

STUDIES ON
THE CONFORMATIONAL DEPENDENCE
OF ELECTRONIC STRUCTURE AND
INTRAMOLECULAR INTERACTION IN
N-HETEROCYCLIC MOLECULES

1 9 7 6

KENICHI YOSHIKAWA

DEPARTMENT OF HYDROCARBON CHEMISTRY

FACULTY OF ENGINEERING

KYOTO UNIVERSITY

STUDIES ON
THE CONFORMATIONAL DEPENDENCE
OF ELECTRONIC STRUCTURE AND
INTRAMOLECULAR INTERACTION IN
N-HETEROCYCLIC MOLECULES

1 9 7 6

KENICHI YOSHIKAWA

DEPARTMENT OF HYDROCARBON CHEMISTRY

FACULTY OF ENGINEERING

KYOTO UNIVERSITY

PREFACE

In the early stage of the nineteenth century, when chemistry was just beginning, organic materials were understood as substances created by living organisms, and were believed to be possessed of a mysterious vital force. By the middle of the nineteenth century, the vital force theory was largely discredited by repeated preparations from mineral sources of "organic" compounds originally obtained only from living organisms. Nevertheless, it is true that millions of "organic" compounds are synthesized by living organisms. A single-celled bacterium is itself a sophisticated and highly organized mixture of tens of thousands of organic compounds, and many of these compounds have been isolated and scrutinized by chemists in this century. In addition to this, many more of the organic materials around us are created by modern chemical knowledge and are substances unknown in past centuries, e.g., plastics, chemical fibers, most dyes and pigments, medicinal drugs, synthetic detergents. Organic chemistry today is indispensable to our modern life, to eat, to have cloths, to cure diseases, etc.

An organic molecule consists of nuclei and electrons, and these electrons can be classified into two groups, π -electrons and σ -electrons. There have been a lot of theoretical and experimental studies concerning the nature of π -electron system. On the other hand, studies on σ -electron system are rather limited. σ -Electrons constitute a funda-

mental molecular framework even in unsaturated organic compounds. It may be, therefore, important to study the intrinsic nature of σ -bond system. In this article, the author studied the chemical and physical properties of N-containing molecules, mainly saturated cyclic and bicyclic amines. These molecules possess the typical lone pair electrons oriented to a certain direction. The nitrogen lone pair plays an important role on hydrogen bonding and as a proton acceptor or an electron donor. It is well known that the nitrogen lone pair electrons concern essentially with the bioactivity of proteins such as hemoglobin, chlorophyll, chymotrypsin, and vitamin B₁₂. It has been a difficult problem in theoretical chemistry to interpret the lone pair electrons accurately, because electron-electron Coulomb repulsion should be taken into account explicitly to calculate the electronic state of lone pair. Recent development of molecular orbital (MO) theories makes it possible for chemists to evaluate the electronic structure of medium sized organic compounds including lone pair electrons. In these circumstances, the studies on the electronic structure in N-heterocyclic compounds seem to contribute the progress in physical organic and biochemistry. The lone pair electrons in aliphatic amines are considered to be unique σ -electrons. Thus, the studies on N-heterocyclic compounds are also expected to shed light on the electronic and steric structures in σ -electron systems.

In Part I, ^1H and ^{13}C nmr spectroscopic studies of

various N-heterocyclic compounds have been carried out in order to elucidate the conformational and geometrical dependence of electron charge and spin distributions through σ -bond system. It had been established that nmr spectroscopy is especially useful in the deeper understanding of the electronic nature of a molecular structure and the interactions among electrons and atomic nuclei. However, nmr studies on other nuclei beside proton were quite limited before 1970. ^{13}C nmr spectroscopy is expected to reflect the small change of electronic or steric structures of organic compounds. The author applied ^{13}C nmr spectroscopy in order to gain insight into the σ -electronic structure of the carbon skeleton.

In Part II, studies on the structural effects on the electronic states of N-heterocyclic molecules were carried out. Here the author is mainly concerned with the energetics of a molecule, e.g., orbital energies, nonbonded intramolecular electronic interactions, conformational energies of the lone pair invertomers, etc. Various spectroscopic methods, i.e., photoelectron, ^1H and ^{13}C nmr, esr, and UV absorption spectroscopies, were applied to elucidate the problems such as the electronic structures and the manner of intramolecular nonbonded interactions in N-heterocyclic compounds.

ACKNOWLEDGEMENTS

studies presented in this thesis are the summarizes
thor's work carried out from the spring of 1971 to
ne Department of Hydrocarbon Chemistry of the
f Engineering of Kyoto University. During the
study, the author has enjoyed many helpful
, encouragements, discussions and suggestions.
y, the author wishes to express his sincere
to Professor Teijiro Yonezawa and Dr. Isao Morishima
continuing guidances and encouragements through-
course of study. Grateful acknowledgement is also
rofessors Kenichi Fukui and Hiroshi Kato for their
stimulations given to the author. It is also his
asure to thank Dr. Shiro Ikegami, Messrs. Koji Okada,
himoto, Koji Toyoda, Hideki Masuda, Katsutoshi Bekki,
Karatsu, Akira Matsui, and Masahiro Kohno for
ive collaborations. He also thanks heartily to
Mamoru Ohashi, Drs. Takashi Kawamura, Hiroshi
, Kimihiko Hirao, Seiji Matsunaga, Messrs. Toshiro
Susumu Kitagawa, and Kazuhiro Matsushita for
pful discussions and encouragements. It is also
pleasure to thank to the members of the Quantum
Group of his Department for useful discussions
stions. The author is grateful to Professor
gakura and Dr. Tsunetoshi Kobayashi for making
toelectron spectrometer available to him.

He is grateful to Messrs. Takeshi Matsui, Toshiaki Hattori and Hiroyuki Katsube for valuable help in the nmr measurement.

The author expresses his sincere gratitude to his parents for their unfailing understanding and continual encouragement. He would also like to thank his intimate friends, Messrs. Shinichi Nagata and Shigeki Kato for their advise and encouragement. Finally, the author acknowledges the hearty encouragement given by his fiancée, Miss Yuko Ito.

CONTENTS

	Page
CONFORMATIONAL DEPENDENCE OF CHARGE AND SPIN DISTRIBUTIONS THROUGH σ -BOND SYSTEMS	
1 Introduction	1
2 Conformational Dependence of Inductive Effect in the σ -Electron System	9
3 Conformational Dependence of Electron Spin Transmission in 4 to 9 Membered Cyclic Amines	16
4 Stereospecific Electron Spin Transmission in Cyclic and Bicyclic Amines	30
5 Some Aspects of the Electronic and Struc- tural Effects on the ^{13}C Contact Shifts for the σ -Bonded Molecules	59
6 Conclusion	84
ELECTRONIC STRUCTURES AND INTRAMOLECULAR INTERACTIONS IN N-HETEROCYCLIC COMPOUNDS	
1 Introduction	89
2 Photoelectron Spectroscopic Study of Cyclic Amines	97
3 Photoelectron Spectroscopic Study of Dialkyl Nitroxide Radicals	99
4 Electron Spin Resonance Spectra of Bicyclic Nitroxide Radicals	103
5 Homoallyl Interaction between Nonadjacent n, π Electrons, I. Photoelectron Spectro- scopic Study	129

Chapter 6	Homoallyl Interaction between Nonadjacent n, π Electrons, II. 2-Azabicyclo[2.2.2]oct- 5-ene Derivatives	11
7	Homoallyl Interaction between Nonadjacent n, π Electrons, III. 2-Aza-5-norbornene Derivatives	14
8	Homoallyl Interaction between Nonadjacent n, π Electrons, IV. 7-Azanorbornene Derivatives	16
9	Homoallyl Interaction between Nonadjacent n, π Electrons, V. ^1H and ^{13}C Nmr Contact Shift Study	20
10	On the Nature of Nitrogen Lone Pair in n, π Homoconjugative Aliphatic Amines	24
11	Conclusion	25
	CONCLUSION	25

LIST OF PUBLICATIONS

- r 2 J. Amer. Chem. Soc., 95, 165 (1973).
- r 3 J. Amer. Chem. Soc., in press.
- r 4 submitted for publication.
- r 5 to be published.

- r 2 J. Amer. Chem. Soc., 96, 288 (1974).
- r 3 Chem. Phys. Lett., 16, 336 (1972).
- r 4 J. Amer. Chem. Soc., 95, 5815 (1973), a part.
- r 5 J. Amer. Chem. Soc., 97, 4283 (1975).
- r 6 J. Amer. Chem. Soc., 97, 2950 (1975).
- r 7 submitted for publication.
- r 8 J. Amer. Chem. Soc., in press.
- r 9 to be published.
- r 10 to be published.

PART I

CONFORMATIONAL DEPENDENCE OF
CHARGE AND SPIN DISTRIBUTIONS
THROUGH σ -BOND SYSTEMS

CHAPTER 1

INTRODUCTION

of the most important questions confronting the is the problem of describing how atoms are held in molecules. As molecules consist of nuclei and "sea", their electronic structures (eg., charge, orbital energies, etc.) are closely connected to molecular steric structures. Chemical reactivity as other physical properties is also essentially determined by the molecular structure. In this sense, it is interesting to investigate the conformational dependence of electronic charge distribution (or electron spin distribution in open-shell molecules). For planar unsaturated compounds, the manner of electron charge distribution has been extensively studied experimentally¹ and theoretically.² In π electron system, resonance and inductive effects have been empirically well documented by Hammett's rule.¹ One can account qualitatively for the reactivity of benzene derivatives in terms of resonance. Similar empirical approach to the chemical reactivity in σ electron system (saturated organic compounds) has not been carried out.¹ However such a study seems not to be successful yet. For the theoretical approach to calculate molecular electronic structures, quantum chemistry was originally developed within the framework of the Hartree-Fock electron approximation, treating the π electrons separately with the remaining σ electrons and atomic nuclei.

considered as part of a nonpolarized core. Accompanied with the recent development of molecular orbital theories : to all valence electrons of a general three- al molecule and with continuing experimental : ions in organic chemistry, studies concerning the : and geometric structures of σ -electron system increased. The recent controversy^{3,4} concerning al carbonium ion is one of such problems in σ - system, which has attracted the concern of many

On the other hand, as σ -electrons constitute mental framework of a molecule, it seems very to investigate the chemical and physical properties iron system.

advent of nmr spectroscopy together with some other methods of investigation has greatly altered the chemical research. Now, nmr spectroscopy is the rtant physical tool available to the organic

Not only does this technique characterize l groups, but it describes the relationships of te nuclei to each other in constitutional and mical detail.⁵ It has been proved that nmr is

l tool for studying detail of conformation in

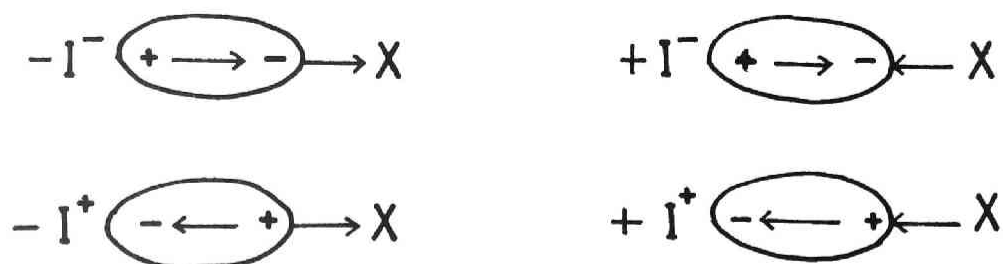
⁵ However, nmr studies on other nuclei beside re quite limited before 1970. Recent instrumental nts make it easier for us to obtain the ^{13}C nmr f organic compounds.^{6,7} The total shielding σ for a particular nucleus is approximated by three terms;⁸

$$\sigma = \sigma_d + \sigma_p + \sigma'$$

where σ_d is the diamagnetic contribution, σ_p the paramagnetic contribution, and σ' the contribution from neighboring groups/nuclei. The paramagnetic term σ_p has been shown to be dominant for most ^{13}C chemical shifts.^{6,7,9} The principal factors affecting this term are the charge polarization, variation in bond order, and average excitation energy. In aromatic and aromatic-like systems, it has been documented that ^{13}C chemical shifts connected with Hammett's σ -constants, that is, with π -charge densities.^{6,7} In these circumstances, the application of ^{13}C nmr spectroscopy to σ -electron system is expected to shed light on the electronic and steric structures of saturated organic compounds. Such a study will also help us to understand the electronic structures of unsaturated organic compounds, since their framework is constituted with σ -electrons.

In Chapter 2, the ^{13}C chemical shift changes induced by N-protonation in the trifluoroacetic acid solution were measured for various aliphatic amines. The main purpose in this chapter is to elucidate the structural and conformational dependence of the electronic structures in the σ -bonded system. Based on the results of semi-empirical molecular orbital calculations, Pople suggested¹⁰ substituents should be classified with respect to the difference in the σ -inductive effect as follows.

1. Electrons may be withdrawn from or donated to the hydrocarbon fragment as a whole. Such substituents would be described as inductive $-I$ and $+I$ types, respectively.



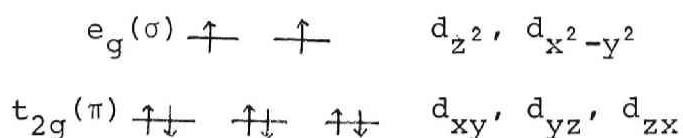
Schematic representation of types of inductive substituent.

2. The distribution of electrons remaining in the hydrocarbon fragments may be polarized so that electrons are drawn to or from the site of substitution. These two possibilities could be denoted by - and + subscripts, respectively, leading to four types of substituent $-I^-$, $-I^+$, $+I^-$, and $+I^+$.

Such an idea is apparently different from the classical description¹¹ of σ -inductive effect. Therefore, it may be worth-while to examine σ -inductive effect experimentally by use of ^{13}C nmr spectroscopy. Here, we studied the aspect of σ -inductive effect and the consequences of conformational change in the σ -skeleton.

Chapters 3, 4 and 5 deals with nmr studies of the diamagnetic molecules of interest in solution "electron spin labelled" by paramagnetic metal chelates. The potential value of such paramagnetic nmr studies was first demonstrated in 1958 by McConnell et al. experimentally¹² and theoretically.^{13,14} Since then the paramagnetic shifts induced by the interaction between an unpaired electron on a transition metal and the nucleus of the ligand coordinated to the metal have been the subject of recent

nmr studies.¹⁵ A great deal of information has been deduced thereby concerning the manner of metal-ligand bonding, the geometrical structure of the transition metal complex, and the electronic structure of the ligand molecules.¹⁵ Among these studies, the six-coordinate nickel (II) complex has been popular as will be mentioned below. Most of these studies have dealt with proton paramagnetic shifts for π -conjugated ligand molecules. However, studies on the contact shifts in σ -electron system have been quite limited. Chapters 3, 4 and 5 deal with the ^1H and ^{13}C paramagnetic shift studies mainly on the Ni(II)-amine complexes where the metal-ligand bond is essentially σ . The oriented lone pair in N-heterocyclic compounds serves as a binding site with the metal. In the near octahedral complex between $\text{Ni}(\text{AA})_2$ and a ligand with the oriented lone pair electrons, the nickel 3d orbitals split into lower threefold degenerate levels (t_{2g}) and the higher twofold degenerate levels (e_g). The e_g orbitals have the σ -type symmetry. $\text{Ni}(\text{AA})_2$ has eight d-electrons with filled t_{2g} orbitals and two unpaired electrons in the e_g orbitals, as illustrated below. It has been shown¹⁶



Energy level diagram for Ni(II) d orbitals
under O_h ligand field.

that the isotropic shift in $\text{Ni}(\text{AA})_2$ complex is caused dominantly by the contact interaction and that the pseudo-contact contribution due to the anisotropic effect of g factor is negligible small. The ^1H or ^{13}C contact shift is expressed by the equation,¹³

$$\frac{\Delta H}{H} = -a_N \frac{\gamma_e}{\gamma_N} \frac{g\beta S(S+1)}{3kT} \quad N = ^1\text{H} \text{ or } ^{13}\text{C}$$

where the hyperfine coupling constant a_N is given by

$$a_N = \frac{4\pi}{3} g\beta\gamma_N h \langle S_Z \rangle^{-1} |\psi(r_N)|^2 \rho_N$$

ρ_N is the unpaired electron spin density on the ^1H or ^{13}C s atomic orbital and the other symbols have their usual meanings. Based on this relationship the downfield and upfield shifts are obtained where positive and negative spin densities are induced on the ^1H or ^{13}C s orbital. From the ^1H and ^{13}C nmr spectra of $\text{Ni}(\text{AA})_2$ -ligand system, both the sign and magnitude of the spin densities induced on proton and carbon atoms can be thus observed.

The major concern in these studies (Chapters 3,4,5) is threefold; (1) to determine the mode of electron spin transmission from metal onto the ligand atoms along the σ -bonds, depending on the orientation and s-character of the nitrogen lone pair, the arrangement of the intervening σ -bonds, substituents and the nature of metal-ligand bond; (2) to utilize the paramagnetic shifts in the elucidation of the steric and electronic structures of σ -bonded molecules; and (3) to use the effect of paramagnetic metal as an aid for nmr signal assignments.

References

- (1) L. P. Hammett, "Physical Organic Chemistry," 2nd ed.
McGraw-Hill, Inc., New York, 1970.
- (2) A. Streitwieser, "Molecular Orbital Theory for Organic
Chemists," John Wiley & Sons, Inc., New York, 1959.
- (3) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin,
New York, 1965.
- (4) H. C. Brown, Accounts Chem Res., 6, 377(1973).
- (5) L. M. Jackman and S. Sternhell, "Application of
Nuclear Magnetic Resonance Spectroscopy in Organic
Chemistry," Pergamon Press Ltd., Oxford, London, 1969.
- (6) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear
Magnetic Resonance for Organic Chemists," John Wiley
& Sons, Inc., New York, 1972.
- (7) J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic
Press, Inc., New York, 1972.
- (8) A. Saika and C. P. Slichter, J. Chem. Phys., 22, 26
(1954).
- (9) M. Karplus and J. A. Pople, J. Chem. Phys., 38, 2803
(1963).
- (10) J. A. Pople and D. L. Beveridge, "Approximate Molecular
Orbital Theory," McGraw-Hill, Inc., New York, 1970.
- (11) C. K. Ingold, "Structure and Mechanism in Organic
Chemistry," G. Bell & Sons, Ltd., London, 1953.
- (12) H. M. McConnell and C. H. Holm, J. Chem. Phys., 27,
314(1957); 28, 749(1958).
- (13) H. M. McConnell and D. B. Chesnut, J. Chem. Phys., 28,
107(1958).

- (14) H. M. McConnel and R. E. Robertson, J. Chem. Phys.,
29, 1361(1958).
- (15) D. R. Eaton and W. D. Phillips, Advan. Mag. Res., 1,
103(1965).
- (16) R. J. Fitzgerald and R. S. Drago, J. Amer. Chem. Soc.,
89, 2879(1967).
- (17) I. Morishima, K. Okada, and T. Yonezawa, J. Amer. Chem.
Soc., 94, 1425(1972), and references therein.

CHAPTER 2

Conformational Dependence of Inductive Effect in the σ -Electron System

Abstract: The ^{13}C chemical shifts induced by the protonation in the trifluoroacetic acid solution have been measured for various aliphatic amines and N-heterocyclic six-membered ring compounds. The protonation-induced ^{13}C shifts are proved to exhibit marked structural and conformational dependences. These results are fairly well interpreted in terms of the charge densities on the carbon skeleton obtained by the semiempirical molecular orbital calculations and are discussed in relation to stereospecificity of the inductive effect in the σ -electron system.

Studies of the electronic inductive effect in the π -electron system have long been carried out experimentally and theoretically. However, the problem of the σ -inductive effect has been less studied. Elucidation of the structural and conformational dependences of the electronic structures of the σ -electron system is one of the essential problems in understanding various stereochemical problems in organic chemistry. The present study is concerned with delineating stereospecificity of the electronic inductive effect in the σ -electron system. A couple of decades ago, Ingold² suggested that an electron-withdrawing substituent, such as the fluorine atom, makes the atom of the σ skeleton positive, and that this effect is diminished gradually along the σ chain.



In contrast to this, Pople, *et al.*,³ using the CNDO-SCF molecular orbital calculations, suggested that the inductive effect induced by such an electronegative substituent alternates and attenuates along the σ skeleton.



Although the concept of the σ -inductive effect has been well accepted in organic chemistry, the mode and mechanism of the transmission of the σ -inductive effect along the saturated molecules are still open to further experimental and theoretical investigations. In this sense, it seems worthwhile to examine experimentally these two aspects of the σ inductive effect and to investigate the consequences of conformational change in the σ skeleton.

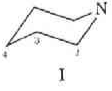
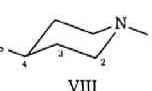
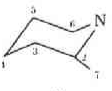
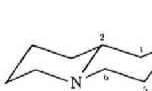
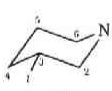
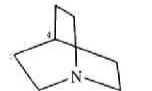
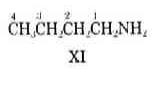
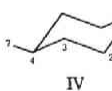
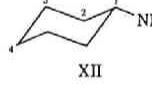
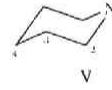
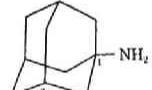
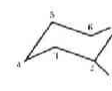
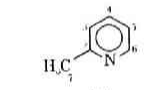
It is well established that the ^{13}C chemical shift is quite a sensitive probe for detecting the structural and electronic perturbations around a carbon atom.

(1) (a) Kyoto University; (b) JEOL Inc.

(2) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Sons, London, 1953.

(3) J. A. Pople and M. S. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).

Table I. ^{13}C Shifts of Free Amines ($\delta^{13}\text{C}$) and N Protonation Shift ($\Delta\delta^{13}\text{C}$)

Molecules	Position	$\delta^{13}\text{C}^a$	$\Delta\delta^{13}\text{C},^b$ ppm	Molecules	Position	$\delta^{13}\text{C}^a$	$\Delta\delta^{13}\text{C},^b$ ppm
	2	143.5	+2.8		2	136.4	-0.2
	3	165.1	+4.8		3	157.8	+3.0
	4	166.9	+3.9		4	162.0	+2.2
	2	139.9	-2.6		7	146.1	+2.5
	3	157.4	+4.6		8	170.0	+1.9
	4	167.0	+3.5		2	129.6	-3.7
	5	165.9	+4.8		3	158.7	+2.7
	6	145.0	+1.2		4	167.4	+3.1
	7	169.4	+4.6		5	166.2	+2.6
	2	137.3	+3.1		6	135.6	+0.2
	3	160.2	+2.9		2	144.6	+0.1
	4	158.3	+3.7		3	165.5	+4.4
	5	165.5	+4.6		4	171.5	+2.0
	6	145.5	+1.0				
	7	172.9	+2.1		1	150.6	+2.8
	2	145.7	+0.9		2	156.1	+6.9
	3	156.6	+5.2		3	172.4	+0.8
	4	160.7	+2.8		4	178.8	+1.3
	7	169.9	+2.4		1	142.0	-2.7
	2	135.8	+0.1		2	155.3	+6.1
	3	166.4	+2.8		3	167.2	+1.2
	4	168.4	+3.3		4	166.4	+1.8
	7	145.7	+2.7		1	144.9	-8.2
	2	133.3	-4.3		2	146.1	+5.3
	3	157.5	+3.0		3	162.4	+0.6
	4	167.6	+2.9		4	156.0	+1.6
	5	166.0	+2.9		2	145.4	-0.2
	6	135.3	-0.1		3	166.8	+1.8
	7	149.3	+1.8		2	34.9	+3.7
	8	172.1	+3.3		3	70.4	-5.4
	2	128.2	+2.5		4	57.5	-5.1
	3	161.4	+0.8		5	72.8	-4.2
	4	159.7	+3.0		6	44.1	+2.2
	5	166.9	+2.3		7	168.2	+5.3
	6	136.5	+0.1				
	7	146.0	+2.4				
	8	173.0	+1.9				

^a ^{13}C chemical shifts are given in ppm from CS_2 . ^b The plus and minus signs mean the upfield and downfield protonation shifts, respectively.

Therefore, a ^{13}C nmr study appears to be most relevant to the present study. Here we are concerned with the perturbational effect of N protonation on the ^{13}C chemical shift changes for the various saturated N-heterocyclic molecules. It was found that the protonation-induced ^{13}C shift depends on the orientation of the nitrogen lone-pair electrons and on the conformation of the intervening carbon skeleton. In addition to this finding, we will discuss the mechanism of electron transmission through the σ skeleton accompanied by nitrogen protonation. Then, based on the ^{13}C chemical shift measurements, the stereospecificity of the inductive effect in the σ skeleton will be discussed with the aid of CNDO MO calculations.

Experimental Section

(a) ^{13}C Nmr Spectral Measurements. All ^{13}C spectra were obtained at natural abundance in 8-mm ϕ tubes with a Jeolco-C-60-HL spectrometer operating at 15.09 MHz. Complete proton decoupling was accomplished by the heteronuclear spin decoupler (Jeolco-SD-HC) and the proton irradiator (Jeolco-IS-60). All chemical shifts were determined with reference to internal cyclohexane or benzene and converted to the CS_2 reference scale with the relation, $\delta^{13}\text{C}_{\text{CS}_2} = \delta^{13}\text{C}_{\text{C}_6\text{H}_6} + 65.0 = \delta^{13}\text{C}_{\text{C}_6\text{H}_{12}} + 165.5$ ppm.

Neat liquid was used to observe TFA-induced protonation shifts except for quinuclidine (X) and 1-adamantanamine (XIII), the solid samples, for which CDCl_3 solvent was employed (ca. 4 and 2 M, respectively). CDCl_3 solvent shifts for ^{13}C resonances were small compared with the protonation shifts.

(b) Materials. N-H piperidines, N-methylpiperidine, n-butylamine (XI), cyclohexylamine (XII), 1-adamantanamine (XIII), pyrrolidine (XIV), and α -picoline (XV) were commercially available. 1,2-, 1,3-, and 1,4-dimethylpiperidines were synthesized by N-methylation of the N-H piperidine homolog.⁴ Quinuclidine (X) was obtained from commercial (K and K) quinuclidine hydrochloride. Quinolizidine (IX) was prepared by hydrogenation of 5,6,7,8-tetrahydroquinoline. (We would like to thank Professor M. Ohashi for gift of this sample.)

(c) ^{13}C Spectral Assignment of Free Amines. The experimental values of the carbon-13 chemical shift data are summarized in Table I for amines used in this study. Each carbon signal of piperidine, 4-methylpiperidine, N-methylpiperidine, 1,4-dimethylpiperidine, and quinuclidine was already assigned.⁵ Assignments of the ^{13}C signals of piperidine and N-methylpiperidine were also referred to the study of Roberts, *et al.*⁶ With the aid of the sub-

(4) H. T. Clarke, H. B. Gillespie, and S. Z. Weiss, *J. Amer. Chem. Soc.*, **55**, 4571 (1933).

(5) I. Morishima, K. Okada, and T. Yonezawa, *Chem. Commun.*, 1535 (1970); *J. Amer. Chem. Soc.*, **93**, 3922 (1971).

(6) W. O. Crain, Jr., W. C. Wildman, and J. D. Roberts, *ibid.*, **93**, 990 (1971).

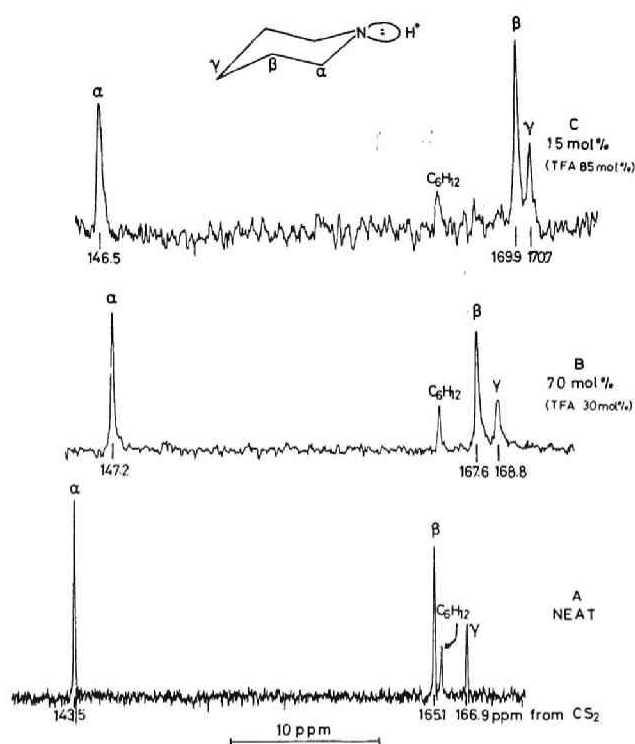
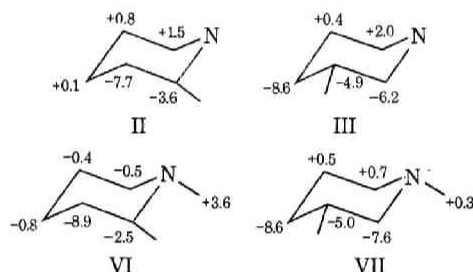


Figure 1. ^{13}C nmr spectra of piperidine perturbed by the protonation in trifluoroacetic acid.

stituent parameters for the methyl group established for methylcyclohexanes by Grant, *et al.*⁷ ($\alpha_e \approx -6$, $\beta_e \approx -9$, $\gamma_e \approx 0$, and $\delta_e \approx 0$ ppm), signal assignment for other piperidines is feasible (see Table I). The effect of methyl substitution on the ^{13}C chemical shift of the carbon skeleton for piperidines (II and III, figures are shifts from piperidine) and *N*-methylpiperidines (VI and VII, figures are shifts from *N*-methylpiperidine) is shown below. These



methyl-substituent effects correspond fairly well with Grant's substituent parameters stated above. Most of the ^{13}C resonances of *N*-H piperidines and *N*-methylpiperidines were readily assigned in this way with a high degree of confidence. Assignments were also assisted by the use of the off-resonance proton decoupling technique. The signals of quinolizidine were assigned by comparison with the spectrum of 1,2-dimethylpiperidine. By utilizing the shift parameters of the NH_2 substituent⁸ and the off-resonance decoupling technique, the assignment can also be made for cyclohexylamine, *n*-butylamine, pyrrolidine, and 1-adamantanamine. The ^{13}C resonances of α -picoline were assigned by referring the CH_3 induced shift for toluene relative to benzene.⁹

Results

The ^{13}C chemical shifts of various amines were measured at various concentrations in trifluoroacetic acid solution. ^{13}C nmr spectra of piperidine perturbed by

(7) D. K. Dalling and D. M. Grant, *J. Amer. Chem. Soc.*, **89**, 6612 (1967).

(8) W. Horsley and H. Sternlicht, *ibid.*, **90**, 3738 (1968).

(9) H. Spiesscke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961). See also D. Doddrell and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 6839 (1970).

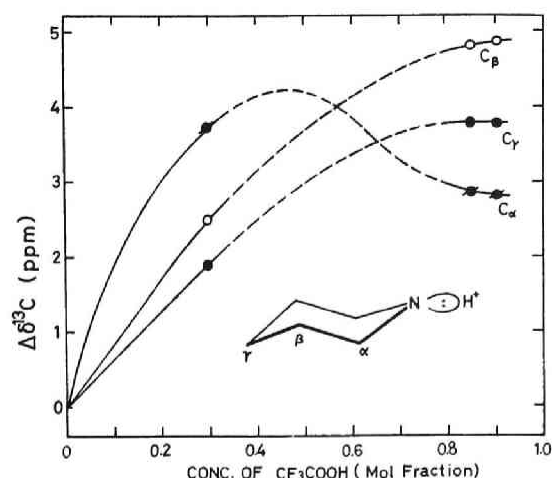


Figure 2. ^{13}C chemical shifts relative to free amine ($\Delta\delta^{13}\text{C}$) varying with acid-base ratios for piperidine. (We could not obtain the protonation ^{13}C shifts for the solution with TFA concentration of 0.4–0.8 mol fraction (the dotted line) because in this region the piperidinium salt was precipitated.)

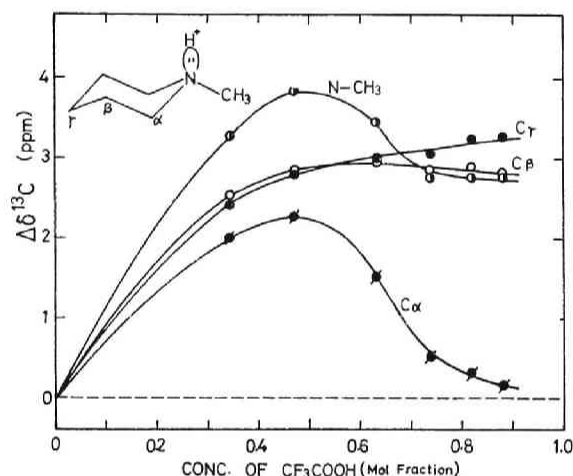


Figure 3. ^{13}C chemical shifts relative to free amine ($\Delta\delta^{13}\text{C}$) varying with acid-base ratios for *N*-methylpiperidine.

the N protonation are shown in Figure 1. In Figures 2 and 3, the variation of ^{13}C shifts induced by the addition of trifluoroacetic acid are shown for piperidine and *N*-methylpiperidine, respectively. Figures 2 and 3 also reveal that all the ^{13}C signals move to higher field upon protonation and that protonation-induced ^{13}C shifts exhibit saturation at the acid:base ratio of *ca.* 1:1. Similar protonation curves were obtained for other saturated amines. The ^{13}C chemical shifts for completely protonated bases (with trifluoroacetic acid concentration of above 80 mol %) are summarized in Table I.

Discussion

A. Variations in ^{13}C Chemical Shift and Electronic Structure of Saturated N-Heterocyclic Molecules Caused by Protonation. Based on a theory of carbon chemical shift with the mean excitation energy approximation, Pople¹⁰ predicted (1) a low-field shift for molecules with low electronic excitation energy, (2) a high-field shift if the carbon atom has high electron density, and (3) a mul-

(10) J. A. Pople, *Mol. Phys.*, **7**, 301 (1964).

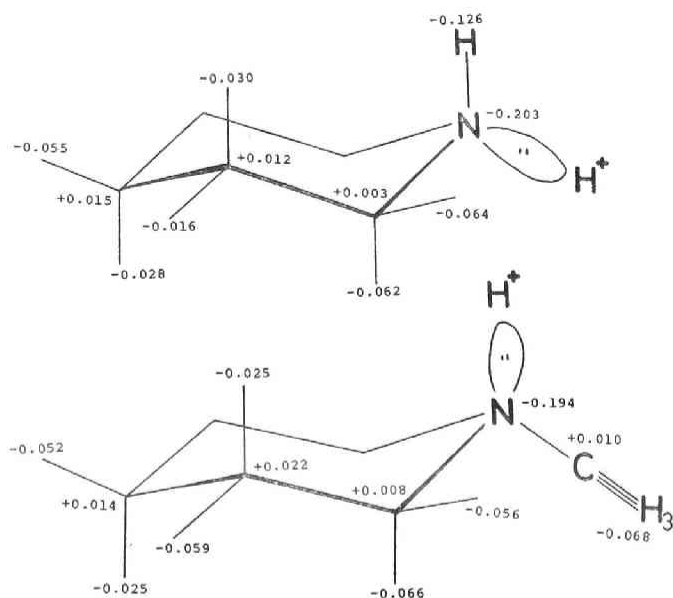


Figure 4. The changes of charge density caused by protonation (CNDO/2 calculations, $N-H^+ = 1.032 \text{ \AA}$).

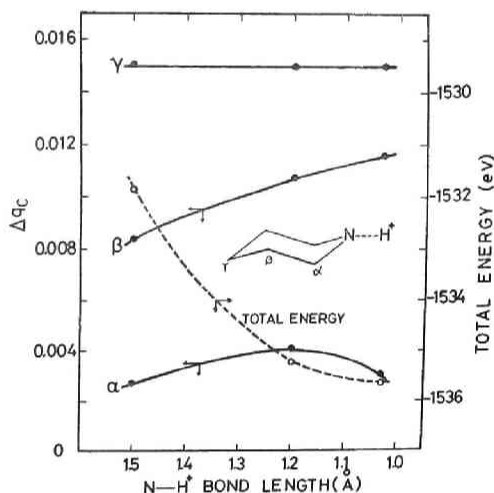


Figure 5. The protonation-induced charge density on the carbon atom of piperidine with variation of $N-H^+$ bond length.

multiple bond effect. Indeed, several workers¹¹ have reported a good correlation between the ^{13}C chemical shift and the π -electron density for aromatic compounds. Similar linear relation between ^{13}C chemical shift and charge density on the carbon atom has also been suggested for saturated molecules.^{12,13} It has been often believed that protonation at the nitrogen atom

(11) H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, 468 (1961); *J. Chem. Phys.*, 35, 731 (1961); P. C. Lauterbur, *ibid.*, 43, 360 (1965); R. J. Pugmire and D. M. Grant, *J. Amer. Chem. Soc.*, 90, 4232 (1968).

(12) (a) J. M. Siegel and M. A. Whitehead, *Theor. Chim. Acta*, 5, 35 (1966); (b) T. Yonezawa, I. Morishima, and H. Kato, *Bull. Chem. Soc. Jap.*, 39, 1398 (1966).

(13) Strictly speaking, the ^{13}C chemical shift on a saturated carbon skeleton is determined mainly by the factors 1 and 2 (K. Okada, I. Morishima, and T. Yonezawa, *J. Amer. Chem. Soc.*, submitted for publication). In the present study, however, we are concerned with the small amount of ^{13}C shift associated with N protonation. Therefore, factor 1 may be essentially important in determining protonation-induced ^{13}C shifts. In fact, the substituent effect on the shift for the carbons in various saturated molecules is plausibly reproduced by the simple CNDO/2 calculation of electron densities on the carbon (I. Morishima, *et al.*, to be submitted for publication).

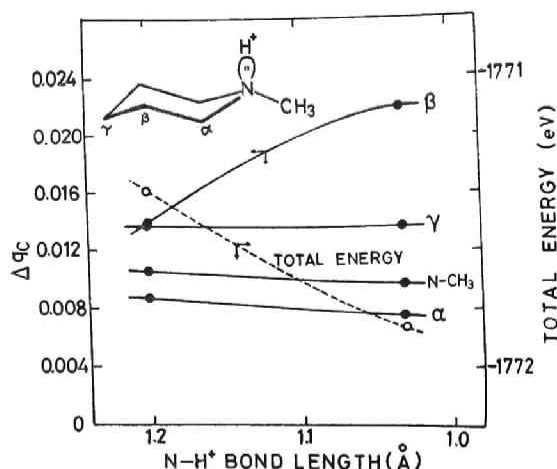
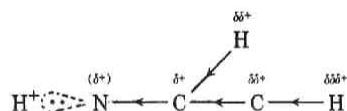


Figure 6. The protonation-induced charge density on the carbon atom of *N*-methylpiperidine.

withdraws electronic charge density from the neighboring atom in the following manner.



Consequently one will expect downfield shifts corresponding to the decreases in electron densities for all of the resonances in the ^{13}C and ^1H spectra. It is well known that the proton resonance of saturated amines shows a downfield shift upon protonation.¹⁴ On the other hand, as Table I shows, protonation causes upfield shifts for most of the ^{13}C signals. In the ^{13}C magnetic resonance studies of amino acids, Horsley, *et al.*,^{8,15} found that the ^{13}C signals of α carbons of the amino acids shift to a higher field upon protonation. From these results, they proposed that protonation of the amino group is accompanied by transmission of negative charge from the hydrogen through the carbons to the NH_3^+ group and that the carbon charge density remains essentially constant or may actually become slightly more negative.

In order to discuss theoretically these experimental results, we have obtained changes of charge densities on carbon atoms upon protonation using the CNDO/2 MO method (Figure 4).¹⁶ In both cases of piperidine and *N*-methylpiperidine, the charge densities of all of the hydrogen atoms decrease upon protonation. On the other hand, the charge densities of all of the carbon atoms increase. The increment of the electron density on the α -carbon atom is smaller than that of β - and γ -carbon atoms. These results suggest that upon N protonation the carbon-hydrogen bond could be polarized to produce the C^--H^+ structure and that the electron on the hydrogen atom could be transmitted through the carbon skeleton onto the positively charged nitrogen atom. Therefore, the upfield ^{13}C shift resulting from protonation is attributable to the

(14) For example, L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, London, 1967, p 180.

(15) W. Horsley and H. Sternlicht, *J. Amer. Chem. Soc.*, 92, 680 (1970).

(16) (a) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, 44, 3289 (1966); (b) for the geometry of piperidine, see T. Yonezawa, I. Morishima, and Y. Ohmori, *J. Amer. Chem. Soc.*, 92, 1267 (1970).

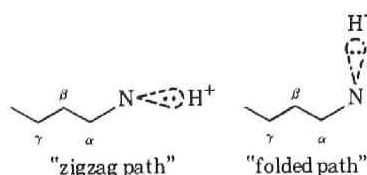
increase in the total charge densities on the carbon.¹³ In order to discuss the peculiar behavior of the plot of ¹³C protonation shift vs. concentration of trifluoroacetic acid (Figures 2 and 3), we obtained the variation of charge densities on the carbon with varying N-H⁺ bond length (Figures 5 and 6). Of course, variation of the N-H⁺ bond length does not directly correspond to the change in acid-base ratio. We are attempting to represent a variation in strength of an intermolecular interaction. As the N-H⁺ distance becomes shorter, the effect of protonation becomes prominent, which may correspond to the accomplishment of protonation. From Figures 5 and 6, it is easily noticed that there are interesting features of Δq_c -N-H⁺ length plots for piperidine or *N*-methylpiperidine. With variation of N-H⁺ bond length, the charge density on the α carbon has a maximum value when the N-H⁺ length is about 1.2 Å. On the other hand, the charge density on the β carbon increases as the N-H⁺ bond length increases. The electron density on the γ carbon remains almost constant with variation of the N-H⁺ length from 1.5 to 1.03 Å. The observed nonlinear variation is not reproduced by the simple weighted average of charge densities for free base and protonated base.

These results of MO calculations and the chemical shift change of the α carbon indicate that the charge density on the α carbon increases due to the C-H bond polarization (C-H⁺) with respect to free amine, and when protonation is sufficient, the positive charge induced on the α carbon in the manner of C^{δ+}→N→H⁺ will compensate for this polarization effect.

B. Conformational Dependence of the ¹³C Shifts Induced by N Protonation. Inspection of Table I shows that the features of ¹³C shifts induced by N protonation are apparently different between N-H piperidine and *N*-methylpiperidine and between 4-methylpiperidine and 1,4-dimethylpiperidine. The most striking difference is encountered for the β carbon, the shift for N-H piperidine being greater by about 2 ppm than that for *N*-methylpiperidine. This relation holds for 4-methyl- and 1,4-dimethylpiperidines. These different features of the ¹³C shifts are most probably due to the structural differences between secondary and tertiary amines. These differences are also seen for the cases of quinuclidine and quinolizidine. For quinuclidine, the lone-pair electrons are in the equatorial position and the shift of the α carbon is rather similar to those of *N*-methylpiperidine derivatives. Perhaps this is resulting from the fact that they are all tertiary amines. But the protonation shift of β carbon in quinuclidine is +4.4 ppm, closer to that in N-H piperidine derivatives (for example, +4.8 ppm for N-H piperidine) than those of *N*-methylpiperidine derivatives. On the other hand, in the case of quinolizidine, where the lone pair electrons occupy an axial position, the protonation shifts of α and β carbons are close to those of 1,2-dimethylpiperidine.

It has been well documented^{16,17} that the nitrogen lone-pair electrons have a greater preference for the equatorial position in N-H piperidine while those in *N*-methylpiperidines preferentially occupy an axial position. Therefore, the charge redistribution induced by

N protonation may occur through a "zigzag path" for piperidines and quinuclidine and through a "folded path" for *N*-methylpiperidines and quinolizidine. This

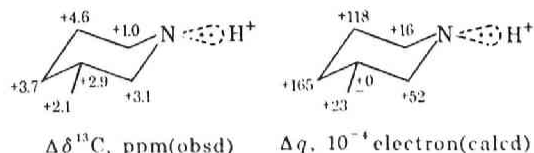


difference in the lone-pair orientation could be responsible for the different features of ¹³C shifts induced by N protonation.

It has also to be noted in Table I that there is an alternation effect in the N-protonation ¹³C shifts for *n*-butylamine; protonation shifts are in the order of C_α < C_β, C_β > C_γ, C_γ < C_δ. Such an alternation effect is also seen for cyclohexylamine and 1-adamantanamine. These features of ¹³C shifts induced by N protonation appear to correspond with the theoretical prediction by Pople, *et al.*^{3,13}

C. Effect of Methyl or Methylene Substituent on the ¹³C Protonation Shift. When the α -carbon shifts of *n*-butylamine, cyclohexylamine, and 1-adamantanamine are compared with each other, the methylene carbon of *n*-butylamine exhibits an upfield protonation shift, but the methine carbon of cyclohexylamine shows an opposite trend. Furthermore, the α carbon of 1-adamantanamine shifts downfield more prominently than that of cyclohexylamine. It may be generalized from these results that the secondary carbon (which has two directly bonded hydrogens) tends to shift downfield upon protonation more than the tertiary carbon. The quaternary carbon shows downfield protonation shift more than the tertiary carbon. This trend is also found for other amines. For example, the C₅ resonance of 3-methylpiperidine exhibits +4.6 ppm upfield shift, while the C₃ resonance shifts only +2.9 ppm. We pointed out in the preceding section that the carbon-nitrogen bond is polarized upon protonation (C-H⁺). These experimental results could also be understood by this mechanism. If the C-H bond is more easily polarized than the C-C bond, the carbon with fewer directly bonded hydrogen atoms should accept less negative charge density from the hydrogen atom, and therefore the carbon atom becomes positive upon protonation.

In order to substantiate these views theoretically, the changes of charge densities on the carbon atoms of 3-methylpiperidine upon protonation were calculated by the CNDO/2 MO method (see below). It is apparent



that the charge densities induced by N protonation follow the variation of ¹³C protonation shifts. The charge density on the C₃ atom is not affected by protonation, quite different from C₅. The present MO calculation appears to support reasonably the mechanism described above.

D. Stereospecificity of the σ -Inductive Effect. A Molecular Orbital Study. In order to substantiate

(17) T. Yonezawa, I. Morishima, and Y. Ohmori, *J. Amer. Chem. Soc.*, **92**, 1267 (1970); I. Morishima, K. Okada, M. Ohashi, and T. Yonezawa, *Chem. Commun.*, **33** (1971).

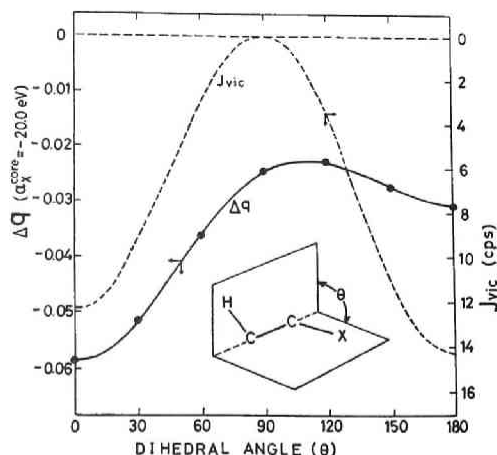


Figure 7. $\Delta q_{H\beta}$ varying with dihedral angle θ .

theoretically the σ -inductive effect¹⁸ established by the ^{13}C protonation shift, we tried semiempirical MO calculations of electron charge densities on the carbon atoms for some model systems. Here we adopted the pseudo-atom approach¹⁹ to introduce theoretically a σ -inductive effect into MO calculations. We have undertaken to see how well experimental trends can be simulated by altering pertinent atomic parameters in CNDO and INDO²⁰ methods. The parameter to be varied in CNDO or INDO is the $1/2(I + A)$ ²¹ value employed in the diagonal elements of the core-Hamiltonian matrix. Other parameters remain unchanged in the present study. The system employed here is ethane ($\text{CH}_3\text{-CH}_2\text{X}$), where X is the pseudoatom for which the parameter variations are carried out ($1/2(I + A)$ was varied from normal -7.176 eV to a value of -20.0 eV). The resulting charge density changes on the vicinal proton are given as a function of dihedral angle θ in Figure 7. The change of charge density Δq_H amounts to a maximum for the cis form (dihedral angle $\theta = 0^\circ$) and minimum at $\theta = 120^\circ$. It is of interest to note that this angular dependence of the Δq_H value is quite similar to that of the H-H vicinal coupling constant. (The variation of J_{vic} ²² is also shown in Figure 7.) The $\text{H}_\text{A}\text{-H}_\text{B}$ nuclear spin-spin coupling constant J_{AB} is represented by²³

$$J_{\text{AB}} = \frac{\hbar\gamma_{\text{A}}\gamma_{\text{B}}}{2\pi} \left(\frac{8\pi\beta}{3} \right)^2 S_{\text{A}}^2(0) S_{\text{B}}^2(0) \pi_{s_{\text{A}}s_{\text{B}}}$$

(18) M. J. S. Dewar and P. J. Grisdale, *J. Amer. Chem. Soc.*, **84**, 3539 (1962).

(19) G. E. Maciel and K. D. Summerhays, *ibid.*, **93**, 520 (1971).

(20) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

(21) In CNDO/2 calculation, Fock's diagonal element $F_{\mu\mu}$ is given by the relation

$$F_{\mu\mu} = -1/2(I_{\mu} + A_{\mu}) + [(P_{\text{AA}} - Z_{\text{A}}) - 1/2(P_{\mu\mu} - 1)]\gamma_{\text{AA}} + \sum_{\text{B}(\neq \text{A})} (P_{\text{BB}} - Z_{\text{BB}})\gamma_{\text{BB}}$$

It is well known that the first term has an essential role to determine $F_{\mu\mu}$. If the orbital ϕ_{μ} contains one electron ($P_{\mu\mu} = 1$) and if all atoms have zero net charge ($P_{\text{AA}} = Z_{\text{A}}$, $P_{\text{BB}} = Z_{\text{B}}$) the diagonal element $F_{\mu\mu}$ becomes $-1/2(I_{\mu} + A_{\mu})$. The value of $(I + A)$ corresponds to the Mulliken-type atomic electronegativity. An atom with a large value of $1/2(I + A)$ shows the electron-withdrawing inductive effect.

(22) A. A. Bothner-By, *Advan. Magn. Resonance*, **1**, 195 (1965).

(23) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964); **9**, 301, 311 (1965).

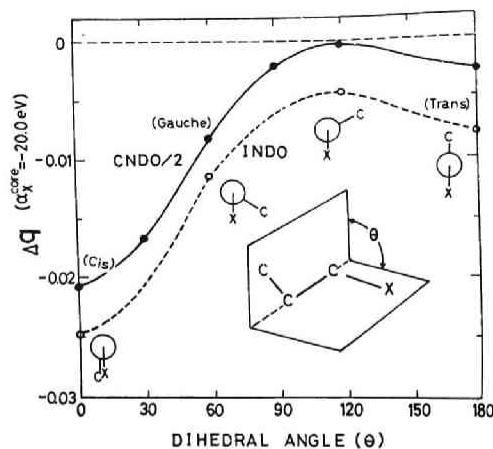


Figure 8. $\Delta q_{C\gamma}$ varying with dihedral angle θ .

where $\pi_{\mu\nu}$ is the mutual polarizability

$$\pi_{\mu\nu} = 4 \sum_i^{\text{occ}} \sum_j^{\text{unocc}} (\epsilon_i - \epsilon_j)^{-1} C_{i\mu} C_{i\nu} C_{j\mu} C_{j\nu}$$

Under the simple LCAO scheme the change in the charge density on atom "s," when the Coulomb integral α_{γ} is perturbed to $\alpha_{\gamma} + \delta\alpha_{\gamma}$, can be given by the relation²⁴

$$\Delta q_s \approx \pi_{s\gamma} \delta\alpha_{\gamma}$$

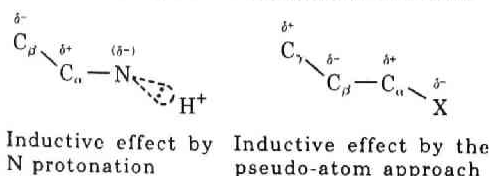
It is, therefore, reasonable to expect that there is a correlation between H-H coupling and the σ -inductive effect.

We have also carried out similar calculations for propane. Changes in the charge density on the γ carbon, when the $1/2(I + A)$ value of α hydrogen is varied from -7.176 to -20.0 eV, is shown in Figure 8. The $\Delta q_{C\gamma}$ value follows an angular dependence similar to the case of Δq_H in ethane. $\Delta q_{C\gamma}$ has the maximum value for the cis form and the minimum for the conformation with $\theta = 120^\circ$.

The stereospecificity of the protonation-induced ^{13}C shift of various amines can be reasonably recognized by the above MO calculations.²⁵ As Figure 9 shows, the protonation-induced shifts and the charge density variation in the pseudo-atom approach show the opposite trend when we compare the β carbon in the N-protonation model and the γ carbon in the pseudo-atom model. However, we are concerned here with the alternating and attenuating features of charge density in the σ -carbon skeleton. Therefore the stereospecific ^{13}C protonation shift may serve as a probe for studying the stereospecificity of the σ -inductive effect. The protonation-induced ^{13}C shift depends on the dihedral angle θ . This angular dependence follows the trends of stereospecific $\Delta q_{C\gamma}$ values (Figure 8). In the

(24) K. Fukui, K. Morokuma, T. Yonezawa, and C. Nagata, *Bull. Chem. Soc. Jap.*, **33**, 963 (1960).

(25) Of course, the mechanism of electron transmission is different between the nitrogen protonation and the pseudo-atom approach. These two cases can be represented schematically as follows.



case of pyrrolidine, for example, the dihedral angle between the lone-pair lobe and the $C_{\alpha}-C_{\beta}$ bond is nearly 120° and the protonation ^{13}C shift is the smallest of all of the four amines (in Figure 9), which corresponds well with the MO theoretical prediction given in Figure 8. However, in the case of α -picoline, where the dihedral angle between the lone-pair lobe and the $C-\text{CH}_3$ bond is 0° , the protonation causes the largest upfield ^{13}C shift for the β carbon. This example also corresponds with the theoretical results of the stereospecificity in the σ -inductive effect. For piperidine and quinuclidine, with the corresponding dihedral angle of 180° , the protonation-induced shifts for the β carbon are $+4.8$ and $+4.4$ ppm, respectively. For *N*-methylpiperidine and quinolizidine, with the dihedral angle of 60° , the protonation-induced shifts for the β carbon are $+2.8$ and $+2.6$ ppm, respectively. Hence the protonation-induced shifts of the β -carbon atoms fall in the order, $\theta = 0^\circ$ (cis) $> \theta = 180^\circ$ (trans) $> \theta = 60^\circ > \theta = 120^\circ$. The change in the charge density obtained by the pseudo-atom approach falls in the order, $\theta = 0^\circ$ (cis) $> \theta = 60^\circ > \theta = 180^\circ$ (trans) $> \theta = 120^\circ$ (Figure 8).

Conclusions

In summarizing the above results and discussion, the following conclusions may be drawn. (1) By the protonation of saturated amines the $\text{C}-\text{H}$ bond is polarized to produce the C^--H^+ structure and the electron on hydrogen atom is transmitted through the carbon skeleton onto the positively charged nitrogen atom. (2) The protonation ^{13}C shifts alternate and attenuate along the σ -carbon skeleton. These features of ^{13}C shifts can be interpreted in terms of charge density variation and correspond well with alternation in the σ -inductive effect predicted by Pople, *et al.*³

From (1) and (2), the σ -inductive effect induced by N protonation may be schematically represented as follows.

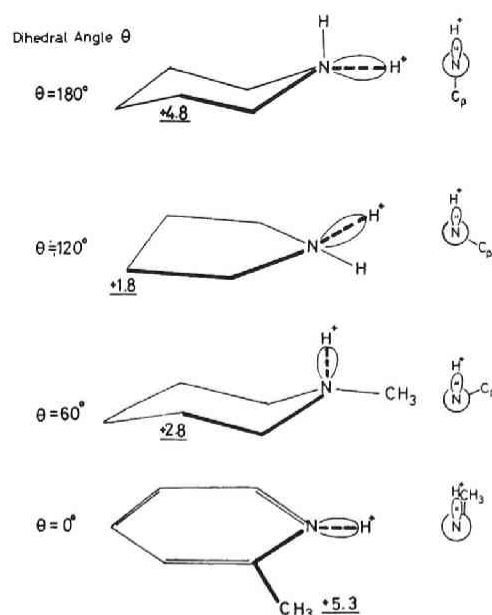
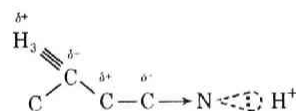


Figure 9. Stereospecific ^{13}C shifts induced by protonation for several cyclic N bases (ppm).



- (3) The $\text{C}-\text{H}$ bond is electronically polarized more readily than the $\text{C}-\text{C}$ bond by the inductive effect and therefore the $\text{C}-\text{H}$ carbon has more electron density than the $\text{C}-\text{C}$ carbon by the protonation. This may be responsible for the observed trend of protonation-induced ^{13}C upfield shifts in the order of the secondary carbon $>$ the tertiary carbon $>$ the quaternary carbon. (4) The protonation ^{13}C shifts exhibit a marked conformational dependence, which can be interpreted in terms of stereospecificity of the σ -inductive effect.

CHAPTER 3

Conformational Dependence of Electron Spin Transmission in 4 to 9 Membered Cyclic Amines

Abstract: In order to elucidate the mode of intramolecular electron spin transmission through the σ -skeleton, ^1H and ^{13}C nmr contact shifts were obtained for 4 to 9 membered cyclic amines. It was found that the feature of the $\text{Ni}(\text{AA})_2$ -induced ^1H and ^{13}C shifts is markedly different between N-H and N-methyl amines. Such an experimental trend was attributed to the different lone pair orientation in these cyclic amines. The experimental results were also discussed in terms of the stereospecific electron spin transmission through the zigzag or folded σ -skeleton. INDO-UHF-MO calculations were carried out for cycloalkyl σ -radicals with the conformation of equatorial or axial radical lobe. The feature of the observed ^1H and ^{13}C contact shifts in cyclic amines was well reproduced by these model calculations.

In the last decade, studies on the geometries and electronic structures of saturated organic compounds have been increased. However, problems on the nature of σ -electron system, eg., σ -inductive effect,¹ mode of electron spin transmission through σ -bonds, seem to be still open to further experimental and theoretical investigations. Elucidation of the structural and conformational dependences of the electronic structures of the σ -bonded molecules is thus one of the essential problems in understanding various stereochemical problems in organic chemistry.

We are currently interested in stereospecificity of the mode of electron spin distribution through the carbon skeleton in the σ -bonded molecules. We have previously reported the conformational or geometrical dependence of proton and carbon-13 contact shifts for N-heterocyclic molecules complexed with paramagnetic nickel acetylacetonate ($\text{Ni}(\text{AA})_2$).^{2,3,4,5} In these studies, it has been revealed that these contact shifts are associated with electron spin densities distributed on proton and carbon atoms and are characteristic of axially or equatorially oriented nitrogen lone pair, of chair or boat, and of zigzag or folded conformation of the carbon skeleton. Such a stereospecific feature of proton and carbon-13 contact shifts has been discussed in relation to the mode of electron spin distribution through the σ -bonded carbon skeleton. $\text{Ni}(\text{AA})_2$ -induced ^1H and ^{13}C contact shifts appear to be relevant for elucidation of the mode of intramolecular electron spin distribution, because nmr contact shift is quite

sensitive for a small quantity and sign of spin density. In this sense, $\text{Ni}(\text{AA})_2$ -induced contact shifts serve as a spin probe for the elucidation of the electronic and geometrical structures of the σ -bonded molecules. In this manuscript, we wish to extend the nmr contact shift study in order to elucidate the structural effects on the mode of electron spin distribution. We have studied ^1H and ^{13}C nmr contact shifts for 4 to 9 membered cyclic amines. This study is expected to shed light on the electronic structures of σ -electron system.

Experimental Section.

Materials. Azetidine (1) and N-(2-ethoxycarbonyl)azetidine (2) were prepared following the method of Wadsworth.⁶ N-methylpyrrolidine (4), N-methylhexamethyleneimine (8), N-methylheptamethyleneimine (10), and N-methyloctamethyleneimine (12) were prepared by N-methylation of the parent N-H amines.⁷ The other compounds used in this study (Table I) were commercially available.

Proton Nmr Measurements. All the proton spectra were obtained at 220 MHz using a Varian HR-220 spectrometer in our department. TMS was used as an internal standard. All samples were made in CDCl_3 solution, ca. 200 mmol/l. Nmr samples were prepared by the addition of a given amount of $\text{Ni}(\text{AA})_2$ to the CDCl_3 solution of the cyclic amines.

^{13}C Nmr Measurements. ^{13}C nmr spectra were obtained at 25.1 MHz on a Jeolco ^{13}C Fourier transform nmr system,

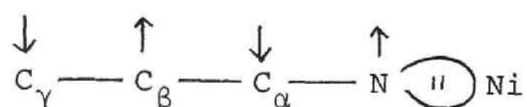
JNM-PFT-100. An internal ^2D lock was employed. The ^{13}C chemical shifts were measured with respect to internal TMS. All samples were made in CDCl_3 solution, ca. 1 M, in 10 mm ϕ sample tubes. All the spectra were taken at room temperature (24°C) in the presence of varying amounts of $\text{Ni}(\text{AA})_2$. Spectral assignments were made referencing the ^{13}C chemical shifts of the related compounds.^{3,4,5} $\text{Eu}(\text{fod})_3^-$ induced shifts were also observed to help the signal assignments.

Results and Discussion.

The relative ^1H and ^{13}C contact shifts with the value for the α -protons and α -carbons normalized to unity for various ligand molecules are summarized in Table I. The plus and minus signs of these values denote the upfield and downfield shifts which correspond to the negative and positive spin densities, respectively, induced on the ligand's atomic orbitals of proton and carbon atoms. The relative values for various protons and carbons in a ligand molecule were obtained from the slopes of the linear plots of the paramagnetic shift vs. the concentration of added $\text{Ni}(\text{AA})_2$. Inspection of Table I shows that $\text{Ni}(\text{AA})_2$ -induced ^{13}C shifts alternate along the σ -bonds in these cyclic amines. The α and β carbons sense upfield and downfield shifts, respectively. The γ carbons show upfield shifts except for 9.

It has been well established that the paramagnetic

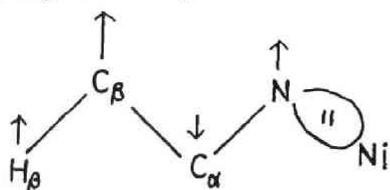
shifts of octahedral Ni(II) complexes are predominantly due to isotropic shifts because of the isotropic g tensor and that any pseudo-contact shifts are negligible small.^{2,3,8} Such an experimental trend of the ^{13}C contact shifts implies that negative spin densities are induced on the s orbitals of the α and γ carbons, while positive spin densities on the s orbitals of the β carbons in these cyclic amines. This indicates that "spin polarization" is the important



mechanism of electron spin transmission through σ -skeleton.

It is to be noted in Table I that ^1H and ^{13}C nmr contact shifts of the N-H amines are apparently different from those of the N-methyl homologues. Relatively large downfield shift of the β -carbon is obtained for the N-H cyclic amines. Whereas the β -carbon feels only a small downfield shift in the N-methyl derivatives. For the ^1H contact shifts, the β -protons in N-H amines sense downfield contact shifts. In contrast to this, the β -protons in N-methyl amines feel upfield shifts. In our previous contact shifts studies,^{2,4,5} it has been shown that the β -proton separated by zigzag σ -bonds from the nitrogen-metal bond exhibits a large downfield contact shift and that separated by folded σ -bonds a small upfield shift.

"zigzag arrangement"



"folded arrangement"

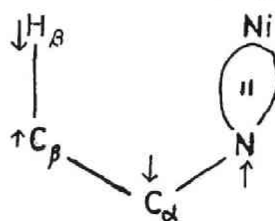
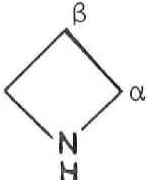
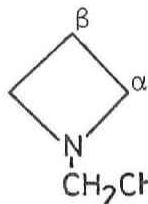
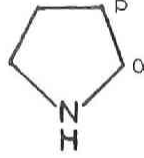
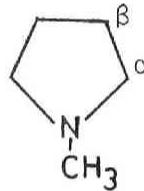
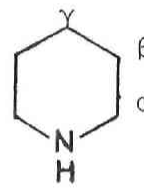
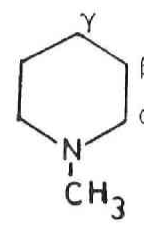
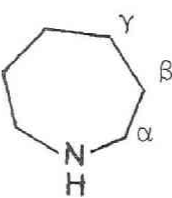
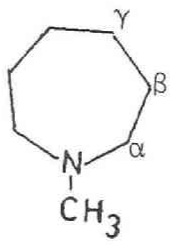
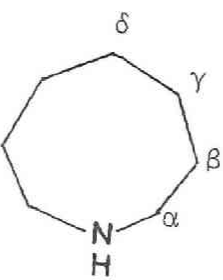
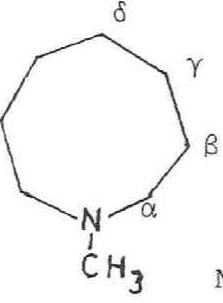
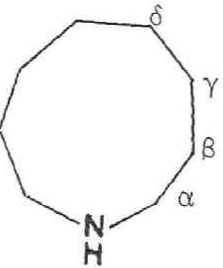


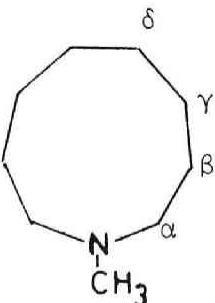
Table I. ^{13}C and ^1H Contact Shifts for Cyclic Amines

Molecules	position	^{13}C a	^{13}C C. S. ^b (rel. values)	^1H C. S. ^b (rel. values)
<u>1</u> 	α	48.5	+1.0	-1.0
	β	22.5	-1.1	-0.2
<u>2</u> 	α	55.8	+1.0	-1.0
	β	17.5	-0.1	+0.03
<u>3</u> 	α	47.9	+1.0	-1.0
	β	26.2	-2.4	-0.2
<u>4</u> 	α	56.7	+1.0	-1.0
	β	24.9	-0.6	+0.05
	N-CH ₃	39.5	+1.4	-1.2
<u>5^c</u> 	α	47.0	+1.0	-1.00
	β	27.0	-1.6	-0.47
	γ	25.3	+0.2	-0.11
<u>6^c</u> 	α	56.7	+1.0	-1.00
	β	25.9	-0.3	+0.04
	γ	23.7	+0.1	-0.14
	N-CH ₃	46.8	+1.1	

(Table I continued)

<u>7</u>		α	49.9	+1.0	-1.0
		β	32.0	-1.8	-0.3
		γ	27.0	+0.06	-0.0
<u>8</u>		α	59.4	+1.0	-1.0
		β	28.3	-0.3	+0.02
		γ	27.3	+0.05	-0.0
		N-CH ₃	42.9	+1.1	-1.0
<u>9</u>		α	49.0	+1.00	-1.00
		β	29.8	-1.58	-0.20
		γ	25.4	-0.04	+0.01
		δ	28.7	+0.02	-0.04
<u>10</u>		α	56.2	+1.00	-1.00
		β	27.6	-0.43	+0.02
		γ	26.3	+0.04	~0.0
		δ	27.6	-0.00	~0.0
		N-CH ₃	47.0	+1.14	-0.87
<u>11</u>		α	48.5	+1.00	-1.00
		β	28.5	-1.57	-0.30
		γ	25.1	+0.06	-0.02
		δ	26.7	-0.04	+0.01

(Table I continued)

<u>12</u> ^d		α	55.5
		β	26.6
		γ	25.8
		δ	23.7
		N-CH ₃	45.9

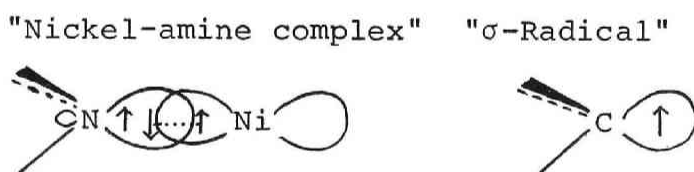
a. ppm from TMS. b. Puls and minus signs denote the upfield and downfield shifts, respectively. c. Ref. 4. d. No apparent Ni(AA)₂-induced shifts were observed.

The large downfield shift of the β -proton has been attributed to the large positive spin density transferred through a zigzag path of the σ -skeleton. Along this line, the different feature of the β -proton contact shifts between N-H (5) and N-methylpiperidine (6) in which the proton signal is observed as an average of the resonances of axial and equatorial protons, was considered to be due to the effect of different lone pair orientation. In 5 the lone pair electrons occupy an equatorial position at least in the complex with $\text{Ni}(\text{AA})_2$, while in 6 the lone pair axial conformer is favorable.^{2,4} Similarly, the different feature of the ^1H contact shifts between N-H and N-methyl derivatives in 4,5,7,8,9-membered cyclic amines in Table I may reflect the different lone pair orientation.

It has been also indicated^{3,4,5} that positive spin reaches β -carbon to a greater extent by a zigzag path than a folded path. The difference in the β -carbon contact shifts between 5 and 6 was thus attributable to the effect of the different lone pair orientations, similarly to the discussion for the proton contact shifts in these amines. Consequently, the different feature of the ^{13}C nmr contact shifts between N-H and N-methyl cyclic amines suggests that the nitrogen lone pair electrons orientate differently at least in the complexes with $\text{Ni}(\text{AA})_2$.

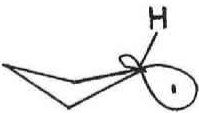
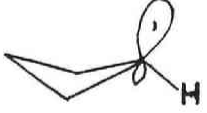
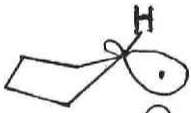
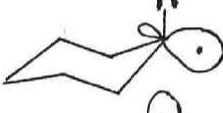
In order to gain further insight into the lone pair orientation and the mechanism of electron spin transmission, we carried out INDO MO calculations. In spite of the recent development in MO theory, at present it is still

difficult to calculate accurately the spin density on a ligand atom in the nickel-amine complexes. This is because of the difficulty to evaluate the d orbitals of nickel. In this situation, we carried model calculations. The manner of nickel-amine bond may be depicted schematically as below. From this, one can easily notice that the circumstance around the nitrogen atom in nickel-amine complexes is similar to that around the carbon atom in the corresponding



σ-radical. We performed MO calculations for cyclobutyl and cyclopentyl σ-radicals⁹ in which the radical lobe occupies the equatorial or axial position, as the model of Ni(AA)₂ complexes with azetidine and pyrrolidine. The calculated relative values of the spin density of the C₃ carbons, when the spin density on the C₂ carbon is normalized to -1.00, are shown in Table II, together with the results for cyclohexyl σ-radical.⁴ In this table, the shifts of the β-carbons (protons) relative to the shifts of the α-carbons (protons) in 4,5,6-membered cyclic amines are also represented. From Table II, it is apparent that the observed shifts for the N-H and N-methyl amines correspond well to the relative values of the calculated spin densities for the cycloalkyl σ-radicals. In the conformer with the equatorial radical lobe, the spin density on the C₃ carbon is greater than that of the C₂ carbon in these σ-radicals.

Table II. Relative Values of Calculated Spin Densities
and Observed Contact Shifts

σ -Radicals	ρ_{C_3}/ρ_{C_2} ^a calcd.	$\rho_{C\beta}/\rho_{C\alpha}$ ^b obsd.	ρ_{H_3}/ρ_{H_2} ^a calcd.	$\rho_{H\beta}/\rho_{H\alpha}$ ^b obsd.	Amines
A 	-1.90		+0.57		
B 	-0.49	-0.1 ^e	+0.13	+0.03 ^e	<u>2</u>
average between A and B	-1.09	-1.1 ^f	+0.28	-0.2	<u>1</u>
	-2.62	-2.4	+0.07	+0.2	<u>3</u>
	-0.04	-0.6	-0.04	-0.05	<u>4</u>
	-1.57	-1.6	+0.27	+0.47	<u>5</u>
	-0.32	-0.3	-0.06	-0.04	<u>6</u>

- a. Relative values of the calculated spin densities on s atomic orbitals for C_3 to C_2 carbons (protons). b. Relative values of the observed $Ni(AA)_2$ -induced shifts for β to α carbons (protons) in the amine indicated in the last column
- c. As to the bond lengths and angles, see ref. 9, 10.
- d. See ref. 4.

On the other hand, in the conformer with the axial radical lobe, the spin density on the C_3 carbon is smaller than that of the C_2 carbon. This is because the arrangement of the radical lobe- C_α - C_β skeleton in the equatorial conformer becomes more planar than that in the axial one, which is quite similar to the dihedral angle dependence of vicinal H-H coupling constants (" $\cos^2\theta$ " rule).^{4,11} The experimental trends of the ^1H contact shifts are also well reproduced by these model calculations. These results suggest that the lone pair electrons preferentially occupy the equatorial and axial positions in the N-H and N-methyl cyclic amines, respectively, at least in the complexes with $\text{Ni}(\text{AA})_2$. In azetidine, the observed trend corresponds better to the averaged values of the spin densities in the two conformers as is shown in Table II. As the ring puckering from the plane is small in azetidine,¹² the energy difference between the lone pair equatorial and axial conformers may be small. Therefore, such a trend of the induced spin density in azetidine may imply that the nitrogen lone pair electrons occupy the equatorial and axial positions nearly equally.

Summarizing the above results and discussion, it is concluded that $\text{Ni}(\text{AA})_2$ -induced ^1H and ^{13}C nmr contact shifts could serve as a quite sensitive probe for the elucidation of the mode of intramolecular electron spin transmission through the σ -skeleton, with the aid of MO model calculations. Nmr contact shift measurement is also proved to be a quite useful tool to study molecular stereo structure of aliphatic amines, i.e., arrangement of the carbon skeleton and lone pair orientation.

References and Notes

- (1) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, Inc., New York, 1970.
- (2) I. Morishima, K. Okada, M. Ohashi, and T. Yonezawa, Chem. Commun., 33(1971).
- (3) I. Morishima, K. Okada, T. Yonezawa, and K. Goto, J. Amer. Chem. Soc., 93, 3922(1971); I. Morishima, K. Okada, and T. Yonezawa, *ibid.*, 94, 1425(1972).
- (4) I. Morishima, K. Yoshikawa, and K. Okada, J. Amer. Chem. Soc., in press; K. Yoshikawa, M. Hashimoto, H. Masuda, and I. Morishima, submitted for publication; I. Morishima, K. Yoshikawa, M. Hashimoto, and H. Masuda, to be submitted for publication.
- (5) I. Morishima and K. Yoshikawa, J. Amer. Chem. Soc., 97, 2950(1975); K. Yoshikawa, K. Bekki, M. Karatsu, T. Kamio, and I. Morishima, *ibid.*, in press; I. Morishima, K. Yoshikawa, K. Toyoda, M. Karatsu, T. Yonezawa, S. Sakata, and S. Ikegami, submitted for publication.
- (6) D. H. Wadsworth, J. Org. Chem., 32, 1184(1967).
- (7) H. T. Clarke, H. B. Gillespie, and S. Z. Weiss Haus, J. Amer. Chem. Soc., 55, 4571(1933).
- (8) R. J. Fitzgerald and R. S. Drago, J. Amer. Chem. Soc., 89, 2879(1967).
- (9) The bond lengths and angles were taken same as cyclobutane¹⁰ and cyclopentane.¹⁰
- (10) "Tables of Interatomic Distances and Configuration in Molecules and Ions," Edt., L. E. Sutton, The Chem. Soc.,

London, 1975.

(11) M. Karplus, J. Chem. Phys., 30, 11(1959).

(12) L. A. Carreira and R. C. Lord, J. Chem. Phys., 51,
2735(1969).

Stereospecific Electron Spin Transmission in Cyclic and Bicyclic Amines

Abstract: ^1H and ^{13}C nmr contact shifts induced by nickel acetylacetonate ($\text{Ni}(\text{AA})_2$) have been observed for various cyclic and bicyclic amines. These contact shifts are well reproduced by INDO molecular orbital calculations of spin densities on the proton 1s and carbon 2s atomic orbitals for the corresponding hydrocarbon σ -radicals. It is shown that the proton contact shifts follow the stereospecificity established for nuclear spin-spin coupling constants.

The importance of the through space spin transfer in the rigid σ bonded skeleton is also proposed to account for non-alternating feature of ^{13}C contact shifts for planar zigzag arrangement of the σ -skeleton. This mechanism is also discussed in relation to the long-range H-H coupling constant across four σ -bonds.

We have currently been interested in stereospecificity of the mode of electron spin distribution through the σ -skeleton in view of elucidation of the σ -electronic structures. We have previously reported² the proton and carbon-13 contact shifts for N-heterocyclic molecules complexed with paramagnetic nickel acetylacetonate ($\text{Ni}(\text{AA})_2$).^{3,4} In these studies it has been demonstrated that the relative contact shifts of various protons and carbons definitely depends on the conformation or configuration of the intervening σ -bond connecting these and the nitrogen atoms. A linear correlation between the $\text{Ni}(\text{AA})_2$ -induced nmr contact shift and the esr hyperfine coupling constant (hfs) in an organic free radical with the corresponding isoelectronic structure has recently been demonstrated.^{2,5,6} It has also been shown that nmr contact shifts are quite useful to probe the mechanism of intramolecular electron spin transmission because it is quite sensitive to a small quantity and a sign of the induced spin density.²

The correlation between hyperfine coupling constant (hfs) of a σ type radical and the nmr nuclear spin-spin coupling constant (J) for protons has been pointed out theoretically^{7,8,9} and experimentally.⁸ The correlation between the contact shifts and the nuclear spin coupling constants (J) has also been studied.^{10,11} The studies on the stereospecific electron spin transmission through the σ -skeleton seem to serve as an aid in understanding the electronic structure of σ -bonded molecules. For this purpose, we have extended here our nmr contact shift studies to the various cyclic and bicyclic amines. Our concern in this study is to find the

conformational or configurational dependence of electron spin distribution and to elucidate the mechanism of intramolecular electron spin transmission in relation to hfs's and nuclear spin-spin coupling constants associated with the corresponding σ skeleton.

Experimental Section

Materials. Piperidine (1), 4-methylpiperidine (2), 3-methylpiperidine (3), N-methylpiperidine (4), and quinuclidine (7) were obtained from commercial sources. 1,4-dimethylpiperidine (5) and 1,3-dimethylpiperidine (6) were prepared by N-methylation of 2 and 3, respectively.¹² 1-Azaadamantane (8) was provided by Dr. W. N. Speckamp. 3,3,4-Trimethyl-2-chloro-1-azabicyclo[2.2.1]heptane (9) was provided by Professor P. G. Gassman. 7-Chloromethyl-1-azabicyclo[3.2.1]octane (10) was the gift from Dr. C. F. Hammer. $\text{Ni}(\text{AA})_2$ was dried in vacuo over 30 hr. at 60°C before use.

Proton nmr measurements. All the proton spectra were obtained at 220 MHz using a Varian HR-220 spectrometer in our department. TMS was used as an internal standard. The samples were made in 10 v/v % CDCl_3 solutions for piperidine derivatives (1~6), in ca. 0.1 M CDCl_3 solutions for 7 and 8, and in 0.5 M CDCl_3 solution for 10. Assignment of proton signals was made by referencing the spectral patterns, the europium dipivalomethane ($\text{Eu}(\text{DPM})_3$) and cobalt acetylacetonate ($\text{Co}(\text{AA})_2$) induced pseudocontact shifts. The variation of the spectral patterns were also referred.

^{13}C nmr measurements. Completely proton decoupled ^{13}C nmr spectra were obtained at 25.15 MHz on a JEOL-JNM-PFT-100 system. After the 100~30000 accumulations of the free induction decays induced by the 45° pulses with the interval of 2~4 sec, the Fourier transformed spectra were recorded. The ^{13}C spectra were obtained from CDCl_3 solution of 9 in 0.5 M, 10 in 3 M and 3 in 50 v/v %. The spectra were taken at room temperature (24°) in the presence of varying amounts of $\text{Ni}(\text{AA})_2$ as well as in the case of ^1H nmr measurements. The ^{13}C chemical shifts were measured with respect to internal TMS or CDCl_3 (77.1 ppm from TMS). The assignments of ^{13}C nmr spectra were made by referring the shifts of related compounds, $^{2\text{d},\text{f},13}$ and by the use of the stereospecific ^{13}C contact shift induced by $\text{Ni}(\text{AA})_2$. $^{2\text{b},\text{c},\text{d},\text{e}}$ The half-decoupled technique was used to help the signal assignment of the ^{13}C nmr spectra.

Results and Discussion

Stereospecific Proton Contact Shifts and Electron Spin

Distribution. In piperidine (1) and N-methylpiperidine (4), the ring inversion rate is so rapid at room temperature that only the time averaged signals of axial and equatorial protons are observed for α, β and γ protons. Introduction of

a methyl group in the piperidine ring slows down this inversion rate and the separated signals of axial and equatorial protons of α and β methylene groups were obtained. Spectral assignments for symmetrical molecules (1,2,4,5,7,8) follow directly from the relative intensities and splitting patterns of well separated signals. For the other molecules (3,6,10) proton spectra are more complicated even at 220 MHz, but with the aid of $\text{Co}(\text{AA})_2$ or $\text{Eu}(\text{DPM})_3$ -induced shifts, we are able to definitely assign each signal. The resonance positions are summarized in Table I. The perturbation of the nmr spectra of 1-azaadamantane (8) and 1-aza-7-chloromethyl-bicyclo[3.2.1]octane (10) induced by $\text{Ni}(\text{AA})_2$ are shown in Figures 1 and 2, respectively. In Figure 3 is exemplified a plot of paramagnetic shift vs. the concentration of $\text{Ni}(\text{AA})_2$ for 10. Each proton resonance is shifted from its normal diamagnetic values by an amount which is proportional to the concentration of added $\text{Ni}(\text{AA})_2$. This linear relation implies that the exchange of ligand between complexed and uncomplexed sites is time averaged. Thus the proton resonances of the ligand shift toward the resonance position of the complex as $\text{Ni}(\text{AA})_2$ is added to the diamagnetic solution and the relative values of these shifts are significant in the present study. The relative values for various protons in a ligand molecule were obtained from the slope of the linear plot of the paramagnetic shift vs. the concentration of $\text{Ni}(\text{AA})_2$, with the value for a α -proton normalized to 1.00. The relative proton contact shifts for various ligand molecules are also summarized in Table I. The plus

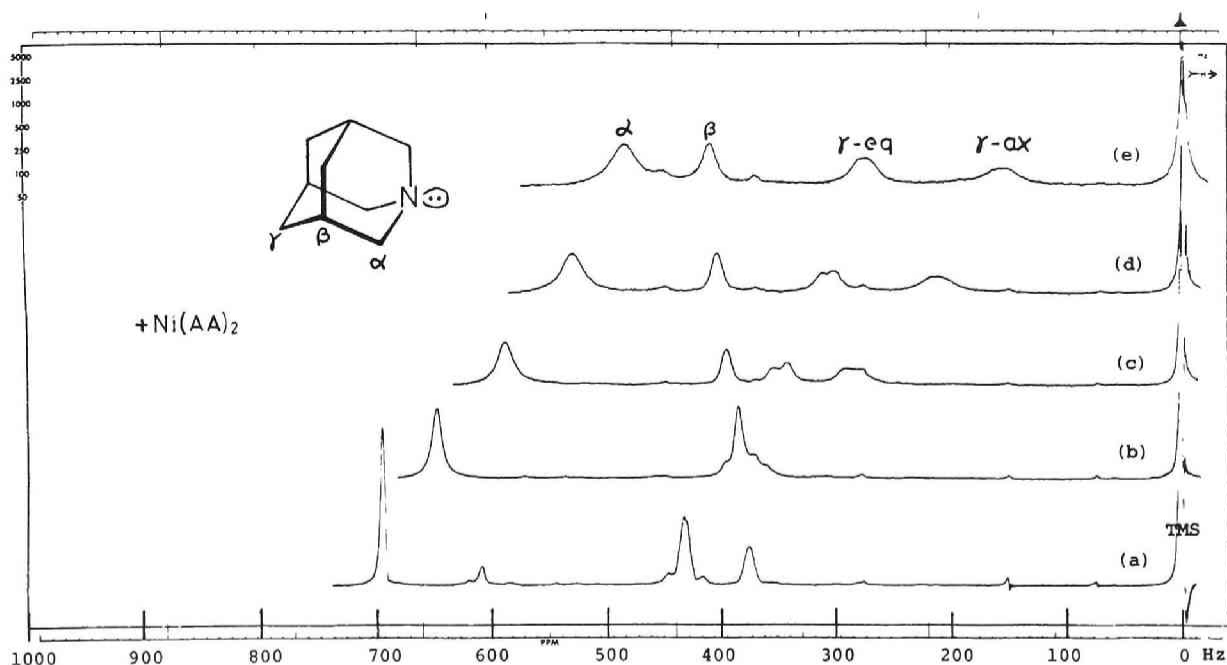


Figure 1. 220 MHz ^1H nmr spectra of 8, (a) in CDCl_3 and (b) (e) in CDCl_3 containing varying amounts of $\text{Ni}(\text{AA})_2$.

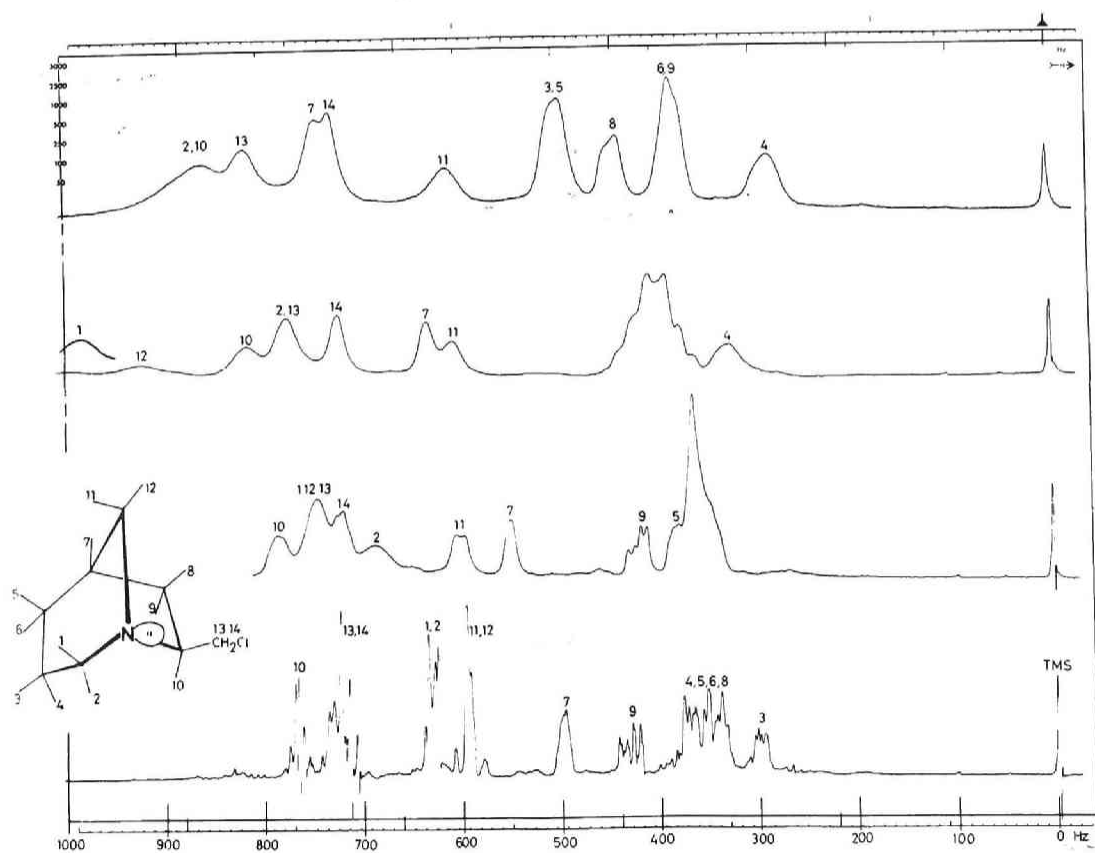


Figure 2. 220 MHz ^1H nmr spectra of 10, (a) in CDCl_3 and (b), (c), (d) in CDCl_3 containing varying amounts of $\text{Ni}(\text{AA})_2$.

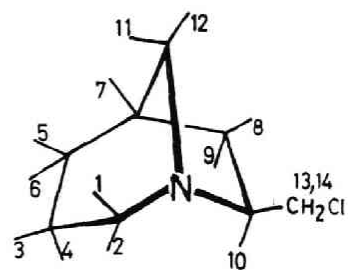
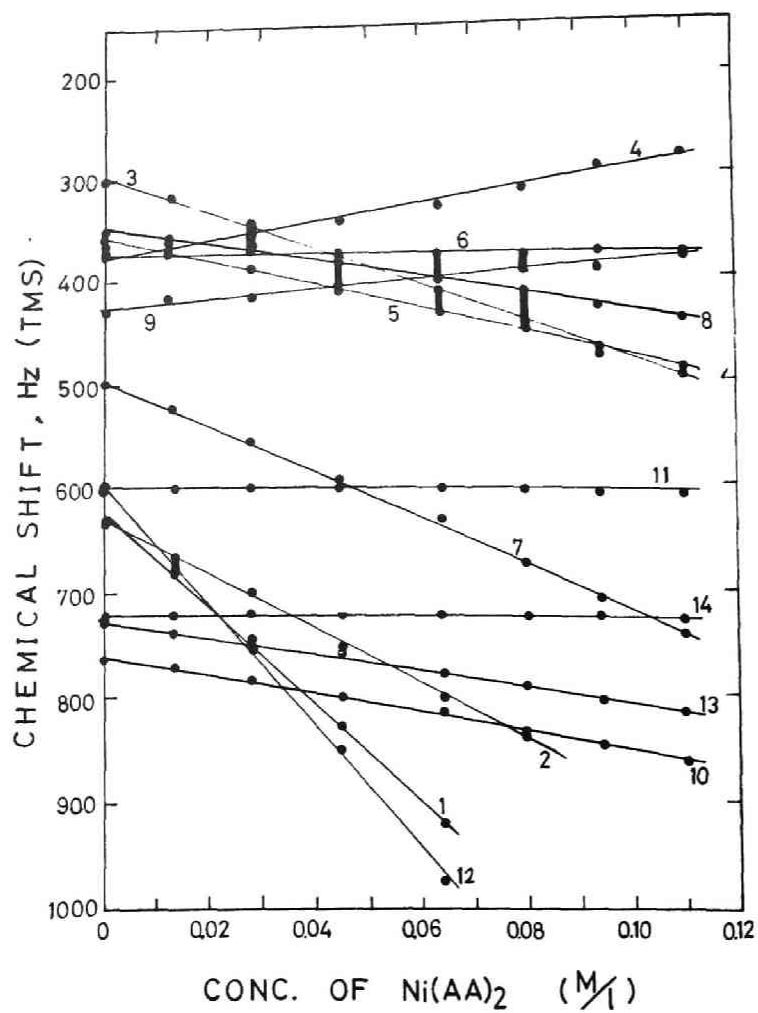
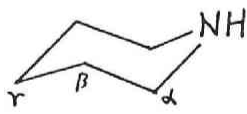
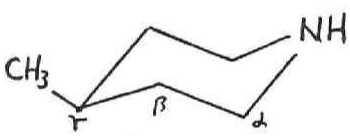
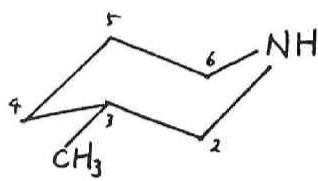
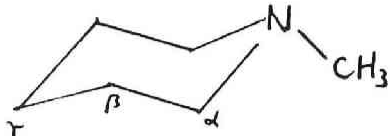


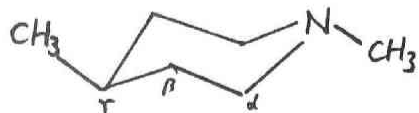
Figure 3. Plots of isotropic paramagnetic ^1H shifts vs. concentration of $\text{Ni}(\text{AA})_2$ for 10.

Table I. Relative ^1H Contact Shifts for Various N-containing
Molecules Complexed with $\text{Ni}(\text{AA})_2^a$

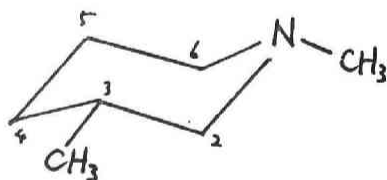
Ligand Molecules	position	chemical shift ^b ^1H (δ)	relative contact sh
Piperidine (1)	α	2.80	-1.00 ^e
	β	1.54	-0.35
	γ		-0.15
4-Methylpiperidine (2)	α { ax	2.58	-1.00 ^e
	eq	3.04	-0.77
	β { ax	1.08	+0.11
	eq	1.62	-0.67
	γ ax	1.45	-0.09
3-Methylpiperidine (3)	α { 2-ax	2.20	-1.00 ^e
	6-ax	2.52	-1.00
	2,6-eq	2.99	-0.64
	β { 3,5-ax	1.50	+0.02 ^c
	5-eq	1.63	—
	γ { ax	1.01	-0.05
	eq	1.77	-0.14
N-Methylpiperidine (4)	α	2.34	-1.00 ^f
	β	1.60	+0.04
	γ	1.42	-0.04

(Table I continued)

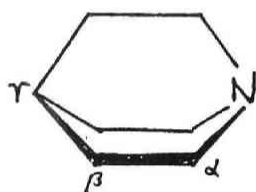
1,4-Dimethylpiperidine (5)	α	ax	1.91	-1.00 ^f
		eq	2.72	-0.38
	β	ax	1.3	+0.09
		eq	1.63	-0.03
	γ	ax	1.36	+0.04



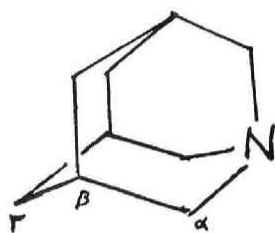
1,3-Dimethylpiperidine (6)	α	2-ax	1.52	-1.00 ^f
		6-ax	1.80	-1.00
		2,6-eq	2.78	-0.36
	β	3,5-ax		+0.08
		5-eq	1.65	-0.07
	γ	eq		+0.08
		ax	0.83	+0.04



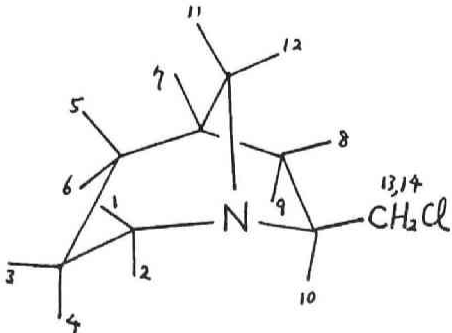
Quinuclidine (7)	α	2.87	-1.00 ^g
	β	1.55	-0.10
	γ	1.76	+0.10



	1-Azaadamantane (8)	α	3.17	-1.00 ^h	
		β	1.71	-0.77	
		γ {	ax	2.00	-0.02
	eq		1.93	-0.30	



(Table I continued)

	1-Aza-7-chloromethyl-bi-	1	2.86	-0.70
	cyclo[3.2.1]octane (10)	2	2.86	-0.34
		3	1.36	-0.24
		4	1.68	+0.11
		5	1.6	-0.12
		6	1.6	-0.11
		7	2.27	-0.31
		8	1.6	-0.17
		9	1.95	+0.04
		10	3.49	-0.11
		11	2.73	-0.01
		12	2.73	-1.00 ⁱ
CH ₂ Cl		13	3.3 ^d	-0.11
		14	3.3 ^d	-0.01

a. Measured in CDCl₃ solution. b. In ppm from TMS. c. A relatively large downfield shift. Because of signal broadening, precise value could not be obtained. d. Two methylene protons were observed separately. As the relative Ni(AA)₂-induced shifts are markedly different each other, the rotation around the C₇-CH₂Cl bond is considered to be forbidden due to the steric hindrance. e. The actual shift is ca. 0.3 ppm per 0.05 M of Ni(AA)₂ in the 10 v/v % solution. f. The actual shift is ca. 0.5 ppm per 0.05 M of Ni(AA)₂ in the 10 v/v % solution. g. The actual shift is 0.4 ppm per 0.01 M of Ni(AA)₂ in the 0.1 M solution. h. The actual shift is 1.2 ppm per 0.01 M of Ni(AA)₂ in the 0.1 M solution. i. The actual shift is 1.0 ppm per 0.05 M of Ni(AA)₂ in the 0.5 M solution.

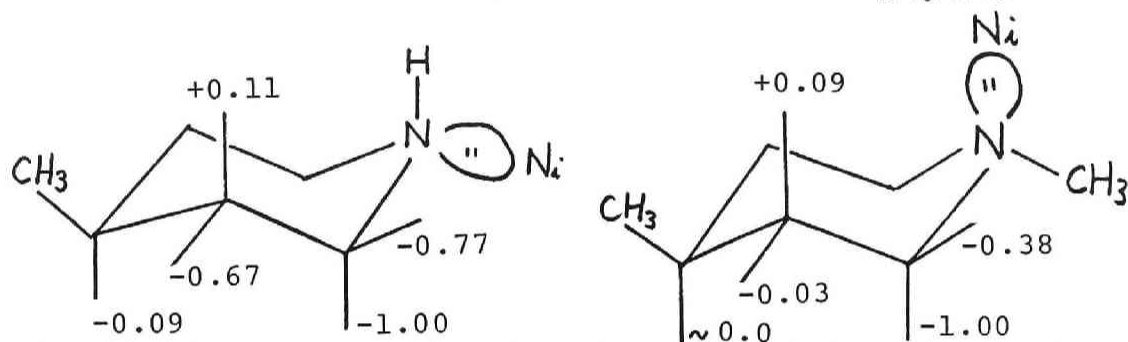
and the minus signs which correspond to the negative and the positive spin densities induced on the ligand proton respectively. In this table, the relative paramagnetic shifts of β and γ protons in 1, where no separated signals of the axial and the equatorial protons are observed, are nearly the average of the shifts of axial and equatorial protons in 2 or 3. This is also the case for N-methylpiperidine (4), as an average of 5 or 6.

It has been well established that the isotropic proton paramagnetic shift in the $\text{Ni}(\text{AA})_2$ system is resulting most dominantly from the Fermi contact shift which is related to the electron spin density distributed on the proton. For piperidine (1), all the ring protons experiences downfield contact shifts, while in N-methylpiperidine (4) β -protons exhibit upfield shifts. This different feature of the contact shift is more apparent in 2 and 5. For 2, the β -equatorial proton shows a large downfield contact shift, while the β -axial one exhibits quite a small upfield contact shift. For 5, on the contrary, the β -equatorial proton experiences a downfield shift and the axial one shows a large upfield shift.

It has been shown^{1a,c,d} that in N-H piperidines the lone pair electrons occupy an equatorial position at least in the complex with $\text{Ni}(\text{AA})_2$, while in N-methylpiperidines the lone pair axial conformer is favorable. Therefore, the different feature of the β -proton contact shifts between N-H and N-methyl piperidine is attributed to the effect of different lone pair orientation. Accordingly, the large

downfield shift for β -equatorial proton in N-H piperidines (1,2,3) and 1-azaadamantane may result from the positive spin density transferred through a "zigzag" path of the σ -skeleton. The downfield and upfield contact shifts in 1 and 4, in which the β -proton signal is observed as an average of the resonances of axial and equatorial protons, also reflect the specific shifts for β -protons due to the different lone pair orientation.

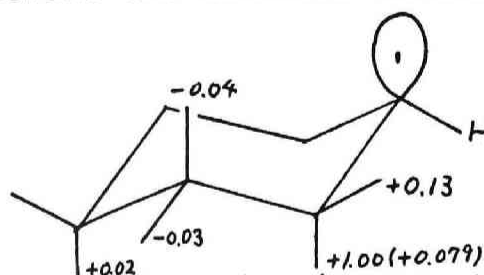
Thus, conformational dependence of the ^1H contact shift due to the different lone pair orientation is shown below. In a lone pair equatorial conformer (1,2,3,8), the



downfield contact shifts for the equatorial protons attenuate slowly through the σ -skeleton, but rapidly for the axial protons. While in a lone pair axial conformer, the contact shifts attenuate rapidly for both the equatorial and the axial protons and this attenuation is more prominent for the equatorial protons than for the axial ones. In this conformer the substantial upfield contact shift for the β protons is quite characteristic. In both cases the β proton separated by "zigzag" σ -bonds from the nitrogen-metal bond exhibits greater contact shift than that separated by "folded" bonds.

These stereospecific features of ^1H contact shifts are plausibly reproduced by the molecular orbital calculations

Hand-drawn skeletal structure of 2,3,4-trimethylpentane. The structure is labeled with handwritten partial charges: -0.13 on the central carbon (C3), $+0.43$ on the carbon to its left (C2), $+0.10$ on the carbon to its right (C4), $+0.72$ on the carbon to the right of C4, and $+1.00 (+0.017)$ on the terminal carbon to the right. A hydrogen atom is explicitly drawn above the terminal carbon on the right.



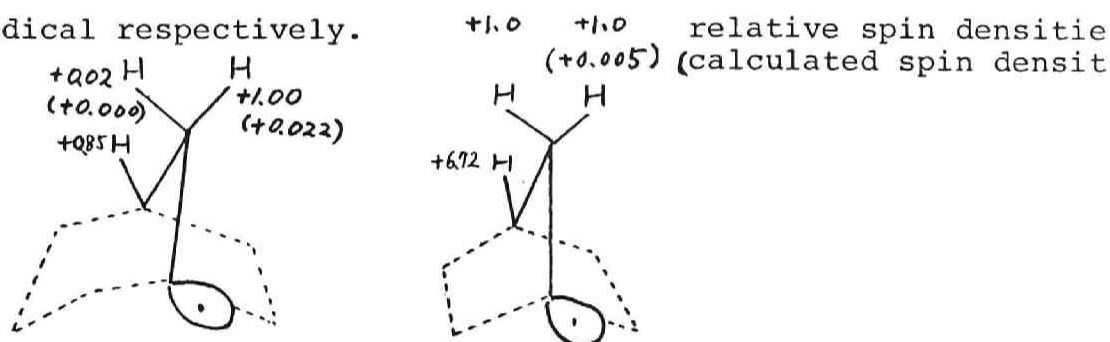
of ^1H contact shifts and those of calculated spin densities is plausible.

From above results, one can see the typical behavior of the electron spin distribution on the protons through the σ -skeleton and the mechanism of electron spin transmission. Electron spin may reach the ligand protons by two different mechanisms, spin delocalization (SD) and spin polarization (SP) as schematically represented below.



- 42 -

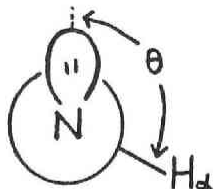
downfield contact shifts of all the protons, but the spin polarization mechanism leads to alternation and attenuation of the shifts along the σ bonds. In the actual cases, these two mechanisms may be simultaneously operating. The upfield or downfield contact shift of γ -protons in piperidines depends on whether the SP or SD mechanism is dominant. It should be noted that in 9 the α -proton contact shifts are quite different in magnitude each other. For example, the contact shift for the α -proton attached to the bridgehead carbon is about fifty times larger than that for H_{11} . This is also reproduced by INDO calculations of the spin densities for the corresponding hydrocarbon σ -radical. For a model of this radical we examined propyl radical^{14,15} with planar and nonplanar geometries which constitutes a part of 1-bicyclo[3.2.1]heptyl radical and 1-bicyclo[2.2.1]hexyl radical respectively.



The calculated spin densities for the nonplanar model agree well with the observed results. It is therefore recognized that proton contact shifts are remarkably sensitive to the molecular configuration.

It has already been shown that in piperidine the α -axial proton in the lone pair axial conformer senses positive spin density three times as large as the α -equatorial

proton. Accordingly, the large shift of H_{12} in **9** is due to the planar cis ($\theta = 180^\circ$) conformation, and the abnormally



small shift for H_{11} is due to the conformation in which the angle (θ) between the lone pair orientation and the C-H bond is close to 90° . Consequently, one can find the trend of ^1H nmr contact shifts in H-C-N skeleton correspond well to the " $\cos^2$ rule" well established for vicinal H-H coupling constant.¹⁶

In order to gain further insight into such a relation, we performed calculation of electron spin densities (ρ_{UHF}) on the protons in ethyl σ -radical which corresponds to the H-C-N $\odot$ fragment complexed with $\text{Ni}(\text{AA})_2$. In Figure 4 is shown the angular dependence of the induced electron spin density (ρ_{UHF}) on the C_2 -proton. The geometry of ethyl radical was taken as C-C = 1.54 Å, C-H = 1.09 Å and any bond angle = $109^\circ 28'$. Inspection of this figure shows that the value of ρ_{UHF} follows the angular dependence of the " $\cos^2\theta$ rule." In this figure, ρ_{UHF} is separated theoretically into the two contributions of spin transmission mechanism, SP and SD, based on the method proposed by Nakatsuji et al.¹⁷ It is worthnoting that the angular dependence of ρ_{SD} as well as that of ρ_{SP} resembles to the " $\cos^2\theta$ rule." This is the reason why the relative values of isotropic hyperfine coupling constants agree well with those of nuclear spin coupling constants, which is determined by the spin polarization mechanism.

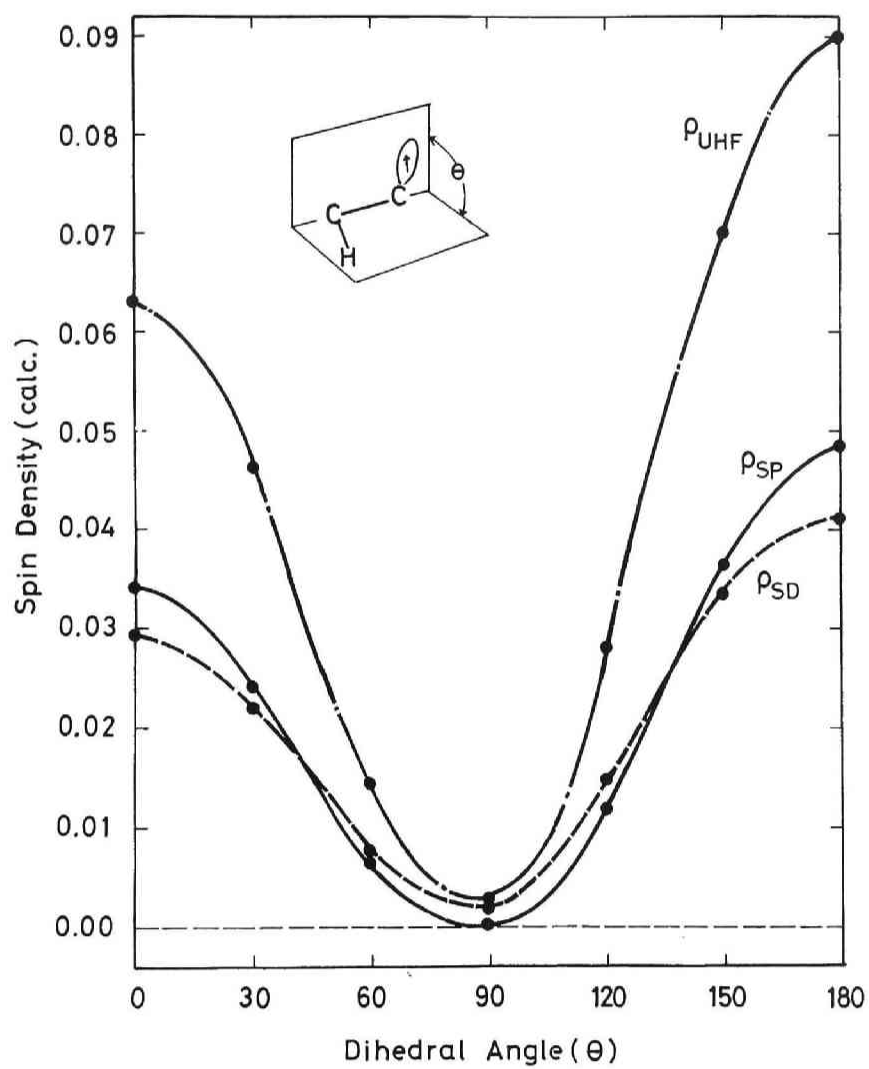
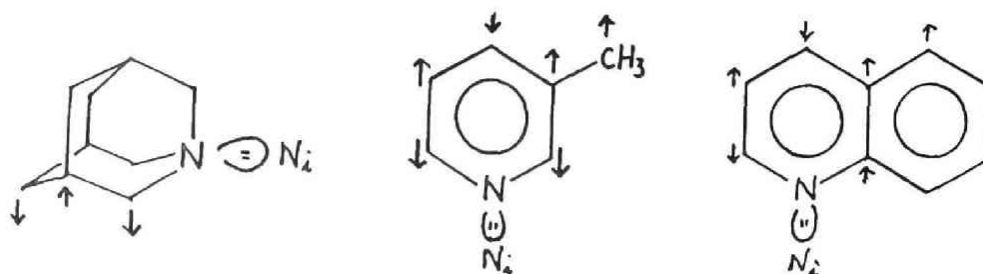


Figure 4. Angular dependence of ρ_{UHF} , ρ_{SP} , ρ_{SD} induced on C₂-H proton (INDO-UHF-MO).

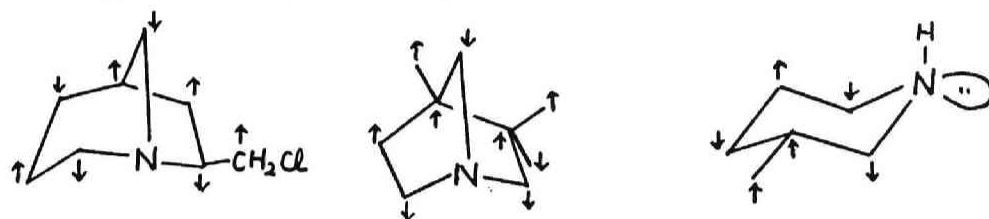
^{13}C Contact Shift and Mechanism of Intramolecular Spin Transmission through the σ -Skeleton. In the previous section, we studied stereospecific ^1H contact shifts for six-membered amines. We concluded that these contact shifts are associated with spin densities distributed on the proton and are characteristic of axially or equatorially oriented nitrogen lone pair and of configuration or conformation of the carbon skeleton. In order to gain further insight into stereospecific mode of electron spin distribution and the mechanism of intramolecular spin transmission through the σ -skeleton, we have studied here ^{13}C contact shift for 1-azanorbornene derivative and 1-azabicyclo[3.2.1]octane derivative.

We have already reported in the previous papers^{2c,d} that the $\text{Ni}(\text{AA})_2$ -induced ^{13}C contact shifts for piperidine, 4-methylpiperidine, *N*-methylpiperidine, 1,4-dimethylpiperidine, quinuclidine and 1-azaadamantane. The alternation in sign and attenuation in magnitude of the ^{13}C contact shifts have been obtained in these compounds. For example, in 1-azaadamantane with a rigid chain conformation, $\text{Ni}(\text{AA})_2$ -induced spin densities on the carbon atoms were alternating in sign along the bond as is always the case for piperidine derivatives and pyridine.^{2c,d} Such an alternation of ^{13}C contact shifts has been attributed to the preferential contribution of the spin polarization mechanism. In contrast to this, nonalternation of the sign of the spin density was encountered for the



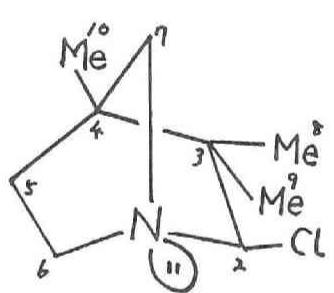
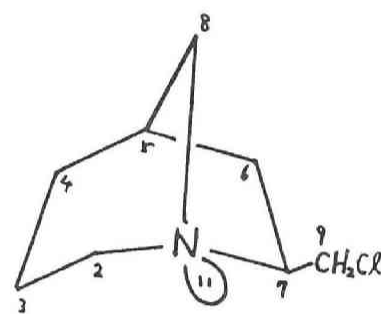
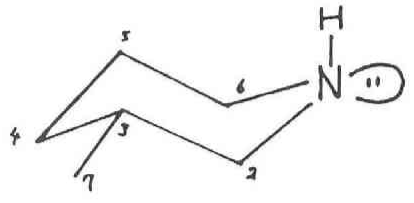
γ -carbons such as the methyl carbon of β -picoline¹⁸ and the C_5 -carbon of quinoline.^{2e} The positive spin density on these γ -carbon atoms could not be expected by inspection of the normal mode of spin transmission along the $N-C_\alpha-C_\beta-C_\gamma$ skeleton with alternating signs. In order to further examine such a stereospecific feature of electron spin transmission through the σ -skeleton, in Table II are presented the ^{13}C contact shifts for 3,3,4-trimethyl-2-chloro-1-azabicyclo[2.2.1]heptane (9), 7-chloro-1-azabicyclo[3.2.1]octane (10), and 3-methylpiperidine (3) which involve $N-C_\alpha-C_\beta-C_\gamma$ skeletons with different figures of arrangement.

In these compounds, the contact shifts for various γ -carbons are quite different each other. The γ -carbons (C_4) in 10, and C_9 in 9 experience upfield shifts (negative spin densities). On the other hand, the downfield shift for the γ -carbon was encountered for C_8 and C_{10} in 9, which are lying on the semi-planar or planar ziazag arrangement of the $N-C_\alpha-C_\beta-C_\gamma$ skeleton.¹⁹ This nonalternating nature of the $Ni(AA)_2^-$ induced spin densities is quite similar to the case of



β -picoline¹⁸ and quinoline.^{2e} It follows, therefore, that when the $N-C_\alpha-C_\beta-C_\gamma$ arrangement is planar or semiplanar zigzag, then the γ -carbon senses the positive spin density, while negative spin is induced for the non-planar arrangement (C_γ of piperidine, N-methylpiperidine, and 1-azaadamantane,

Table II. ^{13}C Contact Shifts for Azacyclic Molecules

Molecules	position	^{13}C chemical shift ^a (ppm)	^{13}C contact shift ^b (relative value)
 (9)	2	92.8	+0.48
	3	49.5 ^c	- d
	4	45.0 ^c	- d
	5	30.5	-0.66
	6	51.3	+1.00 ^e
	7	58.5	+0.37
	8	21.0	-0.13
	9	20.2	+0.05
	10	10.1	-0.14
 (10)	2	56.3 ^c	+1.00 ^f
	3	20.1	-0.65
	4	30.7	+0.08
	5	36.4	-0.84
	6	36.4	-0.98
	7	64.8	+0.25
	8	59.1 ^c	+0.78
	9 (CH ₂ Cl)	48.5	-0.55
 (3)	2	55.0	+1.00 ^g
	3	32.7	-1.2
	4	34.3	+0.11
	5	27.3	-1.2
	6	47.3	+0.94
	7	20.2	-0.23

(Table II continued)

a. Chemical shifts are given in ppm from TMS. b. The plus and minus signs denote the upfield and downfield contact shifts respectively. The relative shifts were obtained from the slope of the linear plot of the observed contact shift vs. the concentration of added $\text{Ni}(\text{AA})_2$. c. The signal assignment is somewhat uncertain. d. The signal broadening was too great to get the precise magnitude of the relative downfield contact shift. e. The actual shift is 7 ppm per 0.02 M of $\text{Ni}(\text{AA})_2$ in the 0.5 M CDCl_3 solution. f. The actual shift is 1.0 ppm per 0.08 M of $\text{Ni}(\text{AA})_2$ in the 3 M CDCl_3 solution. g. The actual shift is 5 ppm per 0.05 M of $\text{Ni}(\text{AA})_2$ in the 50 v/v % CDCl_3 solution.

C_4 of 10, and C_9 of 9) as is depicted below.

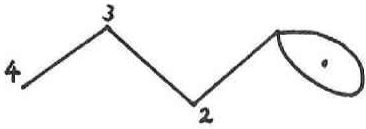
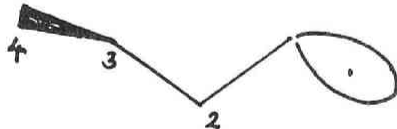
"planar-zigzag" arrangement "non-planar" arrangement



Such a trend is also the case for 3-methylpiperidine (3) in which the lone pair electrons preferentially occupy the equatorial position. The C_4 -carbon in the non-planar arrangement feels the upfield contact shift, whereas the C_7 -methyl carbon in the planar zigzag conformation senses the downfield shift. The specific mode of electron spin distribution (nonalternation) in the planar zigzag skeleton may allow us to expect a "through-space" spin transmission which could produce positive spin density on the γ -carbon due to the direct nitrogen- C_β interaction. The study on such a stereospecific mode of electron spin transmission is expected to shed light on the neighbouring σ -bond participation in the σ -electronic system.

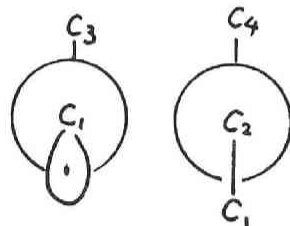
In order to gain further insight into this stereospecific spin distribution, we studied INDO-UHF MO calculations of electron spin densities distributed on the carbon atoms for n-butyl σ -radical as a model of $N-C_\alpha-C_\beta-C_\gamma$ fragment complexed with $Ni(AA)_2$. The experimental trend of alternating and nonalternating spin densities was plausibly reproduced by this model calculations for non-planar and planar n-butyl σ -radicals respectively (see Table III). It is particularly to be noted that on the C_4 carbon negative spin is induced in the non-planar arrangement and that positive spin is induced

Table III. The Calculated Spin Densities with and without
"Through-Space" Interaction

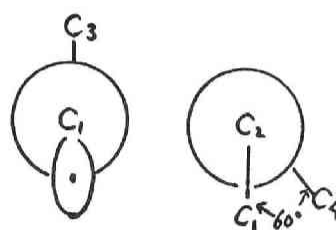
n-Butyl σ -Radical	position	"through-space" +"through-bond"	"through-bond" only
		c_{2s}^a	c_{2s}^b
 (planar zigzag) ^d	C ₂	-0.0085 (-1.00) ^c	-0.0085 (-1.00) ^c
	C ₃	+0.0147 (+1.25)	+0.0160 (+1.89)
	C ₄	+0.0009 (+0.11)	-0.0000 (-0.00)
 (non-planar) ^d	C ₂	-0.0084 (-1.00)	-0.0083 (-1.00)
	C ₃	+0.0145 (+1.72)	+0.0156 (+1.88)
	C ₄	-0.0002 (-0.03)	-0.0004 (-0.05)

a. Spin density on the 2s AO of the carbon atom obtained by the usual calculation. b. Obtained by the modified calculation. c. Relative values are given in parenthesis. d. Tetrahedral configuration at each carbon. The conformation is as shown below.

"planar zigzag"



"non-planar"

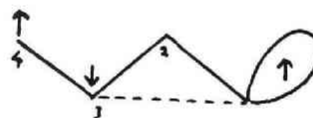
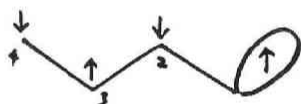


in the planar zigzag conformation (Table III), in accord with the experimental trend. To further substantiate the direct "through-space" spin transmission for the planar zigzag model, we then neglected the Fock's matrix elements between the C_1 -carbon (the radical center) and C_3 in the INDO-UHF MO calculations.²⁰ This procedure, which does not take into account C_1 - C_3 "through-space" interaction, yields alternating signs of the calculated spin densities on the carbon 2s orbitals along the σ -bonds, and results in the negative spin density on the C_4 -carbon (see Table III). The signs of calculated spin densities in the carbon with and without through-space interaction are schematically depicted below.

"through-space
+through-bond"

"through-bond" only

"through-space" only

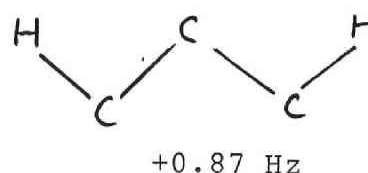
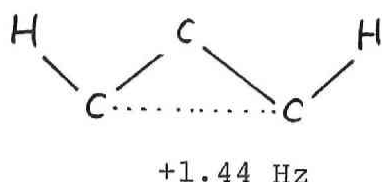


Inclusion of the C_1 - C_3 interaction is therefore responsible for positive spin densities on C_4 . It is also to be noted that the C_1 - C_3 interaction causes a small decrease in the positive spin density on C_3 (Table III), presumably due to contribution of negative spin density induced on C_3 . These through-space effects are explainable in terms of spin transmission by the through-space spin polarization mechanism in the mode of $C_1(\uparrow) \cdots C_3(\downarrow) \cdots C_4(\uparrow)$. Contrary to this, neglect of C_1 - C_3 direct interaction hardly affects the mode of electron spin transmission for the non-planar model (see Table II). We conclude, therefore, from these results that in the planar conformation the "through-space" spin transmission

contributes substantially to the stereospecific spin distribution.²¹

This specific feature of electron spin distribution in the planar zigzag arrangement may also be important in the interpretation of the stereospecificity of the long-range H-H spin coupling constant across four σ -bonds ($^4J_{H-H}$) in the "W" letter arrangement. The value of $^4J_{H-H}$ in this skeleton has been reported to be positive and amounts to 1~2 Hz.^{19,22,23} This large positive value of the long range H-H coupling constant is explainable by the above stereospecific through-space spin transmission in the following way. We calculated the long range H-H coupling constant $^4J_{H-H}$ using Pople's finite perturbation theory,²⁴ in which J_{H-H} is obtained from the spin density induced on H_i when spin density is finitely placed at H_j by introducing slightly different value of Fock matrices for α and β spin orbitals. Here we employed two different ways of INDO UHF finite perturbational calculations of $^4J_{H-H}$ with and without C_1-C_3 "through-space" interaction in a similar way stated above. This through-space interaction corresponds to well-documented "rear side lobe interaction" in the preferable H-H coupling path of W letter arrangement. The calculated results are shown below. This may allow us to see that inclusion of the

"through-space+through-bond"	"through-bond" only
------------------------------	---------------------



C_1 --- C_3 direct interaction (F_{13}) enhances substantially positive value of ${}^4J_{H-H}$ and that "through-space" interaction plays also an important role in the long range H-H coupling associated with the planar zigzag arrangement.²³ The positive value of meta H-H coupling in benzene may be also interpreted along this line.

Summarizing the above results and discussion, we can conclude that $Ni(AA)_2$ -induced nmr contact shifts could serve as a quite sensitive probe for elucidation of modes and mechanisms of intramolecular electron spin transmission through the σ -bonded skeleton.

References and Notes

- (1) A part of our systematic investigation on nmr contact shift studies for the σ -bonded molecules.
- (2) (a) T. Yonezawa, I. Morishima, and Y. Ohmori, J. Amer. Chem. Soc., 92, 1267(1970); (b) I. Morishima, T. Yonezawa, and K. Goto, *ibid.*, 92, 6651(1970); (c) I. Morishima, K. Okada, M. Ohashi, and T. Yonezawa, J. Chem. Soc. Chem. Commun., 33(1971); (d) I. Morishima, K. Okada, T. Yonezawa, and K. Goto, J. Amer. Chem. Soc., 93, 3922(1971); (e) I. Morishima, K. Okada, and T. Yonezawa, *ibid.*, 94, 1425(1972); (f) I. Morishima and K. Yoshikawa, *ibid.*, 97, 2950(1975).
- (3) The observed shifts in $\text{Ni}(\text{AA})_2$ complexes are caused only by contact interaction; references (2), (17) and references therein.
- (4) $\text{Ni}(\text{AA})_2$ -induced ^1H and ^{13}C contact shift study appears to be relevant for elucidation of the mode of intramolecular electron spin distribution because the contact shift is quite sensitive to both quantity and sign of the induced spin density. It appears to excell the esr study especially in its availability of the ^{13}C cocontact shift which is related to spin density on the carbon skeleton. In this sense $\text{Ni}(\text{AA})_2$ -induced contact shift is referred to as a "spin probe" for elucidation of the electronic and geometrical structure of the σ -bonded molecules.
- (5) G. M. Zhidomirov and N. D. Chuvylkin, Teor. Eksp. Khim., 6, 254(1970); G. M. Zhidomirov, P. V. Schastnev, and N. D. Chuvylkin, Zr. Strukt. Khim., 11, 502(1970); (c) N. D. Chuvylkin, R. Z. Sagdeev, G. M. Zhidomirov, and Yu. N. Molin,

Teor. Eksp. Khim., 7, 612(1971); R. Z. Sagdeev and Yu. N. Molin, Chem. Phys. Lett., 5, 471(1970).

(6) M. S. Sun, F. Grein, and D. G. Brewer, Can. J. Chem., 50, 2626(1972).

(7) W. T. Dixon, Mol. Phys., 11, 601(1966).

(8) M. Barfield and B. Chakrabarti, Chem. Rev., 69, 757(1969).

(9) J. W. McIver, Jr. and G. E. Maciel, J. Amer. Chem. Soc., 93, 4641(1971).

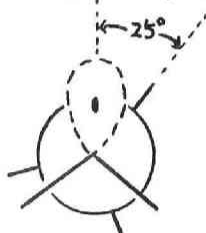
(10) I. Morishima and T. Yonezawa, J. Chem. Phys., 54, 3238(1971).

(11) Z. Luz, J. Chem. Phys., 48, 4186(1968).

(12) H. T. Clarke, H. B. Gillespie, and S. Z. Weiss Haus, J. Amer. Chem. Soc., 55, 4571(1933).

(13) I. Morishima, K. Yoshikawa, K. Okada, T. Yonezawa, and K. Goto, J. Amer. Chem. Soc., 95, 165(1973).

(14) In the MO calculation, all the bond angles were tetrahedral. The dihedral angle in the model of 1-bicyclo[3.2.1]octyl radical was taken to be 25° , which is assumed from the molecular model of 10.



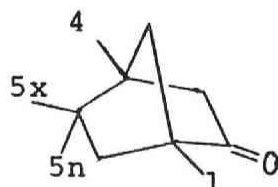
(15) Similar MO calculation for 1-propyl σ radical have been reported; G. R. Underwood, V. L. Vogel and Jo-Anna Iorio, Mol. Phys., 25, 1093(1973).

(16) M. Karplus, J. Chem. Phys., 30, 11(1959).

(17) (a) T. Yonezawa, H. Nakatsuji, T. Kawamura, and H. Kato, Chem. Phys. Lett., 2, 454(1968); J. Chem. Phys., 51, 669(1969);

Bull. Chem. Soc. Japan, 42, 2437(1969). (b) H. Nakatsuji, H. Kato, and T. Yonezawa, J. Chem. Phys., 51, 3175(1969).
 (18) D. Doddrell and J. D. Roberts, J. Chem. Phys., 92, 6839(1970).

(19) Similar experimental trend of H-H coupling constants in norcamphor has been reported. Coupling constants are;



$J_{1,4} = +1.17$, $J_{1,5x} = +0.15$, $J_{1,5n} = -0.30$. It is noticeable that $J_{1,4}$ and $J_{1,5x}$ are positive, which is in contrast with the negative value of $J_{1,5n}$; J. L. Marshall and S. R. Walter, J. Amer. Chem. Soc., 96, 6358(1974).

(20) A referee pointed out that in a SCF theory neglecting the Fock matrix elements would modify the "through-bond" contribution. In order to avoid such an influence, the neglect has been carried out after the conversion of the normal SCF calculations. Therefore, the modification of the "through-bond" contribution is considered to be minimum.

(21) Recently Kawamura et al. suggested, based on the esr study, that the odd electron is delocalized onto the bridgehead atom through a "through-space" mechanism in the case of the 1-norbornyl radical; T. Kawamura, M. Matsunaga, and T. Yonezawa, J. Amer. Chem. Soc., 97, 3235(1975).

(22) See for example, L. M. Jackmann and Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd Edit., chap. 4, Pergamon Press, Oxford, 1969.

(23) From the MO calculations, Barfield et al. concluded that

the substantial positive value for propanoic coupling in "W" conformation arises from a direct mechanism which overcomes a negative indirect mechanism; M. Barfield, A. M. Dean, C. J. Fallick, R. J. Spear, S. Sternhell, and P. W. Westerman, J. Amer. Chem. Soc., 97, 1482 (1975).

(24) J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, J. Chem. Phys., 49, 2960, 2965 (1968).

CHAPTER 5

Some Aspect on the Electronic and Structural Effects on the ^{13}C Contact Shifts for the σ -Bonded Molecules

Abstract: Carbon-13 nmr contact shifts induced by nickel acetylacetonate ($\text{Ni}(\text{AA})_2$) have been observed for various N-heterocyclic compounds in order to elucidate the manner of the stereospecific electron spin transmission through the σ -bonded skeleton. It is revealed that the substituent at the α -carbon atom affects quite sensitively the mode of the carbon-13 contact shifts. Such an experimental trend is discussed in relation to the change in the electronic structure of ligands or in the metal-ligand bonding, which is caused by the introduction of substituents. It is also found that the hybridization of the nitrogen lone pair electrons in ligand molecules play an important role in the manner of intramolecular electron spin transmission. These results are discussed with the aid of molecular orbital calculations of electron spin densities.

We are currently interested in stereospecificity of the mode of electron spin distribution through the carbon skeleton in the σ -bonded molecules. We have previously reported the conformational or geometrical dependence of proton^{1,3} and carbon-13^{2,3} contact shifts for N-heterocyclic molecules complexed with paramagnetic nickel acetylacetonate ($\text{Ni}(\text{AA})_2$). In these studies, it has been revealed that these contact shifts are associated with electron spin densities distributed on the proton and carbon atoms and are characteristic of axially or equatorially oriented nitrogen lone pair, of chair or boat, and of "zigzag" or "folded" conformation of the carbon skeleton. Such a stereospecific feature of proton and carbon-13 contact shifts has been discussed in relation to the mode of electron spin distribution through the carbon skeleton with the aid of molecular orbital calculations of spin densities.^{2c,d,3}

Recently there have been a great deal of paramagnetic shift reagent studies for organic molecules. Lanthanide shift reagents have proved to be quite useful to determine the complicated molecular structure, since the shifts induced by the lanthanide shift reagents have been believed to be predominantly of pseudocontact origin. It has recently been pointed out⁴ that lanthanide induced shifts are hardly interpreted only by the pseudocontact model, especially for carbon-13 nmr paramagnetic shifts, and that there should be a sizable contact contribution. However, the debate over this problem has remained open to further studies. Therefore, it seems also important from this point of view to delineate the mode of the

^{13}C contact shifts for the various carbon skeleton with recourse to the paramagnetic shifts with only contact shift origin.

In the present study we will show the importance of the effects of substituent and the hybridization of the nitrogen lone pair electrons in ligand molecules on the features of ^{13}C contact shifts through the σ -skeleton. These structural effects on the mode of electron spin distribution through the carbon skeleton should be taken into account in addition to the conformational or configurational effect when one is concerned with the ^{13}C contact shifts as a probe for determination of geometrical or electronic structure of organic molecules. The paramagnetic system examined here are the complexes of $\text{Ni}(\text{AA})_2$ with various N-containing molecules. As the ligand molecules we have chosen piperidines (with sp^3 lone pair), pyridines, aziridines, oxime, imine (with sp^2 lone pair), thiazole, N-methylimidazole (with the hybridization between sp^2 and sp), and benzonitrile (with sp lone pair).

It has been shown that the isotropic ^{13}C paramagnetic shift in $\text{Ni}(\text{AA})_2$ complexes is caused mainly by the contact interaction which is related to the electron spin density on the carbon atom. The ^{13}C contact shift is expressed by the equation,⁵

$$\frac{\Delta H}{H} = -a_N \frac{\gamma_e}{\gamma_N} \frac{g\beta S(S+1)}{3kT} \quad N = ^{13}\text{C}$$

where the hyperfine coupling constant a_N is given by

$$a_N = \frac{4\pi}{3} g\beta\gamma_N \hbar \left\langle S_z \right\rangle^{-1} \left| \psi(r_{N_s})^2 \right| \rho_{N_s}$$

and ρ_N is the unpaired electron spin density on the ^{13}C atomic orbital and the other symbols have their usual meanings. From this relationship the downfield and upfield shifts are obtained when positive and negative spin densities are induced on the ^{13}C s orbital.

Experimental Section

(a) Materials. 2-Methylpiperidine, α -picoline, 2-chloro-pyridine, 2-bromopyridine, 2-ethylpyridine, acetoxime, thiazole, N-methylimidazole, and benzonitrile are commercially available. These compounds were dried over sodium hydroxide and distilled. 1,2-Dimethylpiperidine was prepared by the N-methylation of 2-methylpiperidine. N-Ethylacetoxime was prepared by the method of Campbell et al.⁶ 2-Methylaziridine and 2,3-dimethylaziridine were synthesized following the method of Cairns et al.⁷

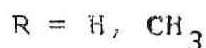
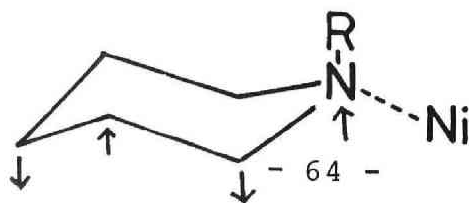
(b) ^{13}C Nmr Measurement. Completely proton decoupled ^{13}C nmr spectra were obtained at 25.15 MHz on a JEOL-PFT-100 system. After the 100~10000 accumulations of the free induction decay induced by the 45° pulses with the repetition of 2~4 sec, the Fourier transformed spectra were recorded. Samples were made in CDCl_3 solution in 8 mm ϕ sample tubes. The spectra were taken at room temperature (24°C) in the presence of varying amounts of $\text{Ni}(\text{AA})_2$. The ^{13}C chemical shifts were measured with respect to an internal TMS.

(c) ^{13}C Spectral Assignments. The experimental values of the ^{13}C chemical shift data are summarized in Table I for the N-containing molecules used in this study. Each carbon signal of 2-methylpiperidine,⁸ 1,2-dimethylpiperidine,⁸ α -picoline,⁸ 2-bromopyridine,⁹ benzonitrile,⁹ acetoxime,⁹ thiazole¹⁰ and N-methylimidazole¹¹ have already been assigned. With the aid of chloro-substitution parameters for benzene,¹² signal assignment of 2-chlorobenzene is feasible. 2-Methylaziridine and 2,2-dimethylaziridine can be readily assigned referring the half-decoupled spectra.

Results and Discussion

(a) General Features of ^{13}C Contact Shifts. The perturbation of the ^{13}C nmr spectrum by the addition of $\text{Ni}(\text{AA})_2$ is exemplified for 2-ethylpyridine in Figure 1. Figure 2 gives an example of the linear plot for 2-ethylpyridine. The various carbon resonances are shifted from their normal diamagnetic values by an amount which is proportional to the concentration of added $\text{Ni}(\text{AA})_2$. This implies that the exchange of ligand between complexed and uncomplexed sites are time averaged. Thus the ^{13}C resonances of the ligand shift toward the resonance position of the complex as $\text{Ni}(\text{AA})_2$ is added to the diamagnetic solution and the relative values of these paramagnetic shifts are of significant in the present study. The relative values for various carbons in a ligand molecule were obtained from the slopes of the linear plot of the paramagnetic shift vs. the concentration of $\text{Ni}(\text{AA})_2$, with the value for the α -carbon normalized to 1.00.

The relative ^{13}C contact shifts for various ligand molecules are summarized in Table I. The plus and minus signs of these values denote the upfield and downfield shifts which correspond to the negative and positive spin densities, respectively, induced on the ligand carbon s atomic orbital. As shown in Table I and reported already in the previous papers^{2c,d} for piperidines, $\text{Ni}(\text{AA})_2$ -induced ^{13}C contact shifts alternate in sign along the σ -skeleton.¹³ The alternating ^{13}C contact shifts suggest the relative importance



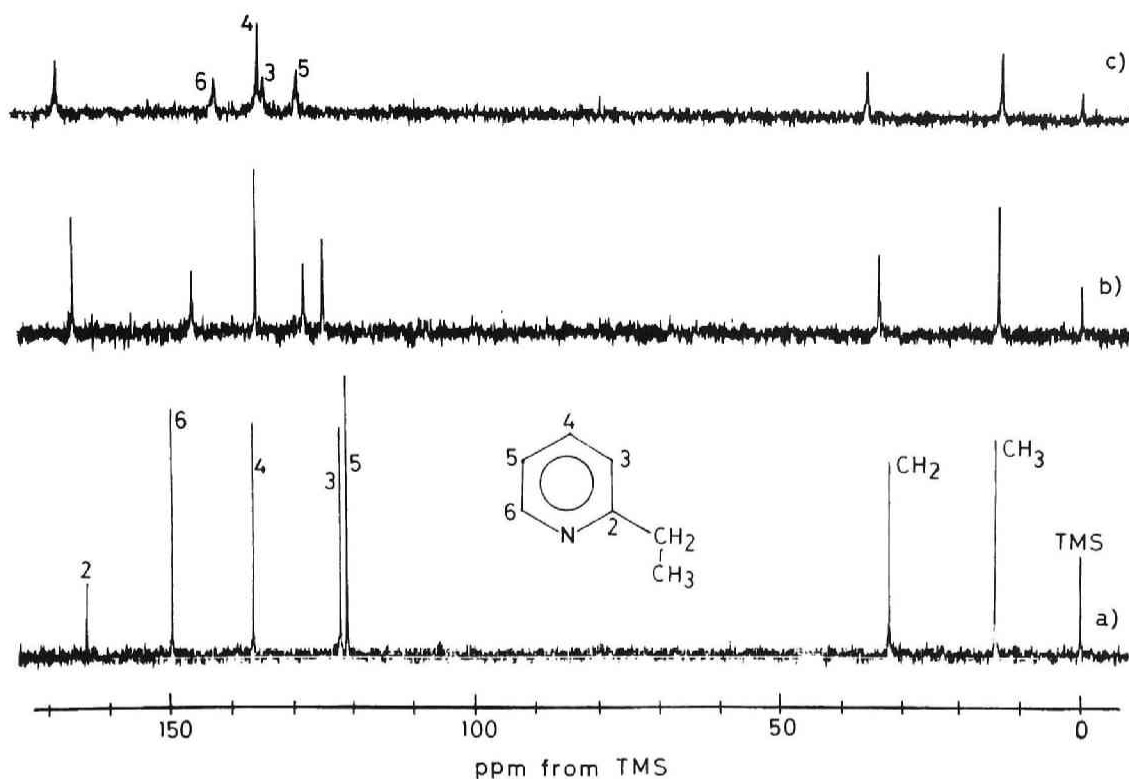


Figure 1. ^{13}C NMR spectra of 2-ethylpyridine in CDCl_3 (a) and in CDCl_3 containing varying amounts of $\text{Ni}(\text{AA})_2$ (b and c) (at 25.1MHz).

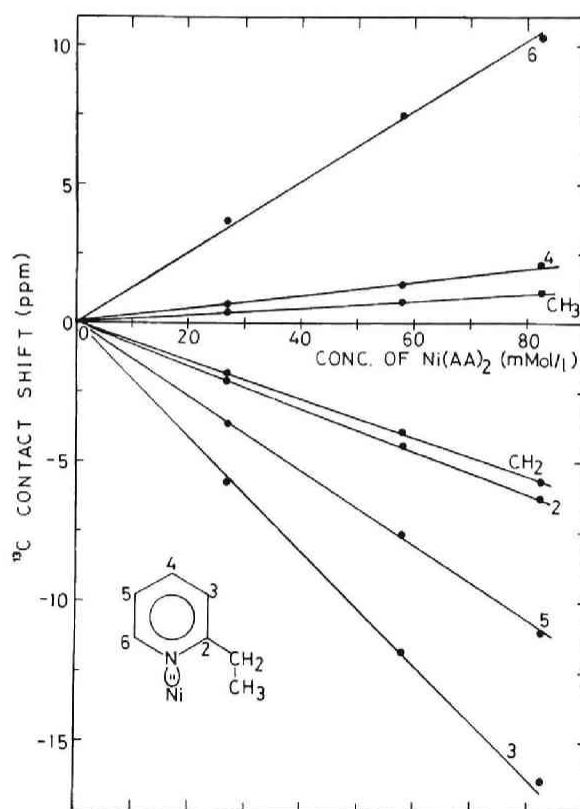
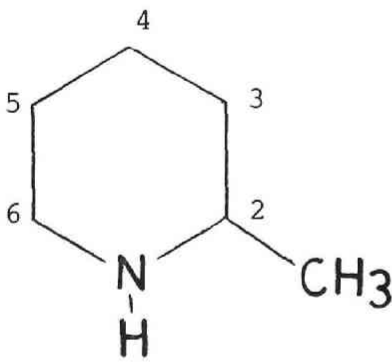
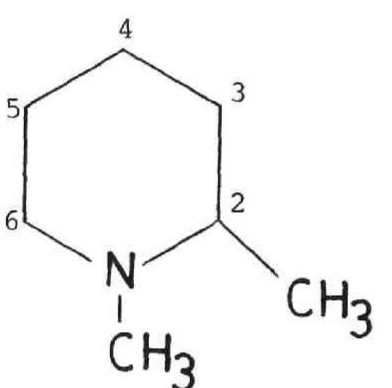
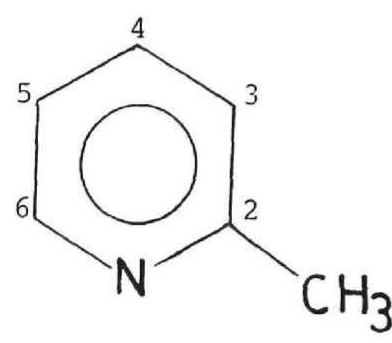


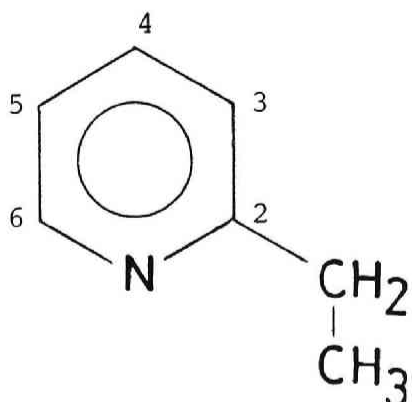
Figure 2. Plots of isotropic paramagnetic ^{13}C shifts vs. concentration of $\text{Ni}(\text{AA})_2$ for 2-ethylpyridine.

Table I. Relative ^{13}C Contact Shifts for Various N-Containing Molecules Complexed with $\text{Ni}(\text{AA})_2$

Molecules	position	$\delta^{13}\text{C}$ (ppm from TMS)	Relative ^{13}C Contact Shifts ^a
2-Methylpiperidine	2	52.9	+0.75
	3	35.4	-0.16
	4	25.8	+0.47
	5	26.9	-0.49
	6	47.8	+1.00 ^b
	CH_3	23.8	+0.30
1,2-Dimethylpiperidine	2	59.5	+0.65
	3	35.3	-0.56
	4	25.2	+0.12
	5	26.8	-0.42
	6	57.5	+1.00 ^c
	N-CH_3	43.5	+1.26
	2-CH_3	20.7	0.0
α -Picoline	2	157.9	-0.49
	3	122.4	-1.12
	4	135.3	+0.10
	5	120.0	-1.66
	6	148.7	+1.00 ^d
	CH_3	23.8	-0.59

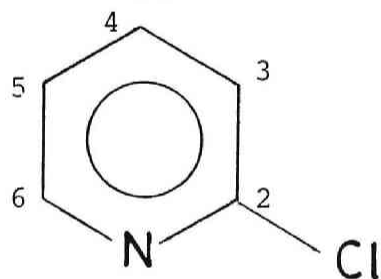
(Table I continued)

2-Ethylpyridine



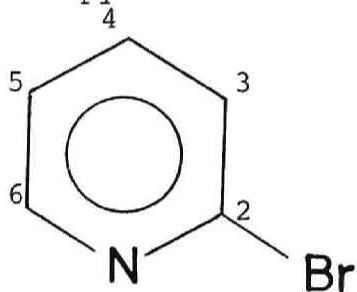
2	163.5	-0.59
3	122.0	-1.53
4	136.1	+0.20
5	120.9	-1.00
6	149.4	+1.00 ^e
CH ₂	31.5	-0.50
CH ₃	13.9	+0.11

2-Chloropyridine



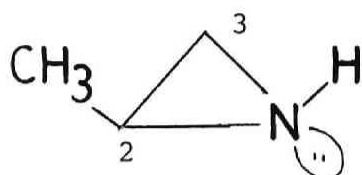
2	151.7	+0.59
3	124.4	-0.90
4	138.8	+0.05
5	122.4	-0.82
6	149.6	+1.00 ^e

2-Bromopyridine



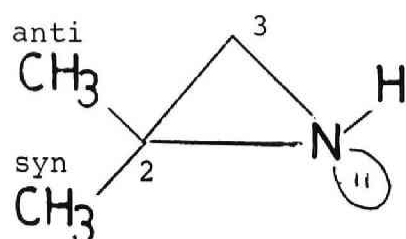
2	142.0	+0.68
3	128.0	-0.88
4	138.5	+0.05
5	122.7	-1.01
6	150.0	+1.00 ^e

2-Methylaziridine



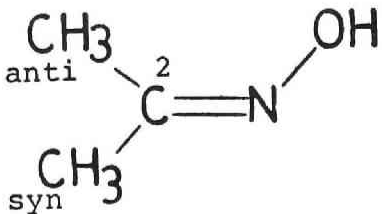
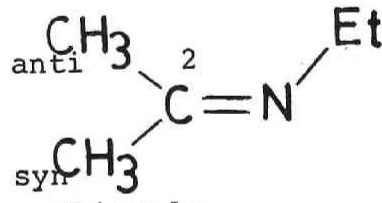
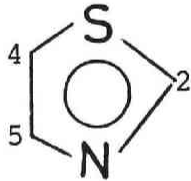
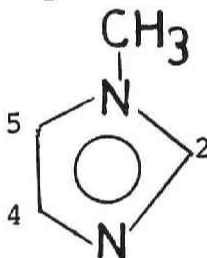
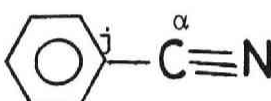
2	25.1	+0.60
3	25.9	+1.00 ^f
CH ₃	19.5	-1.32

2,2-Dimethylaziridine



2	31.9	-0.58
3	34.2	+1.00 ^g
ant-CH ₃	25.7	-0.66 ^h
syn-CH ₃		-0.75 ^h

(Table I continued)

Acetoxime	2	155.0	-1.00 ⁱ
	ant-CH ₃	14.9	-0.48
	syn-CH ₃	21.5	-0.13
N-Ethylacetoneimine	2	164.8	-1. ^j
	ant-CH ₃	29.1	0. ^j
	syn-CH ₃	30.5	0. ^j
Thiazole	2	152.8	-1.00 ^k
	4	118.7	-1.42
	5	143.4	-0.59
N-Methylimidazole	2	137.7	-1.00 ^k
	4	129.1	-0.46
	5	120.1	-0.38
	CH ₃	33.2	-0.40
Benzonitrile	C _α	118.8	-1.00 ^l
	C _j	112.4	-0.04

a. The plus and minus signs denote the upfield and downfield contact shifts respectively. The relative shifts were obtained from the slope of the linear plot of the observed contact shift vs. the concentration of added Ni(AA)₂. b. The actual shift is ca. 5 ppm per 0.1 M of Ni(AA)₂ in the 20 v/v% CDCl₃ solution. c. The actual shift is ca. 1 ppm per 0.1 M of Ni(AA)₂ in the 20 v/v% CDCl₃ solution. d. Ref. 14. e. The actual shift is ca. 10 ppm per 0.1 M of added Ni(AA)₂ in the

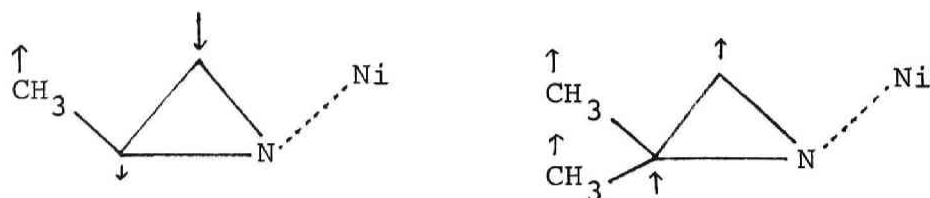
(Table I continued)

20v/v% CDCl_3 solution. f. The actual shift is ca. 10 ppm per 0.1 M of added $\text{Ni}(\text{AA})_2$ in the 10 v/v% CDCl_3 solution. g. The actual shift is ca. 2 ppm per 0.1 M of added $\text{Ni}(\text{AA})_2$ in the 10 v/v% CDCl_3 solution. h. In the spectrum of diamagnetic solution of 2,2-dimethylaziridine, two methyl carbons are observed to be equivalent, which is due to the rapid inversion of the nitrogen lone pair. By the addition of $\text{Ni}(\text{AA})_2$, this signal becomes broad and separate. This implies that the rate of lone pair inversion becomes slow in the presence of $\text{Ni}(\text{AA})_2$. Here, because of the nonlinearity of the plots, the relative values of the carbon contact shifts of the two methyl carbons (anti and syn) are somewhat inaccurate. i. The actual shift is ca. 1 ppm per 0.1 M of added $\text{Ni}(\text{AA})_2$ in the 1 M CDCl_3 solution. j. The signal broadening was too great to get the precise magnitude of the relative contact shifts. k. The actual shift is ca. 10 ppm per 0.1 M of added $\text{Ni}(\text{AA})_2$ in the 20 v/v% CDCl_3 solution. l. The actual shift is ca. 2 ppm per 0.1 M of added $\text{Ni}(\text{AA})_2$ in the 20 v/v% CDCl_3 solution.

of the spin polarization mechanism (SP) of electron spin transmission through the carbon skeleton compared with the spin delocalization mechanism (SD).^{2c,d,3} This has also been confirmed by the molecular orbital calculations.^{2c,d,3}



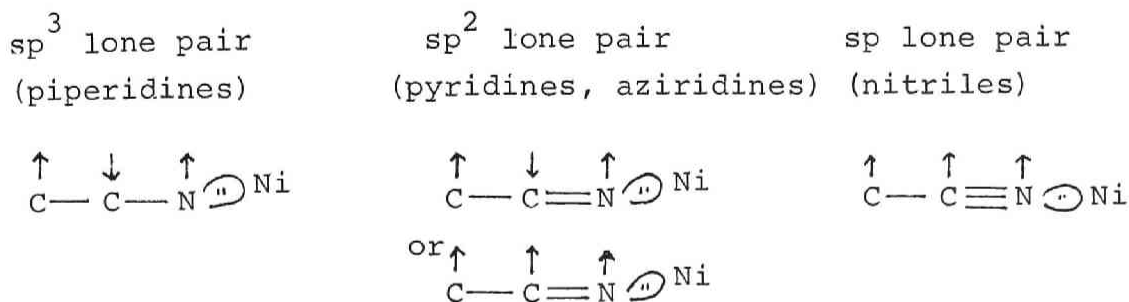
For pyridine, the alternating ^{13}C contact shifts have also been obtained,^{2d,14} whereas, non-alternating shift is observed for 2-methylpyridine (α -picoline).¹⁴ Methyl substitution reduces the magnitude of the upfield contact shift for the α -carbon of piperidine derivatives, but changes its sign for α -picoline. Similar substitution effect is also encountered for ethyleneimines. The α -carbon of aziridine shifts to the higher field as well as both of the two α -carbons in 2-methylaziridine. Here, the shift of methylsubstituted carbon (C_2) is smaller than that of the other carbon (C_3). However, the methylsubstituted α -carbon (C_2) of 2,2-dimethylaziridine exhibits a downfield shift in contrast to the upfield shift for C_3 . The downfield contact shifts of the α -carbon are also obtained for



imines and oximes and for the C_9 -carbon in quinoline.

For the five membered N-containing molecules, thiazole and N-methylimidazole, in which the hybridization of the nitrogen lone pair electrons is considered to be between sp^2 and sp , both of the α -carbons (2- and 5-carbons) show downfield

contact shifts (Table I). For nitriles with sp lone pair, the α -carbon feels downfield contact shifts. From these experimental trends, the modes of the ^{13}C contact shifts are represented schematically as follows.



(b) The Substituent Effects on the ^{13}C Contact Shifts.

In order to gain further insight into the methyl substitution effect on the ^{13}C contact shifts discussed in the previous section, we obtained the relative values of the ^{13}C contact shifts for 2-ethyl-, 2-chloro- and 2-bromopyridines (Table I). Strong electronegativity of the halogen atom may allow us to expect that these substituents affect the features of ^{13}C contact shifts more prominently than the case for methyl substitution. However, it is found that these substituents only to reduce the magnitude of the upfield α -carbon (C_2) contact shifts, which should be compared with the other α -carbon (C_6). Therefore, it is speculated that the abnormal shifts for the methyl substituted α -carbons may be caused not only by the electronic influence of the methyl substitution but also by the steric effect on the manner of metal-ligand bonding and that the latter effect may dominate the electronic effect. To elucidate this steric effect, we tried to determine the position of the paramagnetic metal. From the nmr spectra of $\text{Ni}(\text{AA})_2$ -ligand

complex system where the contact shift contribution is most important, it is difficult to determine the position of $\text{Ni}(\text{AA})_2$ directly. Thus, as a paramagnetic reagent, $\text{Eu}(\text{fod})_3$ was chosen in stead of $\text{Ni}(\text{AA})_2$. In Table II, $\text{Eu}(\text{fod})_3^-$ induced shifts for 2-substituted pyridine are shown. On the basis of the McConnell-Robertson theory¹⁵ the pseudocontact shift ΔH_{pcs} is given by¹⁶

$$\Delta H_{\text{pcs}} = K(3\cos^2\theta_i - 1)/r_{ij}^3,$$

where r_{ij} is the distance between Eu and the i th proton, θ_i is the angle formed by this vector and the principal magnetic axis of the complex, and K is a constant. Using this relation, we calculated the position where the calculated relative values $((3\cos^2\theta - 1)/r^3)$ correspond best to the relative $\text{Eu}(\text{fod})_3^-$ induced shifts. The position is also shown in Table II.¹⁷ The deviation from the $\text{C}_4\text{-N}_1$ axis (the direction of the lone pair orientation) in α -picoline ($\theta=22^\circ$) is larger than those in 2-chloro- and 2-bromopyridine ($\theta=16^\circ$ and 19° , respectively). From this trend, it is expected that the steric hindrance of methyl group is considerably large in the $\text{Ni}(\text{AA})_2$ -ligand system and that this steric influence may affect the mode of the ^{13}C contact shifts of α -methyl substituted carbons.

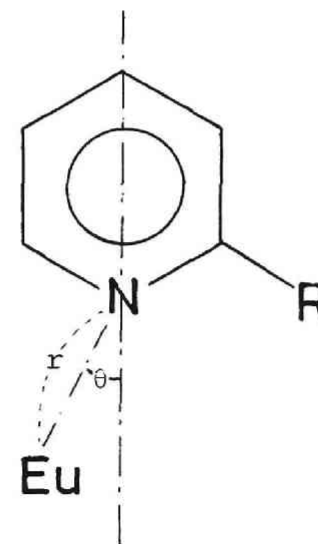
Next, we will discuss "the electronic effect" of α -methyl substitution on the ^{13}C contact shifts of the α -carbon. It has been established that the features of ^{13}C contact shifts are well reproduced^{2c,d,3} by the electron spin distribution that is calculated MO theoretically for the corresponding hydrocarbon σ -radical. We carried out^{2d}

Table II. $\text{Eu}(\text{fod})_3$ -Induced ^1H Shifts of 2-Substituted Pyridine Derivatives

Molecules	Relative value of $\text{Eu}(\text{fod})_3$ -induced shift ^a				Position of $\text{Eu}(\text{fod})_3$ ^b	
	3-H	4-H	5-H	6-H	r (Å)	θ (deg)
R = H	-0.32	-0.35	-0.32	-1.00	2.4	0
= Cl	-1.00	-0.68	-0.55	-1.00	2.3	16
= Br	-0.88	-0.51	-0.35	-1.00	2.3	19
= CH_3	-0.63	-0.39	-0.44	-1.00	2.4	22

a. The plus and minus signs denote the upfield and downfield shifts respectively. The relative shifts were obtained from the slope of the linear plot of the observed paramagnetic shifts. The shifts of the 6-H protons are normalized to 1.00.

b. Estimated based on the McConnell-Robertson's equation.¹⁵ Optimized positions are shown.



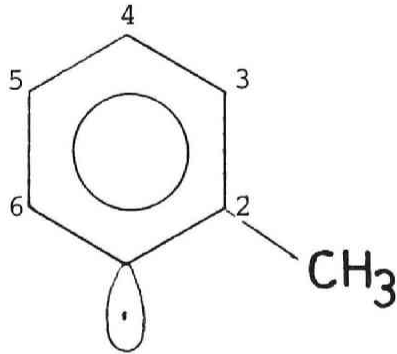
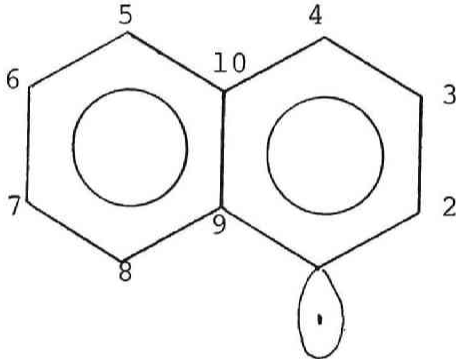
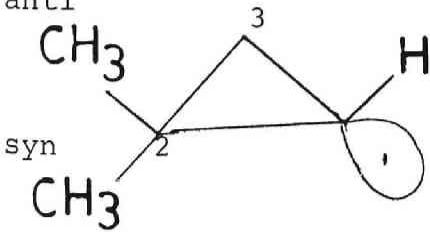
the INDO-UHF calculations for 2-methylphenyl σ -radical. In this calculation, observed positive spin density on C_2 is not reproduced. Introduction of a methyl group at the 2-position gives a positive trend of the spin density on the C_2 carbon, but still induces negative spin density (Table III). INDO calculations of spin densities for 1-naphthyl radical also fail to explain the downfield ^{13}C contact shift of C_9 in quinoline.^{2d} In Table III, calculated spin densities on the carbon s orbitals of 2,2-dimethylcyclopropyl radical are also shown. Here the dimethyl substituents reduce the negative value on the C_2 carbon but still negative spin density is induced. From above discussion, it may be concluded that the specific downfield shift of the methyl substituted α -carbon is mainly due to the change of metal-ligand bonding ("off-centric bond") caused by the steric effect of the methyl group. Such

"off-centric bond" between nitrogen n and nickel d orbitals"



"off-centric" bonding may change the mechanism of spin transmission from the nickel d orbital to the nitrogen atomic orbitals compared with the normal nickel-amine complexes.^{1,2,3} It may be also possible that pseudocontact contribution or direct spin transfer to the nearer α -carbon atom causes the

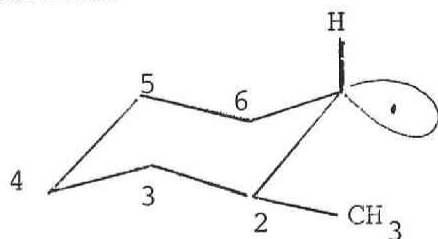
Table III. Calculated Spin Densities on the C 2s AO's
for σ -Radicals (INDO-UHF)

Radicals	position	Relative value of spin density
2-Methylphenyl radical ^a	2	-0.80
	3	+2.72
	4	-0.65
	5	+2.64
	6	-1.00 (-0.005) ^b
	CH ₃	+2.72
1-Naphthyl radical ^a	2	-1.00 (-0.007) ^b
	3	+2.09
	4	-0.50
	5	+0.06
	6	+0.13
	7	-0.19
	8	+0.98
	9	-0.39
	10	+1.52
2,2-Dimethylcyclopropyl radical ^c	2	-0.73
	3	-1.00 (-0.006) ^b
	anti-CH ₃	+1.07
	syn-CH ₃	+0.61

(Table III continued)

2-Methylcyclohexyl

radical^d



2	-0.96
3	+1.61
4	-0.20
5	+1.62
6	-1.00 (-0.007) ^b
CH ₃	+0.44

- a. Ref. 2d. b. The calculated value of the spin density is given in parenthesis. c. The bond lengths and angles used for the MO calculation are: C-H=1.08 Å, C-C=1.54 Å, C-CH₃=1.52 Å, ∠HCH=∠CH₃-C-CH₃=118.2°. d. The bond lengths and angles are: C-C=1.54 Å, C-H=1.09 Å; ∠C-C-C=∠C-C-H=109°28'.

abnormal ^{13}C shift in the "off-centric bonding" system.

To further substantiation, more detailed MO theoretical treatment including nickel d orbitals may be awaited.

(c) The influence of the Hybridization of the Lone Pair Electrons in Ligand Molecules on the Stereospecificity of Electron Spin Transmission. In order to discuss the influence of lone pair hybridization on the stereospecificity of electron spin transmission as is pointed out in section (a), we studied INDO-UHF MO calculation of electron spin densities distributed on the carbon atoms for ethyl σ -radical, ethenyl radical, and ethynyl radical as the model of C-N, C=N, $\text{C}\equiv\text{N}$ fragments complexed with $\text{Ni}(\text{AA})_2$, respectively (Table IV). The negative spin density on the C_2 -carbon of ethyl σ -radical corresponds to the upfield ^{13}C shift of α -carbons in aliphatic amines. The downfield shift of the α -carbons of nitriles agree with the calculated positive spin density for the C_2 -carbon of ethynyl radical.

Nakatsuji et al.¹⁸ proposed a method to separate the spin density calculated with the UHF method into two components due to the SP (spin polarization) and the SD (spin delocalization) mechanisms. For doublet radicals,

$$\rho_{\text{SP}} = 3/2 (\rho_{\text{UHF}} - \rho_{\text{AA}})$$

$$\rho_{\text{SD}} = \rho_{\text{UHF}} - \rho_{\text{SP}}$$

where ρ_{AA} is approximately the spin density of the spin component of lowest multiplicity obtained by annihilation of the major contaminating component.

To gain further insight into the mechanism of electron

Table IV. Calculated Spin Densities on the 2-Carbon 2s
AO's (INDO-UHF)

Radicals	ρ_{UHF}	$\rho_{\text{SP}}^{\text{a}}$	$\rho_{\text{SD}}^{\text{b}}$
Ethyl σ -radical ^c	-0.0104	-0.0126	+0.0022
Ethenyl radical ^d	-0.0175	-0.0236	+0.0061
Ethynyl radical ^e	+0.0054	-0.0163	+0.0218

a. Spin density induced by the spin polarization mechanism.

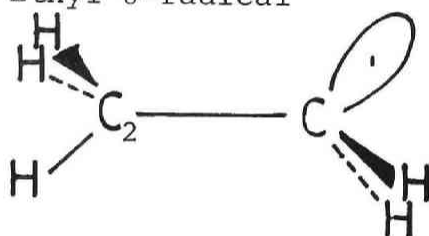
b. Spin density induced by the spin delocalization mechanism.

c. The bond lengths are: C-H=1.09 Å, C-C=1.54 Å. All the bond angles are tetrahedral. d. The bond lengths are:

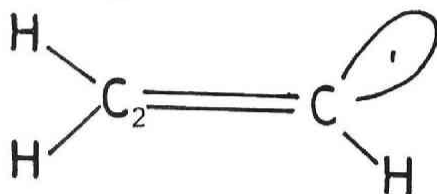
C-H=1.07 Å, C-C=1.31 Å. All the bond angles are 120°.

e. The bond lengths are: C-H=1.06 Å, C-C=1.21 Å.

Ethyl σ -radical



Ethenyl radical



Ethynyl radical



spin transmission, we obtained the SP and SD contributions with the aid of above procedure. The results are shown in Table IV. Here one should notice that in going from ethyl radical to ethynyl radical, the values of the SD contribution increases monotonously, and the ρ_{SD} of ethynyl radical is about ten times as large as that of ethyl radical. This trend may be due to (1) the greater contribution of s-atomic orbital in the radical orbital and (2) the shorter carbon-carbon bond length of ethynyl radical with respect to ethyl radical. On the contrary, the spin densities due to the SP mechanism (ρ_{SP}) does not differ so much each other compared to the large variation in ρ_{SD} .¹⁹

From these calculated results, it may be concluded that the upfield contact shifts of the α -carbon of aliphatic amines and the downfield shifts of nitriles are attributed to the relatively larger contribution of SP or SD mechanism, respectively. The anomalous features of ^{13}C contact shifts in the compounds with sp^2 lone pair electrons may be explained as follows. For the amines with sp^2 lone pair electrons, the contribution of SP and SD mechanisms may be comparable. Therefore, by a small perturbation, the direction of the contact shift (upfield or downfield shift) may be alternable.

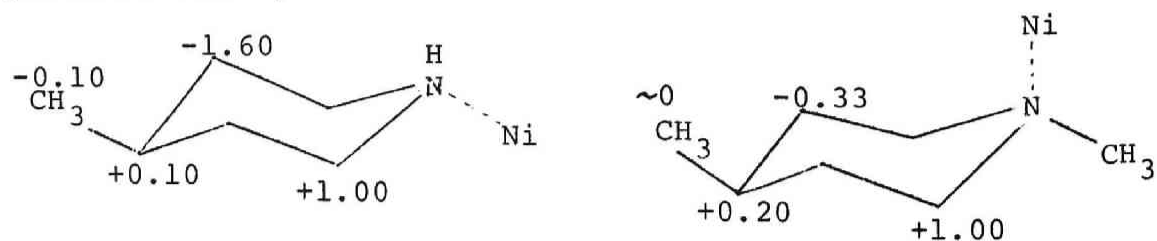
Summarizing above results and discussion, it is concluded that $\text{Ni}(\text{AA})_2$ -induced ^{13}C nmr contact shift reflects quite sensitively the steric or electronic structures associated with the substituent and hybridization of the nitrogen lone pair of the nitrogen-containing molecules and, therefore,

could serve as a quite sensitive probe for the elucidation of modes and mechanism of intramolecular electron spin transmission through the σ -bonded skeleton.

References and Notes

- (1) (a) T. Yonezawa, I. Morishima, and Y. Ohmori, J. Amer. Chem. Soc., 92, 1267(1970); (b) I. Morishima, K. Okada, M. Ohashi, and T. Yonezawa, Chem. Commun., 33(1971); (c) I. Morishima and T. Yonezawa, J. Chem. Phys., 54, 3238(1971); (d) T. Yonezawa, I. Morishima, Y. Akana, and K. Fukuta, Bull. Chem. Soc. Japan, 43, 379(1970).
- (2) (a) I. Morishima, T. Yonezawa, and K. Goto, J. Amer. Chem. Soc., 92, 6651(1970); (b) I. Morishima, K. Okada, T. Yonezawa, and K. Goto, Chem. Commun., 1535(1970); (c) I. Morishima, K. Okada, T. Yonezawa, and K. Goto, J. Amer. Chem. Soc., 93, 3922(1971); (d) I. Morishima, K. Okada, and T. Yonezawa, *ibid.*, 94, 1425(1972).
- (3) (a) I. Morishima, K. Yoshikawa, and K. Okada, J. Amer. Chem. Soc., in press; (b) I. Morishima and K. Yoshikawa, *ibid.*, 97, 2950(1975); (c) K. Yoshikawa, K. Bekki, M. Karatsu, K. Toyoda, T. Kamio, and I. Morishima, submitted for publication.
- (4) (a) J. Briggs, G. H. Frost, F. A. Hart, G. P. Moss, and M. L. Stainforth, Chem. Commun., 749(1970); (b) B. F. G. Johnson, J. Lewis, P. McArdle, and J. R. Norton, J. Chem. Soc., Chem. Commun., 535(1972), *ibid.*, Dalton, 1263(1974); (c) Hirayama, E. Edagawa, and Y. Hanyu, *ibid.*, Chem. Commun., 1343(1972), (d) R. J. Cushley, D. R. Anderson, and S. R. Lipsky, *ibid.*, 636(1972); (e) M. Kainosho, K. Ajisaka, and K. Tori, Chem. Lett., 1061(1972); (f) G. E. Hawkes, D. Leibfritz, D. W. Roberts, and J. D. Roberts, J. Amer. Chem. Soc., 95, 1659(1973); (g) G. E. Hawkes, C. Marzin, S. R.

- Johns, and J. D. Roberts, *ibid.*, 95, 1661(1973); (h) O. A. Gawsow, P. A. Loeffler, R. E. Davis, M. R. Willcott, III, and R. E. Lenkinski, *ibid.*, 95, 3389(1973); (i) G. N. LaMar and J. W. Faller, *ibid.*, 95, 3817(1973).
- (5) H. M. McConnel and D. B. Chesnut, *J. Chem. Phys.*, 29, 107(1958).
- (6) K. N. Campbell, A. H. Sommers, and B. K. Campbell, *J. Amer. Chem. Soc.*, 66, 82(1944).
- (7) T. J. Cairns, *J. Amer. Chem. Soc.*, 63, 871(1941).
- (8) I. Morishima, K. Yoshikawa, K. Okada, T. Yonezawa, and K. Goto, *J. Amer. Chem. Soc.*, 95, 165(1973).
- (9) H. L. Retcotsky and R. A. Friedel, *J. Phys. Chem.*, 71, 3592(1967), *ibid.*, 72, 290, 2619(1968).
- (10) L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra," John Wiley & Sons, New York (1972).
- (11) R. J. Pugmire, D. M. Grant, L. B. Townsend, and R. K. Robins, *J. Amer. Chem. Soc.*, 95, 2791(1973).
- (12) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley-Interscience, John Wiley & Sons, New York(1972).
- (13) For example, the relative ^{13}C contact shift of the various carbons in 4-methylpiperidine and 1,4-dimethylpiperidine are $^{2\text{C}}$;



- (14) D. Doddrell and J. D. Roberts, *J. Amer. Chem. Soc.*, 92, 6839(1970).

- (15) H. M. McConnell and R. E. Robertson, J. Chem. Phys., 29, 1361(1958).
- (16) Strictly speaking, this relation is not complete because of the assumption of axial symmetry. However, even in the detailed treatment the result may not change essentially; R E. Cramer, private communication.
- (17) T. Heigl et al. reported a study concerning the position of lanthanide ion in substituted pyridines. They concluded the substituents at C₂ force the lanthanide complex to one side because of the steric hindrance; T. Heigl and G. K. Mucklow, Tetrahedron Lett., 9, 649(1973).
- (18) T. Yonezawa, H. Nakatsuji, T. Kawamura, and H. Kato, Chem. Phys. Lett., 2, 454(1968); J. Chem. Phys., 51, 669 (1969); Bull Chem. Soc. Japan, 42, 2437(1969). H. Nakatsuji, H. Kato, and T. Yonezawa, J. Chem. Phys., 51, 3175(1969).
- (19) It is well known²⁰ that in aromatic radical ions (π -radicals), only the SP mechanism is important for the electron spin transmission from π -orbital to the neighbouring proton and that the SD contribution is essentially zero. This is the extreme case because the radical orbital includes no s atomic orbital contributions, and with the increasing s-character (bending of radical center) the SD mechanism becomes important.
- (20) H. McConnell, J. Chem. Phys., 24, 764(1956); H. M. McConnell and D. B. Chesnut, J. Chem. Phys., 27, 984(1957).

CHAPTER 6

CONCLUSION

In Chapter 2 the following conclusions were drawn.

- (1) By the protonation of saturated amines the C-H bond is polarized to produce the C^--H^+ structure and the electron on the hydrogen atom is transmitted through the carbon skeleton onto the positively charged nitrogen atom.
- (2) The N-protonation induced ^{13}C shifts alternate and attenuate along the σ -carbon skeleton. These features of ^{13}C shifts can be interpreted in terms of charge density variation and correspond well alternation in the $-I^+$ type σ -inductive effect proposed by Pople.¹
- (3) The C-H bond is electronically polarized more readily than the C-C bond by the inductive effect and therefore the C-H carbon has more electron density than the C-C carbon by N-protonation.
- (4) The protonation induced ^{13}C shifts exhibit a marked conformational dependence, which can be interpreted in terms of stereospecificity of the σ -inductive effect.

In Chapter 3, a marked difference of $Ni(AA)_2$ -induced 1H and ^{13}C contact shifts was found between N-H and N-methyl derivatives of cyclic amines. Such an experimental trend was attributed to their difference in the lone pair orientation. It was also found that the electron spin distribution in $Ni(AA)_2$ -amine complexes is well reproduced by the INDO MO calculation for the corresponding σ -radicals. $Ni(AA)_2$ -induced nmr shifts are thus proved to serve as a quite sensitive probe for the elucidation of the modes and

mechanisms of intramolecular electron spin transmission through σ -bonded skeleton.

In Chapter 4, studies on $\text{Ni}(\text{AA})_2$ -induced ^1H and ^{13}C nmr contact shifts for various cyclic and bicyclic amines were presented in order to elucidate the modes and mechanisms of intramolecular electron spin transmission through the σ -bonded skeleton. The results of nmr contact shifts were discussed along with two different mechanisms of electron spin transmission, spin delocalization and polarization, with the aid of INDO MO calculations.¹ It was shown that these two mechanisms are simultaneously operating in the actual case and show marked conformational dependence. The proton contact shifts follow the stereospecificity established for nuclear spin-spin coupling constants. The importance of the through-space spin transmission in the rigid σ -bonded skeleton was also proposed to account non-alternating ^{13}C contact shifts for planar zigzag arrangement of the σ -skeleton. Such a feature was also discussed in relation to the long range H-H coupling constants across four σ -bonds which is determined essentially by spin polarization mechanism.

In Chapter 5, ^{13}C nmr contact shifts induced by $\text{Ni}(\text{AA})_2$ were observed for various N-heterocyclic compounds in order to elucidate the manner of stereospecific electron spin transmission through the σ -skeleton. It was revealed that the substituent at the α -carbon atom affects quite markedly the mode of ^{13}C contact shifts. Such an experimental trend was attributed to the complementary effects of the

changes in the electronic structures of ligands and in the metal-ligand bonding due to the introduction of substituents. It was also found that the hybridization of the nitrogen lone pair electrons in a ligand molecule plays an important role in the distribution of unpaired electron. These results were interpreted in terms of the relative importance of spin polarization and spin delocalization mechanisms with the aid of INDO MO calculations.

From the results and discussion in Part I, it becomes apparent that the manners of electron "charge" and "spin" distribution through σ -bonded skeleton are quite similar each other. In Chapter 2, the alternating nature of σ -inductive effects was discussed as an important character in intramolecular charge distribution. Alternation of the sign of induced spin densities is encountered in the mode of electron spin transmission through σ -bonds (Chapters 3,4,5). Such an alternation in charge or spin distribution is theoretically concerned with the alternating character of mutual polarizability (π_{rs}) along the σ -bonds, as has been mentioned in Chapter 2. The change (Δq_s) in the charge density on atom "s", when the Coulomb integral α_r on atom "r" is perturbed to $\alpha_r + \delta\alpha_r$, is given by the relation,²

$$\Delta q_s \approx \pi_{rs} \delta\alpha_r . \quad (1)$$

This shows that the inductive effect of atom r, i.e., the effect due to the change of the Coulomb integral on atom r, is related to the mutual polarizability, π_{rs} .

Similarly, nuclear spin-spin coupling constant, J_{AB} , between atoms A and B is represented by the following relation,³

$$J_{AB} \propto \frac{\partial \rho_{SA}}{\partial \alpha_B} \approx \pi_{SASB} \quad (2)$$

where π_{SA} is the induced spin density on the s atomic orbital of atom A due to the variation ($\partial \alpha_B$) of the Coulomb integral on atom B, and π_{SASB} is the mutual polarizability between the s atomic orbitals of atoms A and B. From the relationship of the equation (1) and (2), correspondence between the feature of charge distribution and that of the coupling constants may be expected. While, the induced spin density on atom A in a σ -radical is considered to be an extreme case of the equation (2) where ρ_{SA} becomes fairly large.⁴ Therefore it is supposed that the manner of electron spin distribution in a σ -type free radical resembles to those of inductive effect and nmr coupling constants through σ -bonds. The experimental trends in Chapters 3,4,5 confirm the above theoretical estimation.

From the studies in Part I, it becomes clear that alternating nature is generally important in the manner of electron charge and spin distributions in σ -electron system. It was also established that the features of charge and spin distributions through σ -skeleton exhibit marked conformational and geometrical dependence. These results are expected to be useful not only in stereochemistry but also in the further investigation concerning chemical reactivity and physical nature of organic compounds.

References

- (1) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, Inc., New York, 1970.
- (2) K. Fukui, K. Morokuma, T. Yonezawa, and C. Nagata, Bull. Chem. Soc. Japan, 33, 963(1960).
- (3) J. A. Pople and D. P. Santry, Mol. Phys., 8, 1(1964); 9, 301, 311(1965).
- (4) J. W. McIver, Jr. and G. E. Maciel, J. Amer. Chem. Soc., 93, 464(1971).

PART II

ELECTRONIC STRUCTURES AND INTRAMOLECULAR INTERACTIONS IN N-HETEROCYCLIC COMPOUNDS

CHAPTER 1

INTRODUCTION

Application of various refined chemical and physical methods of investigation into stereochemistry has, in a number of cases, led to a satisfactory description of carbocyclic compounds.¹ Moreover, progress in computing methods has permitted the a priori calculation of potential barriers between isomers, of conformational energies of substituents, of flattening effects, etc. Also, medium-sized cyclic-hydrocarbons have been treated in this way with considerable success. When heteroatoms are included in the ring, the situation with respect to a detailed approach is more difficult.² It is true that there are many overall similarities in the preferred conformation assumed by homocyclic and heterocyclic ring structures. On the other hand, significant differences exist between heterocyclic and homocyclic compounds.²

In Part II, studies on the electronic and steric structures of N-heterocyclic compounds were carried out. Since these compounds have the typical lone pair electrons oriented to a certain direction, such studies may be useful in the investigations of heterocyclic compounds. The results obtained here is also expected to shed light on the studies of other kinds of hetero-compounds, oxygen-, sulfur-, phosphorus-containing molecules. Among the physical methods of investigation in chemistry, X-ray (neutron or electron) diffraction is quite a useful method for the determination

of accurate molecular geometry. However, X-ray analysis seems to be inadequate to the studies concerning the problems, such as, molecular dynamic motion, solvent effects, and inter- or intramolecular interactions. Nmr spectroscopy at various temperature or in various solvents affords information that has proved to be of value, particularly in the description of group interactions and conformational equilibria in the study of heterocyclic compounds. In these situations, studies on the conformational dependence of charge and spin distribution have been made mainly by the use of ^1H and ^{13}C nmr spectroscopy in Part I. However, the energy parameters, e.g., orbital energies, nonbonded electronic interactions, conformational energies, etc., remain a matter of conjecture for many heterocyclic systems. Though there have been many UV spectroscopic studies of heterocyclic compounds, from these studies chemists could not directly obtain the information concerning the electronic structure in the ground state in a molecule. In the last decade, molecular photoelectron spectroscopy has been recognized as an especially unambiguous method for the study of the molecular electronic structures of substances in the vapor state.^{3,4} It has been also proved that photoelectron spectroscopy is extremely useful in evaluating the electronic interaction between nonadjacent groups in the ground state.^{4,5}

In these circumstances, in Chapter 2 photoelectron spectroscopic study of cyclic amines was carried out with attention to the ionization potentials (IP's) of lone pair electrons. Here the relation between IP's, basicities and

the hybridized nature of lone pair electrons was discussed. The effect of the ring size on the physico-chemical properties of cyclic amines were discussed with much attention to the IP's of the lone pair electrons as a probe for elucidation of the intrinsic nature of cyclic molecules.

In Chapter 3, the photoelectron spectra of nitroxide radicals, di-tert-butyl nitroxide and 2,2,6,6-tetramethylpiperidine-N-oxyl have been studied. Experimental determination of the IP of the odd electron or nonbonded electrons in these nitroxide radicals appears to be important and useful in the studies concerning the electronic structures of open-shell molecules. Here, restricted and unrestricted Hartree-Fock MO calculations were carried out in order to interpret the photoelectron spectra of these nitroxide radicals.

In Chapter 4, electron spin resonance spectra of bicyclic nitroxide radicals, 7-azabenzonorbornadiene-7-oxyl and 7-azabenzonorbornene-7-oxyl, obtained from hydroperoxide oxidation of the corresponding amines, have been studied. These nitroxide radicals are interesting because of the following reasons. (1) These radicals are rather stable and may give us useful information concerning the electronic and steric structures in open-shell molecules, in connection with the photoelectron spectroscopic study of dialkyl nitroxide radicals in Chapter 3. (2) They are novel bicyclic radicals with 7-azanorbornadiene and 7-azanorbornene skeleton. (3) Determinations of the structure around the nitrogen atom and the orientation of N-O bond are of great interest in

relation to other bicyclic nitroxide radicals.^{6,7,8}

(4) Comparison with the lone pair orientation of the parent amines (Part II, Chapter 8) is also interesting in order to study the intrinsic nature of n,π homoconjugative interaction.

(5) Studies on the electron spin distribution in the rigid skeleton may attract considerable interest.

Chapters 5,6,7,8,9 in Part II dealt with the problem of n,π homoconjugative interaction in connection with the fundamental nmr (Part I), photoelectron (Chapters 2,3 in Part II) and esr (Chapter 4 in Part II) spectroscopic studies. During the last decade, the consequences of homoconjugation between an unsaturated group and an active center in cations, radicals and anions have been a subject of controversy. Particularly, studies on the interaction between the cation center and the nonadjacent π bond have been extensively performed in connection with the debate on "the nonclassical carbonium ion."⁹ The great π electron participation in the acceleration of the rate of solvolysis in norbornene derivatives have been well established. However, the studies on the non-bonded interaction between the doubly occupied n orbital (anion center) and the nonadjacent π group have been quite limited. Amines containing the nonadjacent unsaturated group seem to be quite relevant for the study of such intramolecular n,π interactions. The aim of these studies (Chapters 5~9) is to delineate the following problems.

(1) To study whether n and π electrons are repulsive or attractive, in other words, whether n,π homoconjugative interaction destabilizes or stabilizes the interacting system. (2) To

investigate the effect of the n,π nonbonded interaction on the lone pair orientation. (3) To know the conformational or geometrical dependence of the manner of n,π homoconjugative interactions. (4) To study the effects of the homoconjugative interaction on the molecular physico-chemical properties, e.g., basicities, IP values, chemical reactivity, etc. (5) To shed light on the problem of homoaromaticity or homoantiaromaticity.¹⁰ (6) To gain further insight into the intrinsic nature of lone pair electrons.

In Chapter 5, photoelectron spectra have been obtained for saturated and unsaturated derivatives of five- and six-membered cyclic and bicyclic amines in order to study the nonadjacent n,π electronic interaction. Here difference in the intrinsic nature of n,π homoconjugative interaction was especially concerned which depends on molecular symmetry (bishomoallyl or homoallyl interaction), orbital energy and orientation of the lone pair electrons.

In Chapter 6, the orientation of the nitrogen lone pair electrons in 2-azabicyclo[2.2.2]oct-5-ene and its N-methyl derivative has been studied in view of elucidation of the manner of homoallyl-type nonbonded n,π interaction. In order to determine the lone pair orientation, we have examined Ni(AA)₂-induced ¹H and ¹³C contact shifts for these molecules together with other subsidiary methods. Referring the stereospecific electron spin transmission established in the studies of Part I, the manner of electron spin distribution was discussed in relation to the lone pair orientation.

In Chapter 7, the n,π homoconjugative interaction in

2-aza-5-norbornene system have been studied. Here the manner of the homoallyl n,π interaction in these compounds was investigated in relation to the stereospecific orientation of the lone pair electrons. Photoelectron spectra of these amines were also obtained and discussed in connection with the homoconjugative n,π interaction.

In Chapter 8, ^1H and ^{13}C nmr spectroscopic study of 7-azanorbornene and 7-azanorbornadiene derivatives were carried in order to gain insight into the effect of n,π bishomoallyl and bishomobenzyl interactions on the orientation of the lone pair electrons. Such 7-norbornenyl system offers a typical structural framework from which lone-range nonbonded interaction may be examined. $\text{Ni}(\text{AA})_2$ -induced ^1H and ^{13}C contact shifts of these amines have also been examined and discussed in terms of stereospecific electron spin transmission in the rigid skeleton. pK values of these bicyclic amines were measured by use of ^1H nmr spectroscopy in order to study the effect of homoconjugation on the physical property of the interacting system.

In Chapter 9, ^1H and ^{13}C nmr contact shifts induced by $\text{Ni}(\text{AA})_2$ were observed for benzylamine, 1,2,3,4-tetrahydroisoquinoline and their derivatives. The aim of this study is to delineate the following problems, intrinsic in these molecules. (a) How is the effect of the nonbonded interaction between n and π electrons on the nitrogen lone pair orientation? (b) How is the manner of the intramolecular electron spin transmission in the n,π homoconjugative interacting system?

In Chapter 10, UV absorption spectra of aliphatic amines containing nonadjacent benzene ring and UV charge transfer (CT) absorption spectra of iodine complexes with various cyclic and bicyclic amines were observed. Based on these experimental results and on the discussion in the preceding studies in this thesis, intrinsic nature of the nitrogen lone pair electrons were discussed. The relationship between basicities, IP values, and lone pair hybridization was examined. Finally the concept of homoconjugation and homoaromaticity was discussed generally in connection with the previous results and discussion in Parts I and II.

References

- (1) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, 1965.
- (2) C. Romers, C. Altona, H. R. Buys, and E. Havinga, "Topics in Stereochemistry," Interscience, New York, Vol. 4, 39(1967).
- (3) D. W. Turner, "Molecular Photoelectron Spectroscopy," John Wiley & Sons, Ltd., London, 1970.
- (4) C. R. Brundle and M. B. Robin, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., Vol. 3, 2(1971).
- (5) R. Hoffman, Accounts Chem. Res., 4, 1(1971).
- (6) G. D. Mendenhall and K. U. Ingold, J. Amer. Chem. Soc., 95, 6395(1973).
- (7) A. Rassat and P. Rey, Tetrahedron, 29, 2845(1973).
- (8) P. G. Gassman and R. L. Cryberg, J. Amer. Chem. Soc., 90, 1355(1968).
- (9) S. Winstein and C. Ordronneau, J. Amer. Chem. Soc., 82, 2085(1960); H. Tanida, T. Irie, and T. Tsushima, *ibid.*, 92, 3404(1970).
- (10) M. J. Goldstein and R. Hoffman, J. Amer. Chem. Soc., 93, 6193(1971).

CHAPTER 2

Photoelectron Spectroscopic Study of Cyclic Amines

Photoelectron Spectroscopic Study of Cyclic Amines. The Relation between Ionization Potentials, Basicities, and s Character of the Nitrogen Lone Pair Electrons

Sir:

Photoelectron spectroscopy (PES) has recently been proved to be potentially useful for structural studies of organic molecules.¹ Much attention has been paid to the studies of electronic interactions such as π, π , n, π , and n, n interactions in a molecule.² However, there has been no report on the systematic PES studies of amines with attention to the ionization potentials (IP) of the lone pair electrons.³ Here we wish to report the relation between IP's, basicities, and the hybridized nature of lone pair electrons for cyclic amines. We are concerned with the effect of the ring size on the physicochemical properties of cyclic amines with much attention to the IP's of the lone pair electrons as a probe for elucidation of the intrinsic nature of cyclic molecules. We have studied here the PES of three- to seven-mem-

Table I. Vertical Ionization Potentials (eV) for Cyclic Amines^a

Compound	R = H	R = CH ₃
	9.85, 11.90	
	9.57	
	9.29, 11.07	8.68, 10.58
	9.04, 11.50	
	8.77, 11.49	8.41, 11.19
	8.64, 10.75	8.29, 10.59
	8.41, 10.85	8.29, 10.68

^a He(I) photoelectron spectra were recorded on a JASCO PE-1 spectrometer. Vertical IP values are accurate to ± 0.02 eV.

bered cyclic amines. The measured vertical ionization potentials (IP's) are shown in Table I. All of the first IP's of these amines are readily assigned to the ionizations from lone pair orbitals. A remarkable feature of this table is that the values of the IP's of lone pair electrons in N-H derivatives fall in the order of increasing ring size, *i.e.*, aziridine > azetidine > pyrrolidine > piperidine > hexamethylenimine. The similar trend in IP is also the case for *N*-methyl homologs, *i.e.*, *N*-methylpyrrolidine > *N*-methylpiperidine $\approx$ *N*-methylhexamethylenimine, although the data for three- and four-membered imines are lacking. It is, there-

(1) For example, (a) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, New York, N. Y., 1970; (b) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

(2) M. J. Goldstein, S. Natowsky, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **56**, 294 (1973); D. A. Sweigart and D. W. Turner, *J. Amer. Chem. Soc.*, **94**, 5592, 5599 (1972); S. F. Nelsen, J. M. Buschek, *ibid.*, **95**, 2011, 2014 (1973); A. D. Bain, J. C. Bünzli, D. C. Frost, and L. Weiler, *ibid.*, **95**, 291 (1973).

(3) Though Gallegos, *et al.*, reported 9.94, 9.1, and 9.0 eV for the IP's of aziridine, azetidine, and pyrrolidine, respectively, by using electron impact spectroscopy, these data seem to contain considerable experimental error: E. Gallegos and R. W. Kiser, *J. Phys. Chem.*, **65**, 1177 (1961); **66**, 136 (1962).

fore, tempting to suggest that this is because of changes in the overall hybridization of the nitrogen atom as the ring size is increased, *i.e.*, a change of the lone pair orbital from an sp^2 hybrid (in aziridine) toward an sp^3 orbital. It is well established⁴ that in cycloalkanes the *s* character of the carbon-hydrogen bond increases with decreasing ring size. This may allow us to expect that in cyclic amines the *s* character of the lone pair electrons increases with decreasing ring size and the IP of the nitrogen lone pair will reflect this hybridized nature. To examine the relation between the IP's and the *s* character of lone pair electrons in cyclic amine, we plotted in Figure 1 the first IP's of cyclic amines against the values of the directly bonded ^{13}C - ^1H nuclear spin coupling constants^{4a} of the corresponding cycloalkanes. This figure shows that the IP's of lone pair electrons are well correlated linearly with their *s* character.⁵

It is also tempting to expect some relation between the IP of amines and their basicity. It was reported⁶ that in aqueous solution the basicity of cyclic amines falls in the order: azetidine ($pK_a = 11.29$) > pyrrolidine (11.27) > piperidine (11.22) > hexamethylenimine (11.07) > aziridine (8.04). It is apparent that these basicities do not parallel the IP values for cyclic amines; the basicity of azetidine appears to be too strong for its IP value. Recently, Bowers, *et al.*,⁷ have determined the relative basicity of cyclic amines in the vapor phase using icr (ion cyclotron resonance) spectroscopy;⁸ the basicity falls in the order, piperidine > pyrrolidine > azetidine. Here the basicities correspond well to the trend of IP's in cyclic amines.⁹ Therefore, the abnormal feature of the relative basicities of cyclic amines could be attributed to the solvent effect.^{10,11} It is also to be noted in Table I that the values of the IP's decrease on going from secondary to tertiary amines. This trend does not parallel the relative strength of basicity.^{6,12,13} This could be also attributable to a solvent effect involved in basicity in solution.^{10,11}

From the above results and discussion it may be reasonable to conclude the IP values of cyclic amines could be used as a measure of the basicity and the hybridized nature of their lone pair electrons. Similar studies for bicyclic amines are now in progress.

(4) (a) J. J. Burke and P. C. Lauterbur, *J. Amer. Chem. Soc.*, **86**, 1870 (1964); (b) A. Streitwieser, Jr., R. A. Caldwell, and W. R. Young, *ibid.*, **91**, 529 (1969).

(5) This relationship would be acceptable, if we assume that the C-N-C bond angle in cyclic amines is not so different from the C-C-C angle in the corresponding cycloalkanes. This is because the C-C-C angle is directly related to the $J_{\text{C-H}}$ value, a measure of *s* character of the C-H bond: C. S. Foote, *Tetrahedron Lett.*, 579 (1963); K. Mislow, *ibid.*, 1415 (1964).

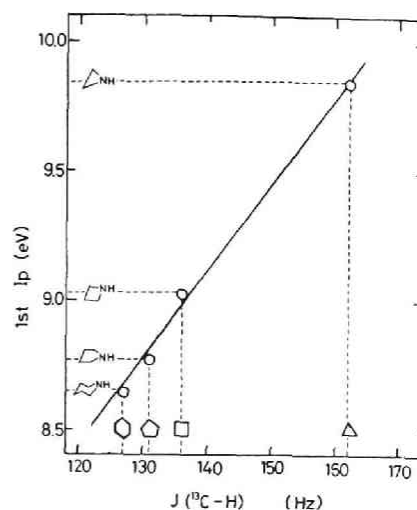


Figure 1. A plot of first IP's against $J_{\text{C-H}}$ in cycloalkanes.

Acknowledgment. We thank Professor S. Nagakura and Dr. T. Kobayashi of the Institute for Solid State Physics of the University of Tokyo for making their JASCO PE spectrometer facility available to us. We acknowledge encouragement and support of Professor T. Yonezawa. I. Morishima is also indebted to Professor J. L. Beauchamp for his helpful discussion.

(6) S. Searles, M. Tamres, F. Block, and L. A. Quarterman, *J. Amer. Chem. Soc.*, **78**, 4917 (1956); H. K. Hall, *J. Phys. Chem.*, **60**, 63 (1956).

(7) M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, Jr., *J. Amer. Chem. Soc.*, **93**, 4314 (1971).

(8) The gas-phase basicity of amines has also been extensively studied by others (see ref 10-13).

(9) The gas-phase basicities of aliphatic amines determined by icr have been related to the N-H bond dissociation energies and the IP's of amines (see ref 11).

(10) E. M. Arnett, F. M. Jones, III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 4724 (1972).

(11) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Amer. Chem. Soc.*, **94**, 4726 (1972).

(12) J. I. Brauman, J. M. Riveros, and L. K. Blain, *J. Amer. Chem. Soc.*, **93**, 3914 (1971).

(13) W. G. Henderson, M. Taagepera, D. Holtz, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 4728 (1972).

CHAPTER 3

Photoelectron Spectroscopic Study of Dialkyl Nitroxide Radicals

The photoelectron spectra of the nitroxide radicals, di-*tert*-butylnitroxide (DTBN) and 2,2,6,6-tetramethylpiperidine-N-oxyl, have been studied and molecular orbital calculations made. The adiabatic first ionization potentials were found to be 6.77 and 6.73 eV for these two nitroxide radicals respectively. Four vertical ionization potentials which are common to each nitroxide radical were attributed to ionization of the odd electron in the N–O antibonding π orbital, oxygen lone pair electrons and N–O bonding π electrons. Doublet splitting of the lone pair electron peak with different peak intensities can be quantitatively understood in terms of triplet and singlet states of the photoionized nitroxide cation.

Although the potential of photoelectron (PE) spectroscopy for studying molecular electronic structures has now been well recognized, there has been only limited work on the photoelectron spectrum of the doublet state molecule. This is only for simple inorganic free radicals such as NO [1], NO₂ [2], NF₂ [3] and ClO₂ [4]. However, there have been no reports on the photoelectron spectral studies of organic free radicals. Here we study PE spectra of some nitroxide radicals. Although quite recently X-ray photoelectron spectra (NO and di-*tert*-butylnitroxide) have been reported [5], we are concerned here with the ionization potential of the valence electrons of the organic free radical.

Recently several experiments have been made on the molecular complex or interaction involving the nitroxide radical where the odd electron or nonbonding electrons play an essential role [6]. In this respect, the experimental determination of the ionization potential for these valence electrons appears to be important and helpful in these studies. Here we are also interested in the MO theoretical studies of the

PE spectrum of the organic free radical with the aid of restricted and unrestricted Hartree–Fock (RHF and UHF) MO calculations.

The nitroxide radicals examined here are di-*tert*-butylnitroxide (DTBN, I) and 2,2,6,6-tetramethylpiperidine-N-oxyl(II), which were prepared by the usual method. The helium-504 Å PE spectrum of II obtained on a JASCO PE-1 spectrometer is shown in fig. 1. Calibration of the spectrum was effected by using the ²P_{3/2,1/2} doublet of xenon.

Fig. 1 shows evidence for three ionization potentials with vertical values of 7.31, 8.94 and 9.27 eV, and an estimated uncertainty of ± 0.02 eV. The adiabatic value for the first ionization potential is 6.77 and 6.73 eV for I and II respectively. These ionization potentials are uniformly much smaller than those for the NO radical [1]. The results for I and II are summarized in table 1.

The first band of I and II may be assigned to ionization from the unpaired electron in the π^* orbital of the N–O bond. This band contains a weak vibrational progression with a spacing of 1370 ± 80 cm⁻¹. This

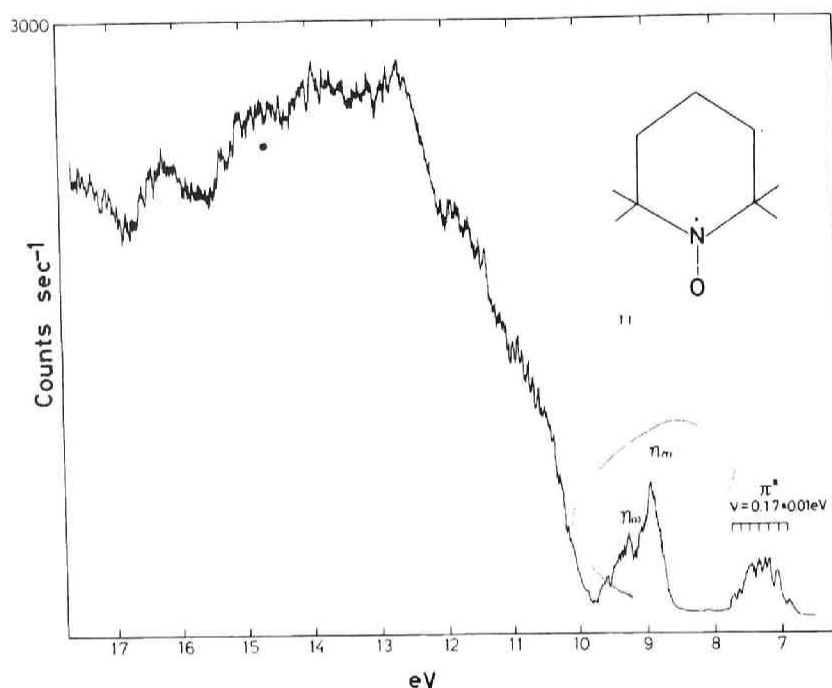


Fig. 1. Photoelectron spectrum of 2,2,6,6-tetramethylpiperidine-N-oxyl.

Table 1
Ionization potentials (eV) of nitroxide radicals

	Ionization potential			
	1st	2nd	3rd	4th
Di- <i>tert</i> -butyl-nitroxide (DTBN)	7.20 a) (6.77) b)	8.85 (8.62)	9.26 (9.15)	— (10.09)
2,2,6,6-tetramethylpiperidine-N-oxyl	7.31 a) (6.73) b)	8.94 (8.63)	9.27 (9.21)	— (9.93)

a) Vertical ionization potential.

b) Adiabatic ionization potential.

is attributable to the N—O stretching vibration of the nitroxide cation that is formed by the removal of the unpaired electron. From the IR spectrum of I the frequency of the N—O stretching vibration is 1245 cm^{-1} [7]. Here one may expect to observe an increase in the vibrational frequency of the N—O bond on going from the IR to PE spectrum of the nitroxide radical because an electron is removed from an antibonding orbital in the photoionization process. This was not realized because of the substantial experimen-

tal error in the PE spectrum.

The second and third bands may correspond to removal of the nonbonding electrons of oxygen (oxygen lone-pair electrons). This doublet splitting of the oxygen lone-pair peak is most probably due to the energy difference ($2K_{ij}$) between singlet and triplet states that are formed by the removal of the electron in the nonbonding orbital, if we apply the "frozen orbital" approximation. This splitting has also been encountered in inorganic radicals and attributed to triplet and singlet states of the photoionized radical cation [1–5].

It is also to be noted in fig. 1 that the intensity of the second band is larger than that of the third band. This difference in the peak intensities may be attributable to that in the multiplicities of the singlet and triplet states. It has often been shown [8] that the intensities of the PE spectral peaks for different ionized states with the same electronic configuration are directly proportional to their spin multiplicities. Because of this rule we may expect an intensity ratio of 3:1 for second and third bands, which is in rough agreement with experiment.

The fourth band, which is clearly separated from the following broad band, has tentatively been assigned to the triplet state of the nitroxide cation formed by photoionization of the N–O bonding π electron.

In order to substantiate and theoretically aid the above interpretation of the spectrum of nitroxide radical, we have performed INDO MO calculations [9] on dimethylnitroxide (DMNO) and its cation (DMNO⁺) with an equilibrium geometry of $r_{\text{N-O}} = 1.215 \text{ \AA}$, $r_{\text{C-N}} = 1.550 \text{ \AA}$ and $\angle \text{CNC} = 120^\circ$. We have assumed a planar structure and ignored the possibility of geometry variation on ionization.

The excitation energy for the DMNO cation in which an electron is removed from the π^* orbital of the DMNO radical will correspond to the energy difference between ionization potentials of the odd electron in the π^* orbital and other electrons in the lower energy state such as n and π electrons in the DMNO radical. Namely, the first excited state of DMNO⁺ will be the triplet state which will have an energy relative to the ground state of ${}^3\Delta E_{n \rightarrow \pi^*} = \epsilon_{\pi^*} - \epsilon_n - J_{\pi^*n}$ where ϵ_{π^*} , ϵ_n are the orbital energies of the virtual π^* orbital and the highest occupied lone-pair orbital, respectively. The second excited state of DMNO⁺ will be the singlet state having an energy relative to the ground state of ${}^1\Delta E = \epsilon_{\pi^*} - \epsilon_n - J_{\pi^*n} + 2K_{\pi^*n}$. Accordingly, the $n \rightarrow \pi^*$ triplet (or singlet) excitation energy, ${}^3\Delta E_{n \rightarrow \pi^*}$ (or ${}^1\Delta E_{n \rightarrow \pi^*}$) for DMNO⁺ will correspond to the energy difference between first and second (or first and third) ionization potentials.

Table 2 summarizes the MO theoretical values of the singlet and triplet excitation energies for the DMNO cation. The ΔE values obtained by the INDO method are uniformly larger than corresponding values of the energy differences in the observed vertical ionization potentials. This deviation is largely removed by the modified CNDO method [10] in which the parametrization of the core integral and one- and two-centre repulsion integrals are different from Pople's original CNDO method. This method has been shown to be more successful in the estimation of ionization potential than Pople's CNDO method. As is shown in table 2, the assignment of the fourth band to the triplet ionization of the π electron in the N–O bonding orbital is reasonable theoretically.

Further, we tried to interpret spectral splitting of the lone-pair peak in terms of unrestricted Hartree–

Table 2
Calculated transition energies for dimethylnitroxide cation (DMNO⁺) [10]

Transition energy	INDO (eV)	Modified CNDO [10] (eV)	Δ_{1i}^a (eV)
${}^3\Delta E_{n \rightarrow \pi^*}$	2.61	1.82	$\Delta_{12} = 1.65$ (1.85)
${}^1\Delta E_{n \rightarrow \pi^*}$	3.22	2.35	$\Delta_{13} = 2.06$ (2.38)
${}^3\Delta E_{\pi \rightarrow \pi^*}$	6.59	3.38	$\Delta_{14} = -$ (3.32)
${}^1\Delta E_{\pi \rightarrow \pi^*}$	11.90	6.60	—

a) Δ_{1i} = the difference between first and i th observed vertical ionization potentials (obtained from the data in table 1). The values in parentheses are the differences in the adiabatic ionization potentials.

Table 3
The orbital energies of dimethylnitroxide calculated by INDO UHF method

Orbital for α or β spin	Orbital energy, ϵ_i (eV)	$\Delta\epsilon^a$ (eV)	Δ_{1i}^b (eV)
$\pi^*(\alpha)$	11.01	—	—
$n(\beta)$	12.89	1.88	1.65 (1.85)
$n(\alpha)$	13.38	2.37	2.06 (2.38)
$\pi(\beta)$	14.49	3.48	— (3.32)
$\pi(\alpha)$	18.50	7.49	—

a) The difference in the orbital energies with respect to the $\pi^*(\alpha)$ orbital.

b) Δ_{1i} = the difference between first and i th observed vertical ionization potentials (obtained from data in table 1). The values in parentheses are the differences in the adiabatic ionization potentials.

Fock MO (UHF INDO method [11]) calculations. The calculated orbital energies for the DMNO radical are given in table 3. The calculated orbital energies are uniformly larger than the observed ionization potential. It is well-known that the INDO method overestimates the ionization potential. Here one should also see whether or not Koopmans' theorem holds in the UHF method since the orbital energies obtained here are not the eigenvalues of S^2 . However, the difference in the orbital energies ($\Delta\epsilon$) with respect to the $\pi^*(\alpha)$ orbital corresponds fairly well with the experimental difference we found between the first and other vertical ionization potentials (given in table 2).

Table 4
UV transition energy for DTBN radical

	Exp. [12]	Calc. a)
$\Delta E_{n \rightarrow \pi^*}$	465 nm (2.67 eV)	2.93 eV
$\Delta E_{\pi \rightarrow \pi^*}$	238 nm (5.21 eV)	6.29 eV

a) Calculated transition energy using modified CNDO method [10] for dimethylnitroxide anion (see text).

Theoretical substantiation of this correspondence will require a further rigorous theoretical basis and work on this is now in progress.

Finally we briefly discuss the UV spectral data of the nitroxide radical. In table 4 the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ UV transition energies for DTBN are shown. Table 4 also contains corresponding MO theoretical values which were estimated from the orbital energy difference for the DMNO anion where the antibonding π^* orbital is doubly occupied. The agreement between calculated and experimental results appears to be fairly good, though calculated values show a slightly larger bias.

To summarize the above results and discussion, the organic nitroxide radical shows a very small first ionization potential arising from the antibonding π -odd electron, and the PE spectrum has been substantiated theoretically by RHF and UHF MO calculations. We are now examining other organic nitroxide radicals.

The authors wish to thank Professor H. Kato for his stimulating discussions and interest in this work.

References

- [1] D.W. Turner and D.P. May, *J. Chem. Phys.* 45 (1966) 471;
J.E. Collin and P. Natalis, *Intern. J. Mass Spectrom. Ion Phys.* 1 (1968) 483, and references therein.
- [2] M.I. Al-Joboury and D.W. Turner, *J. Chem. Soc.* (1964) 4434;
C.R. Brundle, *Chem. Phys. Letters* 5 (1970) 410;
P. Natalis and J.E. Collin, *Chem. Phys. Letters* 2 (1968) 79, and references therein.
- [3] A.B. Cornford, D.C. Frost, F.G. Herring and C.A. McDowell, *J. Chem. Phys.* 54 (1971) 1872.
- [4] A.B. Cornford, D.C. Frost, F.G. Herring and C.A. McDowell, *Chem. Phys. Letters* 10 (1971) 345.
- [5] D.W. Davis and D.A. Shirley, *J. Chem. Phys.* 56 (1972) 669.
- [6] I. Morishima, K. Endo and T. Yonezawa, *J. Am. Chem. Soc.* 93 (1971) 2048; *Chem. Phys. Letters*, to be published.
- [7] A.K. Hoffmann and A.T. Henderson, *J. Am. Chem. Soc.* 83 (1961) 4671.
- [8] W.C. Price, *Molecular spectroscopy* (Institute of Petroleum, London, 1968) p. 221;
H. Lefebvre-Brion, *Chem. Phys. Letters* 9 (1971) 463.
- [9] J.A. Pople, D.L. Beveridge and P.A. Dobosh, *J. Chem. Phys.* 47 (1967) 2026.
- [10] T. Yonezawa, H. Konishi and H. Kato, *Bull. Chem. Soc. Japan* 42 (1969) 933.
- [11] D.L. Beveridge, P.A. Dobosh and J.A. Pople, *J. Chem. Phys.* 48 (1967) 4802.
- [12] A.K. Hoffmann, A.M. Feldman, E. Gelblum and W.G. Hodgson, *J. Am. Chem. Soc.* 86 (1964) 639.

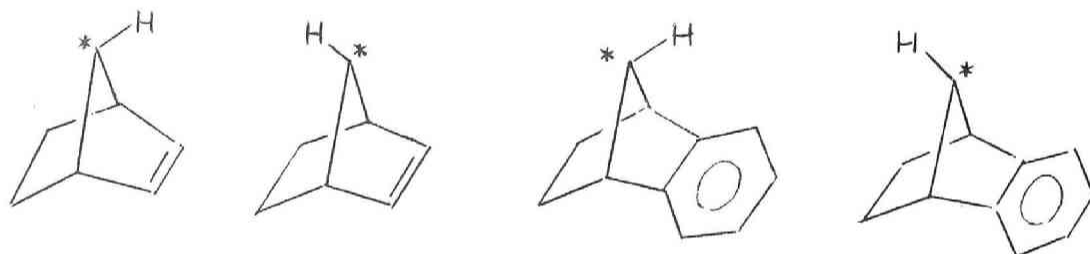
CHAPTER 4

Electron Spin Resonance Spectra of
Bicyclic Nitroxide Radicals

Abstract:

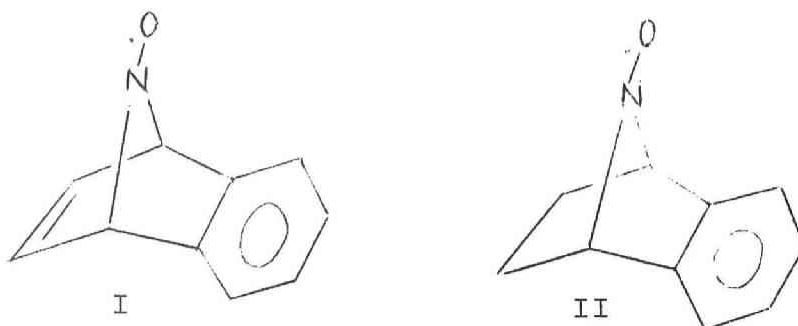
Electron spin resonance spectra of bicyclic nitroxide radicals, 7-azabenzonorbornadiene-7-oxy1 (I) and 7-azabenzonorbornene-7-oxy1 (II), obtained from hydroperoxide oxidation of the corresponding amines, have been studied. The nitrogen hyperfine coupling constants of 22.6 and 23.1 G for I and II, respectively, are the largest for dialkyl nitroxide radicals so far reported and suggest strongly pyramidal structure around the nitrogen atom. Appreciable temperature dependence of proton hyperfine coupling constants for the vinylidene proton in I was observed. The nitrogen atom and other protons in I and II were not sensitive to the temperature variation. The observed proton hyperfine coupling constants and their temperature dependence were interpreted in terms of specific orientation of the N-O bond in I and II with the aid of INDO MO calculations. It was suggested that the N-O bond tilts toward the vinylidene group in I and toward the benzene ring in II. These were also discussed in connection with stereospecific orientation of the radical lobe in the corresponding hydrocarbon radicals and the lone pair electrons in the corresponding amines.

The 7-norbornenyl and 7-norbornadienyl systems offer a structural framework from which long-range nonbonded interactions may be examined. The cation has been shown to exhibit such bonding to an unusual degree.³ Recently the radical and the anion for the 7-norbornenyl^{4,5} and 7-benzonorbornenyl⁶ systems have been investigated and it was revealed that homoconjugative interaction between the π electrons and the nonbonded half or doubly occupied orbital on the 7-carbon has a destabilizing effect which is important to determine the orientation of the radical or anion radical lobe. The stereo-



*=cation, radical, anion
chemistry of these intermediate is quite important and attracted in view of pronounced stereoselectivity for reactions proceeding through the intermediacy of 7-norbornenyl radical⁴ and anion.⁵

As a part of our continuing studies on the nonbonded interaction^{7,8,9,10} and on the stereospecific electron spin transmission,^{11,12,13} we wish to report here an esr study of bicyclic nitroxide radicals, 7-azabenzonorbornadiene-7-oxyl (I) and 7-azabenzonorbornene-7-oxyl (II).¹⁴ These nitroxide



radicals are interesting from the following points of view.

(a) They are novel bicyclic nitroxide radicals with 7-azanorbornadiene and 7-azanorbornene skeletons, much more strained than the other bicyclic nitroxide radical, 8-azabicyclo[3.2.1]octane-8-oxyl (III) and its derivatives which have been reported by Rassat¹⁵ and Ingold.¹⁶ (b) Determination of the structure around the nitrogen atom (planar or non-planar) in I and II and its comparison with other bicyclic nitroxide radicals is of interest. (c) The orientation of the N-O bond, namely of odd electron orbital, in I and II is of great interest in relation to that for 7-norbornenyl radical⁴ and 7-benzonorbornenyl radical.⁶ Thus, I and II offer good models for studying bishomoconjugative interaction involving radical orbital and neighboring vinylidene and benzylidene π electrons. (d) Comparison with the lone pair orientation of 7-azabenzonorbornadiene and 7-azabenzonorbornene derivatives is also interesting in order to study the intrinsic nature of the n, π bishomoconjugative interaction. (e) Studies on the electron spin distribution through the σ -bonded skeleton in these rigid bicyclic radicals may attract considerable experimental and theoretical interests.

Experimental Section

7-Azabenzonorbornadiene (X) and 7-azabenzonorbornene (XI) were prepared by the method of Carpino.¹⁷ 7-Azabenzonorbornene-5,6-exo-d₂ was prepared from Pd-carbon catalyst hydrogenation by deuterium gas of X. Sample preparation for esr measurements were made as follows. Into an aqueous solution (20mg/2ml-H₂O) of X or XI containing 20 mg of sodium tungstate and 20 mg of EDTA, 50 μ l of 30 % hydrogen peroxide solution was added. After 10~20 min at room temperature, the solution was extracted by 2 ml of dichloromethane. The CH₂Cl₂ solution was bubbled by N₂ stream and after then sealed. All the esr spectra were obtained with a JEOL PE-1X spectrometer. ¹H nmr spectra of the CHCl₃ solution were measured with a Varian Associates HR-220 high-resolution spectrometer (Kyoto Univ.) operating at 220 MHz.

Results

The esr spectra of I and II are shown in Figures 1 and 2, respectively. The spectra were obtained at room temperature. Each spectrum consist of 1:1:1 triplet splitting of 22.6 and 23.1 G respectively which further split into two 1:2:1 triplets of 4.6 and 0.94 G for radical I and into nine splittings for radical II. The computer simulated spectrum with Lorentzian line shape shown in the lower half of the figures was based on the hyperfine splitting constants (hfsc's)

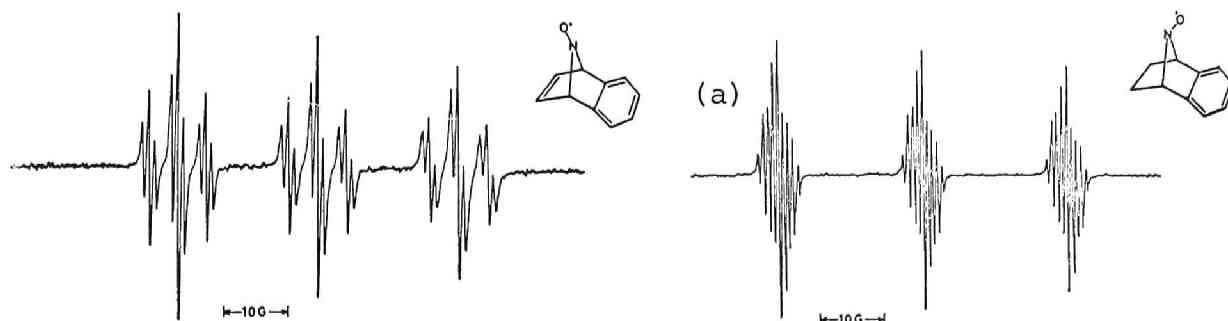


Figure 1. Esr spectrum of I.

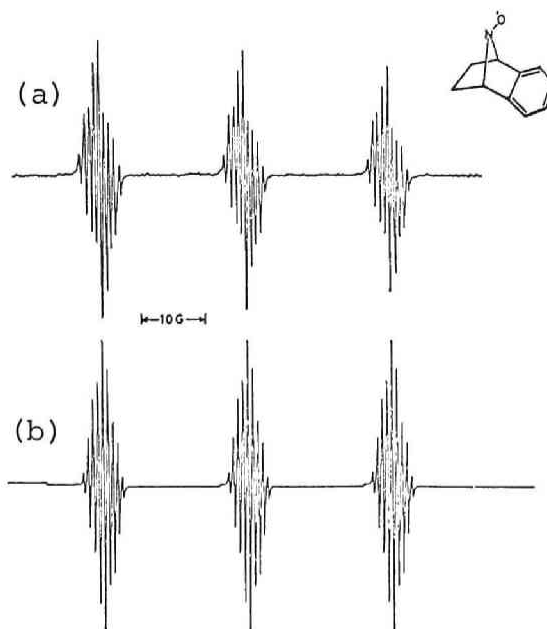


Figure 2. Esr spectrum of (a) II and (b) its computer simulated spectrum.

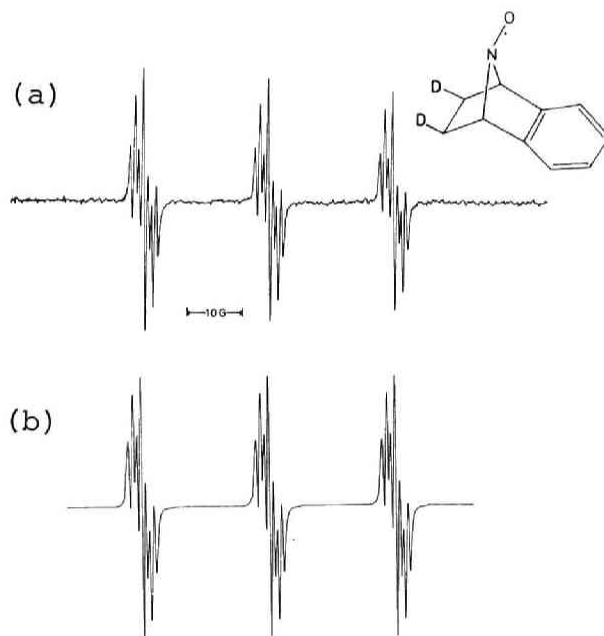


Figure 3. Esr spectrum of (a) exo-d₂ derivative of II and (b) its computer simulated spectrum.

listed in Table I and was obtained by a systematic variation of the coupling constants consistent with the total spread of the spectrum. The splitting constants for II are a little bit different from those presented in our preliminary report.¹ The hfsc's given here improves appreciably the match between the experimental and calculated spectra with regard to the relative intensities of the third line of each triplet signal.

The large hfsc's of 22.6 and 23.1 G are undoubtedly resulting from coupling with nitrogen nucleus. The splitting constant of 0.96 G in I and the related value of 0.90 (or 0.88) G in II are most probably assigned to the bridgehead protons (1- and 4-protons), since these protons are common in each radical. From the steric structure, the bridgehead proton hfsc's would not be seriously changed even if the favored orientation of the nitroxyl group is different in I and II. Accordingly, the possibility of the assignment of these coupling constants to one pair of the benzene ring protons would be ruled out. The triplet of 4.6 G in I is, thus, due to the vinylidene protons and 0.88 (or 0.90) G and 1.58 G splitting in II to the exo and endo protons, respectively. We favor the assignment of the 1.58 G splitting to the endo protons and the remaining one to the exo protons, which is based on a comparison with 7-norbornyl and 7-norbornenyl radicals⁴ in which the relationship $|a_{\text{endo}}^{\text{H}}| > |a_{\text{exo}}^{\text{H}}|$ may hold. In order to ascertain this assignment, we obtained the esr spectrum of the exo-d₂ derivative (II') of II (Figure 3). The hfsc's of II', optimized for the simulated spectra (lower half of Figure 3), are also given in Table I.

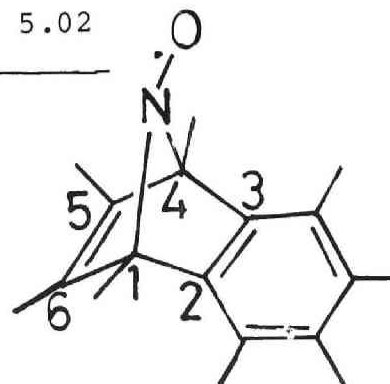
Table I. Hyperfine Splitting Constants (hfsc's) and
g-Values^a

Radical	hfsc (gauss) ^b					g-value
	7-N	1,4-H	5,6-H	5,6-H (<u>exo</u>)	5,6-H (<u>endo</u>)	
I	22.6	0.98	4.11	—	—	2.0058
II	23.1	0.88 ^c	—	0.90 ^c	1.58	2.0058
II' (<u>exo</u> -d ₂)	23.1	0.89	—	0.15 (d) ^e	1.45	2.0058

a. Obtained at room temperature (18°C). b. Optimized values obtained from the matching of the observed and simulated spectra. c. The assignments of the splitting constants of 1,4- and 5,6-protons are tentative. d. Exo-d₂ derivative of II. e. The splitting constant of deuteron.

Table II. Temperature Dependence of Hfsc's in I

temperature	hfsc (gauss)		
	7-N	1,4-H	5,6-H
18°C	22.6	0.98	4.11
-46°C	22.6	1.00	4.99
-60°C	22.6	1.03	5.02



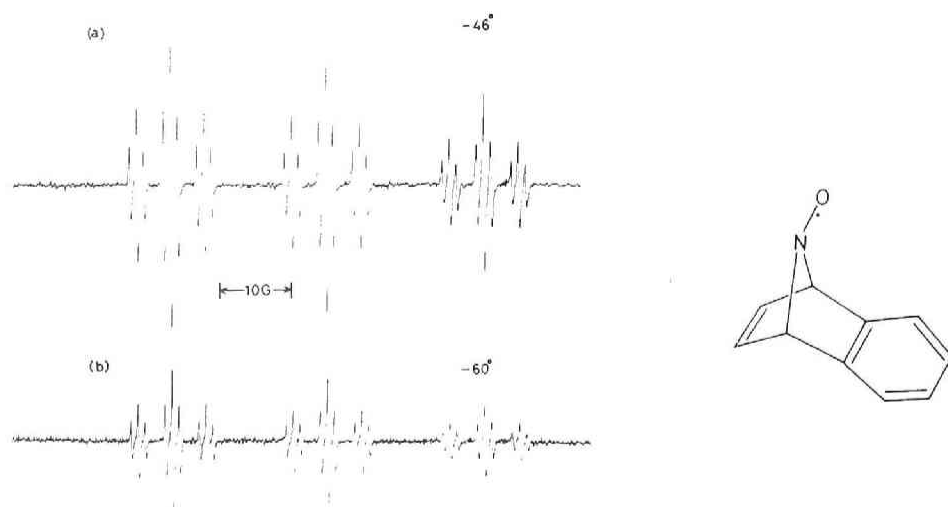


Figure 4. Temperature dependence of esr spectra of I.

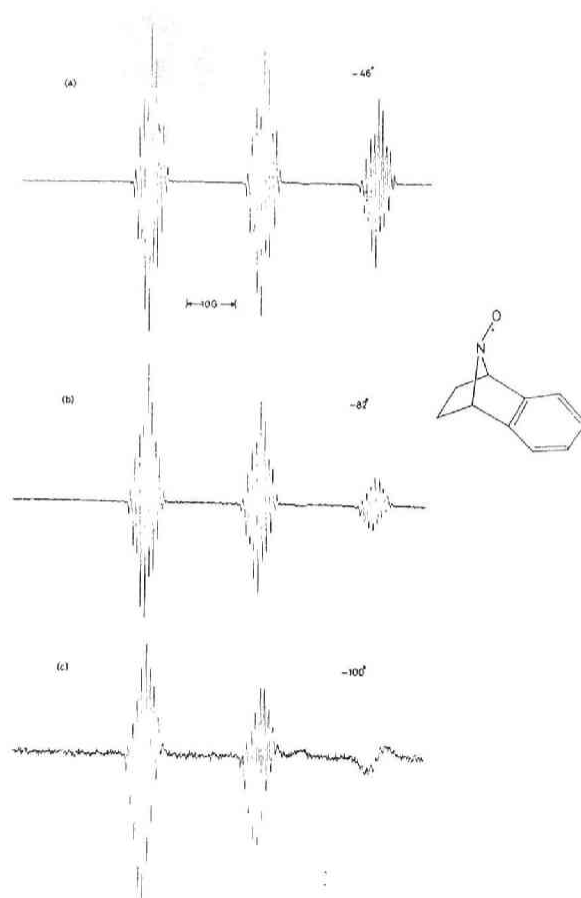


Figure 5. Temperature dependence of esr spectra of II.

The splitting of 0.90 (or 0.88) G in II corresponds well to that of 0.15 G of the deuteron nucleus in II'. It is, therefore, concluded that the 0.90 (or 0.88) G hfsc is attributed to the 5,6-exo protons. The g values of I and II are characteristic of the typical dialkyl nitroxide radicals.¹⁸

The effect of temperature variation on the esr spectra and hfsc's of I and II are presented in Figures 4 and 5. These esr spectra of I and II show that the absorption lines of the higher magnetic field are strongly broadened at low temperature. Even at room temperature there is considerable differential broadening of the line width. This phenomenon is attributable to the strong anisotropic effect as has been frequently encountered for nitroxide radicals.¹⁹ At low temperature the viscosity of solvent would increase and the motion of the solute radical will be reduced, and consequently the effect of anisotropic hyperfine interaction²⁰ will appear, causing a different set of relaxation times for each hyperfine line. It is to be noted that there is an appreciable temperature dependence of proton hfsc's in I, but not for those in II (Table II). The nitrogen hfsc in I and II did not show temperature dependence. These features of temperature dependence of the proton hfsc's will be discussed in the following section in connection with favorable orientation of the N-O group in I and II.

Discussion

First, it should be noted that the 22~23 G of nitrogen hfsc's are unusually large for dialkyl nitroxide radicals (see Table III). Besides I and II, the largest one is for III reported by Ingold¹⁶ with a_N of 19.57 G. The large a_N values in I and II implicate the enhanced s character of the nitrogen atom in the half-occupied orbital compared with radical III. Decrease in $C_\alpha-N-C_\alpha$, bond angle (θ) would be accompanied by an increase in the s character of the nitrogen atom. This structural change could be responsible for increase in the a_N values on going from III ($\theta \sim 105^\circ$) to I or II ($\theta \sim 95^\circ$). It has been pointed out that in hydrocarbon radicals the decrease in the $C_\beta-C_\alpha-C_\beta$, bond angle is accompanied by increase of the pyramidalty around the carbon atom at the radical center.^{21,22} The s-character of the nitrogen atom in I and II is also expected to be enhanced by out-of-plane distortion of the N-O bond. Thus the large nitrogen hfsc's in I and II is attributable to combined causes arising from decrease in the $C_\alpha-N-C_\alpha$, angle and the out-of-plane torsion of the N-O bond.

In order to substantiate theoretically these features, we performed the INDO-UHF MO calculations³⁰ for dimethyl nitroxide (DMNO) as a model molecule (Figure 6). Figure 6 shows spin density on the nitrogen 2s AO and total energy for DMNO with θ ($C_\alpha-N-C_\alpha$, angle) = 80° and 120° , varying out-of plane angle ψ of the N-O bond. The bond lengths ($\text{\AA}$) are chosen as follows: N-O = 1.2, N-C = 1.47, C-H = 1.09, and C=C = 1.33 $\text{\AA}$. It is apparent in Figure 6 that for the unstrained DMNO ($\theta = 120^\circ$) the geometry with a planar radical center

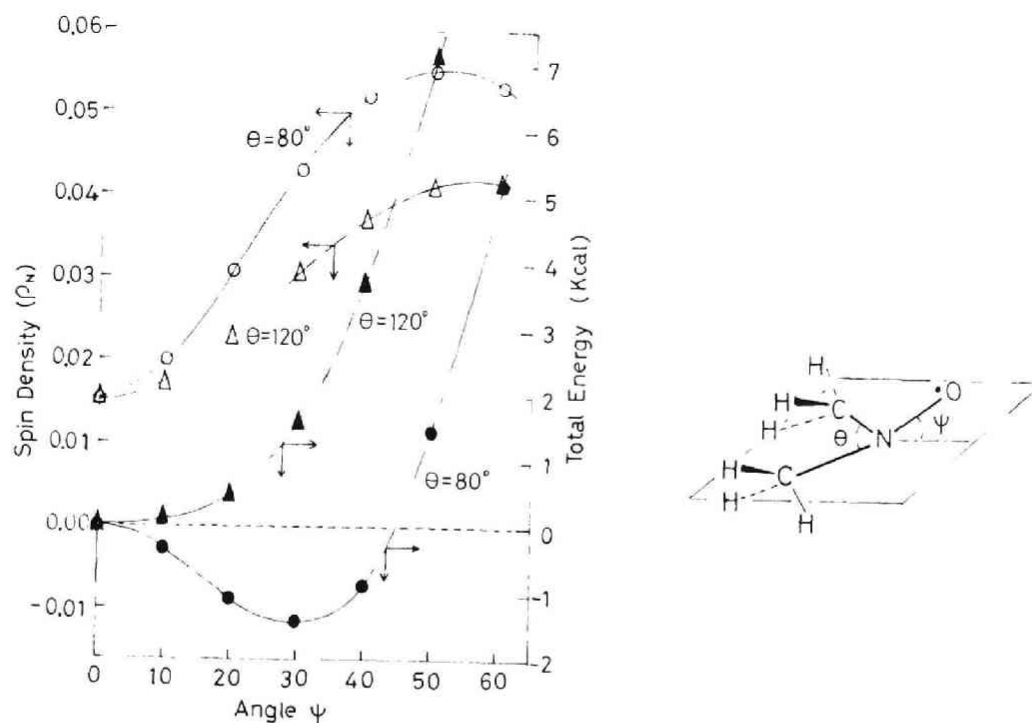


Figure 6. INDO spin densities on the nitrogen s atomic orbital in DMNO for the structures of $\theta = 120^\circ$ (Δ) and $\theta = 80^\circ$ ($\circ$), and the total energies for the structures of $\theta = 120^\circ$ ($\blacktriangle$) and $\theta = 80^\circ$ ($\bullet$) relative to the energy of the planar structure ($\theta = 0^\circ$) as a function of angle ψ (see text).

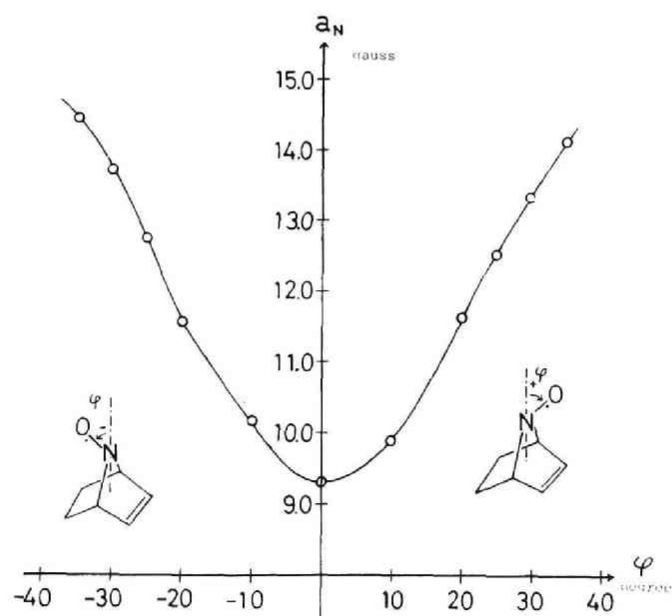


Figure 7. Variation of nitrogen hfsc in VI as a function of ψ (INDO-UHF-MO).

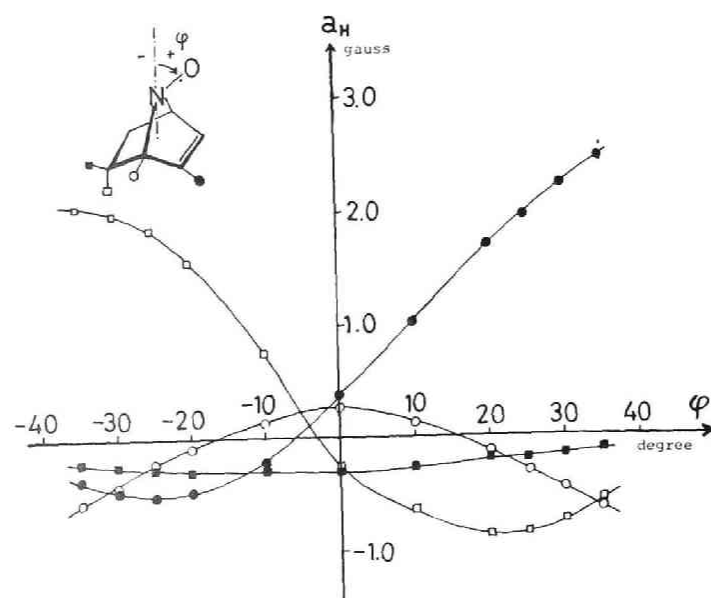


Figure 8. Variation of the proton hfsc's in VI as a function of ψ (INDO-UHF-MO).

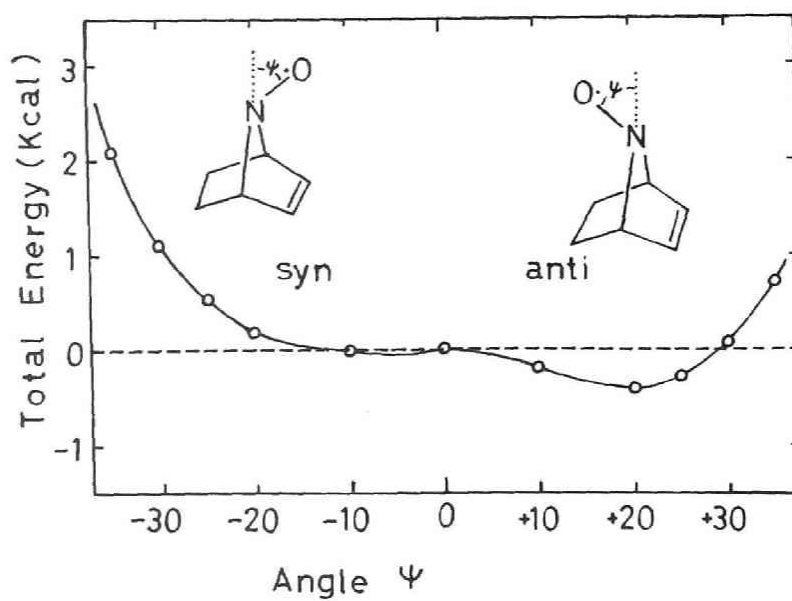
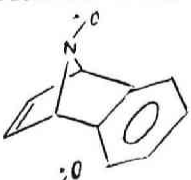
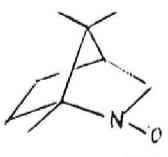
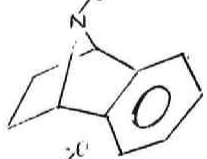
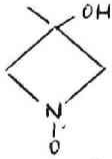
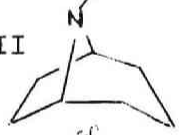
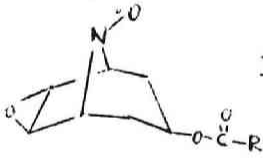


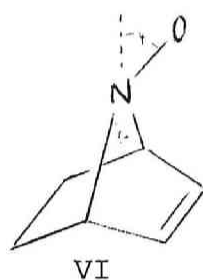
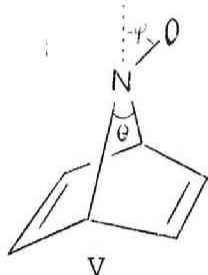
Figure 9. Variation of the total energy of VI as a function of ψ (INDO-UHF-MO).

Table III. Nitrogen Hfsc's for Selected Bicyclic and
Dialkyl Nitroxide Radicals

Radical	a_N (gauss)	ref.	Radical	a_N (gauss)	ref.
I 	22.6	present work		16.97	(24)
II 	23.1	present work		16.5	(25)
III 	19.57	(16)		19.8	(26)
	19.5	(15)	$(CH_3)_2NO$	12.3	(27)
IV 	17.6	(16)	$(t-Bu)_2NO$	15.2	(28)
	17.4	(23)	Ph_2NO	9.66	(29)

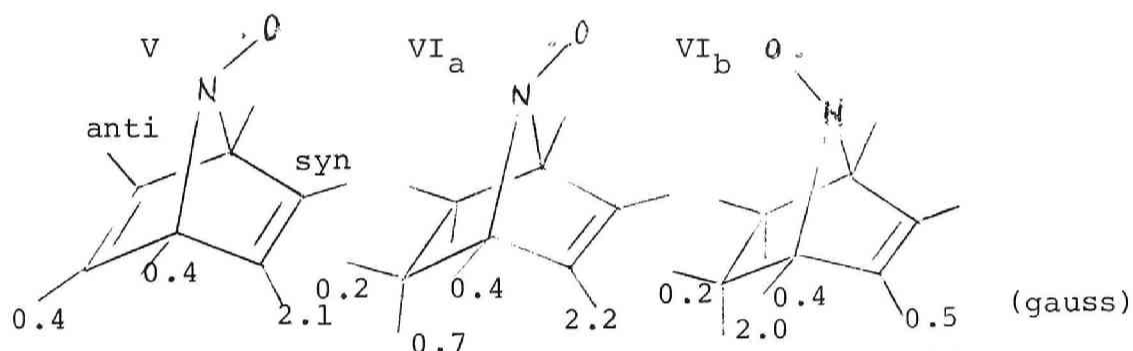
($\psi = 0^\circ$) has the lowest energy. However, when the $C_\alpha-N-C_\alpha$ bond is strained to $\theta = 80^\circ$, the pyramidal structure ($\psi = 30^\circ$) becomes most stable. This corresponds to the generalization that nonplanarity of the radical center of an alkyl radical increases as bond angle θ is decreased.^{21,22} The calculated spin density on the nitrogen 2s atomic orbital increases with the angle ψ to a greater extent for the strained conformation ($\theta = 120^\circ$). From these results and discussion the pyramidal structure around the nitrogen atom is concluded.

In order to obtain further insight into geometrical structures of I and II and to interpret their proton hfsc's, INDO calculations were also carried out for 7-azaborbornadiene-7-oxyl (V) and 7-azanorbornene-7-oxyl (VI) as a function of the out-of-plane angle ψ of the N-O group. The structural parameters which were used in the calculations were derived from the related hydrocarbons, norbornadiene and norbornene; C-C = 1.54 Å, C=C = 1.33 Å, C-H = 1.09 Å, $\theta = 95^\circ$, and $\theta' = 120^\circ$. Here we did not research the optimum geometry by

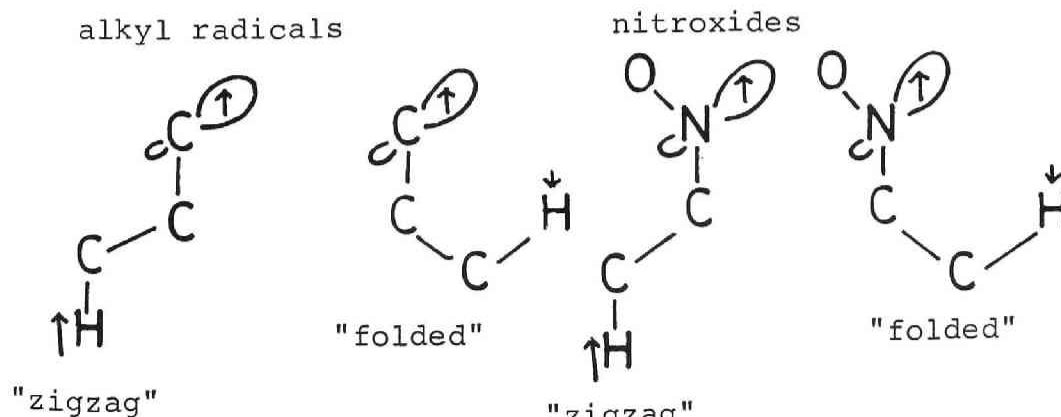


varying bond lengths and angles except the out-of-plane distortion angle ψ . The resulting nitrogen and proton hfsc's of VI are shown in Figures 7 and 8, respectively. The calculated total energy with variation of angle ψ is given in Figure 9. Figure 8 shows that in VI the bridge-head proton (1,4-H) hfsc remains relatively small (+0.2~-0.4 G) from

-30° to +30°. This ascertains the assignment of the 0.98 G triplet in I and 0.88 G (or 0.90 G) triplet in II to the 1,4-proton hfsc. The small value of the α proton hfsc is attributable to the geometry in which the dihedral angle between the odd electron orbital on the nitrogen atom and the $C_{\alpha}-H_{\alpha}$ bond is nearly 90° both for I and II. It is also to be noted that there is a great difference between the calculated hfsc's of β -hydrogens on the syn and anti sides in VI. The calculated proton hfsc's in V and VI in which the N-O bond tilts 30° from the $C_{\alpha}-N-C_{\alpha}$ plane are exemplified below. The spin density induced on the syn proton (with respect to the bent N-O bond) is much larger than that on the



anti proton. It is well established that large positive spin density is induced on a β -proton that lies on a "zigzag" arrangement of the carbon skeleton in an alkyl σ -radical, while a proton that lies on the "folded" arrangement senses a small amount of negative spin density.^{7,8,9,11,13}

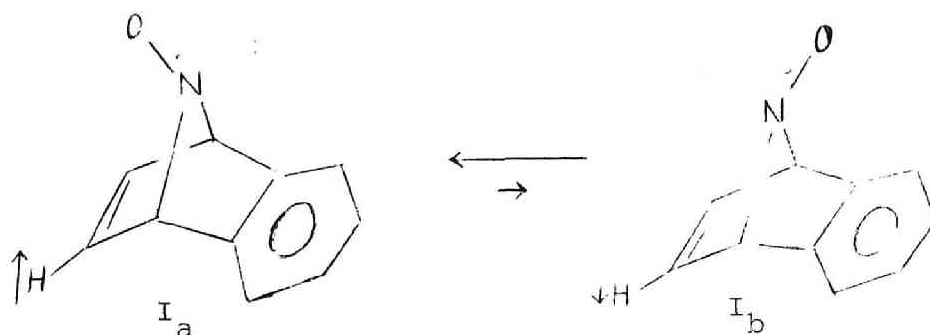


Since the N-O bond tilts from the $C_{\alpha}-N-C_{\alpha}$ plane in I and II as have been discussed previously, similar relation of the intramolecular electron spin distribution may be expected. The calculated results for V and VI reproduce the similar trend. The large difference in the hfsc's of syn and anti β -hydrogens in V is, therefore, attributable to the different arrangement of the $O-N-C_{\alpha}-C_{\beta}-H_{\beta}$ skeleton, "zigzag" or "folded". Referencing the large difference in the syn and anti proton hfsc's in V, the observed large hfsc (4.6 G) in I could be attributed to the β -syn proton, and it may be speculated that the N-O bond predominantly tilts to the opposite side of the benzene ring. By comparison with radical I and with predicted splitting constants obtained for model VI_a and VI_b, 0.88 and 0.90 G splittings in II are attributed to the bridgehead and β -exo protons and 1.58 G splitting to the β -endo proton, as has been estimated previously.¹ The predicted splitting constants for V are a factor of 2 smaller than the experimental values of I. Arguing by analogy, one might expect that the conformation of V_a is responsible for the esr splittings of II. On the basis of above discussion, we propose that the N-O bond of II tilts toward the benzene ring, contrary to the case of I.

Inspection of Figure 9 shows that the conformation of $\psi = +20^{\circ}$ (anti to the double bond) is the most stable, which is in contrast with the above discussion concerning the orientation of the N-O bond. However, it should be noted that the energy variation for $\psi = -20^{\circ}$ to $+30^{\circ}$ is within 0.5 Kcal/mol. Considering that any optimization concerning

the bond lengths and angles in this MO calculation has not been carried out, we might say that the calculated results (Figure 9) suggests that the total energy does not change so much for a rather large variation of angle ψ .

It is worth noting that the temperature dependence of proton hfsc's in I and II connects with the theoretical prediction of hfsc's varying with nonplanar structure around the nitrogen atom, as will be discussed below. The vinylidene proton hfsc in I exhibits appreciable temperature dependence (Table II). The bridge-head proton hfsc in I increases markedly at low temperature (-40° and -60°). Referencing the calculated results for V (Figure 8), a large positive spin density may be induced on the vinylidene proton in I_a in which the N-O bond tilts opposite to the benzene ring, whereas only a small negative spin density in I_b . Consequently,



the remarkable difference ($\Delta = 0.91$ G) of hfsc's of 5,6-protons between at -60° and at -10°C implies that I_a is more stable than I_b and that the relative population of I_b increases at high temperature, resulting in the decrease of the vinylidene proton hfsc. For radical II, however, the proton hfsc's are not sensitive to temperature variation. This could be explainable if we assume that the equilibrium orientation of the N-O group is at the position anti with

respect to the benzene ring and that the energy difference between the anti and syn conformations is larger than that of I. In the N-O anti conformation, all the calculated proton hfsc's are not sensitive to the variation of ψ , which may be responsible for the above experimental result for radical II. Thus, the features of temperature dependence of the proton hfsc's appear to provide evidence for specific orientation of the N-O group in radicals I and II. From these results and discussion, it is concluded that the N-O group tilts toward benzene ring in radical II, whereas preferably in the opposite direction for I.

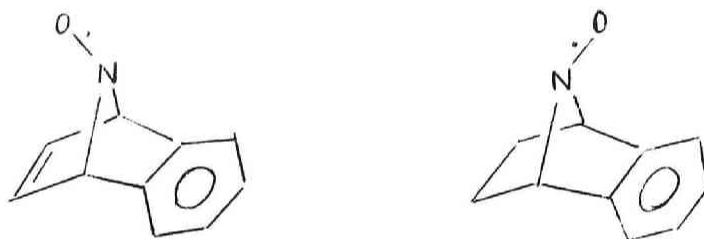


Figure 10 shows the nmr spectra of the CH_2Cl_2 solution of I and II. Since purification of these radicals is difficult, the spectra are contaminated with signals of some other diamagnetic species. However, one can find the signals with rather large line width in Figure 10. Assuming these absorptions to be the signals of the phenyl protons in I and II, hfsc's are estimated (Table IV). These values of the hfsc's in Table IV are fairly different between in I and in II. This experimental trend supposes the above conclusion concerning the different N-O orientation in I and II.

It is also of interest to take a look at the preferential orientation of radical lobe in I and II in relation to that in the corresponding hydrocarbon radicals. The bent structure

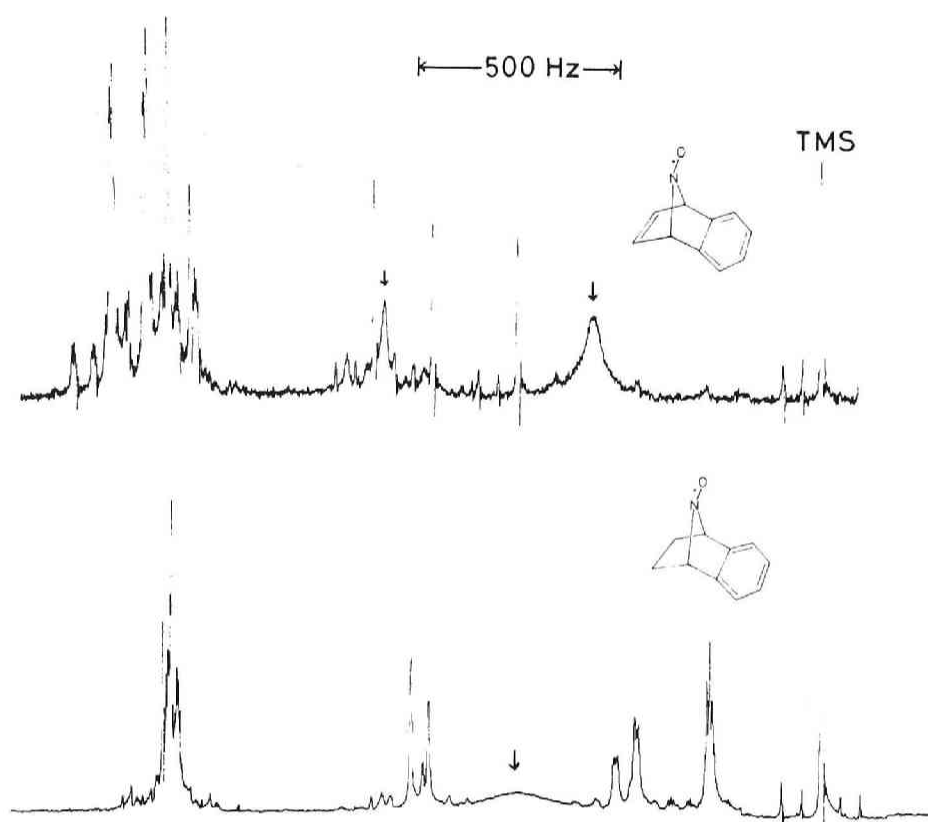


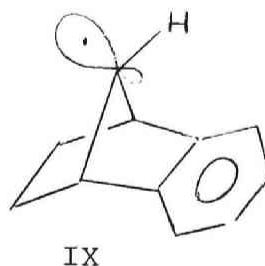
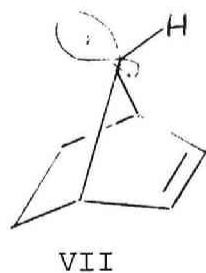
Figure 10. Nmr spectra of the CDCl_3 solution of I and II (at 220 MHz).

Table IV. Hfsc's Obtained from Nmr Measurements

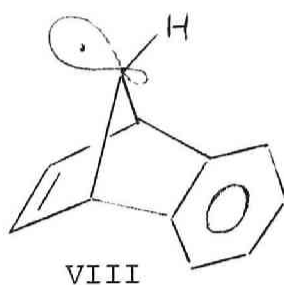
Radical	$\delta^1\text{H}$ ^a (ppm from TMS)	hfsc ^b (gauss)
I	2.52	-0.048
	4.84 ^c	-0.023 ^c
II	3.27	-0.039

a. Observed with a Varian HR-220 nmr operating at 220 MHz (at 20°C). b. Calculated from the relation, $\Delta H/H = -a \frac{\gamma_e g S(S+1)}{H \gamma_H 3kT}$. ΔH is calculated references to the diamagnetic resonance position of the phenyl protons in the parent amine of I and II. c. There remains an ambiguity in assigning this signal to the phenyl proton in I.

of radical II compares to 7-norbornenyl radical (VII)⁴ and 7-benzonorbornenyl radical (IX)⁶ in which radical lobe occupies the anti position as proved by an esr spectroscopy and stereoselectivity in radical transfer reaction. It is



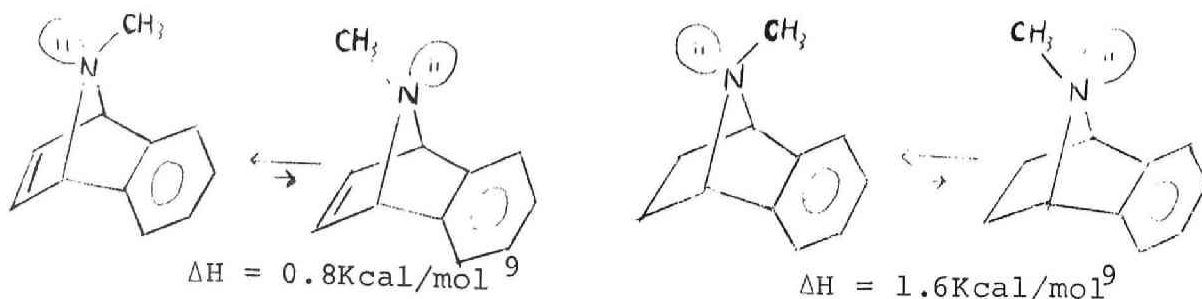
interesting to note that in these radicals the odd electron orbitals are away from the π -orbital. The greater stability of the N-O bond syn conformer with respect to the benzene ring than the anti one would imply that the interaction between the π orbitals and the half-occupied orbital on nitrogen has the destabilizing effect, as is the case for VII and IX. On the other hand, it has been estimated that the C₇-H₇ bond lies anti to the phenylene ring in 7-benzonorbornadienyl radical (VIII) from an esr study.⁶ The



orientation of the radical orbital in I is opposite to that in VIII. There are possibly two factors that determine the orientation of the radical lobe in these 7-benzonorbornadienyl system. One is that the interaction between the half-occupied orbital and the π orbital (bishomoallylic

interaction) is of more anti-bonding character than that involving π orbital on the benzene carbon (bishomobenzylic interaction). Another one is that a small difference in the steric structure or the steric strain causes the different orientation of the radical lobe. For radical VIII it has been proposed⁶ that the bishomobenzylic interaction is larger than the bishomoallylic interaction. However, the opposite orientation of the half-occupied orbital in I and VIII may imply that the latter factor becomes considerably important in I. This estimation is in consistent with the assumption that in I the two conformers (N-O syn and anti) exist and the relative population varies with temperature as have been already discussed.

Finally we will discuss the stereospecific orientation of radical lobe on the nitrogen in I and II in connection with the orientation of nitrogen lone pair in the corresponding parent amines, 7-azabenzonorbornadiene (X), 7-azabenzonorbornene (XI) and their N-methyl derivatives (XII and XIII).⁹ It may be expected that the interaction of the π -orbitals with the doubly occupied orbital on 7-carbon is of much more repulsive character (i.e., destabilizes the system) than that with the half-occupied orbital. Recently we have demonstrated that the lone pair anti conformer of N-methyl-7-azabenzonorbornadiene (XII) is favored over the syn one.⁹ For XIII, the anti



conformation is favored in which the lone pair electrons are located at the anti position with respect to the benzene ring. Similar experimental trend of the lone pair orientation is also encountered for the N-H derivatives (X and XI).⁹ These results have been discussed in terms of the "repulsive" n, π interaction in bishomoallyl and bishomobenyl systems.⁹ In X and XII, the bishomobenzylic repulsive interaction is considered to be more important than the bishomoallylic interaction. This is in accordance with the trend of the corresponding hydrocarbon radical (VIII). Contrary to this, the orientation of the radical lobe in I is apparently different from that of the lone pair in XI and XIII. Such a difference appears to be interesting, since it might be resulting from the difference in the repulsive bishomoallylic or bishomobenzylic interaction in these systems, or from the small difference in their steric structures.

Further experimental and theoretical studies concerning the orientation of the radical lone in 7-benzonorbornadienyl and 7-benzonorbornenyl systems are hopefully awaited in order to gain further insight into the intrinsic nature of the bishomoconjugative interaction. We are now studying the effect of substitution at the benzene ring and vinylidene group on the stereospecific orientation of the N-O bond in these bicyclic nitroxide radicals.

References and Notes

- (1) Presented partly as a communication, I. Morishima, K. Yoshikawa, K. Bekki, M. Kohno, and K. Arita, J. Amer. Chem. Soc., 95, 5815(1973).
- (2) (a) Kyoto Univ. (b) Kyoto Institute of Technology.
(c) JEOL Inc.
- (3) S. Winstein, Quart. Rev. Chem. Soc., 23, 141(1969).
- (4) P. Bakuzis, J. K. Kochi, and P. J. Krusic, J. Amer. Chem. Soc., 92, 1434(1970); J. K. Kochi, P. Bakuzis, and P. J. Krusic, *ibid.*, 95, 1516(1973).
- (5) J. K. Still and K. N. Sannes, J. Amer. Chem. Soc., 94, 8489(1972).
- (6) T. Kawamura, Y. Sugiyama, M. Matsunaga, and T. Yonezawa, J. Amer. Chem. Soc., 97, 1627(1975).
- (7) I. Morishima and K. Yoshikawa, J. Amer. Chem. Soc., 97, 2950(1975).
- (8) I. Morishima, K. Yoshikawa, M. Hashimoto, and K. Bekki, J. Amer. Chem. Soc., 97, 4283(1975).
- (9) K. Yoshikawa, K. Bekki, M. Karatsu, T. Kamio, and I. Morishima, J. Amer. Chem. Soc., in press.
- (10) I. Morishima, K. Yoshikawa, K. Toyoda, M. Karatsu, T. Yonezawa, S. Sakata, and S. Ikegami, submitted for publication.
- (11) (a) T. Yonezawa, I. Morishima, and Y. Ohmori, J. Amer. Chem. Soc., 92, 1267(1970); (b) I. Morishima, K. Okada, M. Ohashi, and T. Yonezawa, Chem. Commun., 33(1971); (c) I. Morishima and T. Yonezawa, J. Chem. Phys., 54, 3238(1971); (d) T. Yonezawa, I. Morishima, Y. Akana, and

- K. Fukuta, Bull. Chem. Soc. Japan, 43, 379(1970).
- (12) (a) I. Morishima, T. Yonezawa, and K. Goto, J. Amer. Chem. Soc., 92, 6651(1970); (b) I. Morishima, K. Okada, T. Yonezawa, and K. Goto, Chem. Commun., 1535(1970); (c) I. Morishima, K. Okada, T. Yonezawa, and K. Goto, J. Amer. Chem. Soc., 93, 3922(1971); (d) I. Morishima, K. Okada, and T. Yonezawa, *ibid.*, 94, 1425(1972).
- (13) (a) I. Morishima, K. Yoshikawa, and K. Okada, J. Amer. Chem. Soc., in press; (b) K. Yoshikawa, M. Hashimoto, H. Masuda, and I. Morishima, submitted for publication.
- (14) An esr study of the derivatives of II has been reported. However, the assignment is different from ours; D. J. Kosman, Tetrahedron Lett., 3317(1972).
- (15) A. Rassat and J. Ronzaud, J. Amer. Chem. Soc., 93, 5041(1971).
- (16) G. D. Mendenhall and K. U. Ingold, J. Amer. Chem. Soc., 95, 6395(1973).
- (17) L. A. Carpino and D. E. Barr, J. Org. Chem., 31, 764 (1966).
- (18) A. R. Forrster, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," chap. 5, Academic Press, London.
- (19) Y. Deguchi, Bull. Chem. Soc. Japan, 35, 260(1962); K. Umemoto, Y. Deguchi, and H. Takaki, *ibid.*, 36, 560 (1963).
- (20) H. M. McConnell, J. Chem. Phys., 25, 709(1956).
- (21) A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, Chem. Commun., 1353(1963); J. Chem. Soc. A, 124(1971).

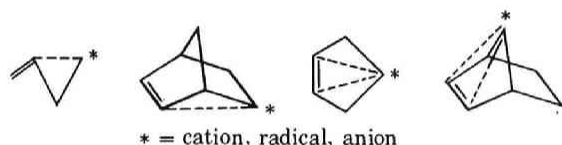
- (22) T. Kawamura, T. Koyama, and T. Yonezawa, J. Amer. Chem. Soc., 95, 3220 (1973).
- (23) A. Rassat and P. Rey, Tetrahedron, 29, 2845 (1973).
- (24) P. G. Gassman and R. L. Cryberg, J. Amer. Chem. Soc., 90, 1355 (1968).
- (25) J. C. Espie and A. Rassat, Bull. Soc. Chim. France, 12, 4385 (1971).
- (26) E. G. Rozanieb and B. D. Solle, Dok. Akad. Nauk. SSSR, 187, 1319 (1969).
- (27) J. Q. Adams, S. N. Nicksic, and J. R. Thomas, J. Chem. Phys., 45, 654 (1966).
- (28) H. Lemaire, A. Rassat, P. S. Gavin, and G. Berthier, J. Chim. Phys., 59, 1247 (1962).
- (29) P. H. H. Fischer and F. A. Neugebauer, Z. Naturforsch, 21b, 1036 (1966).
- (30) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

CHAPTER 5

Homoallyl Interaction between Nonadjacent n, π Electrons, I. Photoelectron Spectroscopic Study.

Abstract: In order to study the nonadjacent n, π electronic interaction, photoelectron spectra have been obtained for saturated and unsaturated derivatives of five- and six-membered cyclic and bicyclic amines. It was found that perturbation of nitrogen lone pair ionization potentials (IP's) induced by the interaction with nonadjacent carbon-carbon double bond is quite different in β, γ -unsaturated five-membered cyclic amines and β, γ -unsaturated six-membered amines. The bishomoallyl homoconjugation in five-membered amines favors n, π through-space interaction with destabilization of lone pair orbital, and homoallyl conjugation in six-membered amines involves n, π and n, π^* interactions with a little stabilization or destabilization of the lone pair orbital. Different features of lone pair IP's were also encountered for N -H and N -methyl derivatives of six-membered amines. These were discussed in terms of relative importance of n, π and n, π^* interactions which depend on molecular symmetry (bishomoallyl or homoallyl interaction), orbital energy level, and orientation of lone pair in cyclic and bicyclic amines.

During the last decade, the consequences of homoconjugation between an unsaturated group and an active center in cations, radicals and anions have been a subject of controversy. Particularly, studies on the interaction between



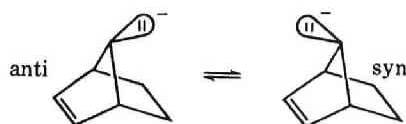
the cation center and the nonadjacent π bond have been extensively performed³ in connection with the debate on "the nonclassical carbonium ion". The great π electron participation in the acceleration of the rate of solvolysis in norbornene derivatives has been well established. Concerning the interaction between the half-occupied orbital and the nonadjacent π bond, Kochi et al.⁴ have reported the ESR studies of 7-norbornenyl radical, and claimed that the configuration with the sp hybrid orbital directed toward the anti side is the most stable form, and that the interaction between the orbitals of carbon 2,3 and the half-occupied orbital on carbon 7 would have a destabilizing effect.

However, the studies on the nonbonded interaction between the doubly occupied n orbital (anion center) and the nonadjacent π group have been quite limited. Recently Stille et al.⁵ have speculated, based on the experimental results of the 7-norbornenyl anion system, that bishomoallyl type interaction makes the $n-\pi$ interacting system less stable due to the antiaromatic character. The conformation of 7-norbornenyl anion has also been examined quantum

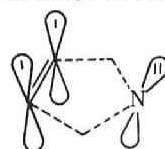
chemically using CNDO/2 and MINDO/2 MO calculations by Santry⁶ and Dewar,⁷ respectively. However, these semiempirical MO calculations failed to predict definitely the orientation of lone pair electrons affected by the neighboring double bond in the 7-norbornenyl anion.⁸ Consequently, the interaction between the lone pair electrons and the nonadjacent π electrons (homoallyl type interaction) is still open to further experimental and theoretical studies.

Recently photoelectron spectroscopy (PES) has proved to be extremely useful in evaluating the electronic interaction between nonadjacent groups⁹ in the ground state molecules. The usefulness of PES in studying π, π interactions in dienes and n, π interactions in various nitrogen and oxygen containing molecules has been demonstrated.¹⁰ The PES studies concerning n, π interactions in unsaturated ketones and ethers have also been reported.¹¹ However, there have been no systematic studies¹² on the n, π interaction between nitrogen lone pair and nonadjacent olefin or benzene π electrons.

In order to elucidate the structural effect on the homoconjugative interaction between lone pair and π electrons, we have performed here a PES study of nonadjacent n, π interaction in various cyclic and bicyclic amines (1-18). Here we are concerned with difference in the intrinsic nature of homoallyl and bishomoallyl n, π interactions. Amines containing the nonadjacent unsaturated group seem to be quite relevant for the study of the intramolecular n, π interactions. The PES study on this n, π homoconjugative interac-



bishomoallyl interaction



homoallyl interaction

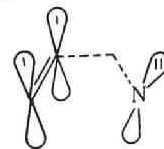
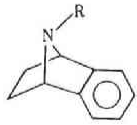
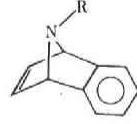
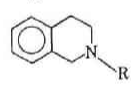
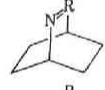


Table I. Ionization Potentials (eV) of Cyclic Amines

Compd	Ionization potential ^a			
	Compd no.	R = H	Compd no.	R = CH ₃
	1	8.7 ₇ (n), 11.4 ₉	2	8.4 ₁ (n), 11.1 ₆
	3	8.6 ₁ (n), 9.7 ₇ (π)	4	8.2 ₁ (n), 9.6 ₆ (π)
	5	8.4 ₄ (n), 9.1 ₀ (π)	6	8.3 ₃ (n), 8.9 ₆ (π)
	7	8.2 ₅ (n), 9.0 ₅ (π), 9.9 ₇ (π)	8	8.1 ₈ (n), 8.7 ₈ (π), 9.0 ₆ (π), 9.6 ₆ (π)
	9	8.6 ₄ (n), 10.7 ₅	10	8.2 ₉ (n), 10.5 ₉
	11	8.6 ₄ (n), 9.3 ₃ (π)	12	8.6 ₇ (n), 9.3 ₇ (π)
	13	8.5 ₇ (n, π), ^b 9.3 ₃ (π)	14	8.6 ₀ (n, π), ^b 9.3 ₀ (π)
	15	8.2 ₂ (n), 10.2 ₉	16	7.7 ₈ (n), 10.0 ₉
	17	8.3 ₅ (n), 9.3 ₆ (π)	18	7.9 ₇ (n), 9.2 ₈ (π)

^a Vertical ionization potentials (± 0.05 eV). ^b This band seems to contain two ionizations.

tion is expected to serve as an aid in studying neighboring group participations of π electrons associated with carbon lone pair in carbanion, the significant reaction intermediate.

Experimental Section

Measurement of Ionization Potential. Helium 504 Å photoelectron spectra were obtained on a JASCO PE-1 photoelectron spectrometer. Calibration of the spectra as effected by using the $^2P_{3/2,1/2}$ doublet of xenon (12.12, 13.44 eV). The estimated uncertainty is about ± 0.05 eV.

Materials. Cyclic and bicyclic amines examined in the present study are listed in Table I. 7-Azabenzonorbornene (5) and 7-azabenzonorbornadiene (7) were prepared following the method of Carpino et al.¹³ 2-Azabicyclo[2.2.2]octane (15), *N*-methyl-2-azabicyclo[2.2.2]octane (16), 2-azabicyclo[2.2.2]oct-5-ene (17), and *N*-methyl-2-azabicyclo[2.2.2]oct-5-ene (18) were synthesized by referring to Cava et al.¹⁴ *N*-Methylpyrrolidine (2), *N*-methylpyrroline (4), *N*-methyl-7-azabenzonorbornene (6), *N*-methyl-7-azabenzonorbornadiene (8), *N*-methyl-1,2,3,6-tetrahydropyridine (12), and *N*-methyl-1,2,3,4-tetrahydroisoquinoline (14) were prepared by *N*-methylation¹⁵ of the parent *N*-H derivatives. Benzonorbornene (21) and benzonorbornadiene (22) were the gift from Dr. H. Tanida of Shionogi Research Laboratory and were used to aid the PE spectral analysis of 5–8. The other compounds (1, 3, 9, 10, 11, 13) were commercially available. The purity of all the samples was checked under the ^1H NMR measurement using a Varian HR-220 NMR spectrometer.

Results and Discussion

The photoelectron spectra of pyrrolidine (3), 1,2,3,6-tetrahydropyridine (11), 7-azabenzonorbornene (5), and 7-azabenzonorbornadiene (7) are exemplified in Figures 1 and 2. Table I lists vertical ionization potentials (IP's) in eV unit for the cyclic and bicyclic amines studied here. Due to the rather large band width, the uncertainty of the IP values is estimated to be ca. ± 0.05 eV. The first IP's (in Table I) can be readily assigned to the ionization from the nitrogen lone pair electrons and the second ones in unsaturated amines to the ionization from the π electrons. For comparison, the IP's of several five- and six-membered cyclic hydrocarbons are listed in Table II.

At first we will discuss IP's of five-membered cyclic and bicyclic amines in terms of the bishomoallyl type n, π interaction and then of six-membered cyclic and bicyclic compounds in terms of the homoallyl type interaction.

(A) Bishomoallyl Type n, π Interaction. In five-membered *N*-H and *N*-methyl cyclic amines, introduction of the double bond increases the first IP's by 0.1–0.2 eV (compare 3 to 1, and 4 to 2). The π IP of 3 or 4 is 0.5–0.6 eV larger than that of cyclopentene (9.18 eV).¹⁶ The correlation between the n and π orbitals in pyrrolidine (1), pyrroline (3), and cyclopentene is schematically shown in Figure 3.

For the interaction between nitrogen lone pair and neighboring π electrons, the π and π^* orbitals are considered to

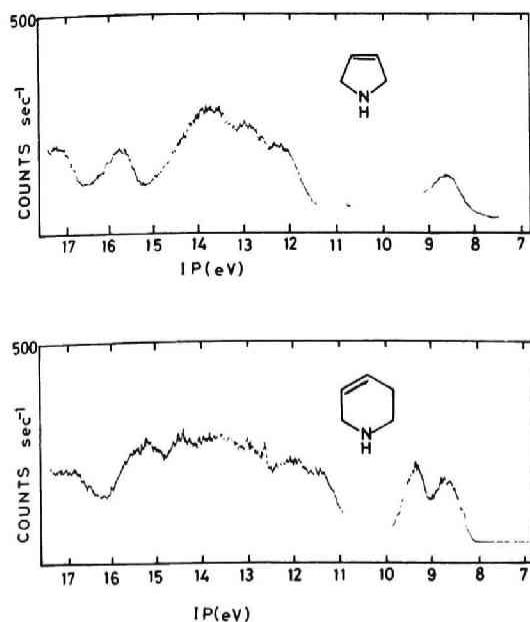
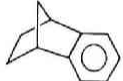
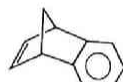


Figure 1. The photoelectron spectra of pyrroline and 1,2,3,6-tetrahydropyridine.

Table II. Ionization Potentials (eV) of Cyclic Hydrocarbons

Compd no.	Ionization potential	Ref
	9.1 ₈	16
19		
	9.1 ₂	16
20		
	8.4 ₂ , 8.9 ₃ , 10.1 ₅	This study ^a
21		
	8.3 ₀ , 8.9 ₁ , 9.2 ₇ , 10.8 ₈	This study ^a
22		
	9.2 ₀	18
23		
	8.9 ₅ , 9.7 ₈	18
24		
	8.4 ₄ , 8.9 ₆	19
25		
	8.4 ₆ , 9.0 ₄	19
26		

^aVertical ionization potentials (± 0.05 eV).

play a significant role. The n, π and n, π^* through-space interactions lead to destabilization and stabilization of the n level, respectively.⁹ The stabilization of the n level in **3** and **4** indicates that the through-space interaction between n and π orbitals is significantly important. This is because the molecular symmetry forbids the n, π^* interaction in the five-membered compounds. Besides this n, π through-space interaction, the "inductive effect" of the olefinic bond upon

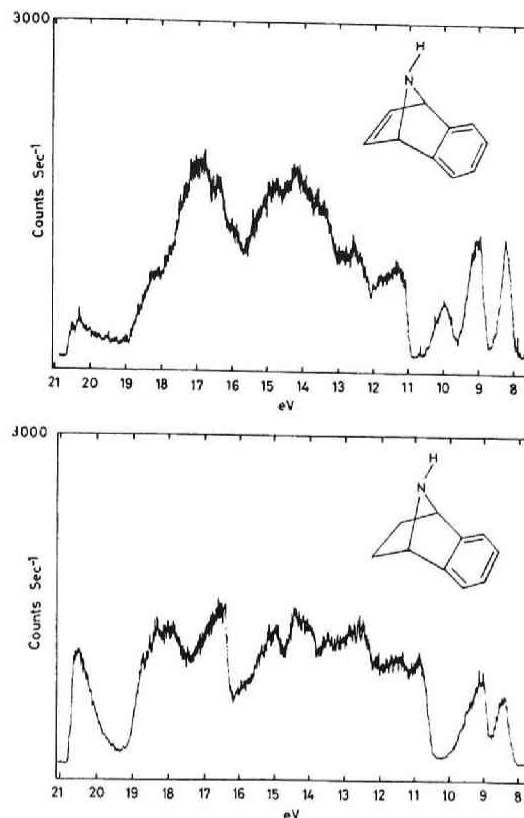


Figure 2. The photoelectron spectra of 7-azabenzonorbornene and 7-azabenzonorbornadiene.

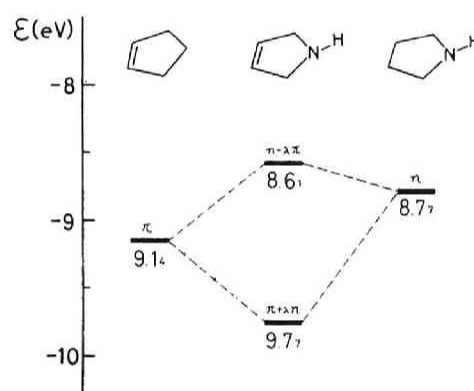


Figure 3. Orbital correlation diagram of the bishomoallyl interacting system.

the n orbital or the "inductive effect" of the nitrogen atom on the π orbital should be taken into account, which causes the unsymmetrical n, π splitting. The midpoint (9.19 eV) of the n and π IP's for **3** is about 0.2 eV larger than that of the n IP for **1** and the π IP for **19**. However, the contribution of the inductive effect seems to be less important in this case, as the orbital correlation diagram in Figure 3 shows a typical feature of through-space interaction between n and π orbitals.⁹ The similar n, π interaction is also encountered for 7-azabenzonorbornene (**5**) and 7-azabenzonorbornadiene (**7**).

In order to interpret the n, π interaction in these compounds, let us first take a look at the feature of the π, π interaction realized in the PES of benzonorbornene (**21**) and benzonorbornadiene (**22**), the related hydrocarbon homologues. The π orbital levels of benzene,¹⁷ **21**, **22**, norbornene (**23**), and norbornadiene (**24**) are schematically shown in Figure 4. These levels may be correlated with each other in

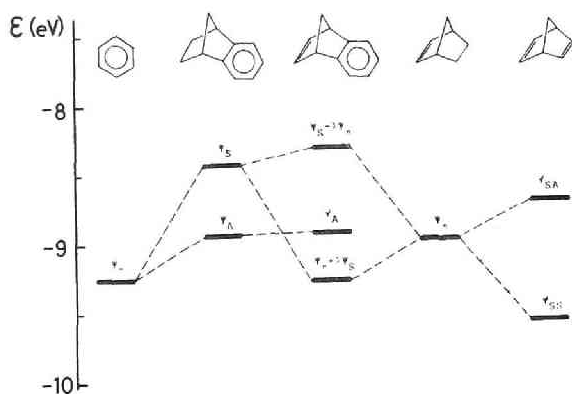


Figure 4. Orbital correlation diagram of benzene, benzonorbornene, benzonorbornadiene, norbornene, and norbornadiene.

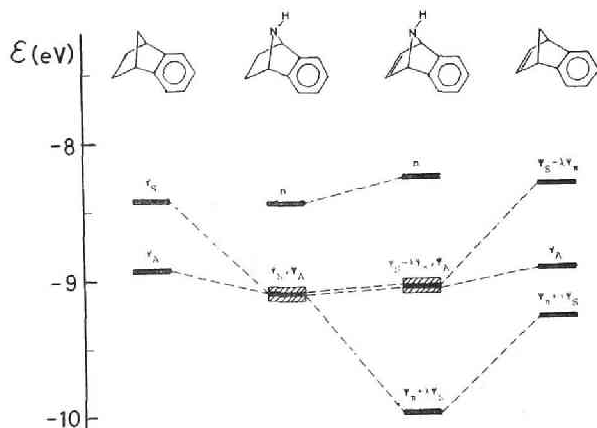


Figure 5. Orbital correlation diagram of 7-azabenzonorbornene and 7-azabenzonorbornadiene.

the manners that are depicted with the dotted lines in this figure. It has already been pointed out¹⁷ that the degeneracy of the highest occupied orbitals ($2e_{1g}$) in benzene is removed by the presence of two ortho disubstituents, and that the $\Psi_S(b_1)$ orbital lies above the $\Psi_A(a_2)$ orbital in benzocycloalkene derivatives. Further the combination of Ψ_S in the benzene ring of **21** and the π orbital (Ψ_π) in norbornene may produce the new levels in **22**, which appear to correspond to the first band ($\Psi_S - \lambda\Psi_\pi$, 8.30 eV) and to the third band ($\Psi_\pi + \lambda\Psi_S$, 9.27 eV). Contrary to this, Ψ_A in **21** remains essentially constant and corresponds to the second band in **22**.



Keeping the above discussions in mind, we then discuss the n, π interaction in **5**, **6**, **7**, and **8**. The first ionization of these compounds is assigned to the removal of an n electron. The n level in **7** and **8** is destabilized by 0.15–0.2 eV relative to that in **5** and **6**, respectively. This value appears to be comparable with that of pyrrolidine (**3** and **4**) and is attributed to the direct (or through space) n, π interaction. As to the π orbitals only the symmetrical orbitals may be stabilized by the interaction with the n orbital from the symmetry allowance. However, the antisymmetric π orbitals may remain constant. Accordingly, we can assign the observed spectra of **5** and **7** as shown in Figure 5 by referring to the energy diagram in Figure 4 and the above symmetry rule. In **5** the second band (9.10 eV) consists of Ψ_S and Ψ_A orbitals and in **7** the second band (9.05 eV) is attributed to $\Psi_S -$

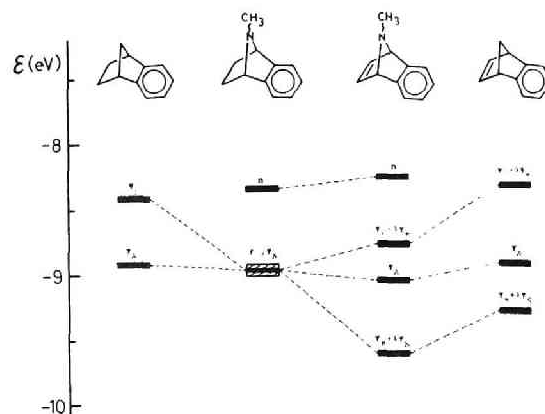


Figure 6. Orbital correlation diagram of *N*-methyl-7-azabenzonorbornene and *N*-methyl-7-azabenzonorbornadiene.

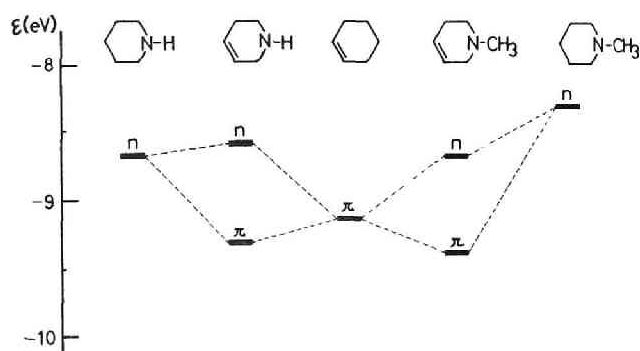


Figure 7. Orbital correlation diagram of the homoallyl interacting system.

$\lambda\Psi_\pi$ and Ψ_A orbitals and the third band (9.97 eV) to $\Psi_\pi + \lambda\Psi_S$ orbital. In this energy diagram, the symmetrical orbitals (Ψ_S , $\Psi_S - \lambda\Psi_\pi$, $\Psi_\pi + \lambda\Psi_S$) are stabilized by about 0.7 eV when the bridging carbon is replaced by the nitrogen atom in Figure 6. All the n and π orbitals can be assigned similarly to the case of *N*-H derivatives (**5** and **7**). There is no apparent difference in the lone pair destabilization energy produced by n, π interaction between *N*-H and *N*-methyl derivatives of pyrrolidine and 7-azabenzonorbornene derivatives. This is in contrast with the case of six-membered cyclic amines which follows.

(B) Homoallyl Type n, π Interaction. Inspection of Table I shows that in the six-membered cyclic amines the lone pair IP's (the first IP's) are affected in a different manner by the interaction with the double bond compared to the case of the five-membered amines already discussed above. For the five-membered *N*-H and *N*-methyl cyclic amines, introduction of a double bond makes the first IP's decrease. In the six-membered ring compounds, on the other hand, the n level remains essentially constant or is rather a little destabilized for the *N*-H derivatives (compare **11** and **13** to **9**), while for the *N*-methyl derivatives the lone pair IP is increased by about 0.3–0.4 eV by introduction of the π bond (compare **12** and **14** to **10**). In the six-membered bicyclic molecules (**17** and **18**), nitrogen lone pair electrons gain stabilization for both *N*-H and *N*-methyl derivatives. The π levels in **11** and **12** are lowered by 0.2–0.25 eV compared with that in cyclohexene (9.12 eV).¹⁶ Those in **13** and **14** are also stabilized by 0.1–0.4 eV compared to those in benzocyclohexene (8.44 (b_1) and 8.96 (a_2) eV).¹⁹ Similar observations were also encountered for bicyclic amines (**17**, **18**).²⁰ These features of the perturbation of the lone pair and the π levels are schematically exemplified for *N*-H and *N*-methyl derivatives of 1,2,3,6-tetrahydropyridine in Fig-

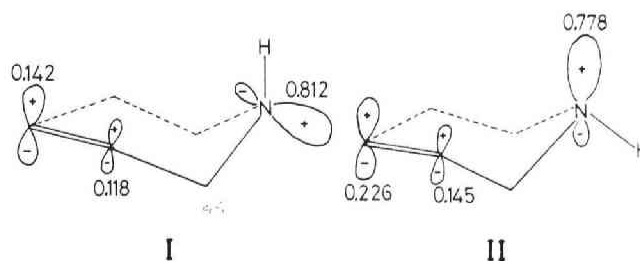
Table III. Calculated Total Energies and Orbital Energies for the Two Conformers of 3-Propenylamine^a (INDO-MO)

Lone pair =	Conformer ^a	
	I equatorial	II axial
Total energy, eV	-1004.97	-1005.11
Orbital energy, eV		
LU (π^*)	5.50	5.47
HO (n)	-12.26	-12.54
NHO (π)	-13.98	-14.25

^aThese geometries (I and II) are taken as the simplified models (half-chair conformation) of 1,2,3,6-tetrahydropyridine with the equatorial and axial lone pair electrons, respectively (see Figure 8). The dihedral angle between the lone pair lobe and the C_2-C_3 bond is 180° for conformer I and 60° for II. The dihedral angle between the N_1-C_2 and $C_3=C_4$ bonds is taken as 120° and tetrahedral bond angles were employed at unsaturated and saturated carbons. Bond lengths are taken as follows: N_1-C_2 , 1.47; C_2-C_3 , 1.53; $C_3=C_4$, 1.33; N_1-H , 1.01; C_2-H , 1.09; C_3-H and C_4-H , 1.07 Å.

ure 7. The destabilization energy of lone pair for the six-membered amines is much less than the corresponding value for the five-membered ones. For the six-membered molecules, both the n,π and n,π^* interactions are allowed by symmetry. This may be responsible for the different manner of perturbation of the n and π levels in the homoallyl system associated with six-membered amines and in the bishomoallyl system with five-membered amines. It is also worth noting that in the six-membered amines the manner of the perturbation of the n level is different between *N*-H and *N*-methyl derivatives. In addition to the "through-space" n,π interaction, we should also take into account the "inductive effect" which enhances¹¹ the IP's of both the n and π levels in going from the separated system (saturated cyclic amine + cycloalkene) to the combined one (β,γ -unsaturated cyclic amines). In the six-membered ring compounds, "through-space" n,π interaction may be diminished due to the molecular nonsymmetry compared with five-membered ring compounds. Hence, the n,π^* interaction and the "inductive effect" may become relatively important, resulting in a small stabilization or no apparent variation of the n level. However, the inductive effect on the n IP induced by replacing the two sp^3 hybridized carbons by the sp^2 ones in *N*-H derivatives of the six-membered cyclic amines is considered to be not so different from that of the *N*-methyl homologues. Accordingly, the different features of the perturbation of the lone pair ionization potential between the *N*-H (11, 13) and *N*-methyl derivatives (12, 14) of six-membered compounds could be attributable to some other contributions.²²

It is tempting to suggest that the different features of the lone pair orientation are also responsible for the different manner of n,π interaction between *N*-H and *N*-methyl derivatives in the six-membered ring system. It has been well documented²³ that the nitrogen lone pair electrons have a greater preference for the equatorial position in *N*-H piperidines²⁴ while those in *N*-methylpiperidines preferentially occupy an axial position. In order to gain further insight into the effect of the lone pair orientation, we have carried out here INDO²⁸ MO calculations of 3-propenylamine, a simple model of the homoallyl n,π interacting system. The calculated results are presented in Table III. This table indicates that the conformer II with axial lone pair is more stable than I with equatorial lone pair by ca. 0.14 eV and that both the highest and the next highest occupied orbitals (HOMO, NHOMO) in II are more stable than those in I. The greater IP of lone pair resides preferentially at an axial position and appears to correspond to the lower HOMO energy level for II. This implies that the difference in the lone pair orientation seems to be responsible for different features of the n,π interactions.²⁹

**Figure 8.** The diagram of the highest occupied molecular orbital (HOMO). (The geometries are the same as is shown in Table III. The atomic orbital coefficients of π and n orbitals are also shown.)

In order to delineate further these different behaviors of the n,π interaction due to the different lone pair orientation, the orbital scheme and the atomic orbital coefficients of the nitrogen lone pair sp^3 orbital and the π orbitals in the HOMO are given in Figure 8. This leads us to see that the π and π^* orbitals mix with the n orbital by the n,π interaction and the mode of this orbital mixing is apparently different between I and II. The atomic orbital coefficient of the nitrogen sp^3 orbital in II is smaller than that in I, which implies that the lone pair electrons in II are delocalized to a greater extent than in I. It is also to be noted that the difference between C_3 and C_4 π orbital coefficients for conformer II (0.081) is larger than that for I (0.024), suggesting that n,π^* interaction in II is greater than that in I. Since the n,π^* interaction stabilizes the n level, this greater contribution of the n,π^* interaction in II would result in the greater stability of the n level in II (Table III). It is conceivable from the above results and discussions that in the homoallyl interacting system the orientation of the lone pair electrons plays an important role in the n,π and n,π^* interactions which determine the stability of the n,π interacting system.³¹

It is also to be noted that the homoallyl system is rather stabilized by the interaction between n and π electrons, which is quite different from the bishomoallyl system. In other words, in the bishomoallyl interacting system n and π electrons are "repulsive". On the contrary, n and π electrons are rather "attractive" in the homoallyl interacting system.

It seems, therefore, reasonable to conclude that PES is very useful for the study of homoconjugative interaction between the nitrogen lone pair and the π bond, and that an intrinsic nature of homoallyl and bishomoallyl n,π interactions in cyclic and bicyclic amines is quite sensitive to the molecular symmetry, the orbital level, and the orientation of the lone pair electrons.

Acknowledgment. The authors are grateful to Dr. T. Kobayashi and Professor S. Nagakura of the University of Tokyo for making their PE-I PE spectrometer available to us. They also wish to thank Professor T. Yonezawa for support and encouragement of this work. This work is also partially supported by a research grant donated to I.M. from Kawakami Memorial Foundation.

References and Notes

- (1) Presented partly at the Symposium on Structural Organic Chemistry, Hakata, Japan, September, 1973.
- (2) Address correspondence to this author.
- (3) For example, S. Winstein and C. Ordonneau, *J. Am. Chem. Soc.*, **82**, 2085 (1960); S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, **77**, 4183 (1955).
- (4) J. K. Kochi, P. Bakuzis, and P. J. Krusic, *J. Am. Chem. Soc.*, **95**, 1516 (1973).
- (5) J. K. Stille and K. N. Sannes, *J. Am. Chem. Soc.*, **94**, 8489 (1972).
- (6) H. O. Ohorodnyk and D. P. Santry, *J. Am. Chem. Soc.*, **91**, 4711 (1969).
- (7) M. J. S. Dewar and W. W. Schoeller, *Tetrahedron*, **27**, 4401 (1971).
- (8) Santry et al.⁶ have predicted, based on the CNDO/2 molecular orbital calculation, that the syn conformer of 7-norbornenyl anion (the anion

- lobe occupies the syn position with respect to the double bond) is more stable than the anti conformer. On the contrary, Dewar et al.⁷ claimed from the MINDO/2 calculations that the anti conformer is preferable.
- (9) R. Hoffmann, *Acc. Chem. Res.*, **4**, 1 (1971).
 - (10) M. J. Goldstein, S. Natowsky, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **56**, 294 (1973); D. A. Sweigart and D. W. Turner, *J. Am. Chem. Soc.*, **94**, 5592 (1972); S. F. Nelson and J. M. Buschek, *ibid.*, **95**, 2011, 2013 (1973).
 - (11) D. Chadwick, D. C. Frost, and L. Weilar, *J. Am. Chem. Soc.*, **93**, 4962 (1971); A. D. Bain, D. C. Frost, and L. Weilar, *ibid.*, **95**, 291 (1973).
 - (12) A study on the nonadjacent n, π interaction in 9-azabicyclo[4.2.1]nona-2,4,7-triene has recently been reported: H. Schmidt, A. Schweig, A. G. Anastassiou, and H. Yamamoto, *J. Chem. Soc., Chem. Commun.*, 219 (1974).
 - (13) L. A. Carpino and D. E. Barr, *J. Org. Chem.*, **31**, 764 (1966).
 - (14) M. P. Cava, C. K. Wilkins, Jr., D. R. Dalton, and K. Bessho, *J. Org. Chem.*, **30**, 3772 (1965).
 - (15) H. T. Clarke, H. B. Gillespie, and S. Z. Weissshaus, *J. Am. Chem. Soc.*, **55**, 4571 (1933).
 - (16) P. Bischof and E. Heilbronner, *Helv. Chim. Acta*, **53**, 1677 (1970).
 - (17) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley, New York, N.Y., 1970, Chapter 10.
 - (18) P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **52**, 1745 (1969).
 - (19) F. Brogli, E. Giovannini, E. Heilbronner, and R. Schurter, *Chem. Ber.*, **106**, 961 (1973).
 - (20) For bicyclo[2.2.2]oct-2-ene only the adiabatic IP (8.92 eV) of the π orbital was reported.²¹ However, since the vertical IP's are generally 0–0.3 eV higher than the corresponding adiabatic ones, it amounts to stabilization of the π level by 0.1–0.3 eV in **17** and **18**.
 - (21) N. Bordor, M. J. S. Dewar, and S. D. Worley, *J. Am. Chem. Soc.*, **92**, 19 (1970).
 - (22) Another possible explanation may be given as follows. Methyl substitution at the nitrogen atom raises substantially the n level, which may allow us to expect that this substitution effect in six-membered cyclic amines diminishes the n, π interaction and reinforces the n, π^* interaction. This could lead to stabilization of the n level in N -methyl derivatives.
 - (23) T. Yonezawa, I. Morishima, and Y. Ohmori, *J. Am. Chem. Soc.*, 1267 (1970); I. Morishima, K. Okada, and T. Yonezawa, *J. Chem. Soc., Chem. Commun.*, 33 (1971); I. Morishima, K. Okada, T. Yonezawa, and K. Goto, *J. Am. Chem. Soc.*, **93**, 3922 (1971).
 - (24) The conformational equilibrium of piperidines has been the subject of prolonged controversy. Some claimed for the lone pair preferentially equatorial,^{23,25} the lone pair preferentially axial,²⁶ and the lone pair equally oriented.²⁷ However, it is at least established that N -H piperidines are the substantial mixtures. Contrary to this, the methyl group in N -methylpiperidines prefers the equatorial position substantially. Therefore it is expected that the different manner of the lone pair orientations between N -H and N -methyl derivatives affects the electronic structures of these compounds differently.
 - (25) T. A. Claxton, *Chem. Ind. (Berlin)*, 1713 (1964); M. J. Aroney and R. J. W. LeFevre, *Proc. Chem. Soc., London*, 82 (1958); *J. Chem. Soc.*, 3002 (1958); M. J. Aroney, C. Y. Chen, R. J. W. LeFevre, and J. D. Saxby, *J. Chem. Soc.*, 4269 (1964); J. B. Lambert and R. G. Keske, *J. Am. Chem. Soc.*, **88**, 620 (1966); J. B. Lambert, R. G. Keske, R. E. Charhart, and A. P. Jovanovitch, *ibid.*, **89**, 3761 (1967); D. H. R. Barton and R. C. Cookson, *Q. Rev., Chem. Soc.*, **10**, 44 (1956).
 - (26) R. J. Bishop, L. E. Sutton, D. Dineen, R. A. Y. Jones, and A. R. Katritzky, *Proc. Chem. Soc., London*, 257 (1964); R. W. Baldock and A. R. Katritzky, *Tetrahedron Lett.*, 1159 (1968); *J. Chem. Soc., B*, 1470 (1968); R. A. Y. Jones, A. R. Katritzky, A. C. Richards, R. J. Wyatt, R. J. Bishop, and L. E. Sutton, *ibid.*, 127 (1970); T. Masamune and M. Takasugi, *Chem. Commun.*, 625 (1967); T. Masamune, *ibid.*, 244 (1968); P. J. Buckley, C. C. Costain, and J. E. Parkin, *ibid.*, 668 (1968).
 - (27) H. Booth, *Chem. Commun.*, 802 (1968).
 - (28) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).
 - (29) Methyl substitution at the nitrogen atom generally raises the n level;³⁰ the IP of nitrogen lone pair electrons in N -methylpiperidine (**10**) is 0.35 eV smaller than that in piperidine (**9**). This is reproduced by INDO-MO calculations. In β, γ -unsaturated six-membered cyclic amines, however, the lone pair IP of N -methyl derivatives (**12** and **14**) is rather larger or nearly equal compared to those in N -H derivatives (**11** and **13**, respectively).
 - (30) K. Yoshikawa, M. Hashimoto, and I. Morishima, *J. Am. Chem. Soc.*, **96**, 288 (1974).
 - (31) In a separate paper, the effect of the lone pair orientation on the electronic structure in 2-azabicyclo[2.2.2]oct-5-enes (**15**–**18**) is discussed in detail: I. Morishima and K. Yoshikawa, *J. Am. Chem. Soc.*, in press. The stereospecific orientation of the lone pair electrons in 7-azanaborborene derivatives (**5**–**8**) has been studied (I. Morishima, K. Yoshikawa, et al., submitted for publication).

CHAPTER 6

Homoallyl Interaction between Nonadjacent n, π Electrons, II. 2-Azabicyclo[2.2.2]oct-5-ene derivatives

Abstract: The orientation of the nitrogen lone pair electrons in 2-azabicyclo[2.2.2]oct-5-ene and its *N*-methyl derivative has been studied with the aid of $\text{Ni}(\text{AA})_2$ (nickel acetylacetonate) induced ^1H and ^{13}C NMR contact shifts and molecular orbital calculations in view of elucidation of nonbonded n, π interaction ($n-\pi$ transannular interaction) in azabicyclic molecules. $\text{Ni}(\text{AA})_2$ -induced ^1H and ^{13}C contact shifts for these molecules were plausibly explained by the spin density distributions obtained by INDO-UHF-MO calculation for the corresponding hydrocarbon σ radical, bicyclo[2.2.2]oct-5-en-2-yl, in which the radical lobe occupies exo and endo positions. This allowed us to conclude that the nitrogen lone pair for *N*-methyl derivative is preferentially oriented at the exo position while the exo and endo positions are equally favored for the *N*-H derivative. This was further confirmed by other NMR evidence. CNDO/2-MO calculations were also performed for above azabicyclic molecules to illuminate the factors that determine the nitrogen lone pair orientation. It is concluded that steric repulsion and $n-\pi$ transannular electronic stabilization energies are essentially important to determine the lone pair orientation in the title molecule.

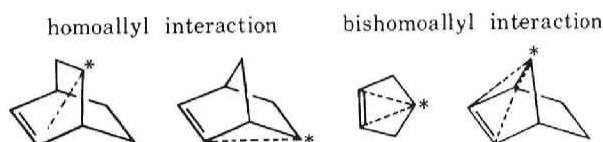
Neighboring group participation in the reaction intermediate or in the electronic and geometrical structures of ground or excited state of molecules constitutes an essential concept in the organic chemistry. As a part of our continuing investigations^{2,3} toward understanding neighboring group participation in the electronic structures of rigid σ -bonded molecules, we have studied here the stereospecific orientation of lone pair electrons and electronic structures in 2-azabicyclo[2.2.2]oct-5-ene derivatives. Much attention has been paid to the transannular interaction between nonbonded π electrons.⁴ However, quite limited studies have been available concerning the neighboring group effect on the stereospecific orientation of lone pair electrons which appears to be one of the interesting problems in the stereochemistry of organic molecules.

The specific orientation of the lone pair electrons on the C_7 carbon in 7-norbornenyl anion has been studied⁵ by stereospecific deuterium capture of anti and syn anion intermediates. The preference for anti 7-norbornenyl anion has been suggested and interpreted as resulting from bishomoantiaromatic character of this anion. Quantum chemical studies of this anion have also been performed. However,



semiempirical MO calculations failed to determine definitely the orientation of lone pair electrons in 7-norbornenyl anion.^{6,7} It may be readily accessible from this example that the problem on the transannular effect between lone pair electrons and the neighboring π bond in bicyclic molecule is still open to further experimental and theoretical studies.

We have recently carried out a photoelectron spectroscopic study of nonbonded n, π interaction involved in several cyclic and bicyclic amines containing nonadjacent π bonds.² It was revealed that the feature of the nonadjacent n, π interaction is quite different between homoallyl and bishomoallyl n, π interacting systems; for the homoallyl interaction, both n, π and n, π^* interactions contribute com-



petitively to the relative stability of the interacting system. It is, therefore, of interest to study the orientation of lone pair electrons in homoallyl n, π interacting molecules in relation to the bishomoconjugative system.⁸

In these circumstances, we have studied here the orientation of nitrogen lone pair electrons and electronic structures in 2-azabicyclo[2.2.2]oct-5-ene (2), its *N*-methyl derivative (3), and their saturated homologs (4, 5) with the aid of

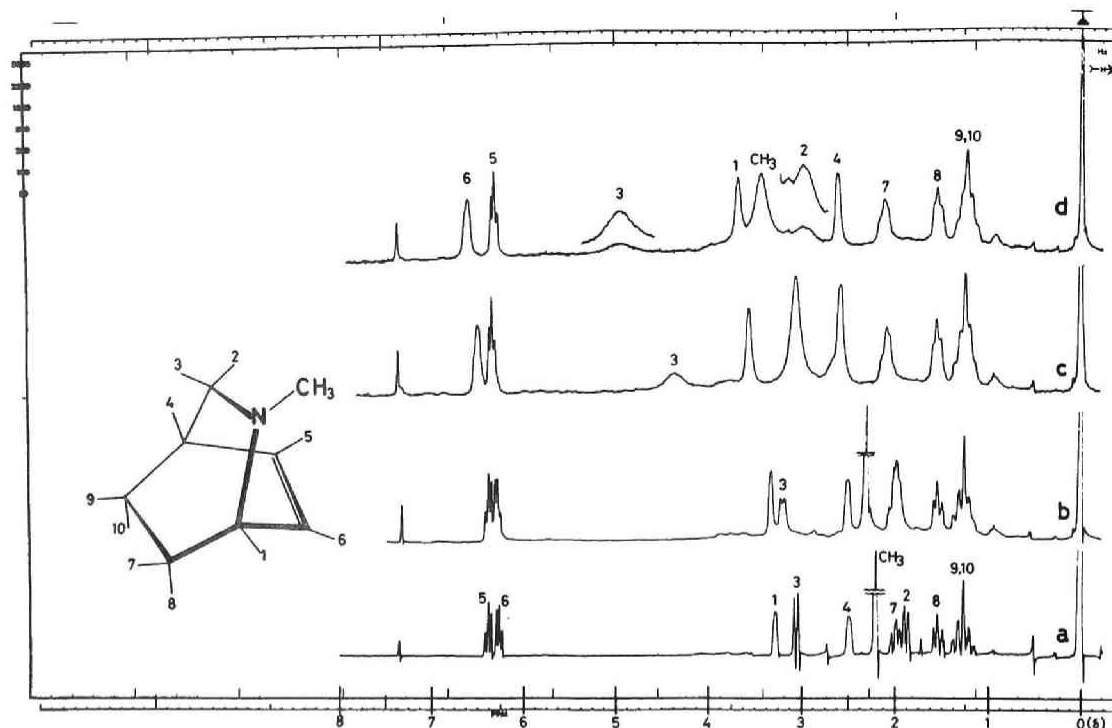
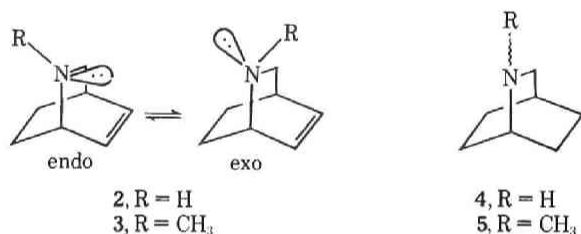


Figure 1. ^1H NMR spectra of **3** (a) in CDCl_3 and (b–d) in CDCl_3 containing varying amounts of $\text{Ni}(\text{AA})_2$ (at 220 MHz).



$\text{Ni}(\text{AA})_2$ (nickel acetylacetonate) induced ^1H and ^{13}C NMR contact shifts and molecular orbital calculations.⁹ **2** and **3** have two possible orientations of nitrogen lone pair electrons, endo (syn) and exo (anti) with respect to the double bond. In order to determine the lone pair orientation, we have examined conformational dependence of $\text{Ni}(\text{AA})_2$ -induced ^1H and ^{13}C contact shifts for these molecules together with other subsidiary methods. Stereospecific intramolecular electron spin transmission was also studied with the aid of MO calculation in relation to the lone pair orientation. The factor that determines the specific lone pair orientation in **2** and **3** was illuminated with the aid of CNDO/2-MO calculations of these molecules and the results were also discussed in relation to the electronic structure of the corresponding hydrocarbon carbanions in which the nitrogen lone pair is replaced by the carbon anion.

Experimental Section

Materials. 2-Azabicyclo[2.2.2]oct-5-ene (**2**), 2-methyl-2-azabicyclo[2.2.2]oct-5-ene (**3**), 2-azabicyclo[2.2.2]octane (**4**), and 2-methyl-2-azabicyclo[2.2.2]octane (**5**) were prepared by the method of Cava et al.¹⁰ Commercially available $\text{Ni}(\text{AA})_2$ (nickel bisacetylacetonate) was dried in vacuo over 30 hr at 60° before use.

Proton NMR Measurements. All samples were made in CDCl_3 solution, ca. 150 mmol/l. for **2** and **4**, and ca. 300 mmol/l. for **3** and **5**. NMR samples were prepared by the addition of a given amount of $\text{Ni}(\text{AA})_2$ to the CDCl_3 solution of these cyclic amines. All the proton spectra were obtained at 220 MHz using a Varian HR-220 spectrometer from our department. TMS was used as an internal standard. Assignment of well separated proton signals was easily made by referencing the spectral patterns. Assignment of rather complicated signals was assisted by the use of a benzene sol-

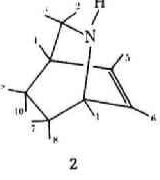
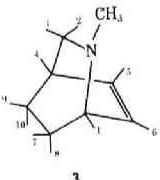
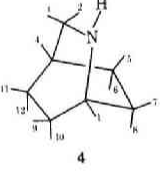
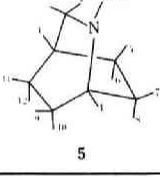
vent induced shift. The spectra were taken at room temperature (24°) in the presence of a varying amount of $\text{Ni}(\text{AA})_2$. The observed paramagnetic shift is relative to the free ligand. For **2** and **3**, $\text{Eu}(\text{DPM})_3$ (europium dipivaloylmalonate) induced shifts were also obtained.

Carbon-13 NMR Measurement. For **4**, completely proton decoupled ^{13}C NMR spectra were obtained at 15.1 MHz on a Jeolco-C-60HL spectrometer equipped with an IS-60 field/frequency synchronous sweep system of the proton irradiation frequency and an SD-HC heteronuclear spin decoupler. The spectra were accumulated in 32–128 scans using the Jeolco S/N booster. These spectra were measured with the external field locking mode and were calibrated with the internal cyclohexane (ca. 5 vol %, 27.3 ppm from TMS). The ^{13}C spectra of **2**, **3**, and **5** were obtained at 25.1 MHz on a Jeolco ^{13}C fourier transform NMR system, JNM-PFT-100, and were recorded after 100–1000 pulses with intervals of 2 or 3 sec. An internal ^2D lock was employed. The ^{13}C chemical shifts of these three compounds were measured with respect to the internal CDCl_3 (77.1 ppm). All samples were made in CDCl_3 solution, ca. 1 M, in 8 mm sample tubes. All the spectra were taken at room temperature (24°) in the presence of varying amounts of $\text{Ni}(\text{AA})_2$. The assignments of ^{13}C NMR spectra were made by comparing unsaturated and saturated bicycles, by referring the methyl substitution effect to the ^{13}C chemical shift,¹¹ and by the use of the stereospecific ^{13}C contact shift induced by $\text{Ni}(\text{AA})_2$.¹² The half-decoupled technique was used to help the signal assignment of the ^{13}C NMR spectra.

Results

^1H Contact Shifts. The signal changes of each proton as $\text{Ni}(\text{AA})_2$ is successively added to the solution of **3** in CDCl_3 are exemplified in Figure 1. Figure 2 shows the linear plots of $\text{Ni}(\text{AA})_2$ induced contact shifts vs. the concentration of added $\text{Ni}(\text{AA})_2$ for **3**. The spectra are time averaged between complexed and uncomplexed species, and the proton resonances of the ligand shift toward the resonance position of the paramagnetic adduct. Therefore, only the relative values of these shifts are significant in the present work. The proton chemical shifts and the relative values of $\text{Ni}(\text{AA})_2$ -induced ^1H contact shifts for **2** to **5** are summarized in Table I. The $\text{Eu}(\text{DPM})_3$ -induced shifts and benzene solvent shifts, which are defined as the shift on going

Table I. Ni(AA)₂- and Eu(DPM)₃-Induced Proton Shifts and Benzene-Induced Solvent Shifts

Molecule	Position	¹ H chemical shift, δ ^a	Ni(AA) ₂ -induced ¹ H shift (rel) ^b	Eu(DPM) ₃ -induced ¹ H shift (rel) ^b	Benzene-induced ¹ H shift, ppm ^c
	1	3.53	-1.00 ^d	-1.00	+0.28
	2 (endo)	2.46	-3.0 ^h	-0.85	+0.26
	3 (exo)	2.92	-3.0 ^h	-1.07	+0.12
	4	2.58	-0.13	-0.38	+0.38
	5	6.38	+0.21	-0.36	
	6	6.43	-0.44	-0.37	
	7	1.93	-0.07	-0.69	+0.01
	8	1.63	-0.11	-0.42	+0.18
	9, 10 ⁱ	~1.3	~+0.03	-0.33, -0.40	
	1	3.30	-1.00 ^e	-1.00	+0.22
	2 (endo)	1.87	-2.90	-0.88	+0.14
	3 (exo)	3.06	-4.94	-0.91	+0.04
	4	2.50	-0.29	-0.42	+0.33
	5	6.39	+0.22	-0.43	
	6	6.26	-0.90	-0.47	
	7	1.99	-0.35	-0.67	-0.03
	8	1.53	-0.07	-0.41	+0.14
	9, 10 ⁱ N-CH ₃	1.25 2.22	0.00 -3.24	-0.35, -0.46 -1.05	
	1	2.86	-1.0 ^f		+0.19
	2, 3	3.01	-4.2 ^h		+0.15
	4	1.73	0.0 ^h		
	5, 6, 8, 10, 11, 12 ⁱ	1.60-1.65			
	7, 9	1.87	~+0.0		
	1	2.44	-1.00 ^g		+0.18
	2, 3	2.70	-2.63		+0.08
	4	1.48	-0.05		
	5, 6, 11, 12 ⁱ	1.52	~0.0		
	7, 9	1.97	+0.12		+0.04
	8, 10	1.62	-0.15		+0.08
	N-CH ₃	2.35	-2.18		+0.12

^aDiamagnetic reference positions observed at 220 MHz at room temperature in CDCl₃ solution. ^bObtained from the relative values of the slopes of linear plots of observed ¹H contact shifts vs. concentration of added Ni(AA)₂ or Eu(DPM)₃. The plus and minus signs denote upfield and downfield contact shifts, respectively. ^cThe plus sign means the upfield benzene-induced solvent shifts. ^dThe actual shift is 0.45 ppm per 0.01 mol of Ni(AA)₂ in the 0.15 M CDCl₃ solution. ^eThe actual shift is 0.6 ppm per 0.1 mol of Ni(AA)₂ in the 0.3 M CDCl₃ solution. ^fThe actual shift is 0.34 ppm per 0.01 mol of Ni(AA)₂ in the 0.15 M CDCl₃ solution. ^gThe actual shift is 0.4 ppm per 0.1 mol of Ni(AA)₂ in the 0.3 M CDCl₃ solution. ^hPrecise values of the relative contact shift could not be obtained due to the rapid broadening. ⁱProton signals could not be distinguished due to the superposition.

from the CDCl₃ solution to the benzene solution, are also included in Table I. As Figure 1 shows, the proton signals of **3** are well separated in a diamagnetic solution (in the absence of Ni(AA)₂) in the 220 MHz NMR spectra except for those of β- and γ-methylene protons. Similar spectra were also obtained for **2**, **4**, and **5**. The two α-methylene protons (adjacent to the nitrogen atom) are magnetically equivalent for **4** and **5** due to the rapid inversion of nitrogen lone pair.

Inspection of Table I shows that all the protons except for H₅ in **2** and **3** exhibit downfield shifts in the Ni(AA)₂ system. As is well documented,^{13,14} the isotropic shift induced by complexation with Ni(AA)₂ is predominantly caused by the Fermi contact shift which is related to electron spin density, ρ_H, induced on the proton. The downfield and upfield contact shifts correspond to the positive and negative spin densities on the proton, respectively. Therefore, the relative contact shifts in Table I mean the relative spin densities with the opposite sign.

¹³C Contact Shifts. Perturbation of the ¹³C NMR spectrum caused by the addition of Ni(AA)₂ is shown in Figure 3 for **3**, as an example. Relative values of ¹³C contact shifts were obtained from the slopes of the linear plot for various carbons, with the value for α-methylene carbon (C₁) normalized to unity. The results are summarized in Table II. The

feature of relative ¹³C contact shifts for **3** is close to that for **5**, but somewhat different from **2**.

Molecular Orbital Calculations. In order to substantiate theoretically the observed trend of ¹H and ¹³C contact shifts, we calculated electron spin densities on the proton 1s and carbon 2s AO's for the corresponding hydrocarbon σ radicals which are expected to have isoelectronic structure with these bicyclic amines complexed with Ni(AA)₂ (see Tables III and IV). Previously we demonstrated¹⁴ that the relative values of the Ni(AA)₂-induced contact shifts are most plausibly reproduced by the INDO-UHF-MO¹⁵ calculations of spin densities for the corresponding hydrocarbon σ radicals. For example, relative values of spin densities calculated for cyclohexyl and phenyl radicals correspond well to the relative contact shifts for piperidine and pyridine complexed with Ni(AA)₂, respectively. We have carried out INDO-MO calculations for the two conformers of 2-bicyclo[2.2.2]oct-5-enyl σ radical with the orientation of the radical lobe in the endo and exo positions and for 2-bicyclo[2.2.2]octyl σ radical. Bond lengths used for the MO calculations are taken as C-H, 1.09, C-C, 1.54, and C=C, 1.35 Å. We also assumed that there is no strain in geometries for these compounds, that is, all the bond angles except for the sp² carbons (120°) are taken as 109°28'. The calculated spin densities on the proton 1s and carbon 2s AO's for

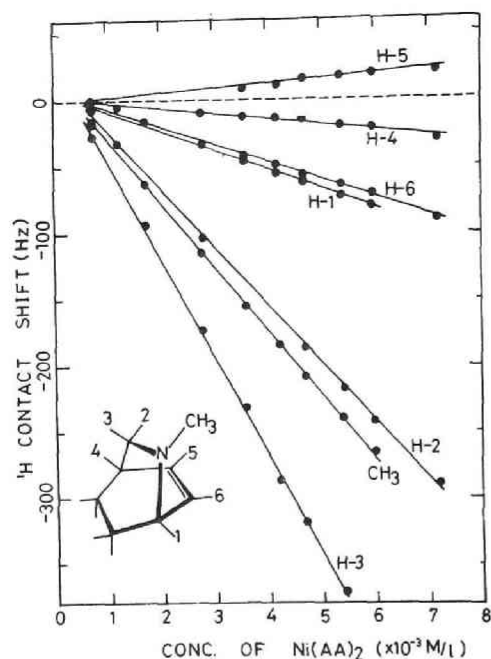


Figure 2. Plots of isotropic paramagnetic shifts vs. concentration of $\text{Ni}(\text{AA})_2$ for 3.

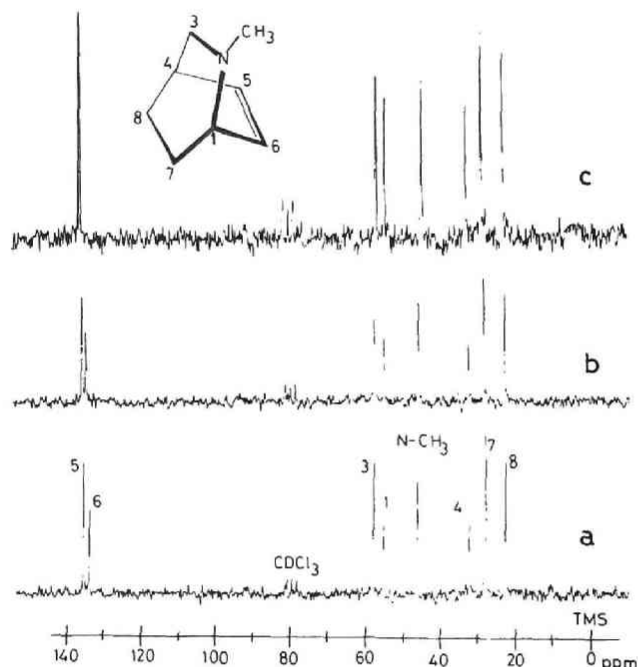
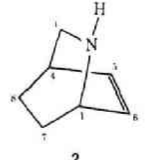
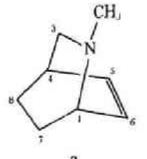
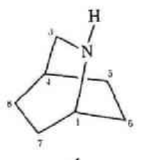
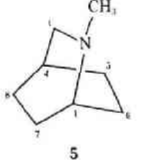


Figure 3. ^{13}C NMR spectra of 3 (a) in CDCl_3 (b and c) and in CDCl_3 containing varying amounts of $\text{Ni}(\text{AA})_2$ (at 220 MHz).

these σ radicals are summarized in Tables III and IV, respectively. Spin densities on H_2 , C_5 , and C_6 in 2-bicyclo[2.2.2]octyl radical were obtained by taking an average between those associated with the atoms located symmetrically to the $\text{C}_1\text{NC}_3\text{C}_4$ plane. It is readily seen that the calculated results for 2-bicyclo[2.2.2]octyl radical plausibly account for the relative values of $\text{Ni}(\text{AA})_2$ -induced ^1H and ^{13}C contact shifts in 4 and 5.

In order to get insight into the stereospecific orientation of the nitrogen lone pair electrons and relative stability of the two conformers, CNDO/2-MO¹⁶ calculations were performed for 2, 3, 4, and 5 with the nitrogen lone pair orientation at endo and exo positions. Here bond lengths are: C-N, 1.54; N-H, 1.01 Å. Other bond lengths and bond an-

Table II. $\text{Ni}(\text{AA})_2$ -Induced ^{13}C Contact Shifts

Molecule	Position	$\delta^{13}\text{C}^a$	$\text{Ni}(\text{AA})_2$ -induced ^{13}C shift (rel) ^b
 2	1	46.6	+1.00 ^c
	3	46.6	+1.33
	4	30.6	-1.25
	5	133.1	-0.09
	6	134.8	-2.38
	7	27.1	-1.15
	8	23.9	-0.28
 3	1	55.2	+1.00 ^d
	3	57.7	+1.15
	4	32.3	-0.23
	5	134.3	+0.02
	6	132.9	-1.18
	7	28.1	-0.32
	8	22.8	+0.05
	N-CH ₃	46.2	+1.68
 4	1	43.6	+1.00 ^e
	3	47.1	+1.30
	4	24.7	-0.26
	5, 8	25.0	+0.00
	6, 7	27.1	-1.31
 5	1	51.9	+1.00 ^f
	3	58.6	+1.31
	4	26.9	-0.29
	5, 8	25.7	+0.07
	6, 7	24.8	-0.80
	N-CH ₃	43.9	+1.53

^aIn parts per million from TMS. ^bObtained from the relative values of the slopes of linear plots of observed ^{13}C contact shifts vs. concentration of added $\text{Ni}(\text{AA})_2$. The plus and minus signs denote upfield and downfield contact shifts, respectively. ^cThe actual shift is 1.9 ppm per 0.02 mol of $\text{Ni}(\text{AA})_2$ in the 1 M CDCl_3 solution. ^dThe actual shift is 0.6 ppm per 0.02 mol of $\text{Ni}(\text{AA})_2$ in the 1 M CDCl_3 solution. ^eThe actual shift is 3.4 ppm per 0.02 mol of $\text{Ni}(\text{AA})_2$ in the 1 M CDCl_3 solution. ^fThe actual shift is 0.5 ppm per 0.02 mol of $\text{Ni}(\text{AA})_2$ in the 1 M CDCl_3 solution.

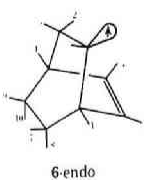
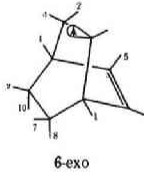
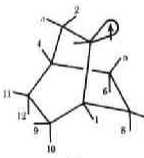
gles are taken similar to the case of the hydrocarbon σ radicals described above. Similar calculations were also carried out for the corresponding carbanions in which the nitrogen lone pair in 2-5 is replaced by the carbon anion C^- .

Discussion

A. The Orientation of the Lone Pair Electrons. Inspection of Table I shows that the difference in the α -methylene proton chemical shifts between endo (H_2) and exo (H_3) protons is quite different for 2 and 3. The shift difference for 2 ($\Delta = 0.46$ ppm) is small and rather close to that for bicyclo[2.2.2]oct-2-ene ($\Delta = 0.23$ ppm).¹⁷ It is well documented^{18,19} that the chemical shift of the proton adjacent to the nitrogen lone pair is affected by the long range shielding effect of the oriented lone pair. Therefore, one may expect that the two α -methylene protons (H_2 , H_3) sense to the same extent the long range shielding effect of the adjacent nitrogen lone pair electrons, probably because equilibrium orientation of the lone pair occurs in almost equal population for the exo and endo conformers. The large shift difference ($\Delta = 1.19$ ppm) for 3, however, allows us to expect preferential orientation of the lone pair at the exo or endo position.

The $\text{Ni}(\text{AA})_2$ -induced ^1H contact shifts for these two α -methylene protons also reflect different modes of lone pair orientation in 2 and 3; for 3, the α -exo proton (H_3) experiences greater downfield contact shift than the α -endo proton (H_2), while these contact shifts for 2 are almost equal. The large difference in the $\text{Ni}(\text{AA})_2$ -induced contact shifts

Table III. Calculated Spin Densities on the H 1s AO's for Hydrocarbon σ Radicals (INDO-UHF-MO)

Radical	Position	Relative value of spin density	Calcd value of spin density
	1	+1.00	+0.0107
	2 (endo)	+5.38	+0.0575
	3 (exo)	+2.58	+0.0275
	4	+0.16	+0.0017
	5	+0.05	+0.0006
	6	+0.00	+0.0000
	7	-0.18	-0.0019
	8	+0.93	+0.0099
	9	+0.04	+0.0004
	10	+0.12	+0.0013
	1	+1.00	+0.0090
	2 (endo)	+3.06	+0.0275
	3 (exo)	+5.84	+0.0524
	4	+0.25	+0.0023
	5	+0.32	+0.0029
	6	+0.84	+0.0076
	7	-0.04	-0.0003
	8	-0.19	-0.0017
	9	+0.14	+0.0013
	10	+0.03	+0.0003
	1	+1.00	+0.0102
	2, 3 ^a	+4.15	+0.0422
	4	+0.18	+0.0018
	5, 11 ^a	+0.06	+0.0006
	6, 12 ^a	+0.09	+0.0009
	7, 9 ^a	-0.14	-0.0014
	8, 10 ^a	+0.42	+0.0042

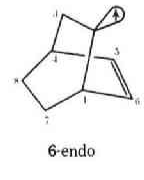
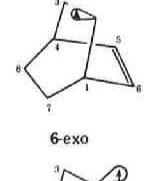
^a Averaged values of these two protons.

for H₂ and H₃ in **3** is again attributable to preferential orientation of the nitrogen lone pair.

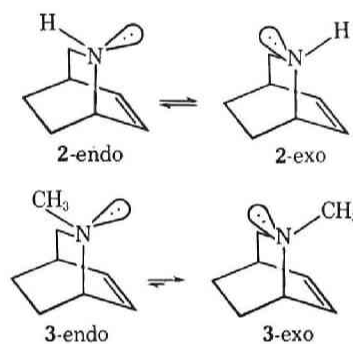
In order to gain further insight into the relative importance of lone pair endo or exo conformer in **2** and **3**, comparison was made between relative values of observed contact shifts and those of calculated spin densities by the INDO method for the corresponding hydrocarbon σ radical, 2-bicyclo[2.2.2]oct-5-enyl, in which the radical lobe occupies an endo (6-endo) or an exo (6-exo) position. In our previous investigations we demonstrated^{12,14} that ¹H and ¹³C contact shifts for the nitrogen-containing molecules induced by the coordination with Ni(AA)₂ depend on the orientation of the nitrogen lone pair and are plausibly reproduced theoretically by the INDO-MO calculations of electron spin densities for the corresponding hydrocarbon σ radicals. The observed trend of the ¹H and ¹³C contact shifts for **3** appears to be fairly well reproduced²⁰ by the calculated spin densities for the corresponding hydrocarbon σ radical 6-exo (Tables III and IV) where the radical lobe is oriented at an exo position. However, the contact shifts for **2** correspond to neither 6-endo nor 6-exo. They are rather explained reasonably by the calculated spin densities averaged between two radical conformers 6-endo and 6-exo (see Tables III and IV). It is therefore likely that the exo and endo orientations of the nitrogen lone pair of **2** are equally favored.

The Eu(DPM)₃-induced ¹H pseudocontact shifts for **2** and **3** (Table I) show that the shift difference between two α -methylene protons in **2** is greater than that in **3**, quite different from the Ni(AA)₂-induced shifts. It is especially worth noting that the exo proton (H₃) experienced greater Eu(DPM)₃-induced shift than the endo one (H₂) for **2**. This observation implies that the presence of Eu(DPM)₃ causes different populations of lone pair exo and endo conformers for **2**.²²

Table IV. Calculated Spin Densities on the C 2s AO's for Hydrocarbon σ Radicals (INDO-UHF-MO)

Radical	Position	Relative value of spin density	Calcd value of spin density
	1	-1.00	-0.0063
	3	-1.36	-0.0085
	4	+0.51	+0.0032
	5	-0.16	-0.0010
	6	+0.55	+0.0034
	7	+1.81	+0.0113
	8	-0.19	-0.0012
	1	-1.00	-0.0061
	3	-1.13	-0.0069
	4	+0.48	+0.0029
	5	-0.07	-0.0004
	6	+2.39	+0.0145
	7	+0.52	+0.0032
	8	-0.04	-0.0003
	1	-1.00	-0.0064
	3	-1.34	-0.0085
	4	+0.51	+0.0032
	5, 8 ^a	-0.13	-0.0008
	6, 7 ^b	+1.18	+0.0075

^a Averaged value between C₅ and C₈. ^b Averaged value between C₆ and C₇.



Another evidence for different modes of nitrogen lone pair orientation in **2** and **3** resulted from benzene solvent induced shift for H₂ and H₃. It is established²³ that the upfield benzene solvent shift is more pronounced for the proton that is more distant from the nitrogen lone pair electrons; for example, the proton trans to the nitrogen lone pair in ketimines, aziridines, and oximes senses greater upfield solvent shift than the cis one.²² As Table I shows, H₃ in **3** experiences less upfield benzene-induced solvent shift than H₃ in **2** or H₂ in **5**. This may also be due to the preferential orientation of the nitrogen lone pair electrons at the exo position in **3**.

B. ¹H and ¹³C Contact Shifts and Mechanism of Electron Spin Transmission in Relation to Nonbonded n, π Interaction. Here we will examine the different feature of the relative ¹H and ¹³C contact shifts for **2** and **3** in view of elucidation of neighboring group participation in the intramolecular electron spin transmission. It is to be noted in Table II that the relative ¹³C contact shifts of β carbons (C₄, C₆, and C₇) are remarkably different between **2** and **3**. Quite rapid attenuation of the contact shift of C₄ in **3** is to be compared with the one in **2**. This different feature of the ¹³C contact shifts is attributable to different nitrogen lone pair orientations as discussed above. It is well established that electron spin reaches the β carbon to a greater extent by a zigzag

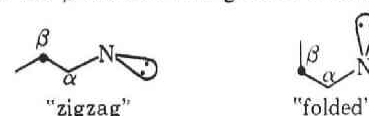


Table V. Calculated Total Energies for 2-Azabicyclo[2.2.2]oct-5-enes, eV (CNDO/2)^a

Molecule	Total electronic energy (A)	Core repulsion energy (B)	Total energy (A + B)
2-endo	-7634.47	5727.00	-1907.47
2-exo	-7632.34	5724.88	-1907.46
3-endo	-9260.66	7116.74	-2143.92
3-exo	-9241.37	7097.35	-2144.02

^a Any minimization of energy with respect to geometry is not performed in the present calculation.

path than a *folded* one.¹² The above features of β -carbon contact shifts correspond to this general trend. For **3** in which the lone pair occupies preferentially an *exo* position, C₇ lying on a *folded* path shows a rather small downfield contact shift. On the other hand, C₇ of **2** exhibits a greater magnitude of the ¹³C contact shift than C₁. The relative value (-1.15) of the contact shift for this C₇ carbon is comparable with that for C₆ (-1.31) of **4**, indicating that the effect of the lone pair orientation on the contact shift of C₇ in **2** is averaged out due to the rapid nitrogen inversion, i.e., equal orientation of the lone pair, as is the case for **4**. This is reasonably confirmed by the spin density calculation when we compare these contact shift values (-1.15, -1.31) with the averaged value of the spin densities for the two conformers (6-endo and 6-exo) ((+0.52 + 1.81)/2 = +1.16). A similar discussion appears to be valid for the ¹H contact shifts.

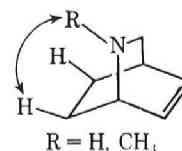
It is of particular interest to note that the ¹³C contact shift of C₆ in **2** is much greater than that in **3**. The C₆ β carbon in **3**, lying on a zigzag arrangement with respect to the lone pair orientation, shows unexpectedly smaller downfield shift than the corresponding carbon in **2** where the lone pair N-C₁-C₆ arrangement has more folded nature resulting from equal contributions of two lone pair orientations. This unusually large downfield ¹³C contact shift, characteristic of large positive spin density on the carbon, could be attributable to the direct delocalization of spin density from the lone pair coordinated with Ni(AA)₂ onto the C₆ carbon. The lone pair orbital facilitates delocalization of positive spin density onto C₆ by the "through-space" spin transmission. It is also to be noted that C₅ and C₈ carbons in **2** experienced downfield contact shift while those in **3** showed upfield shift. The general trend of the alternating ¹³C contact shifts established for piperidine derivatives is also encountered for **3**, **4**, and **5**, but not for **2**. These unusual downfield contact shifts for C₅ and C₈ in **2** could also be attributed to the direct spin transmission which is facilitated by the substantial contribution of the lone pair *endo* conformation.

C. The Relative Stability of an n, π Homoallyl Interacting System. In order to illuminate the factor that determines the nitrogen lone pair orientation in **2** and **3**, we have carried out CNDO/2 MO calculations for the two conformers of those molecules. The results are given in Table V. The *endo* conformer (**2-endo**) is more stable than the *exo* one (**2-exo**) by about 48 kcal/mol (2.13 eV) in terms of total electronic energy. However, the greater value of the core repulsion energy for **2-endo** compared to **2-exo** cancels above electronic stabilization energy and results in nearly equal total energy of two conformers. This may correspond to the experimental finding for **2** that *exo* and *endo* positions of lone pair are nearly equally favored (see section A). As to the *N*-methyl derivative (**3**), the *exo* conformer is more stable than the *endo* one by 0.1 eV (2.2 kcal/mol), corresponding to the experimental trend. This is attributable to the repulsive interaction between N-CH₃ and β, γ *exo* protons, as is revealed in Table VI. It is, therefore, likely that the *endo* conformer of **2** or **3** is electronically more stable than the

Table VI. Calculated Total Energies for Bicyclo[2.2.2]oct-5-en-2-yl Anion, eV (CNDO/2)^a

Conformer	Total electronic energy (A)	Core repulsion energy (B)	Total energy (A + B)
Lone pair = <i>endo</i>	-7195.29	5415.91	-1779.38
Lone pair = <i>exo</i>	-7193.24	5413.83	-1779.41

^a Any minimization of energy with respect to geometry is not performed in the present calculation.



exo one; however, the steric repulsion between N-R and β, γ *exo* protons plays an important role in this system.

In our recent photoelectron spectroscopic study² of **2-5** together with several other related cyclic and bicyclic amines, we have shown that in the homoallyl interacting system the stereospecific orientation of the lone pair electrons plays an important role in the n, π and n, π^* homoconjugative interactions. Therefore, this different feature of electronic stability between the two conformers is attributable to relative contributions of n, π and n, π^* orbital interactions (or mixings) which lead to stabilization and destabilization of the system, respectively. The *endo* conformer may be more stabilized by the greater contribution of n, π^* interaction than the *exo* one. This trend seems to suggest that the interaction between n and π electrons is rather *attractive*.

In order to discuss the relative stability of the conformers of the corresponding hydrocarbon anion, CNDO/2-MO calculated total energy of 2-bicyclo[2.2.2]oct-5-enyl anion is represented in Table VI. Similarly to the case of the bicyclic amine (**2**), the difference in the total electronic energies of the two conformers is canceled out by the difference in the nuclear repulsion energies. Accordingly it follows that there is no difference in the stability of these two conformers. This corresponds to the result for **2**, the *N*-azahomolog of this carbon anion.

It seems, therefore, reasonable to conclude that the Ni(AA)₂-induced ¹H and ¹³C contact shift serves as a useful probe for the study of homoconjugation between the nitrogen lone pair and the π bond, and that in the homoallyl interacting system both the n, π electronic interaction and the steric repulsive interactions between H-H and H-CH₃ are important for the determination of the orientation of lone pair electrons and the relative stability of the molecule.²⁴

Acknowledgment. The authors are grateful to Professor T. Yonezawa for support and encouragement of this work. They wish to express their appreciation to the Data Processing Center of Kyoto University for the use of the FACOM 230-60 computer.

References and Notes

- Presented partly at XIth European Congress on Molecular Spectroscopy, Tallin, USSR, May, 1973. This paper is referred to as part II of a series on homoallyl n, π interaction in cyclic and bicyclic amines.
- Part I: I. Morishima, K. Yoshikawa, M. Hashimoto, and K. Bekki, submitted for publication.
- I. Morishima, K. Yoshikawa, K. Bekki, M. Kohno, and K. Arita, *J. Am. Chem. Soc.*, **95**, 5815 (1973).
- See, e.g., S. Winstein, *Q. Rev., Chem. Soc.*, **23**, 141 (1969); P. Bischof, R. Gleiter, and E. Heilbronner, *Helv. Chim. Acta*, **53**, 1425 (1970).
- J. K. Stille and K. N. Sannes, *J. Am. Chem. Soc.*, **94**, 8489 (1972).
- H. O. Ochorodnyk and D. P. Santry, *J. Am. Chem. Soc.*, **91**, 4711 (1969).
- M. J. S. Dewar and W. W. Schoeller, *Tetrahedron*, **27**, 4401 (1971).

- (8) As to the bishomoallyl interacting system, the lone pair orientations in 7-azanorbornene derivatives have also been studied: I. Morishima, K. Yoshikawa, K. Toyoda, K. Bekki, to be submitted for publication.
- (9) The π participation effect on the rate of carbonium ion reaction in 2-bicyclo[2.2.2]oct-5-enyl structure has been appreciated: A. Lebel, J. E. Huber, Abstract of the 144th National Meeting of the American Chemical Society, March–April 1963, Los Angeles, Calif., 52M.
- (10) M. P. Cava, C. K. Willkins, Jr., D. R. Dalton, and K. Bessho, *J. Org. Chem.*, **30**, 3772 (1965).
- (11) (a) D. K. Dalling and D. M. Grant, *J. Am. Chem. Soc.*, **89**, 6612 (1967); (b) J. B. Grutner, M. Joutelet, J. B. Dence, R. A. Smith, and J. D. Roberts, *ibid.*, **92**, 7107 (1970).
- (12) (a) I. Morishima, T. Yonezawa, and K. Goto, *J. Am. Chem. Soc.*, **92**, 6651 (1970); (b) I. Morishima, K. Okada, T. Yonezawa, and K. Goto, *Chem. Commun.*, 1535 (1970); (c) I. Morishima, K. Okada, T. Yonezawa, and K. Goto, *J. Am. Chem. Soc.*, **93**, 3922 (1971); (d) I. Morishima, K. Okada, and T. Yonezawa, *ibid.*, **94**, 1425 (1972).
- (13) J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1311 (1963); R. W. Kluiber and W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, **87**, 5350 (1965).
- (14) (a) T. Yonezawa, I. Morishima, and Y. Ohmori, *J. Am. Chem. Soc.*, **92**, 1267 (1970); (b) I. Morishima, K. Okada, and T. Yonezawa, *Chem. Commun.*, 33 (1971); (c) I. Morishima and T. Yonezawa, *J. Chem. Phys.*, **54**, 3238 (1971); (d) T. Yonezawa, I. Morishima, Y. Akana, and K. Fukuta, *Bull. Chem. Soc. Jpn.*, **43**, 379 (1970).
- (15) D. L. Beveridge, P. A. Dobosh, and J. A. Pople, *J. Chem. Phys.*, **48**, 4802 (1967).
- (16) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).
- (17) K. Tori, Y. Takano, and K. Kitahonoki, *Chem. Ber.*, **97**, 2798 (1964).
- (18) J. B. Lambert, R. G. Keske, R. E. Carhart, and A. P. Jovanovich, *J. Am. Chem. Soc.*, **89**, 3761 (1967).
- (19) S. F. Nelsen, P. J. Hintz, and R. T. Landis, II, *J. Am. Chem. Soc.*, **94**, 7105 (1972).
- (20) The ESR hyperfine coupling constant of 2-bicyclo[2.2.2]oct-5-enyl radical has been reported.²¹ However, due to the planar structure around the radical center in this radical, these splitting constants do not correspond to the feature of the Ni(AA)₂-induced ¹H contact shifts of 2-azabicyclo[2.2.2]oct-5-enes.
- (21) L. Bonazzola and R. Max, *Mol. Phys.*, **19**, 405, 899 (1970).
- (22) The sizable contribution of contact shift to the Eu(DPM)₃-induced paramagnetic shift could also lead to misleading conclusions concerning the lone pair orientation.
- (23) T. Yonezawa, I. Morishima, and K. Fukuta, *Bull. Chem. Soc. Jpn.*, **41**, 2297 (1968).
- (24) The detailed study concerning the geometries of various bicyclic amines with minimization of calculated total energies will appear in a separate paper.

CHAPTER 7

Homoallyl Interaction between Nonadjacent n,π Electrons, III. 2-Aza-5-norbornene Derivatives

Abstract:

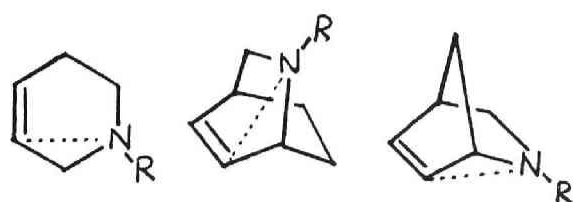
2,3-Dimethyl-2-aza-5-norbornene and its derivatives were prepared. The configuration of these compounds was determined with the aid of Eu- and Pr-induced ^1H paramagnetic shifts and Gd-induced line broadening. From these experimental results, it was concluded that the 2- and 3-methyl carbons occupy the endo and exo positions respectively.

It was also found that the chemical shifts of β and γ protons are affected greatly by the nitrogen lone pair orientation. Such a trend is discussed in relation to the magnetic anisotropy of the nitrogen atom. The photoelectron spectra of 2-aza-norbornene derivatives were obtained in view of elucidation of the manner of nonbonded n,π interaction. It was indicated that the features of the nonbonded interactions are quite different between "homoallyl" and "bishomoallyl" interacting systems.

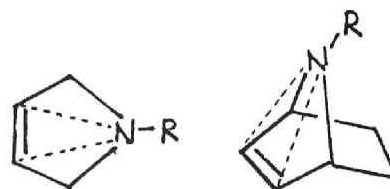
The 7- and 2-norbornenyl systems offer structural frameworks from which long-range nonbonded interactions may be examined. The great π electron participation in the acceleration of the rate of solvolysis in norbornene derivatives has been well established.⁴ However the studies concerning the nonbonded interaction between lone pair (n) and π electrons seems to have been quite limited. The specific orientation of the lone pair electrons on the C₇ carbon in 7-norbornenyl anion has been studied by stereospecific deutron capture for anti and syn anion intermediates.⁵ The preference for anti 7-norbornenyl anion has been suggested, which has been interpreted as resulting from n, π bishomoantiaromaticity in this anion.⁵ In relation to this anion, we have studied stereospecific orientation of the nitrogen lone pair electrons in 7-azanorbornene derivatives⁶ and in 2-azabicyclo[2.2.2]oct-5-ene derivatives,² and indicated the importance of the nonbonded n, π interaction on the lone pair orientation.^{2,6}

We have also performed photoelectron spectral studies of nonbonded n, π interaction involved in several cyclic and bicyclic amines containing nonadjacent π -bonds.⁷ It has been shown that the feature of the nonadjacent n, π interaction is quite different between homoallyl and bishomoallyl interacting systems; in the homoallyl interacting system, both n, π and n, π^* interactions may contribute competitively to the

"Homoallyl Interaction"



"Bishomoallyl Interaction"



relative stability of the interacting system.^{2,7} It is, therefore, of interest to extend our studies to the 2-azanorbornene system⁸ in which relatively strong homoallyl n,π interaction is expected to be involved. In this paper we wish to report the preparation of some 2-azanorbornenyl derivatives. We have also studied the manner of the nonbonded interaction in these compounds in relation to the stereospecific orientation of the lone pair electrons, as a part of our continuing investigations on understanding towards neighboring group participation in the rigid σ -bonded molecules.^{2,6,7,9}

Experimental Section

Routine nmr analysis were performed on a Varian HA-100 nmr spectrometer. Pmr spectra of 2,3-dimethyl-2-aza-5-norbornene (7) and 2,3 diemthyl-2-azanorbornene (8) were obtained using a Varian HR-220 spectrometer. The chemical shift values are expressed in δ values (ppm) relative to a internal TMS. Helium-504 Å photoelectron spectra were obtained on a JASCO PE-1 photoelectron spectrometer. Calibration of the spectra were effected by using the $^2P_{3/2,1/2}$ doublet of xenon (12.13, 13.44 eV). The estimated uncertainty is about ± 0.05 eV.

Results and Discussion

(A) Synthesis and Stereochemistry of 2,3-Dimethyl-2-aza-5-norbornene.¹⁰ 2-Azanorbornene derivatives used for the present study were prepared in the way illustrated in Scheme 1. N-Ethoxycarbonylglycine ethyl ester (1) was treated with t-butyl hypochlorite in acetonitrile to give the corresponding N-chloro derivative (2). Because of difficulty in isolation of ethyl ethoxycarbonyliminoacetate (3),¹¹

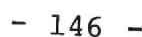
$$\text{EtO}_2\text{CNHCH}_2\text{CO}_2\text{Et} \xrightarrow{\text{t-BuOCl}} \text{EtO}_2\overset{\text{Cl}}{\underset{|}{\text{N}}}\text{CH}_2\text{CO}_2\text{Et} \xrightarrow{\text{Et}_3\text{N}} [\text{EtO}_2\text{CN=CHCO}_2\text{Et}]]$$


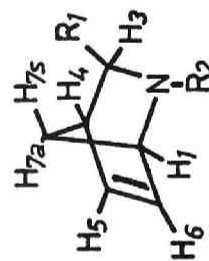
Table I. Pmr assignments of 2-aza-5-norbornenes^a (at 100 MHz)

No. of compd	Ring protons							Other protons
	1	3	4	5	6	7s	7a	
<u>4</u>	4.81m	3.51s	3.33m	6.44m	2.01d	1.50d		4.12q, 4.25q, CH ₂ 1.30t (J=7Hz), CH ₃
					AB, J _{7s,7a} =8Hz			
<u>5</u>	3.77m	1.70t	2.72m	6.48dd	6.13dd	1.75d	1.38d	3.65d, CH ₂ 2.24s, N-CH ₃
		J _{3,CH₂} =6Hz		AB, J _{5,6} =5.5Hz		AB, J _{7s,7a} =8Hz		
				J _{4,5} =3Hz, J _{1,6} =2Hz				
<u>5</u> (HCl)	4.62m	2.75 ^b	3.16m	6.99dd	6.36dd	2.44d	1.92d	4.05d, CH ₂ 2.75d (J _{NH⁺,CH₃} =5.5Hz), N-CH ₃
		J _{3,CH₂} =6Hz		AB, J _{5,6} =5.5Hz		AB, J _{7s,7a} =10.5Hz		
		J _{3,NH⁺} =3.5Hz		J _{4,5} =3Hz, J _{1,6} =2.5Hz				
<u>6a</u> (HCl) ^c	4.56m	2.99t	3.60m	6.94dd	6.37dd	2.10d	1.76d	4.61d, CH ₂ 3.35s, CH ₃ 2.58s, N-CH ₃
		J _{3,CH₂} =6.5Hz		AB, J _{5,6} =5.5Hz		AB, J _{7s,7a} =11Hz		
				J _{4,5} =3Hz, J _{1,6} =2.5Hz				
<u>6b</u>	3.78m	1.78q	2.94m	6.46dd	6.16dd	1.68d	1.42d	3.77q, 3.35q (AB, J=11Hz), CH ₂ 2.25s, N-CH ₃
		J _{3,CH₂} =6&9Hz		AB, J _{5,6} =5.5Hz		AB, J _{7s,7a} =8Hz		
				J _{4,5} =3Hz, J _{1,6} =2Hz				
<u>6b</u> (HCl)	4.67m	(2.8) ^d	3.37m	6.98dd	6.40dd	2.47d	1.95d	4.34q, 3.90q (AB, J=12Hz), CH ₂ 2.79d (J _{NH⁺,CH₃} =5Hz), N-CH ₃
				AB, J _{5,6} =5.5Hz		AB, J _{7s,7a} =11Hz		
				J _{4,5} =3Hz, J _{1,6} =2Hz				

(Table I continued)

$\tilde{\nu}$	3.76m	1.57q	2.50m	6.45dd	6.05dd	1.76d	1.37d	1.19d, CH ₃
		J _{3, CH₂}	=6Hz	AB, J _{5,6} =5.5Hz	AB, J _{5,6} =5.5Hz	AB, J _{7s,7a} =8Hz		2.18s, N-CH ₃
				J _{4,5} =3Hz, J _{1,6} =2.5Hz				
$\tilde{\nu}$ (HCl)	4.56m	2.61q	3.04m	6.96dd	6.31dd	2.46d	1.93d	1.64d, CH ₃
		J _{3, CH₂}	=7Hz	AB, J _{5,6} =5.5Hz	AB, J _{5,6} =5.5Hz	AB, J _{7s,7a} =10.5Hz		2.64d (J _{NH, CH₃} ⁺ =5Hz),
				J _{4,5} =3Hz, J _{1,6} =2.5Hz				N-CH ₃
$\tilde{\nu}$ (HBr)	4.62m	2.75q	3.07m	6.99dd	6.33dd	2.46d	1.95d	1.70d, CH ₃
		J _{3, CH₂}	=7Hz	AB, J _{5,6} =5.5Hz	AB, J _{5,6} =5.5Hz	AB, J _{7s,7a} =10.5Hz		2.67d (J _{NH, CH₃} ⁺ =5Hz),
				J _{4,5} =3Hz, J _{1,6} =2.5Hz				N-CH ₃

a. All spectra were measured in CDCl₃ except 6a-HCl. Chemical shifts and coupling constants were determined by means of decoupling technique. b. Chemical shift was determined from the spectrum of deuterio compound. c, Taken in DMSO-d₆. d, Overlapped with N-Me signal.



2-Azanorbornane derivative (8) could be obtained from catalytic hydrogenation of 7.

Generally, the configuration of a substituent at the 3-position in such bicyclic compounds as norbornane(ene),¹² 2-azanorbornane(ene),¹³ and 2-thia or oxa-5-azanorbornane¹⁴ has been determined by coupling with a bridge head proton in pmr spectrum: C₃-exo-proton exhibits coupling of 3-5 Hz, while C₃-endo-proton does not couple with the C₄-proton.

As is shown in Table 1, pmr spectra of all derivatives obtained in the way of the synthesis of 7 did not show any appreciable coupling, thus indicating exo-configuration of substituents at the 3-position. Cycloaddition of aldimines, in which trichloromethyl and trifluoromethyl groups are connected to a carbon atom, with cyclopentadiene results in the mixed formation of two isomers.^{13b,c,e} On the other hand, cyclic dienophiles such as dehydrohydantoins gives only an endo-isomer.^{13a} Therefore, it should be noted that the present cyclization resulted in the exclusive formation of an exo-isomer would be attributed to anti-conjugation in a cyclizing step.¹⁵

(B) ¹H Nmr Spectra in 7 and 8. The signal changes of each proton as Eu(fod)₃ is successively added to the CDCl₃ solution of 7 are shown in Figure 1 (at 220 MHz). All the protons of 7 exhibit downfield shifts. Figure 2 gives the linear plots of the Eu(fod)₃-induced ¹H shifts vs. the concentration of added Eu(fod)₃ for 7. Similar linearity is also obtained in the plots of the Pr(fod)₃-induced shifts

(upfield shifts) for 7. The spectra are time averaged between complexed and uncomplexed species, and the proton resonances of the ligand shift towards the resonance positions of the paramagnetic adduct. Therefore, only the relative values of these shifts are significant in the present study. Relative values of $\text{Eu}(\text{fod})_3$ - and $\text{Pr}(\text{fod})_3$ -induced shifts were obtained from the slope of these linear plots with the value for the 7-syn proton normalized to unity (Table II).

In order to substantiate these paramagnetic shifts, we calculated the geometric factor, $(3\cos^2\theta - 1)/r^3$.¹⁶ In Table II the relative values of the calculated geometric factors are given, where the C_3 -methyl and N-methyl carbons occupy the exo and endo positions respectively and the metal associates the exo lone pair. In this table, the calculated values correspond to the observed shifts except for 3- and N-methyl protons.¹⁷

To verify further the configuration and the signal assignments for 7, we studied the specific line broadening of the proton nmr resonances induced by the addition of $\text{Gd}(\text{fod})_3$. In Figure 3 is shown the variation of each proton signals with successive addition of $\text{Gd}(\text{fod})_3$ to the CDCl_3 solution of 7. Addition of $\text{Gd}(\text{fod})_3$ causes line broadening of all the proton resonances. Particularly, it is to be noted that the resonance for the 7-syn proton exhibits preferential line broadening compared with that for the 7-anti proton. It has been well established¹⁹ that the long electron relaxation time and highly isotropic magnetic

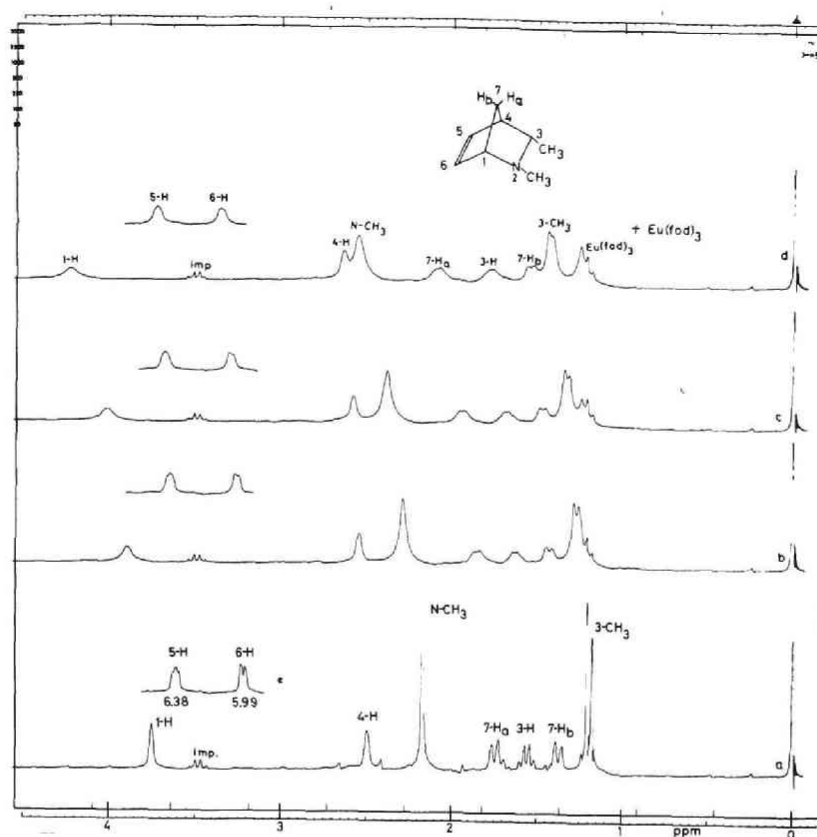


Figure 1. PMR spectra of **7**: (a) 10% CDCl_3 solution (v/v) at 220 MHz, (b-d) in the presence of varying amount of $\text{Eu}(\text{fod})_3$, (e) 5,6-protons are offset +700Hz.

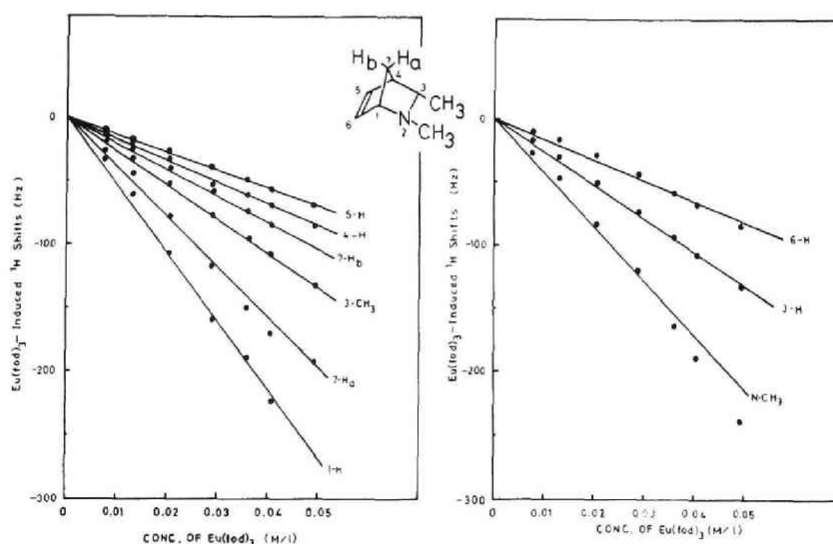
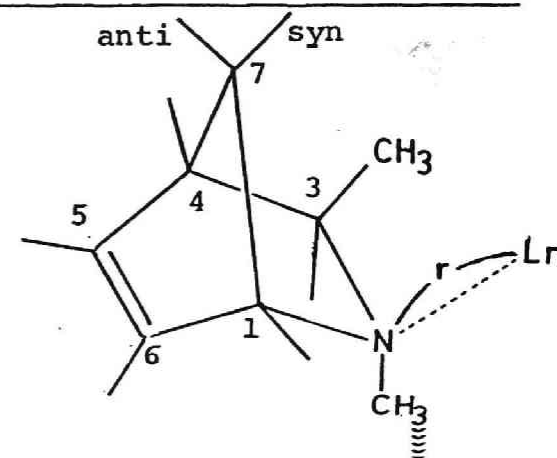


Figure 2. Plots of $\text{Eu}(\text{fod})_3$ -induced ^1H shifts vs. concentration of $\text{Eu}(\text{fod})_3$ for **7**.

Table II. Eu(fod)₃- and Pr(fod)₃-Induced Shifts, and Calculated Pseudo Contact Shifts for 7.

position	chemical shift ^a δ (ppm)	Eu-induced ^b shift(rel.)	Pr-induced ^b shift(rel.)	calculated values (rel.) ^c			
				<u>exo</u> -lone pair r=3.1Å r=3.5Å		<u>endo</u> -lone pair r=3.1Å r=3.5Å	
1	3.75	-1.37	+1.12	1.58	1.29	1.41	1.49
3	1.56	-0.67	+0.51	1.50	1.11	2.04	1.69
4	2.50	-0.43	+0.32	0.64	0.52	0.67	0.72
5	6.37	-0.35	+0.50	0.61	0.46	0.16	0.34
6	6.07	-0.43	+0.64	0.77	0.58	-0.03	0.44
7- <u>syn</u>	1.74	-1.00 ^d	+1.00 ^d	1.00 ^d	1.00 ^d	1.00 ^d	1.00 ^d
7- <u>anti</u>	1.37	-0.51	+0.44	0.61	0.52	0.69	0.73
3-CH ₃	1.20	-0.67	+0.69	0.74	0.93	0.89	0.69
N-CH ₃	2.17	-1.11	+0.94	1.64	1.24	1.69	1.79

a. Diamagnetic reference positions from TMS observed at 220 MHz in CDCl₃ solution. b. Obtained from the relative values of linear plots. The plus and minus signs denote upfield and downfield shifts, respectively. c. Calculated following the equation of McConnell & Robertson (ref. 16). d. The shift of this proton was normalized to unity.



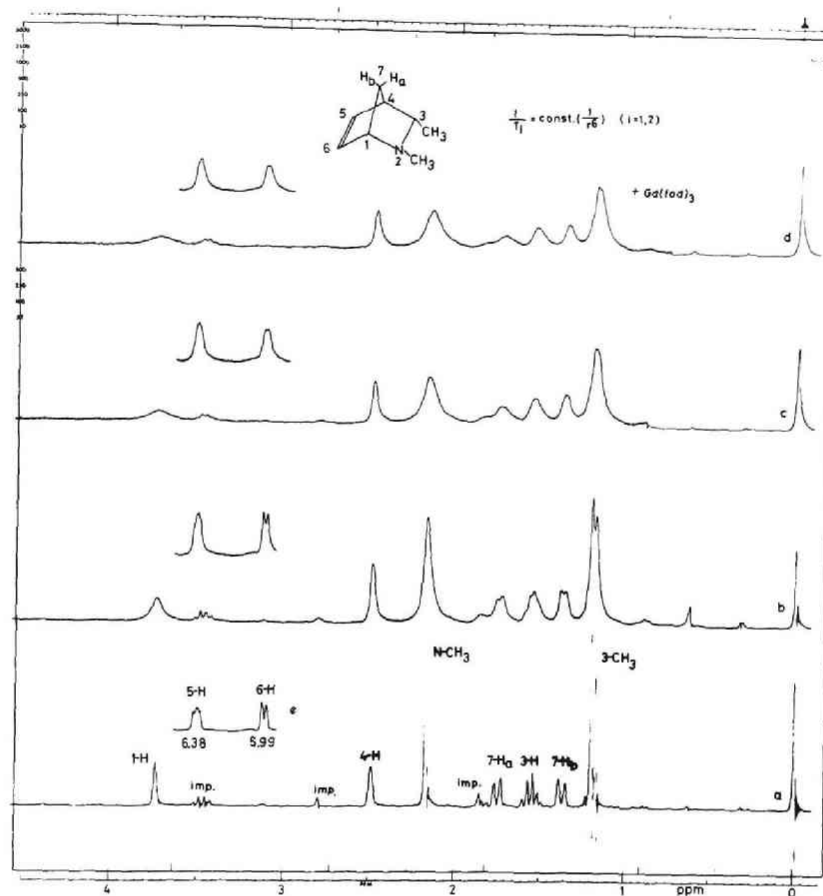
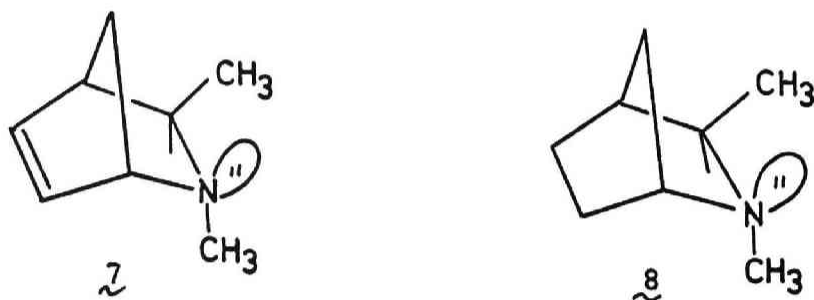


Figure 3. Pmr spectra of **7**: (a) 10% CDCl₃ solution (v/v) at 220 MHz, (b-d) in the presence of varying amounts of Gd(fod)₃, (e) 5,6-protons are offset +700Hz.

moment of Gd makes it the ideal lanthanide "relaxation reagent" with the desired $\langle r^{-6} \rangle$ line width dependence. Accordingly, above differential line broadening effect ascertains the signal assignments of the 7-syn and 7-anti protons in 7. In addition to this, the apparent differential line broadening of the 7-protons confirms further the preferential orientation of the nitrogen lone pair at the exo position in 7. Because it seems reasonable that the line broadening effect on the 7-syn proton is relatively greater by the proximity to the side of the nitrogen lone pair (i.e. the side of the paramagnetic metal) which is preferentially oriented at the exo position, whereas the 7-anti proton feels a much smaller line broadening effect due to its longer distance from the metal associated to the exo lone pair.



In Table III, observed ^1H chemical shifts and Eu-induced shifts for 8 are shown. From the similar experimental trend to the case of 7, it can be concluded that the lone pair electrons occupy the exo position in 8.

There have been many reports concerning the magnetic anisotropy of nitrogen lone pair electrons,^{20,21,22} However, the nitrogen anisotropic effect seems not to have

Table III. Eu(fod)₃-Induced Shifts and Calculated Pseudo Contact Shifts for **8**.

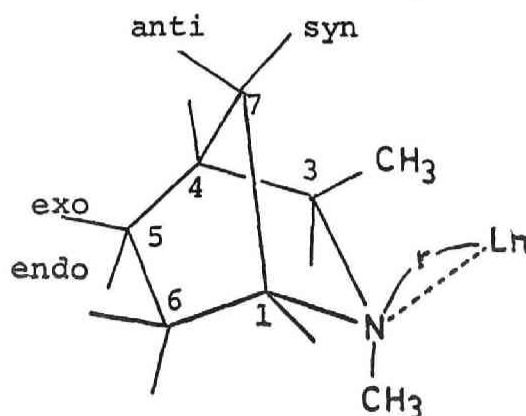
position	chemical shift ^a		Eu-induced ^b shift(rel.)	calculated values(rel.) ^c	
	δ (ppm)			<u>exo</u> -lone pair $r=3.0\text{\AA}$	<u>endo</u> -lone pair $r=3.0\text{\AA}$
1	3.21		-2.55	2.06	1.65
3	1.89		-1.32	2.63	2.27
4	1.96		-0.79	0.84	0.78
5- <u>exo</u>	1.27		-1.2 ^d	0.75	0.34
5- <u>endo</u>	1.76		-1.7 ^d	1.07	0.25
6- <u>exo</u>	1.50		-1.2 ^d	0.92	0.33
6- <u>endo</u>	1.80		-1.69	1.45	0.45
7- <u>syn</u> ^e	1.17	1.21	-1.00 ^f	1.00 ^f	1.00 ^f
7- <u>anti</u> ^e					
3-CH ₃	0.99		-1.76	0.92	0.92
N-CH ₃	2.33		-2.33	2.18	1.97

a. Diamagnetic reference positions from TMS observed at 220 MHz in CDCl₃ solution. b. Obtained from the relative values of linear plots. The minus sign indicates downfield shift.

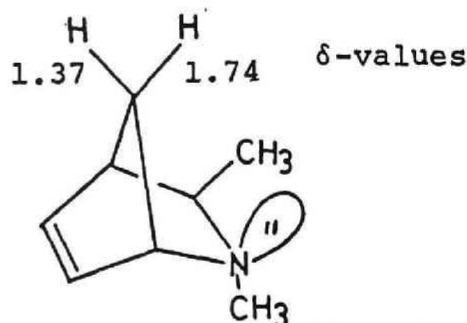
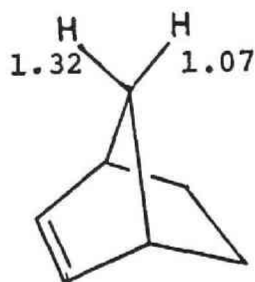
c. Calculated following the equation of McConnell & robertson (ref. 16). d. Accurate values could not be obtained due to

the signal overlapping. e. Syn and anti protons superpose

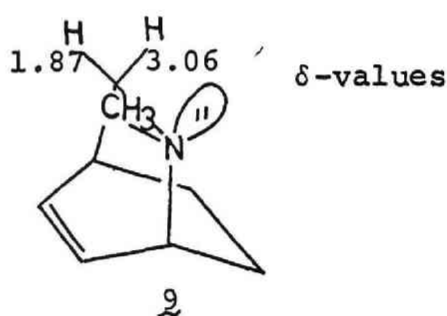
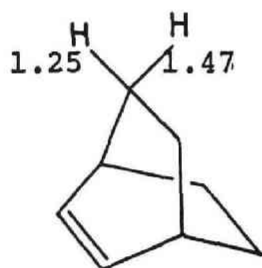
each other. f. Averaged shift of the two 7-protons was normalized to unity.



been clarified yet, in spite of its importance in the spectral analysis and in the configurational analysis of amines. It is noteworthy that the 7-syn proton signal in 7 appears at the downfield side of the anti one, which is in contrast with the difference in the chemical shifts of the hydrocarbon analogue, norbornene,²³ as is shown below. We have previously



reported the ^1H nmr spectra of 2-azabicyclo[2.2.2]oct-5-ene derivatives.² The large shift difference ($\Delta=1.19\text{ppm}$) of the α -methylene protons in 9 is quite different from that ($\Delta=0.22\text{ppm}$) in the hydrocarbon analogue.²⁴ Such an experimental trend



has been attributed to the preferential lone pair orientation to the endo position.² Thus, it becomes apparent that the proton perpendicular to the direction of the lone pair orientation senses deshielding in both cases of the 7-protons in 8 and 3-protons in 9. The relatively deshielded 1-proton resonances in 7 and 8, in which the dihedral angle between the lone pair orientation and the $\text{C}_1\text{-H}_1$ bond is smaller than 60° , are also attributable to the similar

nitrogen anisotropic effect. Uskoković et al. reported that the gauche proton to the lone pair appears in the lower field than the other β -protons in quinolizidine derivatives.^{20,25} This may be also due to the deshielding effect of the nitrogen lone pair in analogue to the above cases. From above discussion, it seems proper to conclude that the tranverse susceptibility of the lone pair is negative and therefore the proton located perpendicular to the lone pair is deshielded.



(C) Homoallyl Type n, π Interaction. Recently photoelectron spectroscopy (PES) has proved to be extremely useful in evaluating the electronic interaction between nonadjacent groups²⁸ in the ground state molecules. Our recent PES study⁷ on the interaction between the nonadjacent n and π electrons involved in several cyclic and bicyclic amines has shown that in the homoallyl interacting system the stereospecific orientation of the lone pair electrons could play a significant role in the n, π and n, π^* homoconjugative interactions.

In order to elucidate further the intrinsic nature of the homoconjugative interaction between n and π electrons, we have performed here a PES study of 7 and 8. The photoelectron spectra of 7 and 8 are shown in Figure 4. The measured vertical ionization potentials (I_p 's) in eV unit

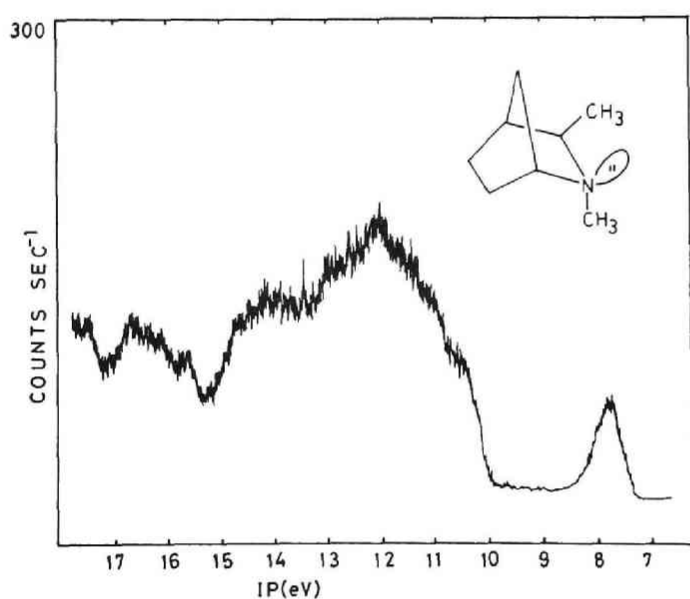
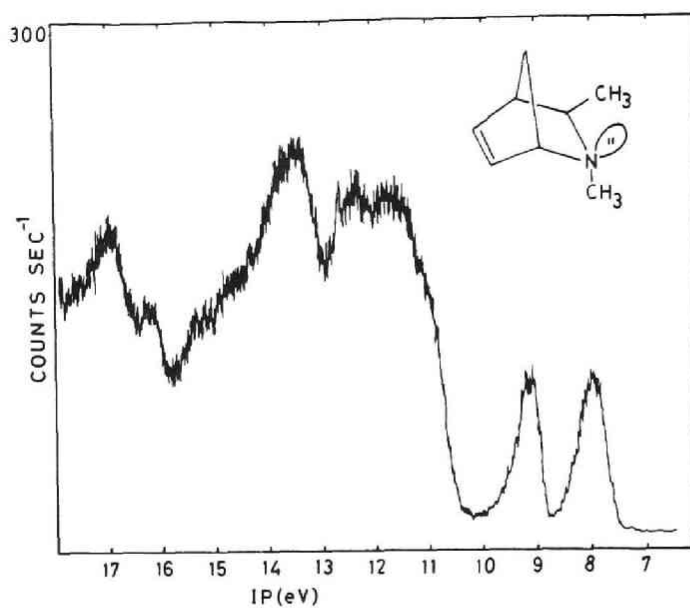
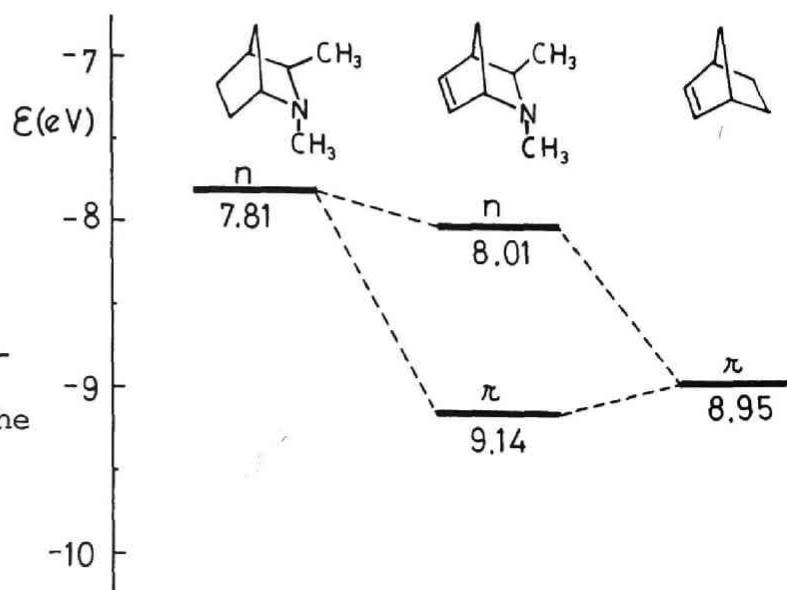


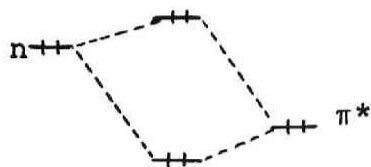
Figure 4. Photoelectron spectra of 7 and 8.

Figure 5. Orbital correlation diagram of the homoallyl interacting system.

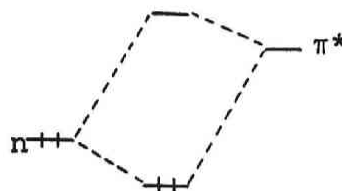


are given in Table IV together with other cyclic and bicyclic amines which involve nonadjacent π bond (homoallyl interacting systems). The first Ip's (in Table IV) can be readily assigned to the ionization from the nitrogen lone pair electrons and the second ones in the unsaturated amines to the ionization from the π electrons.²⁹ Inspection of Table IV shows that the lone pair Ip's are substantially affected by the introduction of a double bond in these cyclic and bicyclic amines. The Ip of the nonbonded electron orbital increases in going from 8 to 7 (by the introduction of a bond). The π level in 7 is lower than that of the corresponding hydrocarbon, norbornene (Figure 5).³⁰ Such a feature is similar to the other homoallyl n, π interacting systems (Table IV),⁷ which is quite different from that of the bishomoallyl n, π interacting system (five membered amines).⁷ For the interaction between nitrogen lone pair and neighboring π electrons, the π and π^* levels are considered to play a significant role in the "through-space" interactions. The n, π and n, π^* direct interactions cause destabilization and stabilization of the n level, respectively.²⁸ As the

" n, π interaction"

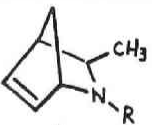
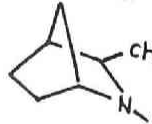
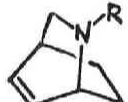
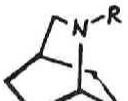


" n, π^* interaction"



n, π^* direct interaction is symmetry forbidden in five membered amines, the n level is destabilized by the n, π direct interaction. For six membered systems, both the n, π and n, π^* interac-

Table IV. Ionization Potentials of Cyclic Amines (eV).

compound	ionization potential ^a	
	R=H	R=CH ₃
	—	8.01(Δ =+0.20,n) ^c , 9.14(π)
	—	7.81(n), 10.69
	8.64(Δ =0.00,n), 9.33(π)	8.67(Δ =+0.38,n), 9.37(π)
	8.64(n), 10.75	8.29(n), 10.59
	8.35(Δ =+0.13,n), 9.36(π)	7.97(Δ =+0.19,n), 9.28(π)
	8.22(n), 10.29	7.78(n), 10.09
	8.61(Δ =-0.16,n), 9.77(π)	8.21(Δ =-0.20), 9.66(π)
	8.77(n), 11.49	8.41(n), 11.16

a. Vertical ionization potentials (± 0.05 eV). b. Ref. 7.

c. " Δ " shows the stabilization energy induced by the introduction of a double bond.

tions are symmetrically allowed.^{2,7} Therefore, in these systems both the n,π and n,π^* interactions appear to contribute competitively. In addition to the "through-space" interaction, we should also take into account the "inductive effect" which enhances³¹ the I_p 's of the n and π levels in going from the separated system (saturated cyclic amine + cycloalkene) to the interacting one (β,γ -unsaturated cyclic amine). In the six membered cyclic and bicyclic amines, "through-space" n,π interaction may be diminished due to the molecular nonsymmetry compared with that of the five membered ones and therefore the n,π^* interaction and the "inductive effect" may become relatively important, resulting in a small stabilization or no apparent variation of the n level (see Δ values in Table IV).

Such a different feature of the nonbonded n,π interaction between in homoallyl and bishomoallyl interacting systems may imply that there should be different physical and chemical properties in these two systems.

References and Notes

- (1) This paper is referred to as part III of a series on homoallyl n, π interaction in cyclic and bicyclic amines.
- (2) Part II; I. Morishima, and K. Yoshikawa, J. Amer. Chem. Soc., 97, 2950(1975).
- (3) (a) Kyoto University; (b) National Institute of Radiological Sciences.
- (4) See e.g.; S. Winstein, Quart. Rev. Chem. Soc., 23, 141(1969).
- (5) J. K. Stille and K. N. Sannes, J. Amer. Chem. Soc., 94, 8489(1972).
- (6) K. Yoshikawa, K. Bekki, M. Karatsu, T. Kamio, and I. Morishima, J. Amer. Chem. Soc., in press.
- (7) I. Morishima, K. Yoshikawa, M. Hashimoto, and K. Bekki, J. Amer. Chem. Soc., 97, 4283(1975).
- (8) Stille et al. have also studied the anion of 2-norbornenyl system. However, due to scrambling between the 2- and 7-positions of the norbornenyl anion, its steric or electronic structure seems not to have been clarified yet; J. K. Stille and K. N. Sannes, J. Amer. Chem. Soc., 94, 8494(1972).
- (9) I. Morishima, K. Yoshikawa, K. Bekki, M. Kohno, and K. Arita, J. Amer. Chem. Soc., 95, 5815(1973).
- (10) The results of some reactions to 2-aza-5-norbornene derivatives will be published by S. I.
- (11) H. Plieninger and D. von der Bruck, Tetrahedron Lett., 4571(1968).
- (12) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,"

2nd edition, Chapter 4-2, Pergamon Press, New York, N. Y., 1969. References are cited herein.

(13) (a) A. B. Evnin, A. Lam, and J. Blyskal, *J. Org. Chem.*, 35, 3097(1970); (b) G. Krow, R. Rodebaugh, and J. Marakoeski, *Tetrahedron Lett.*, 1899(1973); (c) T. Imagawa, K. Sisido, and M. Kawanishim *Bull. Chem. Soc. Japan*, 46, 2922(1973); (d) P. S. Portoghese and D. T. Sepp, *Tetrahedron*, 29, 2253(1973); (e) G. R. Krow, C. Pyun, R. Rodebaugh, and J. Marakowski, *ibid.*, 30, 2977(1974); (f) M. S. Raasch, *J. Org. Chem.*, 40, 161(1975).

(14) (a) P. S. Portoghese and J. G. Turcotte, *Tetrahedron*, 27, 961(1971); (b) P. S. Portoghese and V. G. Telang, *ibid.*, 27, 1823(1971).

(15) Recent report (Ref.13f) describes that the adduct from cycloaddition of n-butyl tosyliminoacetate with cyclopentadiene (R. Albrecht and G. Kresze, *Chem. Ber.*, 98, 1431(1963)) is an exo-isomer.

(16) H. M. McConnel and R. E. Robertoson, *J. Chem. Phys.*, 29, 1361(1958).

(17) There would be a considerable contact contribution in the lanthanide-induced paramagnetic shifts for α and β protons.¹⁸ The abnormal shifts of 3- and N-methyl protons are attributable to the contact contribution.

(18) J. Briggs, G. H. Frost, F. A. Hart, G. P. Moss, and M. L. Stainforth, *Chem. Commun*, 749(1970); R. J. Cushley, D. R. Anderson, and S. R. Lipsky, *J. Chem. Soc. Chem. Commun.*, 636(1972); M. Kainosho, K. Ajisaka, and K. Tori, *Chem. Lett.*, 1061(1972); G. E. Hawkes, C. Marzin, S. R. Johns, and J.

D. Roberts, J. Amer. Chem. Soc., 95, 1661(1973).

(19) G. N. LaMar and L. W. Faller, J. Amer. Chem. Soc., 95, 3817(1973). G. N. LaMar and E. A. Metz, *ibid.*, 96, 5611(1974).

(20) M. Uskoković et al. speculated that the magnetic anisotropy of the nitrogen lone pair is similar to that of a carbon-carbon triple bond. M. Uskoković, H. Bruderer, C. von Planta, T. Williams, and A. Brossi, J. Amer. Chem. Soc., 86, 3364(1964).

(21) S. Yamaguchi et al. claimed that the anisotropy of the nitrogen atom opposes to that of a carbon-carbon triple bond. S. Yamaguchi, S. Okuda, and N. Nakagawa, Chem. Pharm. Bull. (Tokyo), 11, 1465(1963).

(22) S. F. Nelsen et al. speculated shielding on the side of the lone pair and deshielding on the back side. S. F. Nelsen, P. J. Hintz, and R. T. Landis, II, J. Amer. Chem. Soc., 94, 7105(1972).

(23) K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, Tetrahedron Lett., 9(1966).

(24) K. Tori, Y. Takano, and K. Kitahonoki, Chem. Ber., 97, 2798(1964).

(25) Another possible factor²⁶ can be considered as causing the observed chemical shift difference between the gauche and trans protons in piperidines and quinolizidines is that the electron density at the trans hydrogen is greater than that at the gauche hydrogen atom. However, semiempirical MO calculations indicate that the difference of the electron densities of the gauche and trans protons is negligible

small.²⁷

(26) H. P. Hamlow, S. Okuda, and N. Nakagawa, *Tetrahedron Lett.*, 37, 2553(1964).

(27) K. Yoshikawa, M. Karatsu, I. Morishima, and S. Ikegami, unpublished results.

(28) R. Hoffman, *Accounts. Chem. Res.*, 4, 1(1971).

(29) These assignments have been confirmed by the study concerning the UV charge transfer band of amine-I₂ complexes. K. Yoshikawa, A. Matsui, M. Karatsu, I. Morishima, K. Bekki, and S. Ikegami, to be submitted for publication.

(30) P. Bischof, J. A. Hashmall, E. Heilbronner, and R. Schurter, *Chem. Ber.*, 106, 961(1973).

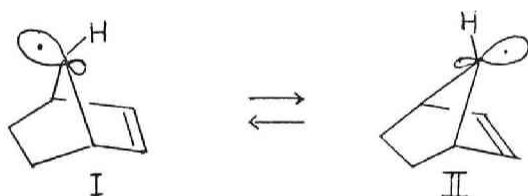
(31) D. Chadwick, D. C. Frost, and L. Weilar, *J. Amer. Chem. Soc.*, 93, 4962(1971). A. D. Bain, D. C. Frost, and L. Weilar, *ibid.*, 95, 291(1973).

Homoallyl Interaction between Nonadjacent n, π Electrons, IV.
7-Azanorbornene Derivatives

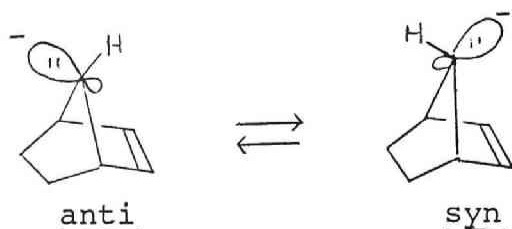
Abstract:

In order to gain insight into the effect of n, π bis-homoallyl interaction on the orientation of the lone pair electrons, we have carried ^1H and ^{13}C nmr spectroscopic study of 7-azanorbornene and 7-azanorbornadiene derivatives. Based on the stereospecific shifts and the line broadening effects of ^1H nmr signals induced by Eu^{3+} and Gd^{3+} , it was concluded that the lone pair electrons preferentially occupy an anti position with respect to the electron rich π -bond in N-methyl-7-azanorbornadiene-2,3-dicarboxylic acid. This preferential orientation of the nitrogen lone pair in 7-azanorbornene derivatives was also confirmed by the stereospecific ^{13}C chemical shift changes induced by N-methyl substitution and by the $\text{Eu}(\text{fod})_3$ -induced ^1H shifts. Similar trend of the specific lone pair orientation is also encountered for N-H 7-azanorbornene derivatives. From these experimental results it is concluded that n and π electrons are "repulsive" in bishomoallyl and bishomobenzyl interacting systems involved in the five membered cyclic and bicyclic amines and that the nitrogen lone pair electrons prefer an anti position with respect to the π bond or π electron rich group so as to avoid the "repulsive" interaction.

The 7-norbornenyl system offers a structural framework from which long-range nonbonded interactions may be examined. The 7-norbornenyl cation has been shown to exhibit such bonding to an unusual degree.⁴ This has been attributed to the nonclassical nature of the 7-norbornenyl cation resulting from the overlapping of the unoccupied and the nonadjacent orbitals. Similarly, the nonclassical nature of the 7-norbornenyl radical has been proposed by Kochi et al.⁵ based on its electron spin resonance spectrum. They claimed that I is more stable than II and that the interaction between the π orbital on carbon-2,3 and the half-occupied orbital on



carbon-7 has a destabilizing effect. However, the studies on the nonbonded interaction between the doubly occupied n orbital (anion center) and the nonadjacent π group has been quite limited. Recently, the specific orientation of the lone pair electrons on C_7 in 7-norbornenyl anion has been studied⁶ by stereospecific deuterium capture of anti and syn anion intermediates. The preference for anti-7-norbornenyl anion has been suggested and interpreted as resulting from possible bishomo-antiaromatic character of this anion. Quantum chemical studies of 7-norbornenyl anion has also been performed.^{7,8} The semiempirical molecular orbital calculations, however, failed to predict definitely the orientation of the lone pair electrons. It may be, therefore, readily

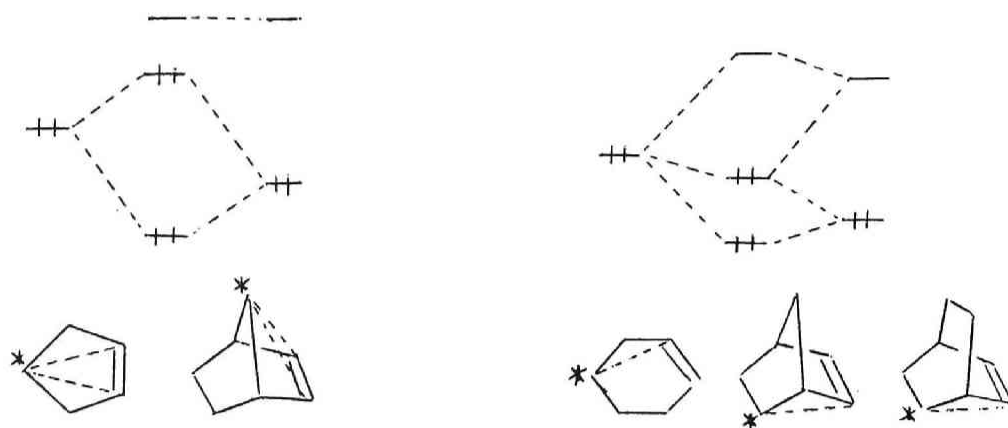


accessible from these examples that the problem on the transannular effect between the lone pair electrons and the neighbouring π bond in bicyclic molecules is still open to further experimental and theoretical studies.

In our recent photoelectron spectroscopic studies^{1,9,10} on the nonbonded n, π interaction involved in several cyclic and bicyclic amines containing nonadjacent π bond, it has been shown that the feature of the nonbonded n, π interaction is quite different between homoallyl and bishomoallyl n, π interacting systems. In the homoallyl interacting system, both n, π and n, π^* interactions contribute competitively to the relative stability of the interacting system and, therefore, the system is electronically rather stabilized.^{9,10,13}

"bishomoallyl"

"homoallyl"

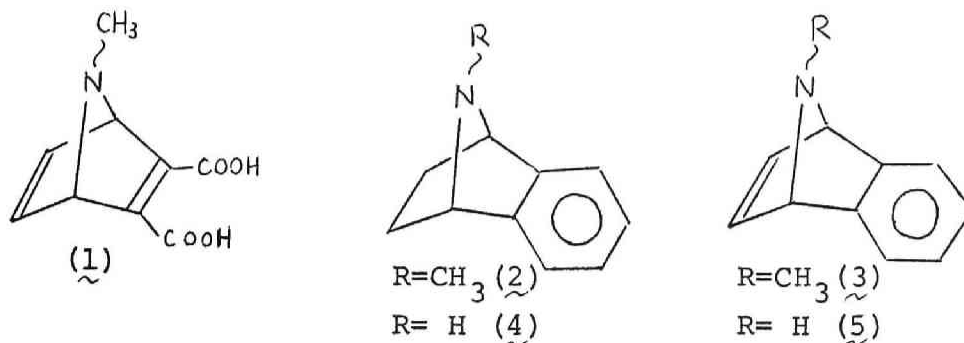


* = N-H, N-CH₃

On the contrary, bishomoallyl n, π interaction makes the interacting system less stable, because the n, π^* interaction is forbidden from the orbital symmetry. In other words,

n and π electrons in the bishomoallyl interacting system⁹ are "repulsive," while, these electrons are rather "attractive" in the homoallyl system.^{9,10,13} It is therefore of interest to study the specific orientation of the lone pair electrons in bicyclic amines in which homoallyl and bishomoallyl n, π interactions may be involved and to elucidate the intrinsic nature of these homoconjugative interactions.

We have previously reported the stereospecific orientation of the lone pair electrons in 2-azabicyclo[2.2.2]oct-5-ene derivatives¹³ and N-methyl-2-aza-5-norbornene derivatives,¹⁰ the homoallyl n, π interacting systems. It has been shown that the direct interaction between n and π electrons play an important role in the specific lone pair orientation and that these electrons are "electronically attractive", as is expected from the molecular symmetry. In these circumstances, we have studied here the orientation of the nitrogen lone pair electrons and electronic structures in 7-azanorbornene derivatives, the bishomoallyl interacting system. The following compounds were studied: N-methyl-7-azanorbornadiene-2,3-dicarboxylic acid (1), N-methyl-7-azabenzonorbornene (2), N-methyl-7-azabenzonorbornadiene (3), 7-azabenzonorbornene (4) and 7-azabenzonorbornadiene (5). The aim of this study is



to delineate the following problems, intrinsic in these molecules. (1) Whether the n, π bishomoconjugative interaction is "attractive" or "repulsive"? (2) How is the effect of this n, π nonbonded interaction on the stereospecific orientation of the lone pair electrons?

Experimental Section

Materials. N-Methyl-7-azanorbornadiene-2,3-dicarboxylic acid (1) was synthesized by referring to Kitzing et al.¹⁴ 7-Azabenzonorbornene (4) and 7-azabenzonorbornadiene (5) were prepared by the method of Carpino.¹⁵ N-methyl-7-azabenzonorbornene (2) and N-methyl-7-azabenzonorbornadiene (3) were prepared by N-methylation of the parent amines (4 and 5). $\text{Eu}(\text{NO}_3)_3$, $\text{Gd}(\text{NO}_3)_3$, $\text{Eu}(\text{fod})_3$ (tris(heptafluorobutanoyl pivaloylmethanato) europium), and $\text{Ni}(\text{AA})_2$ (nickel bisacetyl acetonate) are commercially available. $\text{Eu}(\text{fod})_3$ and $\text{Ni}(\text{AA})_2$ were dried in vacuo over three days at 60° and at room temperature, respectively, before use.

Proton Nmr Measurement. All the proton spectra were measured with a Varian Associates HR-220 high-resolution spectrometer (Kyoto Univ.) operating at 220MHz. Assignments of well separated proton signals were made by referencing the spectral patterns, $\text{Eu}(\text{fod})_3$ -induced shifts, and the spectra of the related carbocyclic compounds. TMS or DSS was used as an internal standard. The perturbed spectra were taken at room temperature (24°) in the presence of varying amounts of the paramagnetic reagents.

Carbon Nmr Measurement. All the ^{13}C spectra were obtained at 25.1 MHz on a Jeolco ^{13}C Fourier transform nmr system, JNM-PFT-100, and were recorded after 100~10000 pulses with intervals of 2 or 3 seconds. An internal ^2D lock was employed. The assignments of ^{13}C nmr spectra were made by comparing each other (1~5) and by referring the spectra of their carbocyclic derivatives. The half-decoupled technique was also used to help the signal assignment of the ^{13}C nmr spectra.

Results and Discussion

A. The Specific Orientation of the N-Methyl Group in 7-Azanorbornadiene-2,3-dicarboxylic acid. The pK values of 2.9, 5.8 and 10.5 for 1 were obtained from the pH measurement of its hydrochloride solution by titration with aqueous NaOH. The values of pK=2.9 and 5.8 are attributable to the dissociation of two carboxyl groups and pK=10.5 to the dissociation of a proton from the ammonium group. Therefore, four steps of ionization are deduced as shown below.¹⁷

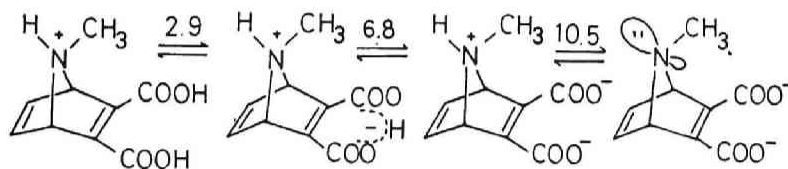


Figure 1 shows the 220 MHz ^1H nmr spectra of 1 in acidic, neutral and basic D_2O solutions. As the pD is raised, the shieldings of all the protons (N-methyl, bridgehead (1,4-H) and vinylidene (5,6-H) protons) increase. This is because dissociation of the proton at the carboxyl or the ammonium

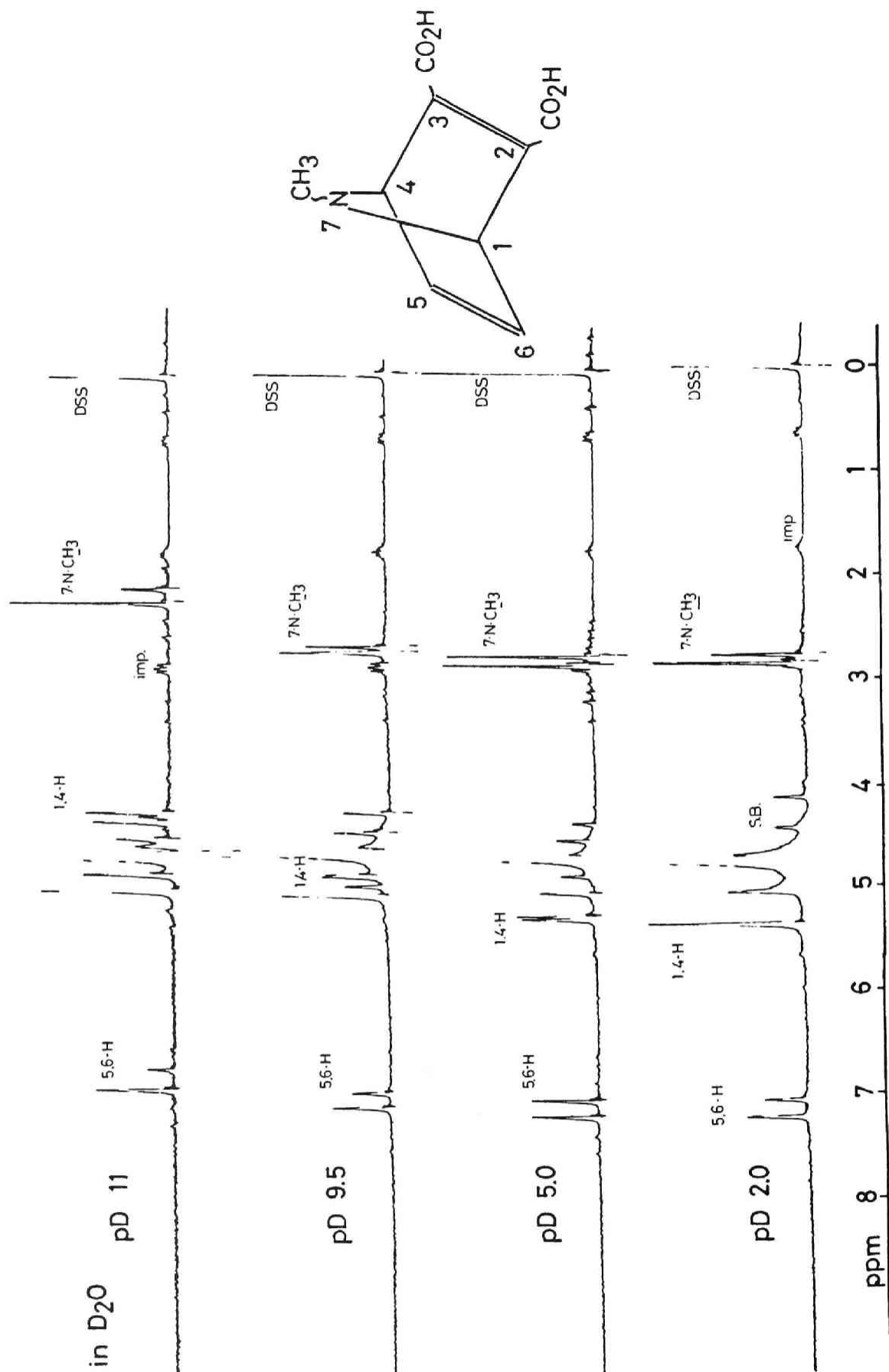


Figure 1. 220 MHz ^1H nmr spectra of **1** in acidic, neutral and basic D_2O solutions.

group enhances electron densities on the neighbouring hydrogen atoms. A remarkable feature to be noted in Figure 1 is that the ^1H nmr spectra of 1 exhibit two separate absorptions for each proton^{/8}, which is most possibly resulting from the presence of two N-methyl invertomers, N-methyl-syn and -anti ones. The invertomer ratio obtained by integration of each proton absorption (most accurately the N-methyl proton signals) was seriously affected by the variation of the pD values as is shown in Figure 1 and Table I. At high pD values (greater than pD=10.5), where the nitrogen atom is free from protonation, one invertomer is strongly favored over the other (80:20). In the acidic media, however, the invertomer ratio becomes close to 1:1. This experimental trend may allow us to expect that n,π bishomoconjugative interaction is responsible for the specific orientation of the nitrogen lone pair electrons and that the steric effect of the N-methyl group on the lone pair orientation is less important.

In order to assign these two sets of separate signals, we studied Eu^{3+} -induced pseudo-contact shifts for 1. Figure 2 shows the plots of Eu^{3+} -induced paramagnetic shifts vs. the concentration of added $\text{Eu}(\text{NO}_3)_3$ for the 0.05 M D_2O solution of 1. Here pD was adjusted to 4.6 which is most suitable for the observation of Eu^{3+} -induced shifts. The relative intensity of each set of the proton signals did not vary with the addition of the paramagnetic shift reagent. The spectra are time averaged between complexed and uncomplexed species. When the concentration of Eu^{3+} is lower than

Table I. Relative Populations of the Two Invertomers

Compounds	Solvents	Relative Populations ^a
<u>1</u>	D ₂ O {	pD = 1.4 58 : 42
		4.6 55 : 45
		9 74 : 26 ^b
		11 80 : 20
	DMSO	24 : 76
<u>2</u>	CDCl ₃	80 : 20
	CF ₃ COOD	70 : 30
<u>3</u>	CDCl ₃	94 : 6
	CF ₃ COOD	76 : 24

a. Obtained from the integration of the N-methyl proton signals of the two invertomers.

b. Obtained from the integration of 1,4-H signals.

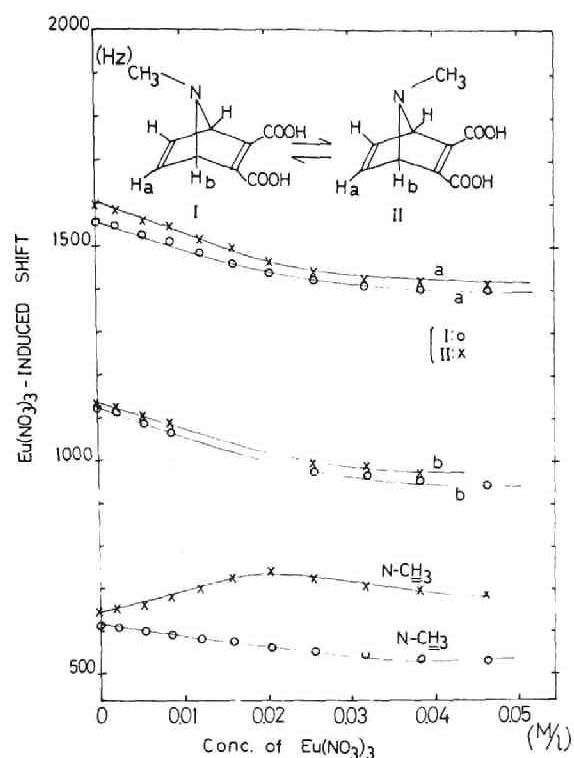


Figure 2. Plots of Eu^{3+} -induced pseudo-contact shifts vs. the metal concentration for 1.

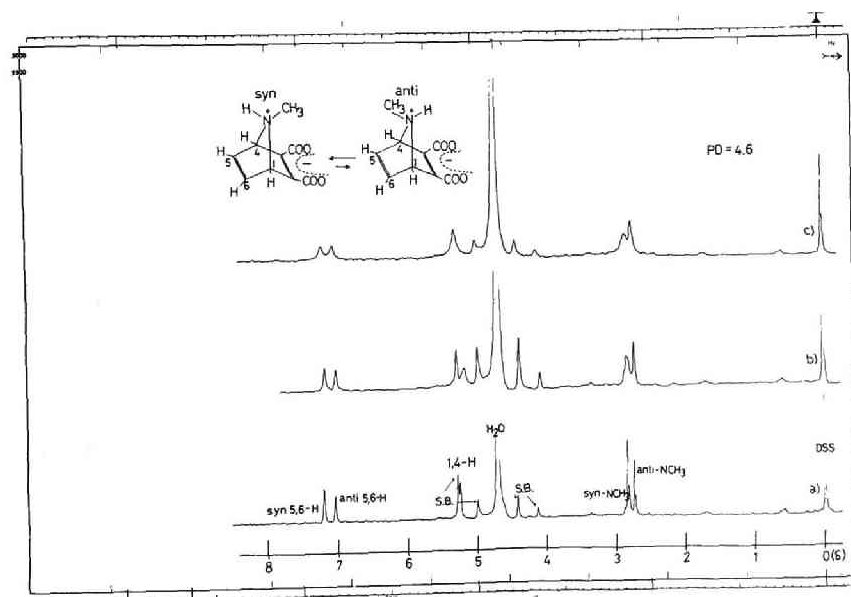


Figure 3. 220 MHz ^1H nmr spectra of 1 (pD=4.6). (a) in D_2O ($3 \times 10^{-1} \text{M}$), (b), (c) in the presence of 1×10^{-1} and $1 \times 10^{-3} \text{mM}$ $\text{Gd}(\text{NO}_3)_3$ in the solution, respectively.

0.017~0.018 M, the addition of $\text{Eu}(\text{NO}_3)_3$ caused upfield shifts for each of the proton signals except for the N-methyl signal of the predominant invertomer. It is well known¹⁹ that carboxyl anions or carboxyl groups associate perpendicularly to the principal magnetic axis of a lanthanide ion and used to form a 3 : 1 complex of ligands and a metal ion. Axial symmetry around the metal ion is also expected in the 3 : 1 complex of 1 and Eu^{3+} . It is, therefore, likely that the relative values of the Eu^{3+} -induced shifts at low ion concentration are significant in the present study. The relative values of Eu^{3+} -induced shifts of the 3 : 1 complex of the ligands and the Eu^{3+} ion, with the value for the bridgehead proton normalized to unity, are shown in Table II. In order to substantiate these paramagnetic shifts, we calculated the geometric factor,²⁰ $(1-3\cos^2\theta)/r^3$, with the assumption that the dicarboxyl group of 1 associates perpendicularly to the principal axis of Eu^{3+} . The relative values of the calculated geometric factors which give the best agreement with the observed paramagnetic shifts are also given in Table II. Correspondence between the relative values of the observed shifts and those of the calculated geometric factors may allow us to assign the major conformer to the one having the N-methyl group on the same side as the dicarboxyl group (N-methyl-syn conformer). To verify further the preferential orientation of the N-methyl group to the syn position, we have also studied the specific line broadening of the proton resonances induced by the addition

Table II. ^1H Chemical Shifts, Eu^{3+} -Induced Shifts, and Calculated Pseudo Contact Shifts for 1 (pD = 4.6)

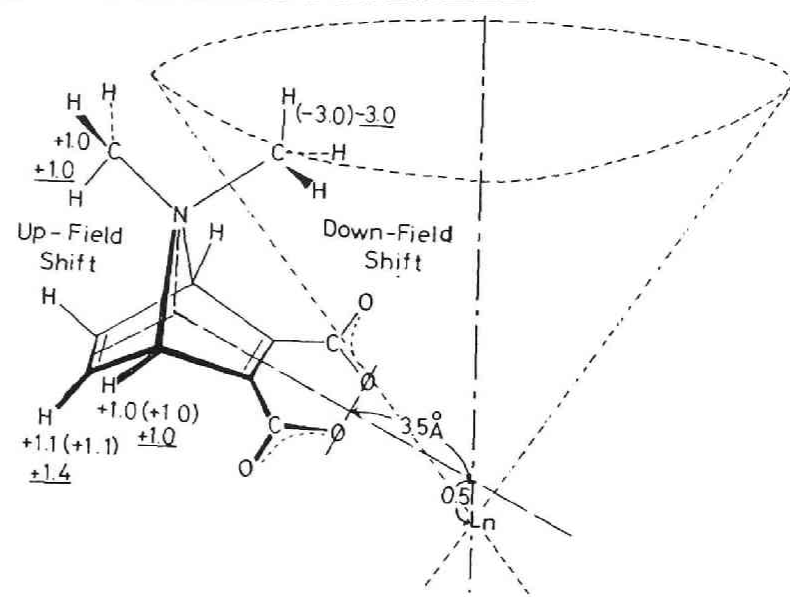
Conformer	position	^1H chemical shift, δ ^a	Eu^{3+} -induced ^1H shift (rel.) ^b	Calculated values (rel.) ^c
N-methyl- <u>syn</u> ^e	N-methyl	2.95	-3.0	-3.0
	1,4-H ^d	5.09	+1.0	+1.0
	5,6-H	7.25	+1.1	+1.4
N-methyl- <u>anti</u>	N-methyl	2.76	+1.0	+1.0
	1,4-H	5.19	+1.0	+1.0
	5,6-H	7.09	+1.1	+1.4

a. Diamagnetic reference positions from DSS observed at 220MHz at room temperature (24°C) in D_2O solution.

b. Obtained from the relative values of linear plots in the low concentration of Eu^{3+} (see Figure 2).

The plus and minus signs denote upfield and downfield pseudo contact shifts, respectively. c. Calculated following the equation of McCornell & Robertson.²⁰

The optimized values are shown. The location of the Eu^{3+} used for the calculation is shown. d. The shifts of this proton was normalized to unity. e. The major conformer.



of $\text{Gd}(\text{NO}_3)_3$ to the aqueous solution of 1. The lower field N-methyl resonance ($\delta=2.83$) with the greater signal intensity exhibits preferential line broadening, compared with the upperfield one. While, the other sets of proton signals (the bridgehead (1,4-H) and the vinylidene (5,6-H) protons) of the two invertomers show the line broadening to an equal extent. It has been well established²¹ that the long electron relaxation time and highly isotropic magnetic moment of Gd^{3+} makes it the ideal lanthanide "relaxation reagent" with the desired $\langle r^{-6} \rangle$ line width dependence. Accordingly, above differential line broadening effect appears to confirm our assignment of the major invertomer to the N-methyl-syn conformer.

B. The Orientation of the Lone Pair Electrons in N-Methyl-7-azanorbornene derivatives.

Figure 4 exemplifies the 220 MHz ^1H nmr spectra for 3. As is evidently shown in this figure, the ^1H nmr spectra of 2 and 3 in CDCl_3 or in CF_3COOD solution also exhibit two separate absorptions for each proton, resulting from the presence of the two N-methyl invertomers. The invertomer ratio of these compounds obtained from the integration of the proton absorptions are given in Table I together with the result for 1. In order to delineate the stereospecific orientation of the nitrogen lone pair electrons, the ^{13}C nmr chemical shifts for 1~5 were measured in various solvents. The ^{13}C nmr spectrum of 1 in d_6 -DMSO is shown in Figure 5. The two invertomers give rise to two distinct sets of ^{13}C

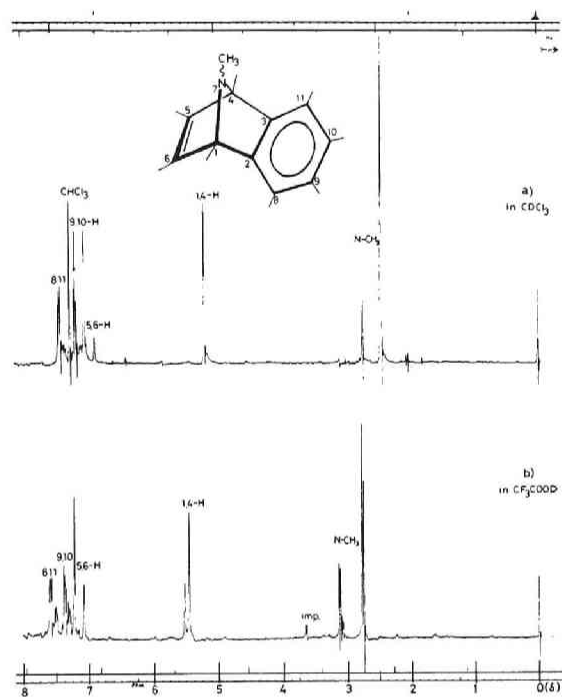


Figure 4. 220MHz ^1H nmr spectra of **3**, (a) in CDCl_3 and (b) in CF_3COOD .

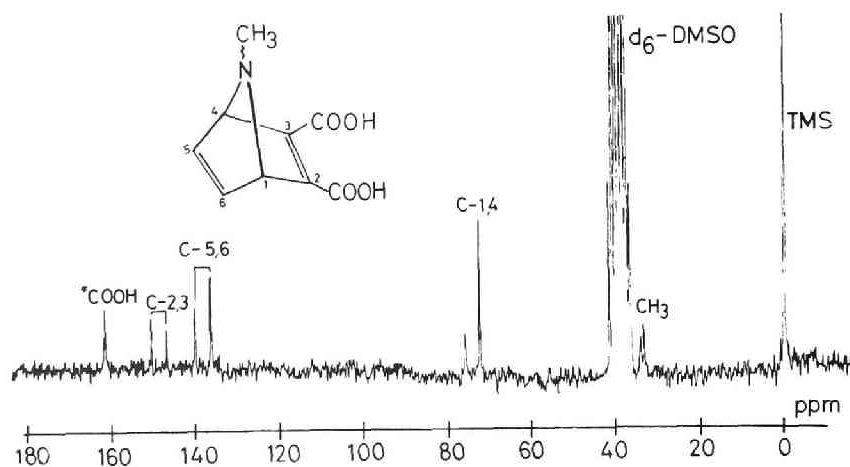


Figure 5. ^{13}C nmr spectrum of 1 in d_6 -DMSO solution (at 25.1MHz).

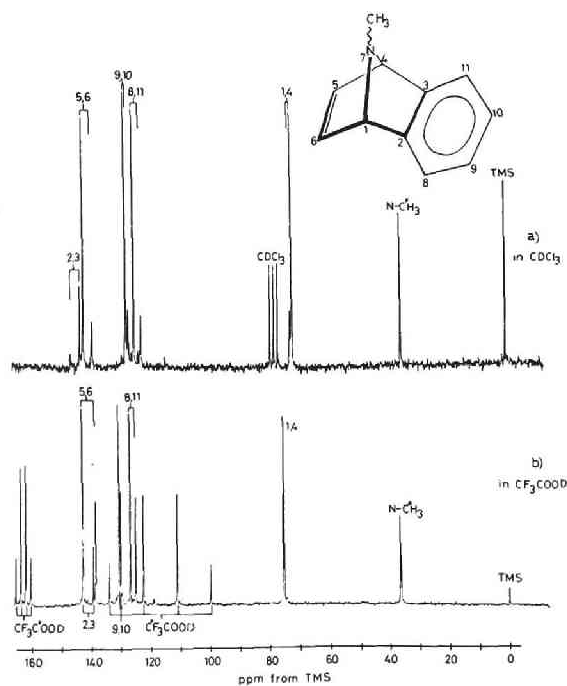


Figure 6. ^{13}C nmr spectra of 3, (a) in CDCl_3 and (b) in CF_3COOD solutions (at 25.1MHz).

chemical shifts for each carbon, as the case for ^1H nmr spectra. In DMSO solution, as is discussed in section A, N-methyl-anti conformer is the major one. Figure 6 shows the ^{13}C nmr spectra of 3 in CDCl_3 and in CF_3COOD . As is the case for 1, inspection of Figure 6 shows the presence of the two N-methyl-invertomers for 3. The ^{13}C nmr shifts of 7-azanorbornene derivatives are summarized in Table III. Unfortunately, the ^{13}C nmr signals of the minor conformer of 2 in CDCl_3 solution were failed to detect because of its considerably small population (6 : 94, see Table I). On the other hand, the ^1H and ^{13}C nmr spectra of 4 and 5 showed a single set of time-averaged signals. In the DMSO solution of 1, the 2,3 carbon resonance of the N-methyl-syn conformer is 3.3 ppm upfield with respect to that in N-methyl-anti one. However, the 5,6 carbons of the former resonate at 3.2 ppm downfield from those of the latter. Similar trend of the ^{13}C chemical shifts of 2,3 and 5,6 carbons is also encountered in the D_2O solution of 1 (Table III). It is well established²¹ that the effect of methyl substitution on the ^{13}C chemical shift is quite sensitive to the structural changes of the carbon skeleton in organic compounds. In the 7-methyl-syn and -anti conformers of 7-methylnorbornene, the γ -carbon that lies on the cis skeleton resonates at higher field than that on the trans one. Such an experimental

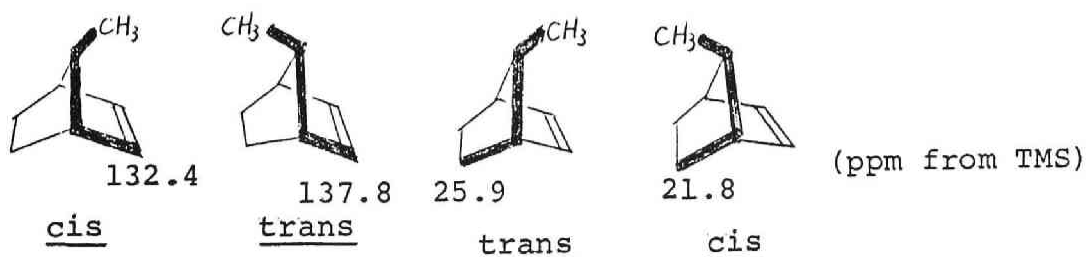
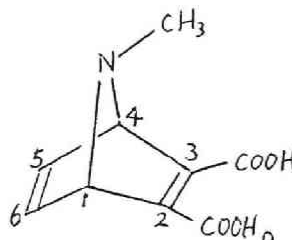
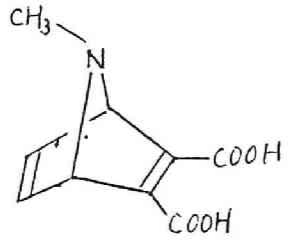
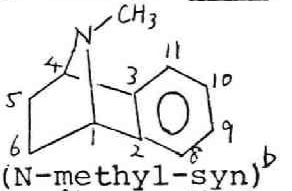
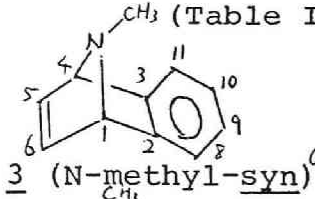
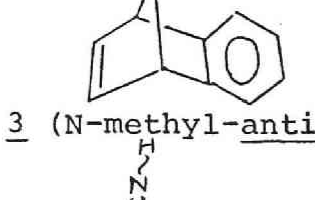
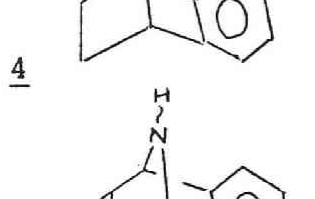
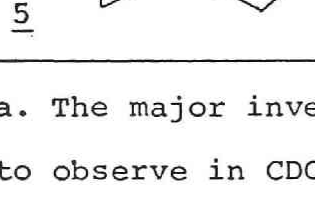


Table III. ^{13}C Chemical Shifts of 7-Azanorbornene Derivatives (ppm from TMS)

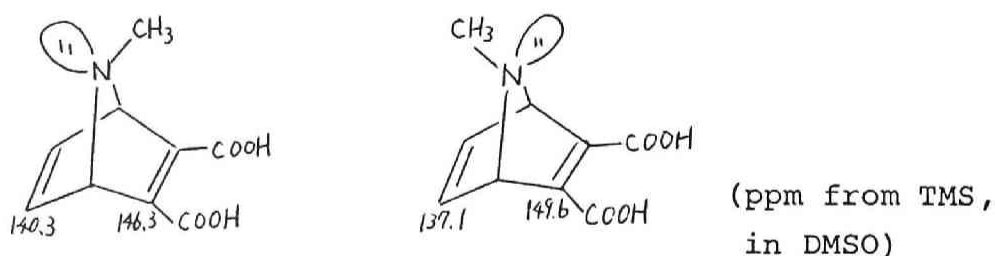
Compounds	Solvent	1,4	2,3	5,6	N-C*H ₃	C*OOH	8,11	9,10
 <u>1</u> (N-methyl- <u>syn</u>)	DMSO	77.2	146.3	140.3	35.1	160.4		
	D ₂ O {							
	pD=2.0	74.4	149.1	141.4	35.7	166.4		
	4.5	74.3	147.4	141.2	34.8	166.7		
	8.0	74.9	146.0	142.9	36.4	167.4 ^c		
	12.0	75.4	148.4	144.5	36.1	174.9		
 <u>1</u> (N-methyl- <u>anti</u>)	DMSO	74.9	149.6	137.1	34.2	160.4		
	D ₂ O {							
	pD=2.0	74.4	153.3	137.4	35.7	166.4		
	4.5	74.3	151.8	137.4	34.8	166.7		
	8.0	74.9	149.8	138.0	36.4	167.4 ^c		
	12.0	75.4	153.8	139.5	36.1	174.9		
 <u>2</u> (N-methyl- <u>syn</u>) ^b	CDCl ₃	67.7	140.1	25.4	33.3		122.1	128.2
	CF ₃ COOD	73.1	138.4	27.2	34.2		124.5	132.2
 <u>2</u> (N-methyl- <u>anti</u>)	CF ₃ COOD	71.9	— ^d	24.1	34.2		123.0	131.9

CH₃ (Table III continued)

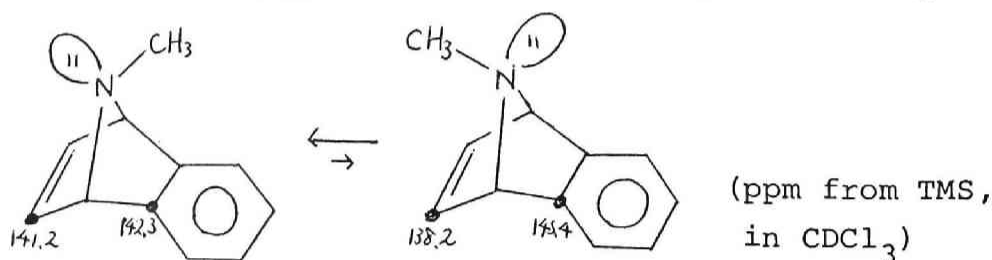
 <u>3</u> (N-methyl- <u>syn</u>) ^a	CDCl ₃	71.3	142.3	141.2	34.9	124.3	127.0
	CF ₃ COOD	75.0	139.0	142.4	36.3	126.6	130.3
 <u>3</u> (N-methyl- <u>anti</u>)	CDCl ₃	71.9	145.4	138.2	34.9	121.8	126.2
	CF ₃ COOD	75.4	142.5	138.2	36.0	124.7	129.8
 <u>4</u>	CDCl ₃	61.1	148.5	26.5		119.1	125.9
	CF ₃ COOD	65.8	139.4	25.4		124.7	129.5
 <u>5</u>	CDCl ₃	66.2	151.2	144.4		120.6	124.4
	CF ₃ COOD	68.4	141.4	141.0		126.2	128.8

a. The major invertomer. b. The major invertomer. The ¹³C signals of the minor one were failed to observe in CDCl₃ due to its rather small relative ratio. c. The chemical shift was somewhat uncertain. d. This signal was failed to obtain.

trend of ^{13}C chemical shifts in carbocyclic compounds has been well known^{22,23} as the "γ-effect" of methyl substitution. It is worth noting that this "γ-effect" is also encountered in our N-methyl-7-azanorbornadiene system and therefore affords further support of the above assignment.²⁴ It is,



therefore, now possible to assign two invertomers of 3 with the aid of the ^{13}C chemical shift difference between the 2,3 and 5,6 carbons. The 2,3 carbon of the major conformer of 3 resonates at the higher field than that of the minor one. On the contrary, the 5,6 carbon resonance of the former is 3.0 ppm downfield from that of the latter. Thus, use of the "γ-effect" established for 1 may suggest that the N-methyl-syn conformer is the major one in 3.

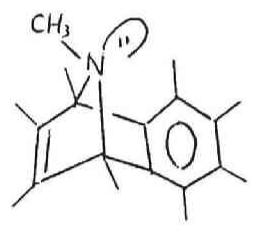
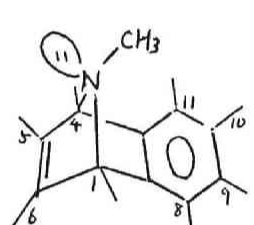
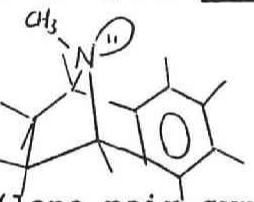


For 2 we cannot directly determine the orientation of the lone pair by comparing the 2,3 and 5,6 carbon chemical shifts of the two invertomers, because only one set (the major invertomer) of the ^{13}C nmr signals was detected. However, the difference of the ^{13}C chemical shifts between the two conformers of 4 in CF_3COOD corresponds well to that of 5 (Table III). For example, the 5,6 carbon resonance

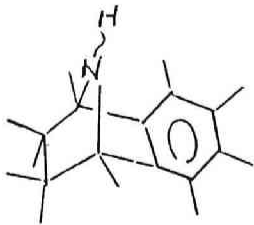
of the minor conformer is 3.1 ppm higher than that of the major one. It is also to be noted that the 5,6 carbon resonance moves by 7.4 ppm to the higher field on going from the N-H 7-azabenzonorbornene (4) to the N-methyl derivative (2), while the 2,3 carbon resonance remains almost unchanged. Referring the " γ -effect" of the ^{13}C chemical shift leads us to expect that the N-methyl group occupies preferentially a syn position in 2, similar to the case for 1 and 3.

In order to obtain further confirmation of this stereospecific orientation of the N-methyl group, we obtained $\text{Eu}(\text{fod})_3$ -induced ^1H nmr shifts for 2 and 3. The relative values of the $\text{Eu}(\text{fod})_3$ -induced shifts obtained from the relative values of the linear plots of the observed ^1H paramagnetic shift vs. the concentration of added $\text{Eu}(\text{fod})_3$ are listed in Table IV. Here, the larger shift of the vinylidene proton (5,6-H) and the smaller shifts of the benzene-ring protons (8,9,10,11-H) in the major conformer than those of the corresponding protons of the minor one are noticeable. Taking into account the $1/r^3$ dependence of pseudo-contact shifts,²⁰ this trend support the assumption that the lone pair anti conformer is the major one. It is also apparent that the relative $\text{Eu}(\text{fod})_3$ -induced shifts of the predominant invertomer of 2 correspond well to those of the major one (the N-methyl-syn conformer) in 3. This experimental trend confirms that the N-methyl group preferentially occupies a syn position in 2.

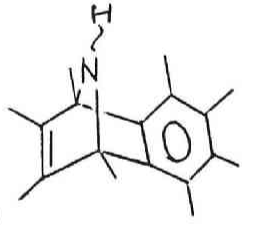
2



(Table IV continued)

	1,4	4.53	-1.00	-1.00
	5,6-exo	2.05	-0.91	+0.34
	5,6-endo	1.24	-0.59	-0.44
	8,11	7.18	-0.26	+0.11
	9,10	7.07	-0.14	-0.14

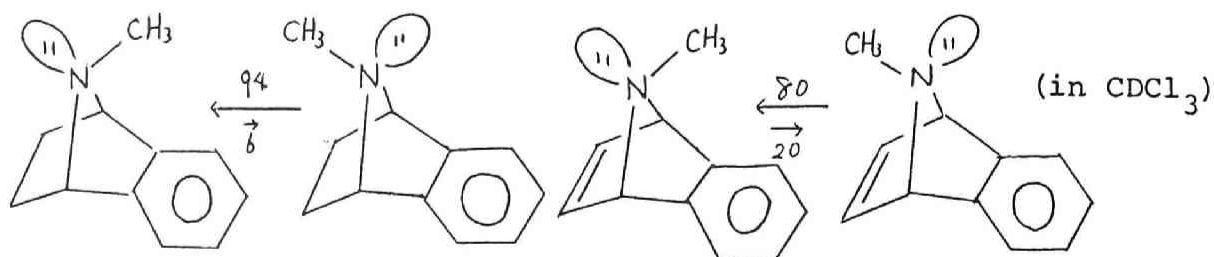
4

	1,4	4.53	-1.00	-1.00
	5,6	6.99	-0.56	-0.74
	8,11	7.24	-0.22	+0.06
	9,10	6.92	-0.12	-0.07

5

a. Diamagnetic reference positions from TMS observed at 220 MHz at room temperature in CDCl_3 solution. b. Obtained from the relative values of the slopes of linear plots of observed ^1H contact shifts vs. concentration of added $\text{Eu}(\text{fod})_3$ or $\text{Ni}(\text{AA})_2$.

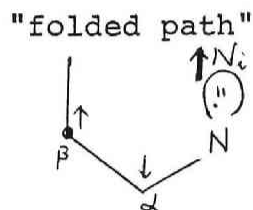
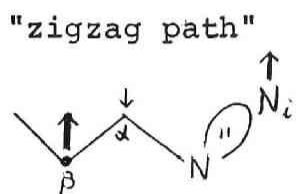
Based on the above discussion, the specific orientation of the lone pair electrons in 2 and 3 is now determined as below.²⁵



C. The Orientation of the Lone Pair Electrons in N-H 7-Azanorbornene Derivatives.

Here we wish to extend our study to the N-H 7-azanorbornene derivatives. The stereo-specific ¹³C shifts induced by the N-methyl group, which has been discussed in section B, could not serve as a tool for the determination of the nitrogen lone pair orientation. We have to be very careful when we want to determine the steric structure of organic compounds based only on the lanthanide-induced nmr shifts, because these paramagnetic shifts have considerable contact contribution beside the pseudo-contact effect.²⁶ Thus, in order to examine the lone pair orientation of the N-H derivatives, we have measured Ni(AA)₂-induced ¹H and ¹³C nmr contact shifts. As is well documented,^{27,28,29} Ni(AA)₂-induced ¹H and ¹³C nmr contact shifts are substantially sensitive to the conformational changes and, therefore, is quite useful in the studies of the molecular conformation associated with the orientation of the lone pair electrons. In order to study the specific orientation of the nitrogen lone pair and the manner of the intramolecular electron spin transmission in N-H 7-azanorbornene derivatives, Ni(AA)₂-induced ¹H and ¹³C nmr contact shifts were observed for

4 and 5. The signal changes of each proton and carbon as $\text{Ni}(\text{AA})_2$ is successively added to the solution of 5 in CDCl_3 are exemplified in Figures 7 and 9. Figures 8 and 10 show the linear plots of $\text{Ni}(\text{AA})_2$ -induced ^1H and ^{13}C contact shifts vs. the concentration of added $\text{Ni}(\text{AA})_2$ for 5. The spectra are time averaged between complexed and uncomplexed species, and the proton and carbon resonances of the ligand shift toward the resonance position of the paramagnetic adduct. Therefore, only the relative values of these shifts are significant in the present study. Relative values of $\text{Ni}(\text{AA})_2$ -induced shifts for various protons of 4 and 5 are shown in Table IV. The relative ^{13}C contact shifts of 4 and 5 are given in Figure 11 and Table V. Here, the positive and negative signs correspond to upfield and downfield shifts respectively. It is to be noted in Figure 11 that the relative ^{13}C contact shifts of the β -carbons are remarkably different between 2,3 and 5,6 carbons in 4. It is well established^{13,28} that electron spin reaches the β carbon to a greater extent by a zigzag path than a folded one. Therefore, the large difference in the β carbon contact



shifts of 4 may suggest that the lone pair electrons occupy preferentially an anti position with respect to the benzene ring. In 5, the relative value (-1.62) of the contact shift for the 2,3 carbon is not so different from that for the 5,6

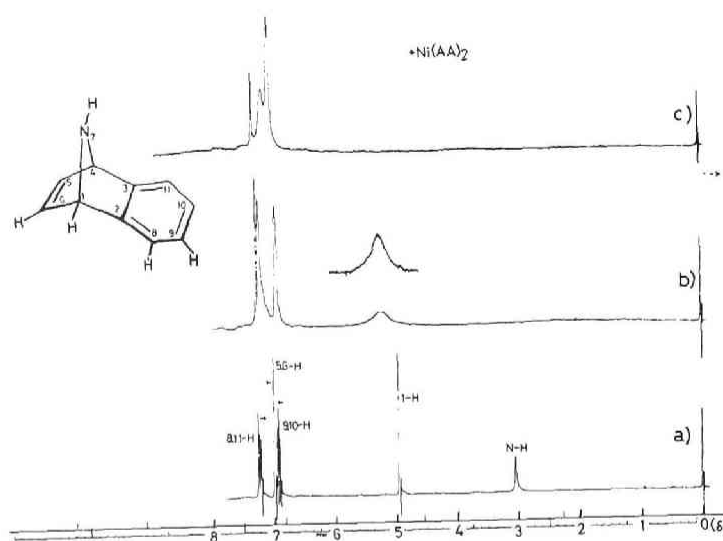


Figure 7. ^1H nmr spectra of 5, (a) in CDCl_3 and (b), (c) in CDCl_3 containing varying amounts of $\text{Ni}(\text{AA})_2$ (at 220MHz).

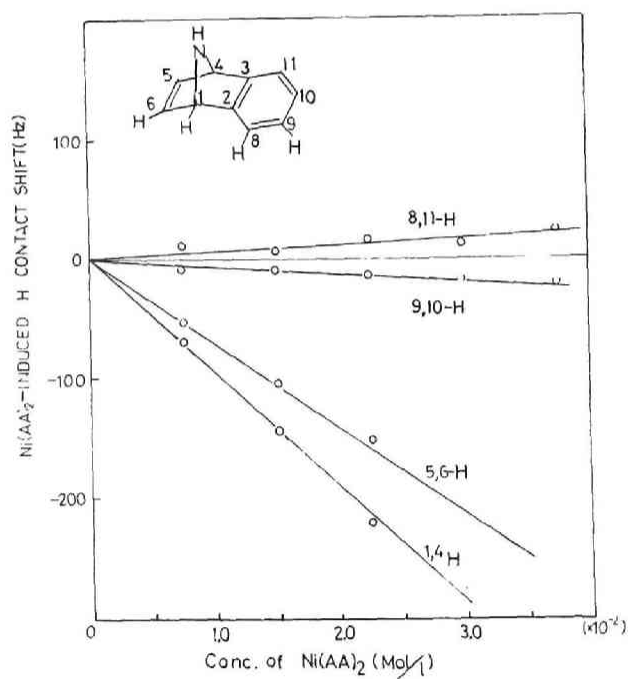


Figure 8. Plots of isotropic paramagnetic ^1H shifts vs. concentration of $\text{Ni}(\text{AA})_2$ for 5.

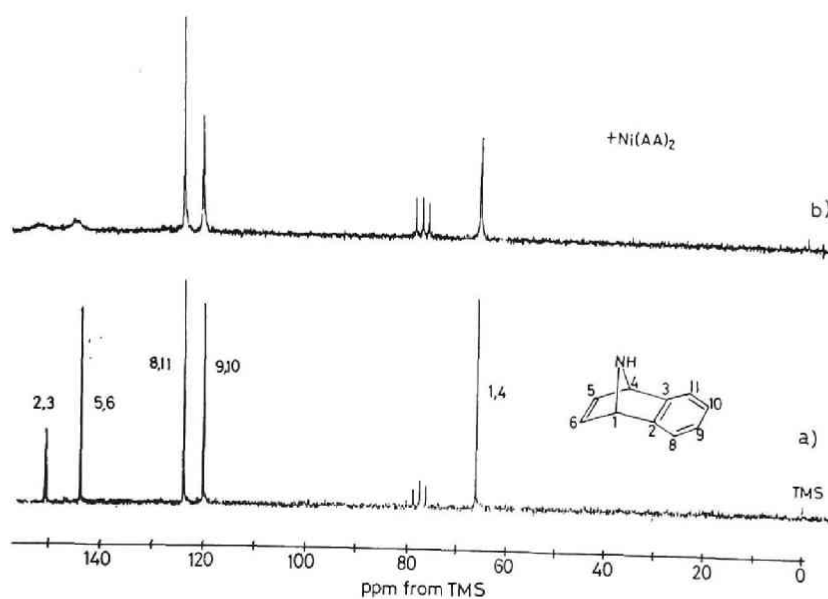


Figure 9. ^{13}C nmr spectra of **5**, (a) in CDCl_3 and (b) in CDCl_3 containing $\text{Ni}(\text{AA})_2$ (at 25.1MHz).

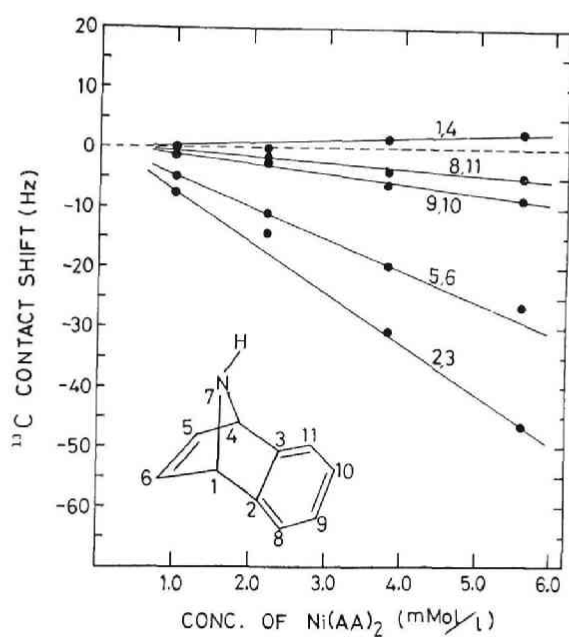


Figure 10. Plots of isotropic paramagnetic ^{13}C shifts vs. concentration of $\text{Ni}(\text{AA})_2$ for **5**.

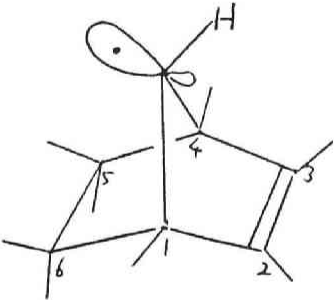
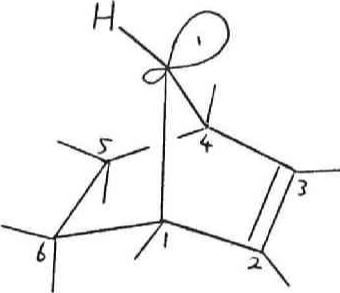
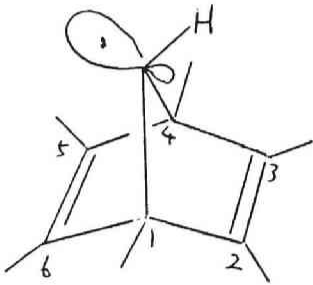
Table V. $\text{Ni}(\text{AA})_2$ -Induced ^{13}C Contact Shifts

Compounds	position	^{13}C contact shift (rel) ^a
7-azabenzonorborene (4)	1,4	+0.12
	2,3	-3.26
	5,6	-1.00 ^b
	8,11	-0.25
	9,10	-0.44
7-azabenzonbornadiene (5)	1,4	+0.08
	2,3	-1.62
	5,6	-1.00 ^c
	8,11	-0.15
	9,10	-0.31

a. Obtained from the relative values of the slopes of linear plots of observed ^{13}C contact shifts vs. concentration of added $\text{Ni}(\text{AA})_2$. The plus and minus signs denote upfield and downfield contact shifts, respectively. b. The actual shift is 1.0ppm (25Hz) per 5mM of $\text{Ni}(\text{AA})_2$ in the 1.7M CDCl_3 solution. c. The actual shift is 1.6ppm per 5mM of $\text{Ni}(\text{AA})_2$ in the 1.6M CDCl_3 solution.

carbon (-1.00), indicating that the relative ratio of the invertomers are nearly equal or the lone pair anti conformer is a little favored. In order to gain further insight into the relative stability of the lone pair anti and the syn conformers in 4 and 5, comparison was made between relative values of the observed contact shifts and the calculated spin densities by INDO method³⁰ for the corresponding hydrocarbon σ -radical, 7-norbornenyl (6) and 7-norbornadienyl (7), in which the radical lobe occupies an anti or a syn position (Table V). In our previous investigations, we demonstrated^{26,27} that Ni(AA)₂-induced ¹H and ¹³C contact shifts for the nitrogen containing molecules are plausibly reproduced theoretically by the INDO-UHF MO³⁰ calculations of electron spin densities for the corresponding hydrocarbon σ -radicals. For the proton 1s spin densities (Table VI), the large positive spin densities on the vinyl and methylene protons lying on the zigzag path are noticeable in 6-anti, 6-syn and 7. The spin density on these protons (+0.006 in 6-anti, +0.008 in 6-syn, and +0.005 in 7) is 2~3 times larger than that of the bridgehead proton. Contrary to this, relatively small negative spin density is induced on the other protons (2,3 or 5,6 protons) which lie on the folded path. It is apparent from these features that the relative ¹H contact shifts for 4 can not be reproduced only by the calculated spin densities for 6-anti or 6-syn. However, if one supposes that both the lone pair anti and syn conformers present and that the former is more favored, it is easily

Table VI. Calculated Spin Densities on the H 1s and C 2s
AO's for Hydrocarbon $\dot{\sigma}$ -Radicals (INDO-UHF-MO)

Radical	position	calculated value of spin density
 <u>6-anti</u> ^a	1,4-C	-0.004
	2,3-C	+0.016
	5,6-C	+0.001
	1,4-H	+0.003
	2,3-H	+0.006
	5,6-exo H	-0.001
	5,6-endo H	-0.002
 <u>6-syn</u> ^a	1,4-C	-0.005
	2,3-C	+0.002
	5,6-C	+0.014
	1,4-H	+0.003
	2,3-H	-0.001
	5,6-exo H	-0.001
	5,6-endo H	+0.008
 <u>7</u> ^a	1,4-C	-0.003
	2,3-C	+0.015
	5,6-C	+0.000
	1,4-H	+0.003
	2,3-H	+0.005
	5,6-H	-0.001

a. The bond angles and lengths are selected referring the structures of norbornane and norbornene reported by A. Yokoyagi and K. Kuchitsu, Bull. Chem. Soc. Japan, 44, 2356 (1971).

recognized that the relative ^1H contact shifts can be well reproduced by the weighted average of the spin densities for 6-anti and 6-syn conformers. Similar trend is encountered between 5 and the corresponding σ -radical, 7. The relative ^1H contact shift (-0.74) of the β -proton for 5 does not simply correspond to the large positive spin density (+0.005) nor to the small negative spin density on the vinylidene protons of either side in 7. The relative ^1H contact shifts of the β -protons in 5 is reproduced by the average of the spin densities of these vinylidene protons in 7. This may suggest that the lone pair electrons occupy the anti and syn positions to an equal extent.

As to the carbon contact shifts, the calculated results for 6-anti and 6-syn radical conformers, and for 7 show that relatively large positive spin densities are induced on the carbons that lie on the zigzag path. On the other hand, small positive spin densities are induced on the carbons that lie on the zigzag path. On the other hand, small positive spin densities are induced on the carbons lying on the folded path (Figure 11). Similarly to the case of the ^1H contact shifts, the relative ^{13}C contact shifts of 4 is again reproduced by the weighted average of the carbon 2s spin densities in 6-anti and 6-syn conformers in which the former is predominant. Comparing with the calculated results for 7, the larger shift of the 2,3 carbons than the 5,6 carbons in 4 suggests that the lone pair anti conformer is also preferred.

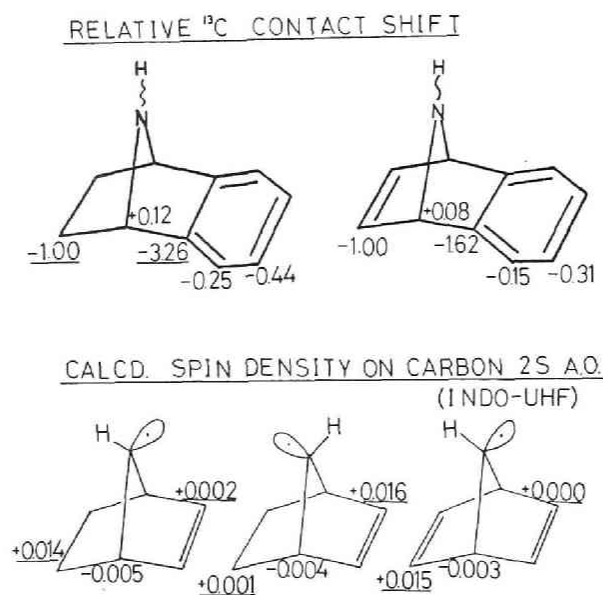


Figure 12. The ^1H chemical shifts of the N-methyl protons of 1 versus pD (at 220MHz).

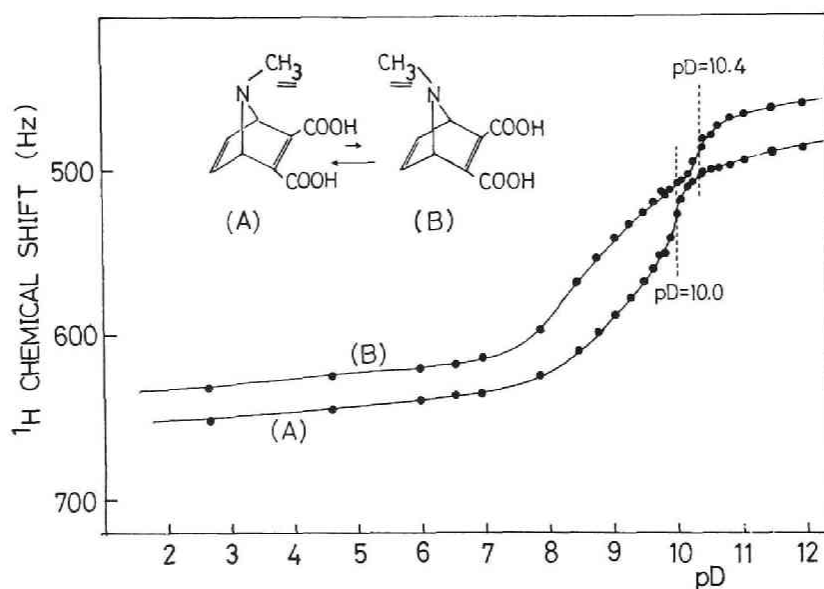
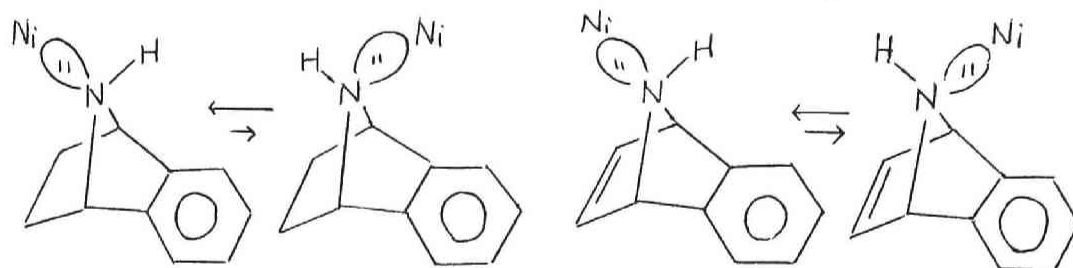


Figure 11. Comparison between the relative $\text{Ni}(\text{AA})_2^-$ induced ^{13}C contact shifts in 4 and 5 and the INDO MO calculated spin densities on carbon 2s AO's in 6-anti, 6-syn and 7.

From the above discussion concerning the feature of the ^1H and ^{13}C contact shifts, it is concluded that, at least in the presence of $\text{Ni}(\text{AA})_2$, the population of the lone pair anti conformer is larger than that of the syn one and that this trend is more pronounced in 4 than in 5.^{31,32}



The experimental trend of the $\text{Eu}(\text{fod})_3$ -induced shifts in 4 and 5 supports this conclusion (Table IV). It is apparent that the relative ^1H pseudo-contact shifts of 4 and 5 correspond well to those of the major conformers (the lone pair anti ones) of 2 and 3, respectively. This shows that the lone pair electrons of 4 and 5 preferentially occupy the anti position with respect to the benzene ring at least in the form of complexes.

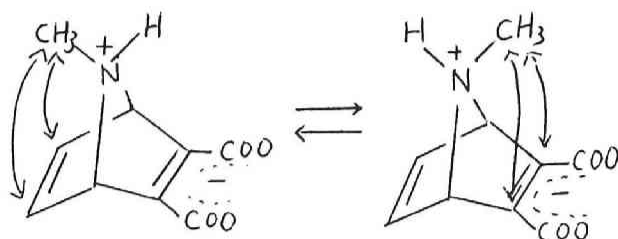
D. Bishomoallyl and Bishomobenzyl n,π Interactions. In our recent photoelectron, UV and fluorescence spectroscopic studies^{1,9,10} of the cyclic and bicyclic amines containing nonadjacent π group, we have shown that bishomoallyl or bishomobenzyl n,π interaction destabilizes the interacting system. This may allow us to expect that n and π electrons are "repulsive" in 7-azanorbornene derivatives. For 1, in the aqueous basic solution ($\text{pD}=11$), where the dicarboxyl group is ionized and electron densities are rather riched on the C-2,3 π bond, as is evidenced by the ^{13}C chemical shifts (see Table III), the lone pair electrons favor the anti position

with respect to the mono anionic dicarboxyl group (see section A). In DMSO solution, however, the lone pair electrons preferentially occupy a syn position. This may be explained as follows; in DMSO solution, where dissociation of the carboxyl proton is prohibited, the dicarboxyl group serves as electron withdrawing from the C-2,3 π bond (see ^{13}C shifts in Table III). Thus, the bishomoallyl "repulsive" interaction between the nitrogen lone pair and the C-5,6 π electrons becomes more important than that between n and the C-2,3 π electrons. This may be responsible for the preferential lone pair orientation at the syn position.

In 3 and 5, the lone pair electrons predominantly occupy the anti position with respect to benzene. The lone pair in 2 and 4 also prefers the anti position to the benzene ring in which the highest occupied π orbital energy is higher than that of the C-5,6 π bond. Consequently, these experimental trends suggest that the lone pair electrons preferentially occupy the anti position with respect to the π bond associated with the higher orbital energy or with the "electron rich" π group, so as to avoid the "repulsive" n, π bishomoallyl interaction. This interpretation is in consistent with the Stille's suggestion⁶ that the lone pair electrons prefers the anti position in 7-norbornenyl anion from its possible bishomo-antiaromatic character. In order to gain further insight into the intrinsic nature of the lone pair electrons in the bishomoallyl and the bishomobenzyl n, π interacting systems, pK values of 1~3 were obtained from the 220 MHz nmr

measurements. The variation of the ^1H nmr chemical shifts of the N-methyl protons vs. pD is exemplified in Figure 12. The pK's of the amino groups of the two invertomers were determined directly from the pD values of the inflection points of the nmr titration curves for two separate N-methyl signals. The pK values of 1, 2 and 3 are summarized in Table VII. It is of particular interest to note that the pK value of the lone pair anti conformer is smaller than that of the syn one. From the specific orientation of the lone pair electrons in 1~5, it has been suggested that the larger repulsive n,π interaction in the lone pair syn conformer destabilize its nonbonded orbital more than in the anti conformer. It is, therefore, apparent that the bishomoallyl "repulsive" n,π interaction affects the electronic structure of 7-azanorbornenyl derivatives substantially and makes the basicity of the amino group stronger.

Strictly speaking, in N-methyl-7-azanorbornene derivatives (1,2,3), "steric" repulsion³³ should be taken into account besides the bishomoallyl or bishomobenzyl n,π "electronic" effect. In 1, however, when the nitrogen lone pair electrons are "completely" protonated (at pD=1.4 or 4.6, see Table I), the invertomer ratio becomes close to 1 : 1. This indicates



that the steric repulsion energy between the N-methyl group and the 2,3-carbons or the dicarboxyl group in the

Table VII. pK Values Obtained from the 220 MHz nmr measurement^a.
(in D₂O, 24°C)

Compounds	the orientation of the lone pair electrons	pK ^d
<u>1</u>	anti ^b	10.0
	syn	10.4
<u>2</u>	anti ^c	9.4
	syn	9.7
<u>3</u>	anti ^c	9.4
	syn	9.6

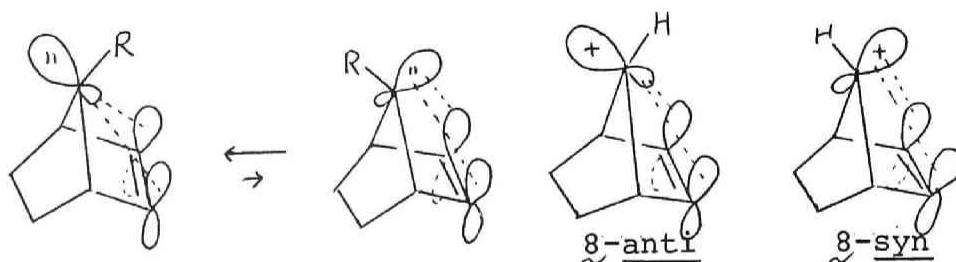
a. Obtained from the inflection point of the titration curve in which the ¹H nmr chemical shifts are plotted vs. pD values.

b. Anti with respect to the dicarboxyl group. c. Anti to the benzene ring. d. The estimated uncertainty is ±0.2.

N-methyl-syn invertomer is nearly equal to that between the methyl group and the 5,6-carbons in the anti invertomer, and that the steric effect of the N-methyl group on stereochemistry seems to become minimal in 7-azanorbornadiene skeleton. While, in 2 and 3 the N-methyl-syn conformer is still preferred (70:30) on N-protonation, although the difference in the invertomer ratio is reduced in going from CF₃COOD solution to the CDCl₃ solution. In this case, the "steric" repulsion may be also responsible for the orientation of the N-methyl group toward the anti position which is the same direction caused by the n,π repulsive "electronic" interaction and this "steric effect" seems to be comparable with the repulsive bishomoallyl or bishomobenzyl n,π electronic interaction. The cancelling effect of the "steric" and the "electronic" repulsive interactions may cause only a slight difference in the relative stability of the two invertomers of 3. However for 2, the lone pair anti conformer is much preferred (94:6) in CDCl₃ solution compared with that in CF₃COOD. This may suggest that bishomobenzyl "electronic" n,π interaction contribute mainly to the specific lone pair orientation in 2.

Summarizing the above discussion, it is concluded that n and π electrons in 7-azanorbornenyl system are "repulsive" by the bishomoallyl n,π interaction and that the nitrogen lone pair electrons preferentially occupy an anti position with respect to the π bond or π electron rich group to avoid this "repulsive" interaction. The specific orientation

of the nitrogen lone pair electrons in 7-azanorbornenyl system may lead us to expect that the overlap between the nonbonded orbital and the π orbital in the lone pair anti conformer is smaller than that in the syn one.³⁴ This is in marked contrast with well-established π -participation in the



solvolysis of 7-norbornenyl tosylate or 7-benzonorbornenyl tosylate.³⁵ Based on the great difference in the solvolysis rate constants for these compounds, the π -participation (stabilization) in 8-anti is considered to be larger than in 8-syn. This suggests that the overlap between the empty orbital and the π orbital in 8-anti is larger than in 8-syn, inversely to the case of n, π overlap in 7-azanorbornene derivatives or 7-norbornenyl anion. These features reflect that the magnitude of the overlap between the n orbital at C-7 and the C-2,3 π orbital is quite responsible for the structural fluctuation in 7-norbornenyl system. The unusual temperature dependence of the esr spectra of 7-norbornenyl radical reported by Kochi et al.⁵ also may be due to the similar structural flexibility of this radical. The present results also appear to be quite interesting in relation to the specific orientation of radical lobe in the related free radicals, 7-azabenzonorbornene-7-oxyl³⁶, 7-azabenz-

norbornadiene-7-oxyl,³⁶ 7-benzonorbornenyl,³⁷ and 7-benzonorbornadienyl.³⁷ Details in the MO theoretical analysis of relative stability of 7-norbornenyl system are now under way.³⁸

References and Notes

- (1) Part IV; K. Yoshikawa, K. Toyoda, K. Bekki, and I. Morishima, submitted for publication. A part of doctor thesis of K. Y. to be submitted to Department of Hydrocarbon Chemistry, Kyoto University.
- (2) Kyoto University.
- (3) Kyoto Institute of Technology.
- (4) S. Winstein, Quart. Rev., Chem. Soc., 23, 141(1969).
- (5) P. Bakuzis, J. K. Kochi, and P. J. Krusic, J. Amer. Chem. Soc., 91, 1434(1970). J. K. Kochi, P. Bakuzis and P. J. Krusic, *ibid.*, 95, 1516(1973).
- (6) J. K. Stille and K. N. Sannes, J. Amer. Chem. Soc., 94, 8489(1972).
- (7) H. Ohorodnyk and D. P. Santry, J. Amer. Chem. Soc., 91, 4711(1969).
- (8) M. J. S. Dewar and W. W. Schoeller, Tetrahedron, 27, 4401(1971).
- (9) I. Morishima, K. Yoshikawa, M. Hashimoto, and K. Bekki, J. Amer. Chem. Soc., 97, 4283(1975).
- (10) I. Morishima, K. Toyoda, K. Yoshikawa, T. Yonezawa, S. Sakata, and S. Ikegami, submitted for publication.
- (11) The n, π^* interaction causes a large stabilization because there are only two electrons for the two interacting orbitals. Contrary to this, the interaction between the doubly occupied orbital induce a small destabilization.¹²
- (12) For example, see: R. Hoffmann, Accounts. Chem. Res., 4, 1(1971).
- (13) I. Morishima and K. Yoshikawa, J. Amer. Chem. Soc., 97, 2950(1975).

- (14) R. Kitzing and R. Fucks, *Helv. Chim. Acta.*, 51, 888(1968),
- (15) L. A. Carpino and D. E. Barr, *J. Org. Chem.*, 31, 764(1966).
- (16) H. T. Clarke, H. B. Gillespie, and S. Z. Weisshaus, *J. Amer. Chem. Soc.*, 55, 4571(1966).
- (17) This has been confirmed by the signal changes of the 220 MHz ^1H nmr spectra induced by pH titration for 1. The orientation of the N-methyl group is arbitrary.
- (18) The 5,6 H at pD 1.4 shows only a single line (Figure 1). This is because the signals of the two invertomers coincide each other.
- (19) R. E. Sievers et al., "Nuclear Magnetic Resonance Shift Reagents," Academic Press, New York, 1973.
- (20) H. M. McCornell and R. E. Robertson, *J. Chem. Phys.*, 29, 1361(1958).
- (21) I. Solomon, *Phys. Rev.*, 99, 559(1955). G. N. La Mar and L. W. Faller, *J. Amer. Chem. Soc.*, 95, 3817(1973). G. N. La Mar and E. A. Metz, *ibid.*, 96, 5611(1974).
- (22) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," John Wiley & Son, Inc., New York, 1972. J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York, 1972.
- (23) J. B. Grutzner, M. Jautelat, J. B. Dence, J. A. Smith, and J. D. Roberts, *J. Amer. Chem. Soc.*, 92, 7107(1970).
- (24) A referee suggested that examination of the N,N-dimethyl derivative related to 1 is desirable to test the assignments of the chemical shift data. However, this compound, which could be obtained by the methylation of 1 by the use of methyl iodide, would not permit us to assign definitely two N-methyl

signals without recourse to the substituent effects of the ^{13}C chemical shift discussed in the text.

(25) From the ^1H nmr spectroscopic study, Gribble et al. speculated that the major conformation in the one having the lone pair on the same side of the electron deficient benzene ring in 7-methyl-7-azatetrafluorobenzonorbornadiene and 7-methyl-7-azatetrachlorobenzonorbornadiene; G. N.

Gribble, N. R. Easton, Jr., and J. T. Eaton, *Tetrahedron Lett.*, 13, 1075(1970).

(26) For example; B. F. G. Johnson, J. Lewis, P. McArdle, and J. R. Norton, *J. Chem. Soc., Chem. Commun.*, 535(1972). M. Kainosho, K. Ajisaka, and K. Tori, *Chem. Lett.*, 1061 (1972).

(27)(a) T. Yonezawa, I. Morishima, and Y. Ohmori, *J. Amer. Chem. Soc.*, 92, 1267(1970). (b) I. Morishima, K. Okada, and T. Yonezawa, *J. Chem. Soc., Chem. Commun.*, 33(1971). (c) I. Morishima and T. Yonezawa, *J. Chem. Phys.*, 54, 3238 (1971). (d) T. Yonezawa, I. Morishima, Y. Akana, and K. Fukuta, *Bull. Chem. Soc. Japan*, 43, 379(1970).

(28)(a) I. Morishima, T. Yonezawa, and K. Goto, *J. Amer. Chem. Soc.*, 92, 6651(1970). (b) I. Morishima, K. Okada, T. Yonezawa, and K. Goto, *J. Chem. Soc., Chem. Commun.*, 1535(1970). (c) I. Morishima, K. Okada, T. Yonezawa, and K. Goto., *J. Amer. Chem. Soc.*, 93, 3922(1971). (d) I. Morishima, K. Okada, and T. Yonezawa, *ibid.*, 94, 1425(1972).

(29) J. A. Happe and R. L. Ward, *J. Chem. Phys.*, 39, 1311 (1963). R. W. Kluiber and W. D. Horrocks, Jr., *J. Amer. Chem. Soc.*, 87, 5350(1965).

(30) D. L. Beveridge, P. A. Dobosh, and J. A. Pople, *J. Chem. Phys.*, 48, 4802(1967).

(31) This conclusion is oppose the assumption of Underwood et al. that the N-H bond lies anti to the aromatic ring in both in 2 and 3. They have speculated this based on the upfield ^1H contact shift of the β -endo proton in 2 or of the vinylidene proton in 3 induced by $\text{Ni}(\text{AA})_2$. However, this trend is reproduced by the weighted average of the induced spin densities of each of the protons in the two invertomers as has been discussed in this section. Lack of the data of ^{13}C nmr contact shifts seems to lead them misinterpretation of the lone pair orientation.: G. R. Underwood and H. S. Friedman, *J. Amer. Chem. Soc.*, 96, 4989(1974).

(32) A referee suggested that it is reasonable to conclude the Ni binds preferentially. It is true that the $\text{Ni}(\text{AA})_2$ -induced ^{13}C contact shifts give no information about the conformational equilibrium in 7-azanorbornene derivatives (4 and 5), themselves. However, $\text{Ni}(\text{AA})_2$ may not affect the lone pair orientation, which is evidenced from the linear dependence of ^{13}C coantact shift on the concentration of added $\text{Ni}(\text{AA})_2$ (Figures 8 and 10). If the conformation equilibrium is changed by the presence of $\text{Ni}(\text{AA})_2$, the contact shift-concentration plot may deviate from the linearity.

(33) The important role of the "steric repulsion" energy on the lone pair orientation in 2-azabicyclo[2.2.2]oct-5-ene derivatives has been demonstrated, see ref. 13.

(34) This feature is also of interest in comparison with the recent study of the anomalous lithium aluminium hydride reduction of carbon-carbon double bonds in 7-azabicyclo

[2.2.1]heptyl system, A. P. Marchand and R. W. Allen, Tetrahedron Lett., 67(1975).

(35) S. Winstein, M. Shatavsky, C. Norton, R. B. Woodward, J. Amer. Chem. Soc., 77, 4183(1955). S. Winstein and E. T. Stafford, *ibid.*, 79, 505(1957). H. Tanida and H. Ishitobi, *ibid.*, 88, 3633(1966). H. Tanida, Y. Hata, S. Ikegami, and H. Ishitobi, *ibid.*, 89, 2928(1967).

(36) I. Morishima, K. Yoshikawa, K. Bekki, M. Kohno, and K. Arita, J. Amer. Chem. Soc., 95, 5815(1973).

(37) The radical lobe on the C₇ carbon in these bicyclic radicals is concluded to lie anti to the phenylene group.: K. Kawamura, Y. Sugiyama, and M. Matsunaga, and T. Yonezawa, J. Amer. Chem. Soc., 97, 1627(1975).

(38) K. Yoshikawa and I. Morishima, unpublished results.

CHAPTER 9

Homoallyl Interaction between Nonadjacent n, π Electrons, V. ^1H and ^{13}C NMR Contact Shift Study

Abstract: ^1H and ^{13}C nmr contact shifts induced by nickel acetylacetonate ($\text{Ni}(\text{AA})_2$) have been observed for benzylamine, 1,2,3,4-tetrahydroisoquinoline and their derivatives.

It was found that the feature of electron spin transmission on to the benzene ring is quite different between benzylamines and 1,2,3,4-tetrahydroisoquinolines. Such a stereospecific spin transmission is discussed in relation to the change in the steric structure and in the manner of nonbonded n, π interaction. Theoretical analysis of the mechanism of spin distribution have also been carried out with the aid of molecular orbital calculation of electron spin densities.

We have currently been studying^{1,2,3,4} the steric and electronic structures of various cyclic and bicyclic amines containing nonadjacent π bond, in view of elucidation of the intrinsic nature of homoallyl or bishomoallyl type n, π interaction. It has been revealed that n and π electrons could be "repulsive" or "attractive", which depends on the molecular symmetry.^{1,2,3,4} In relation to this, it was found that the lone pair orientation depends markedly on the manner of nonbonded n, π interaction (homoallyl^{1,2,4} or bishomoallyl^{2,3} type interaction).

We have previously reported the conformational or geometrical dependence of proton and carbon-13 contact shifts for several N-heterocyclic molecules complexed with paramagnetic nickel acetylacetonate ($\text{Ni}(\text{AA})_2$). In these studies, it has been demonstrated that these contact shifts are associated with electron spin densities distributed on the proton^{1,3,5,7} and carbon^{1,3,6,7} atoms and depend on the lone pair orientation, lone pair hybridization, molecular conformation and substituents quite sensitively. It has also been shown that nmr contact shifts are quite useful to probe the mechanism of intramolecular electron spin transmission because it is quite sensitive to a small quantity and a sign of the induced spin density.^{1,3,5,6,7}

Here we wish to report a nmr contact shift study of aliphatic amines containing a benzene ring. The aim of this study is to delineate the following problems, intrinsic in these molecules. (1) How is the effect of the interaction between n and π electrons on the nitrogen lone pair

orientation? (2) How is the manner of the intramolecular electron spin transmission in the n, π homoconjugative interacting system?

Experimental Section

N-methyl-1,2,3,4-tetrahydroisoquinoline (7) was prepared by N-methylation of the N-H homologue (6). Other compounds used in this study (Table I) were commercially available. All the proton spectra were measured with a Varian Associates HR-220 high-resolution spectrometer (Kyoto Univ.) operating at 220 MHz. Assignments were made by referencing the spectral patterns and $\text{Eu}(\text{fod})_3$ -induced shifts. All the ^{13}C spectra were obtained at 25.1 MHz on a Jeolco ^{13}C Fourier Transform nmr system, JNM-PFT-100. An internal ^2D lock was employed. The assignments of ^{13}C nmr spectra were made by comparing the related compounds. The half-decoupled technique was also employed to help the ^{13}C signal assignment. TMS was used as an internal standard in both ^1H and ^{13}C nmr measurements. The spectra were taken at room temperature (24°C) in the presence of varying amounts of $\text{Ni}(\text{AA})_2$. Samples for ^{13}C nmr were made in ca. 50v/v% CDCl_3 solution using 10mm ϕ sample tube and for ^1H nmr in ca. 10v/v% CDCl_3 solution.

Results.

The perturbation of the 220 MHz ^1H nmr spectrum by the addition of $\text{Ni}(\text{AA})_2$ is exemplified for benzylamine in Figure 1. Among the aromatic protons, the signal in the highest field was easily assigned to by the p-proton from its relative intensity and Eu-induced shift. The assignments of the o- and m-protons were performed referencing the spectral patterns of the separated signals in the presence of small amount of $\text{Ni}(\text{AA})_2$ (Figure 1). The various proton resonances in a ligand molecule studied here were shifted from their normal diamagnetic values by an amount which is proportional to the concentration of added $\text{Ni}(\text{AA})_2$. This implies that the exchange of ligand between complexed and uncomplexed sites are time averaged. Thus the ^1H resonances of the ligand shift toward the resonance position of the complex as $\text{Ni}(\text{AA})_2$ is added to the diamagnetic solution and the relative values of these paramagnetic shifts are of significant in the present study. The relative values for various protons in a ligand molecule were obtained from the slopes of the linear plots of the paramagnetic shift vs. the concentration of added $\text{Ni}(\text{AA})_2$, with the value for the π -carbon normalized to 1.00.

The relative ^1H contact shifts for various ligand molecules are summarized in Table I. The plus and minus signs of these values denote the upfield and downfield shifts which correspond to the negative and positive spin densities, respectively, induced on the ligand ls atomic orbital. Here it is of interest that the shifts of o-,

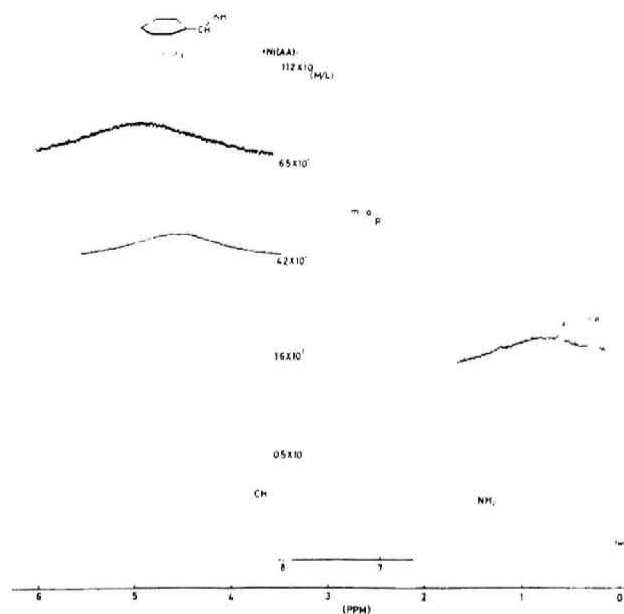


Figure 1. ^1H NMR spectra of benzylamine (1) in CDCl_3 containing varying amounts of $\text{Ni}(\text{AA})_2$ (at 220MHz).

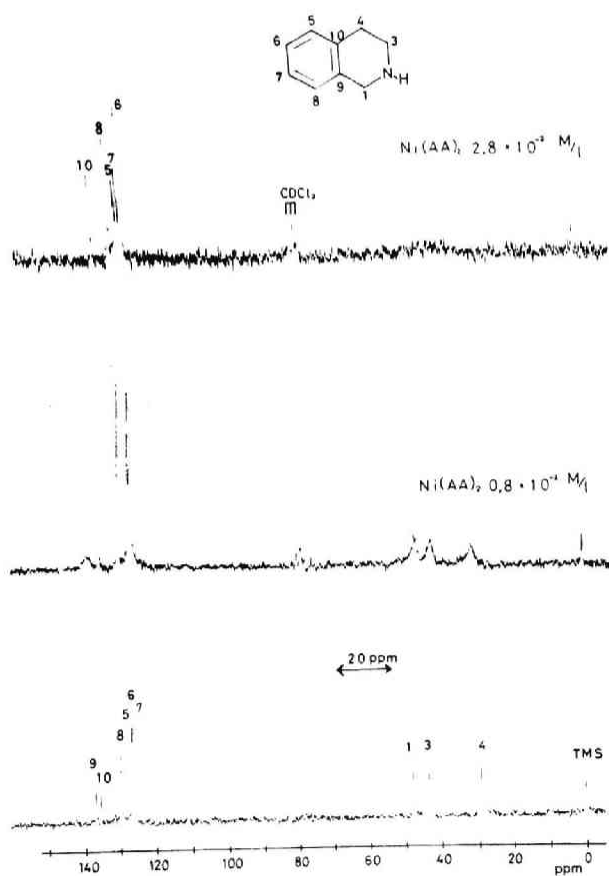
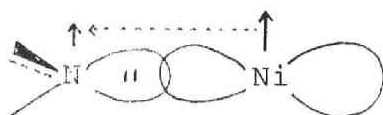


Figure 2. ^{13}C NMR spectra of 1,2,3,4-tetrahydroisoquinoline (6) in CDCl_3 containing varying amounts of $\text{Ni}(\text{AA})_2$ (at 25.1MHz).

m-, and p-protons alternate in sign along the carbon skeleton in benzylamines (1~5). Figure 2 exemplified the perturbation of the ^{13}C nmr signals of 1,2,3,4-tetrahydroisoquinoline (6) by the addition of $\text{Ni}(\text{AA})_2$. Relative ^{13}C shifts obtained from the linear plots of $\text{Ni}(\text{AA})_2$ -induced shifts vs. the concentration of $\text{Ni}(\text{AA})_2$ are given in Table I. The shift for a α -carbon in a ligand molecule was normalized to 1.00. It is noteworthy that all the α and β carbons sense up- and downfield shifts, respectively, in the molecules studied here. It is also interesting that the relative shifts of the aromatic carbon atoms are apparently different between benzylamines and tetrahydroisoquinolines.

Discussion

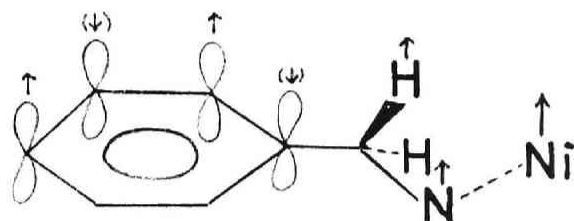
It has been well established^{5,6,8} that the paramagnetic shifts of octahedral $\text{Ni}(\text{II})$ complexes are mainly due to isotropic shift because of the isotropic g tensor and that any pseudo-contact shifts are negligible small. We can then consider the observed Ni-induced shifts to be isotropic shifts and interpret them in terms of the mechanism of electron spin transmission. Since there are two unpaired electrons in the metal e_g orbitals, a σ -type metal-ligand bond with the amine would place the unpaired spin in the σ^* antibonding orbital. Thus, positive spin density is placed on the nitrogen and on all other ligand atoms making a substantial contribution to the σ^* antibonding orbital (spin delocalization mechanism). This gives rise to a



downfield shift at these atoms. Contrary to this, there are some atoms which exhibit upfield paramagnetic shifts (negative spin densities) as is shown in Table I. This implies that the "spin polarization" mechanism is also important in these complexes. In the actual cases, these two mechanisms may be simultaneously operating.



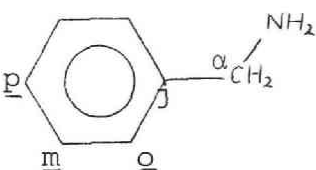
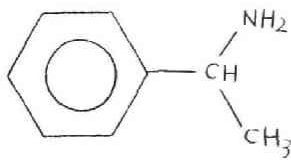
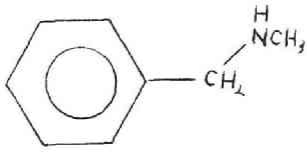
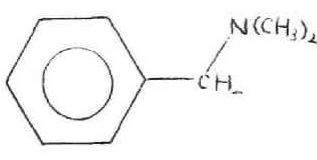
From the ^1H nmr contact shift study of benzylamine, Drago et al.⁸ has proposed that spin is transmitted directly to the phenyl π system through a hyperconjugative-type mechanism. This π delocalization gives rise to the positive spin density at the m-carbon.^{8,9} Downfield shifts of the o- and p-carbons and the negligible small shift of the m-carbon in benzylamine (1~5) indicate that this "hyperconjugative-type" spin delocalization should be significantly important. For the aromatic protons in benzylamines,



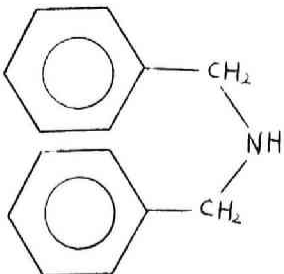
Scheme of electron spin transmission expected from the "hyperconjugative-type" spin delocalization.

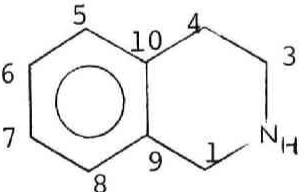
due to the C-H spin polarization effect, negative spin density at the o- and p-hydrogens and positive spin density

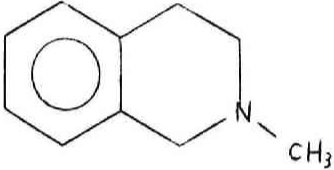
Table I. Relative Ni(AA)₂-Induced ¹H and ¹³C Contact Shifts.

Molecules	position	$\delta^{1\text{H}}$ ^a	Relative ¹ H C.S. ^b	$\delta^{13\text{C}}$ ^a	Relative ¹³ C C.S. ^b	
 (1)	α	3.81	-1.00	46.4	+1.00	
	j	—	—	143.7	-2.18	
	o	7.2	7.3	+0.08	127.0	-0.23
	m			-0.04	128.3	0.00
	p			+0.10	126.4	-0.16
 (2)	α	4.05	-1.00	51.3	+1.00	
	CH ₃	1.35	-0.02	25.8	-1.82	
	j	—	—	148.0	-2.52	
	o	7.2	7.3	+0.03	125.6	-0.22
	m			-0.03	128.3	0.00
p	+0.03			126.6	-0.13	
 (3)	α	3.69	-1.00	56.1	+1.00	
	j	—	—	140.4	-1.48	
	o	7.2	7.3	+0.05	128.1	-0.07
	m			-0.09	128.3	0.00
	p			+0.12	126.9	-0.06
N-CH ₃	2.40		36.0	+1.08		
 (4)	α	3.38	-1.00	64.5	+1.00	
	j	—	—	139.1	-0.79	
	o	7.2 ~ 7.3	0.0	0.0	128.9	-0.00 ₂
	m			0.0	128.1	0.00
	p			+0.08	126.9	-0.00 ₂
N-CH ₃	2.19	-2.17	45.3	+1.00		

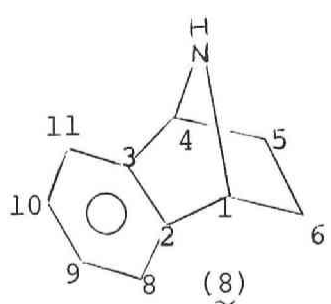
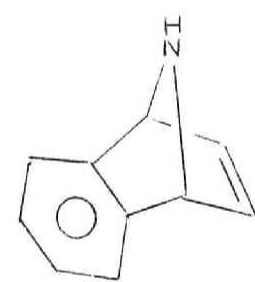
(Table I continued)

 (5)	α	3.72	-1.00	53.1	+1.00
	j	—	—	140.5	-1.14
	$\underline{o}$	7.2~7.3	+0.01	128.0	-0.04
	$\underline{m}$		-0.01	128.1	0.00
	$\underline{p}$		+0.02	126.7	-0.04

 (6)	1	3.95	-1.00	48.1	+1.00
	3	3.05	-0.90	43.6	+0.86
	4	2.70	-0.46	29.3	-1.23
	5	7.0~7.5	+0.02	126.1	-0.25
	6		0.00	125.8	0.00
	7		-0.20	125.5	-0.17
	8		-0.06	129.1	-0.06
	9		—	136.1	-1.37
	10		—	134.7	+0.08

 (7)	1	3.50	-1.00	58.0	+1.00
	3	2.60	-1.00	52.9	+1.00
	4	2.85	+0.02	29.3	-0.56
	5	7.0~7.5	+0.04	126.3	-0.03
	6		0.00	126.1	+0.02
	7		-0.03	125.6	-0.07
	8		-0.03	128.6	-0.02
	9		—	134.7	-0.61
	10		—	133.8	+0.10
	N-CH ₃	2.35	+1.83	46.1	+1.18

(Table I continued)

 (8)	1,4	4.53	-1.00	61.1	+1.0
	2,3	—	—	148.5	-27.2
	5,6- <u>exo</u>	2.05	+0.34		
	- <u>endo</u>	1.24	-0.44	26.5	-8.3
	8,11	7.18	+0.11	119.1	-2.1
	9,10	7.07	-0.14	125.9	-3.7
 (9)	1,4	4.53	-1.00	66.2	+1.0
	2,3	—	—	151.2	-20.3
	5,6	6.99	-0.74	144.4	-12.5
	8,11	7.24	+0.06	120.6	-1.9
	9,10	6.92	-0.07	124.4	-3.9

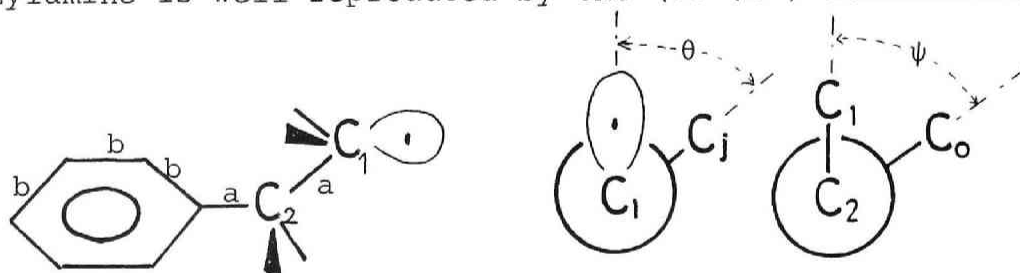
a. Chemical shifts are given in ppm from TMS. b. The plus and minus signs denote the upfield and downfield contact shifts respectively. The relative shifts were obtained from the slope of the linear plot of the observed contact shift vs. the concentration of added $\text{Ni}(\text{AA})_2$. c. See ref. 3.

at the $\underline{m}$ -hydrogen are expected, which corresponds well to the observed ^1H contact shifts. The large downfield shifts of the junction carbon in benzylamines, however, suggest that the spin transmission through σ -skeleton is not negligible at least for the β carbons.

For 1,2,3,4-tetrahydroisoquinolines (6 and 7), alternating ^{13}C contact shifts are observed (Table I). Only the C-8 carbon does not show alternation. It is well documented^{7a} that the γ carbons lying on the planar zigzag arrangement of the $\text{N}-\text{C}_\alpha-\text{C}_\beta-\text{C}_\gamma$ skeleton senses the positive spin density. The downfield shift of the C-8 carbon is thus attributable to this stereospecific electron spin transmission.^{7a} In 6 and 7, it is also to be noted that all of the signs of the coupling constants for the aromatic protons are not opposite to the signs of their direct bonded carbon atoms. These experimental trend suggest that the mechanism of electron spin transmission onto the benzene ring in tetrahydroisoquinoline is apparently different from that of the benzylamines.

In our previous investigations, we demonstrated^{1,3,5,6,7} that $\text{Ni}(\text{AA})_2$ -induced ^1H and ^{13}C contact shifts for amines are plausibly reproduced theoretically by the INDO-UHF MO^{10} calculations for electron spin densities for the corresponding hydrocarbon σ -radicals. In order to substantiate the observed ^1H and ^{13}C contact shifts, we performed MO calculations for various conformations of 2-phenylethyl radical. The calculated results for a typical conformation which corresponds well to the trend of the observed contact

shift is given in Table II. Bond lengths and angles used for MO calculation are $a = 1.54 \text{ \AA}$, $b = 1.40 \text{ \AA}$, $C(sp^3)-H = 1.09 \text{ \AA}$, $C(sp^2)-H = 1.07 \text{ \AA}$, $\phi = 109^\circ 28'$, θ and ψ are the dihedral angles of radical-lobe- $C_1-C_2-C_j$ and $C_1-C_2-C_j-C_O$, respectively. Tetrahedral structure is taken around the C_1 carbon. Table II shows that the experimental trend of benzylamine is well reproduced by the $(90^\circ, 0^\circ)$ conformation



($\psi = 90^\circ$, $\theta = 0^\circ$). This implies that the $(90^\circ, 0^\circ)$ conformation is preferred at least in the complex with $Ni(AA)_2$.

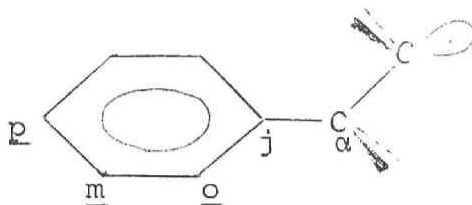
The alternating sign of the $2p_\pi$ orbitals along the bond is considered to be due to the hyperconjugative-type spin delocalization onto the benzene ring. On the other hand, for the junction carbon the sign of the spin density of the $2s$ orbital is opposite to that of the $2p_\pi$ orbital. It is well established that alternation of the induced spin density (spin polarization) is the most important mechanism of spin transmission through carbon σ -skeleton.^{6,7} This suggests that the large downfield shift of the junction carbon is not attributable to the π -delocalization mechanism but to the spin transmission through the $N-C_\alpha-C_j$ σ -skeleton.



Table II. Relative Values of Observed and Calculated
Spin Densities for Benzylamine (1).

position	obsd. ^a	Calcd. Relative Spin Density ^b	
		s-orbital	p _π -orbital
C _α	-1.00 ^c	-1.00 ^c (-0.0087) ^d	
C _j	+2.18	+1.71	-1.00 ^c (-0.0059) ^d
C _{<u>o</u>}	+0.23	+0.02	+1.47
C _{<u>m</u>}	+0.00	+0.02	-0.91
C _{<u>p</u>}	+0.16	+0.05	+1.31
H _α	+1.00 ^c	+1.00 ^c (+0.0136) ^d	
H _{<u>o</u>}	-0.08	+0.07	
H _{<u>m</u>}	+0.04	+0.07	
H _{<u>p</u>}	-0.10	-0.02	

a. Opposite sign to the observed contact shift. b. Obtained from the model calculation of 2-phenylethyl σ-radical with the (90°,0°) conformation. C₂ carbon in this radical corresponds to the C_α carbon in benzylamine. c. This value is normalized to unity. d. The value in parenthesis is the absolute value.



In order to gain further insight into the stereospecific spin distribution in 1,2,3,4-tetrahydroisoquinoline (6), we performed INDO-UHF MO calculations of electron spin densities for 1,2,3,4-tetrahydro-2-naphthyl σ -radical as a model of 6 complexed with Ni(AA)₂ (Table III). It is particularly to be noted that the observed spin densities (opposite sign to the observed contact shifts) are well reproduced both for proton and carbon atoms by Model A, in which the radical lone occupy the equatorial position. Contrary to this, Model B does not correspond to the observed trend.¹¹ This implies that the lone pair electrons in 6 occupies the equatorial position at least in the complex with Ni(AA)₂. It is also interesting that in Model C the calculated result for the (0°,0°) conformation of 2-phenylethyl σ -radical corresponds rather well to the observed shifts. In Model A and C, the sign of the spin density of proton 1s orbital does not always oppose to that of the directly bonded carbon 2s orbital. As the steric structure of 6 is rather fixed by the presence of the piperidine ring, different N-C_α-C_β conformation from that of benzylamine is expected. Above observed and calculated results suggest that the spin transmission through the σ -skeleton becomes relatively important in 6 compared to benzylamine. It may be, therefore, concluded that the difference of the manner of electron spin distribution between benzylamine and tetrahydroisoquinoline is related to the different configuration of their σ -skeletons.

In 7-azabenzonorbornene (8) and 7-azabenzonorbornadiene (9),³

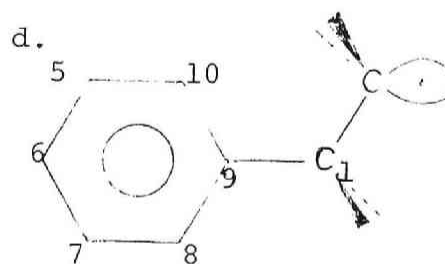
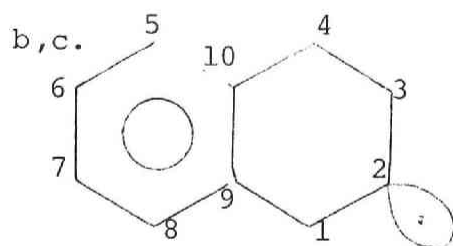
Table III. Relative Value of Observed and Calculated Spin Densities for 1,2,3,4-tetrahydroisoquinoline (5).

position	obsd. ^a	Calcd. Relative Spin Density		
		Model A ^b	Model B ^c	Model C ^d
C ₁	-1.00 ^e	-1.00 ^e (-0.0088) ^f	-1.00 ^e (-0.0077) ^f	-1.00 ^e (-0.0078) ^f
C ₃	-0.86	-0.84	-0.97	—
C ₄	+1.23	+1.11	+0.44	—
C ₅	+0.25	+0.17	+0.08	+0.02
C ₆	±0.00	-0.03	-0.03	+0.00
C ₇	+0.17	+0.12	+0.03	+0.13
C ₈	+0.06	+0.01	-0.07	+0.10
C ₉	+1.37	+1.33	+0.38	+2.10
C ₁₀	-0.08	-0.14	-0.08	+0.17
H ₁	+1.00 ^e	+1.00 ^e (+0.0151) ^f	+1.00 ^e (+0.0544) ^f	+1.00 ^e (+0.0120) ^f
H ₃	+0.90	+0.71	+0.86	—
H ₄	+0.46	+0.21	-0.06	—
H ₅	-0.02	-0.01	-0.00	+0.02
H ₆	±0.00	+0.04	+0.00	+0.01
H ₇	+0.20	+0.11	-0.00	+0.11
H ₈	+0.06	+0.14	+0.01	+0.08

a. Opposite sign to the observed contact shift. b. Calculated results for 1,2,3,4-tetrahydro-2-naphthyl σ -radical with the equatorial radical lobe. c. Calculated results for 1,2,3,4-tetrahydronaphthyl σ -radical with the axial radical lobe. d. Calculated results for 2-phenylethyl σ -radical with the

(Table III continued)

(0°,0°) conformation. The numbering of the atoms is made correspond to that of 1,2,3,4-tetrahydro-2-naphthyl σ -radical. e. This value is normalized to unity. f. The value in parenthesis is the absolute value.



all the aromatic carbons sense downfield shifts. Whereas, the shifts of the aromatic protons show alternation (Table I). Such a feature cannot be explained only by the π -delocalization mechanism. In 8 and 9 the hyperconjugative-type spin delocalization is considered to be forbidden from their steric structure. Unpaired spin may be transmitted to the benzene ring by other mechanisms, σ -polarization or σ -delocalization mechanism may play an important role.

Summarizing the above results and discussion, it is concluded that $\text{Ni}(\text{AA})_2$ -induced ^1H and ^{13}C contact shifts reflect quite sensitively the steric structure associated with the intramolecular nonbonded interaction and, therefore, could serve as a quite sensitive probe for the elucidation of the mode of intramolecular electron spin transmission and the nature of nonbonded interactions.

References and Notes

- (1) I. Morishima and K. Yoshikawa, J. Amer. Chem. Soc., 97, 2950(1975).
- (2) I. Morishima, K. Yoshikawa, M. Hashimoto, and K. Bekki, J. Amer. Chem. Soc., 97, 4283(1975).
- (3) K. Yoshikawa, K. Bekki, M. Karatsu, T. Kamio, and I. Morishima, J. Amer. Chem. Soc., in press.
- (4) I. Morishima, K. Yoshikawa, K. Toyoda, M. Karatsu, T. Yonezawa, S. Sakata, and S. Ikegami, submitted for publication.
- (5)(a) T. Yonezawa, I. Morishima, and Y. Ohmori, J. Amer. Chem. Soc., 92, 1267(1970); (b) I. Morishima, K. Okada, M. Ohashi, and T. Yonezawa, Chem. Commun., 33(1971); (c) I. Morishima and T. Yonezawa, J. Chem. Phys., 54, 3238(1971); (d) T. Yonezawa, I. Morishima, Y. Akana, and K. Fukuta, Bull. Chem. Soc. Japan, 43, 379(1970).
- (6)(a) I. Morishima, T. Yonezawa, and K. Goto, J. Amer. Chem. Soc., 92, 6651(1970); (b) I. Morishima, K. Okada, T. Yonezawa, and K. Goto, Chem. Commun., 1535(1970); (c) I. Morishima, K. Okada, T. Yonezawa, and K. Goto, J. Amer. Chem. Soc., 93, 3922(1971); (d) I. Morishima, K. Okada, and T. Yonezawa, *ibid.*, 94, 1425(1972).
- (7)(a) I. Morishima, K. Yoshikawa, and K. Okada, J. Amer. Chem. Soc., in press; (b) K. Yoshikawa, M. Hashimoto, H. Masuda, and I. Morishima, submitted for publication.
- (8) R. J. Fitzgerald and R. S. Drago, J. Amer. Chem. Soc., 89, 2879(1967).

- (9) A. Carrington, *Quart. Rev. (London)*, 17, 67(1963).
- (10) D. L. Beveridge, P. A. Dobosh, and J. A. Pople, *J. Chem. Phys.*, 48, 4802(1967).
- (11) Model B rather corresponds to the observed trend of N-methyl-1,2,3,4-tetrahydroisoquinoline (7). Consequently, axial orientation of the lone pair electrons may be expected.

CHAPTER 10

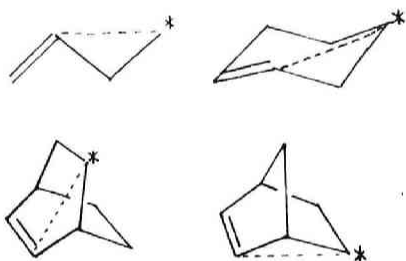
On the Nature of Nitrogen Lone Pair in n,π Homoconjugative Aliphatic Amines

Abstract:

In order to study the intrinsic nature of lone pair electrons, ultraviolet absorption spectra have been obtained for several cyclic and bicyclic amines containing nonadjacent benzene ring. It was found that these spectra are apparently different between bishomobenzyl n,π interacting system (7-azabenzonorbornene derivatives) and homobenzyl system (1,2,3,4-tetrahydroisoquinoline derivatives). We further studied charge transfer complexes of iodine with various cyclic and bicyclic amines containing nonadjacent π groups. The transition energies ($h\nu_{CT}$) of the charge transfer absorptions have been discussed in connection with ionization potentials and basicities. Remarkable difference in the nature of the lone pair electrons between bishomomallyl and homoallyl n,π interacting systems or between bishomobenzyl and homobenzyl n,π interacting systems have been discussed in relation to homoconjugation.

The consequence of homoconjugation between π electrons and nonadjacent active centers of cations, radicals and anions has been a subject of continuing controversy in organic chemistry. Such interactions also connect with the problem concerning aromaticity and antiaromaticity of organic molecules.¹ Particularly, the interaction between a cation center and a nonadjacent π bond have most extensively studied.² The great π electron participation in the acceleration of the rate of solvolysis in homoconjugative and bishomoconjugative systems has been well established.²

"homoallyl interaction"



"bishomoallyl interaction"



* active center
(cation, radical, anion)

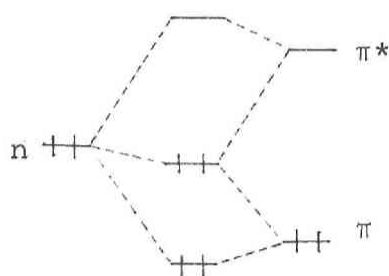
However, studies on the nonbonded interaction between doubly occupied n orbitals and the nonadjacent π groups have been quite limited.^{3,4}

We are currently interested in the stereospecific orientation of nitrogen lone pair electrons in cyclic and bicyclic amines.^{5,6,7,8} We have previously reported structural effects on the homoconjugative^{6,8} and bishomoconjugative⁷ interactions between nitrogen lone pairs and π electrons with the aid of ^1H and ^{13}C nmr measurements. In these studies, it has been revealed that n and π electrons are "repulsive" in 7-azanorbornene derivatives which constitute the bishomoallyl interacting system,⁷ while these electrons are electronically rather "attractive" in the

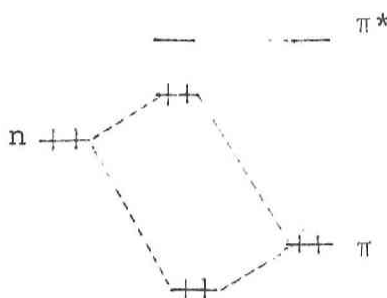
homoallyl interacting system.^{6,8}

Recently we have also carried out a photoelectron spectroscopic study⁹ of nonbonded n, π interactions involved in several cyclic and bicyclic amines containing nonadjacent π bonds. It has been found that the feature of the non-adjacent n, π interaction is quite different between homoallyl and bishomoallyl interactions systems. In the latter system, the direct interaction between n and π^* orbital is forbidden on the basis of the molecular symmetry and, therefore, only the direct n, π interaction is significant. Such bishomoallyl n, π interaction between the doubly occupied orbitals destabilizes the system. In the case of homoallyl interaction, however, the n orbital is allowed to interact with both π and π^* orbitals because of the molecular dissymmetry. This interacting system is thus rather electronically stabilized. These results obtained from the photoelectron

"homoallyl interaction"



"bishomoallyl interaction"



spectroscopic study have also been discussed in relation to the stereospecific lone pair orientation in bicyclic and cyclic amines.^{6,7,8}

In order to gain further insight into the intrinsic nature of homoconjugation between lone pair and π electrons, we have performed here ultraviolet absorption spectroscopic

studies of nonadjacent n,π interaction in various cyclic and bicyclic amines. We also measured the charge-transfer absorption band of iodine-amine complexes. These results were discussed in connection with the photoelectron spectroscopic study of these amines.⁹ From these experimental results, marked differences in the nature of the lone pair electrons between in bishomoallyl (or bishomobenzyl) and homoallyl (or homobenzyl) interacting systems were found. These experimental trends were discussed in relation to homoconjugation and homoaromaticity.

Experimental Section

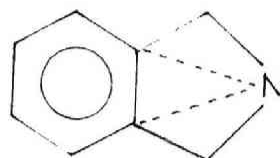
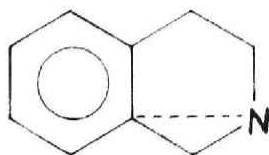
Cyclic and bicyclic amines and the related carbocyclic compounds examined in the present study are listed in Tables I and II. 7-Azabenzonorbornene (14) and 7-azabenzonorbornadiene (15) were prepared following the method of Carpino et al.¹⁰ Procedure of the synthesis of 2,3(exo)-2-azanorbornene (12) and 2,3(exo)-2-aza-5-norbornene (13) is reported in a separate manuscript.⁸ N-methyl-1,2,5,6-tetrahydropyridine (11) and N-methyl-1,2,3,4-tetrahydroisoquinoline (17) were synthesized by N-methylation of the parent N-H amines. Other amines used in this study are commercially available. All samples were purified by distillation or sublimation. Commercially available iodine were sublimed and kept in a desicator. In the measurement of CT absorption of iodine-amine complexes, the actual concentration were in the order of 10^{-5} and $10^{-3} \sim 10^{-4}$ mol/l for iodine and amines, respectively.

Results and Discussion

UV Spectra. We obtained UV spectra of cyclic and bicyclic amines containing a benzene ring nonadjacent to the nitrogen atom. The UV spectra of 7-azabenzonorbornene (14), 7-azabenzonorbornadiene (15), benzonorbornene, and benzonorbornadiene are exemplified in Figure 1. Table I summarizes the results of UV absorption measurements. As is shown in Figure 1, the compounds studied here (listed in Table I) exhibit a $\pi^* \leftarrow \pi$ absorption band with the vibrational fine structure of the benzene ring having their maximums located at 270~280 nm. Here, the $\pi^* \leftarrow \pi$ band in 14 and 15 shifts to the longer wavelength by the introduction of a nitrogen atom ($\Delta\lambda = 4 \sim 4.5$ nm in 14 compared to benzonorbornene, $\Delta\lambda = 7.5$ nm in 15 compared to benzonorbornadiene). Contrary to this, in 1,2,3,4-tetrahydroisoquinoline (16) and its N-methyl derivative (17) the $\pi^* \leftarrow \pi$ absorption shifts slightly to the shorter wavelength compared to tetraline (Table I). Such a different manner is attributable to the different effect of the nonadjacent nitrogen atom on the π orbitals, that is, the difference in bishomobenzyl and homobenzyl n, π interacting systems. It is also to be noted

"homobenzyl interaction"

"bishomobenzyl interaction"



that the $\pi^* \leftarrow \pi$ band shift to the shorter wavelength in the protic solvents (methanol and water) and that the magnitudes

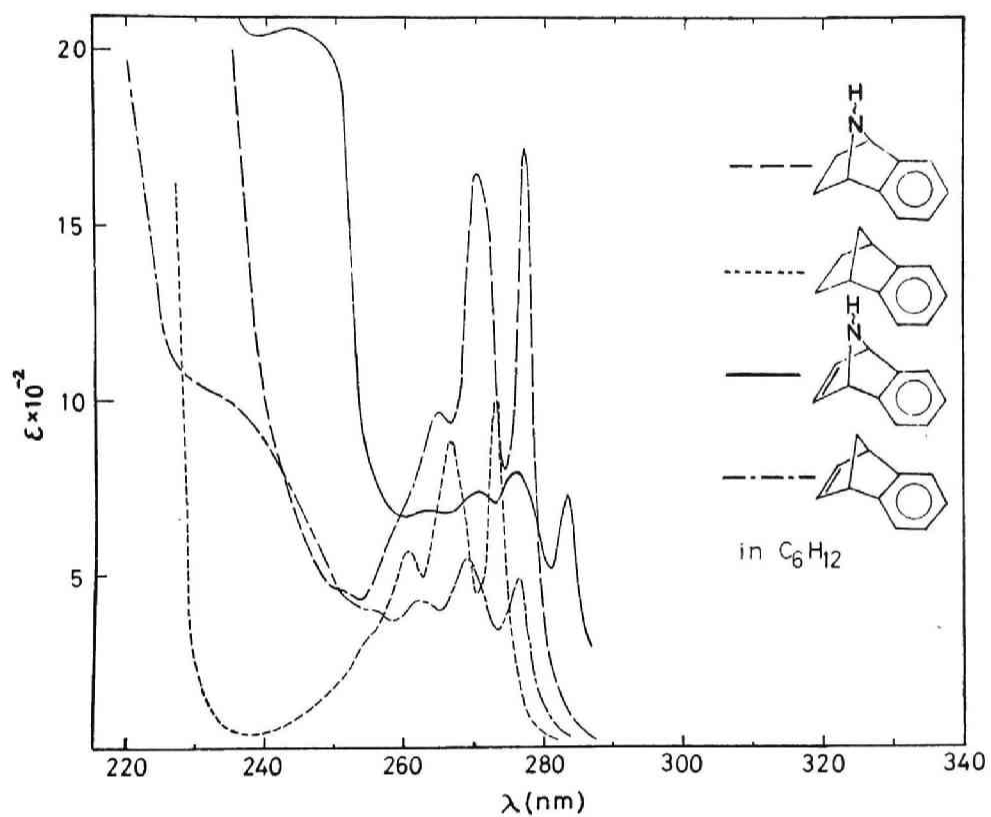
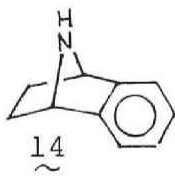
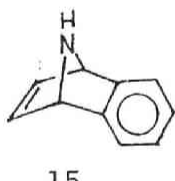
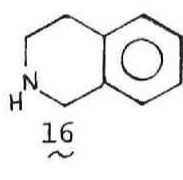
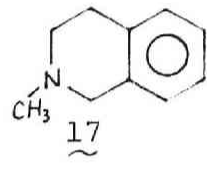
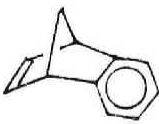
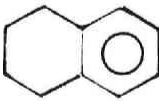
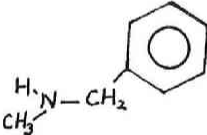


Figure 1. UV spectra of 14, 15, benzonorbornene, and benzonorbornadiene in C_6H_{12} .

Table I. UV Transition Energies

Compounds	UV Transition Energies $\lambda_{\max}$ (ϵ), nm		
	solvent = cyclohexane	methanol	water
 14 ~	264.5 (970)	262.5 (620)	261.5 (600)
	270 (1650)	267 (770)	266.5 (730)
	277 (1720)	274 (730)	273 (640)
 15 ~	244 (2100)	243 (2330)	265 (600)
	272.5 (740)	265 (690)	271.5 (620)
	275.5 (800)	272.5 (720)	279.5 (530)
	283 (730)	280 (630)	
 16 ~	259 (580)	257.5 (630)	257 (660)
	266 (620)	265 (660)	263.5 (680)
	273.5 (600)	272.5 (580)	271.5 (540)
 17 ~	260 (330)	259 (380)	257 (320)
	267 (430)	266 (460)	265 (430)
	274 (460)	273 (490)	272.5 (400)
	260 (570)		
	266 (880)		
	272.5 (1000)		

(Table I continued)

	261.5 (430)			
	268 (550)			
	275.5 (490)			
	261 (390)			
	267.5 (550)			
	274.5 (640)			
	288 (16)			
 <u>18</u>	248.5 (450)	248.5 (200)	248 (210)	
	253.5 (430)	253.5 (230)	252.5 (240)	
	259.5 (440)	259 (250)	258 (270)	
	265.5 (320)	264.5 (200)	263 (230)	
	269.5 (160)	268.5 (150)	267.5 (170)	

of these solvent-induced shifts are also different between bishomobenzyl (14 and 15) and homobenzyl (16 and 17) n, π interacting systems. In our recent photoelectron spectroscopic study, a remarkable difference in the manner of interaction between n and π electrons have been found between bishomoallyl and homoallyl n, π interacting systems.⁹ This is mainly due to the difference of molecular symmetry. The different feature obtained in UV measurements of 14~17 may be also due to such different molecular symmetry. These experimental trends will be discussed later in connection with the concept of homoconjugation.

Iodine-Amine CT Absorptions. There have been a lot of report concerning charge-transfer (CT) UV absorptions of iodine complexes with various organic compounds (amines, alcohols, sulfides and other compounds). In these studies, it has been shown that the energy of the UV absorption of the charge-transfer complexes, $h\nu_{CT}$, correlates with the ionization potential (IP) of donor molecules, the exchange energy (β) and overlap integral (S) between iodine and donor molecules quite vividly.^{12,13} The study of CT absorption in iodine complexes with various cyclic and bicyclic amines is interesting from the following points of view. (a) This study will help the assignment of n orbital in the photoelectron spectra of amines. As the bandwidth of n electrons in amines obtained in photoelectron spectroscopy is rather large, it is difficult to distinguish the bands of n and π electrons in the amines containing π electrons. Therefore, the measurement of the CT band is

expected to help us to assign the n and π bands in the photoelectron spectra of amines. (b) The effect of the steric structure and molecular strain of the donor molecules on the CT absorptions may be of interest to study the intrinsic nature of lone pair electrons in cyclic and bicyclic amines. (c) From this study, we may obtain useful informations concerning the intramolecular nonbonded interactions, homoallyl and homobenzyl n, π interactions.

An example of the absorption spectra measured in the present study is given in Figure 2, the spectrum of iodine and 2,3(exo)-2-aza-5-norbornene (13) complex in cyclohexane. The maximum wavelengths (λ_{CT}) of the CT absorption bands are given in Table II together with the vertical ionization potentials (IP's) of the n and π electrons in various cyclic and bicyclic amines. By comparison with some other iodine-amine complexes reported by Nagakura et al.,¹³ it is evident that the absorption at 230~290 nm wavelength region is the charge-transfer (CT) band. We evaluated the equilibrium constant (K) in iodine-14 complex from the observation of ϵ values with varying the concentration of 14, using Benesi and Hildebrand's equation. The equilibrium constant K obtained from such procedure is 2200 at 16°C. This value correspond well to the K value of usual iodine-amine complexes¹² and excludes the possibility of forming π type complex with the benzene ring in 14. Similar to this, the other amines studied here are also expected to form lone pair- I_2 complexes.

In Figure 3, the transition energies ($h\nu_{CT}$) of the CT

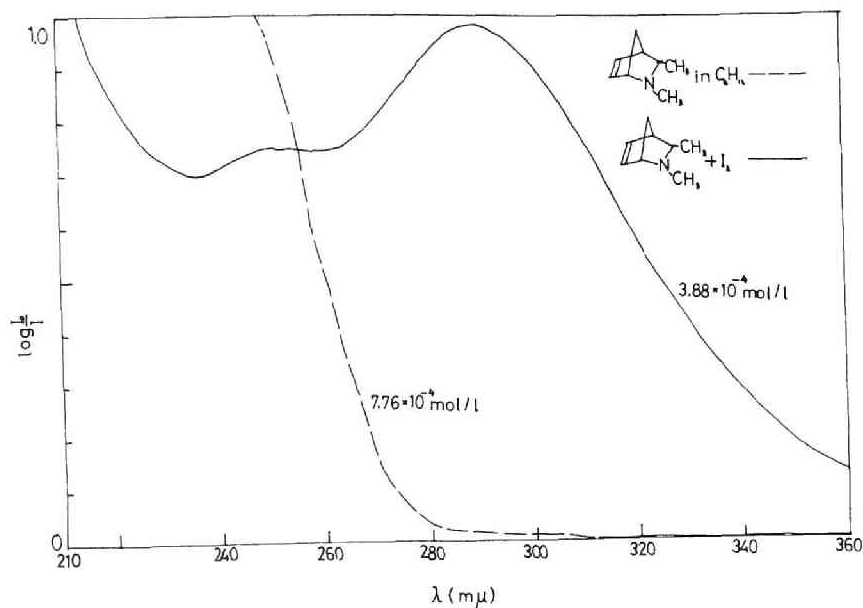


Figure 2. Iodine-13 CT absorption spectrum at room temperature in C_6H_{12} .

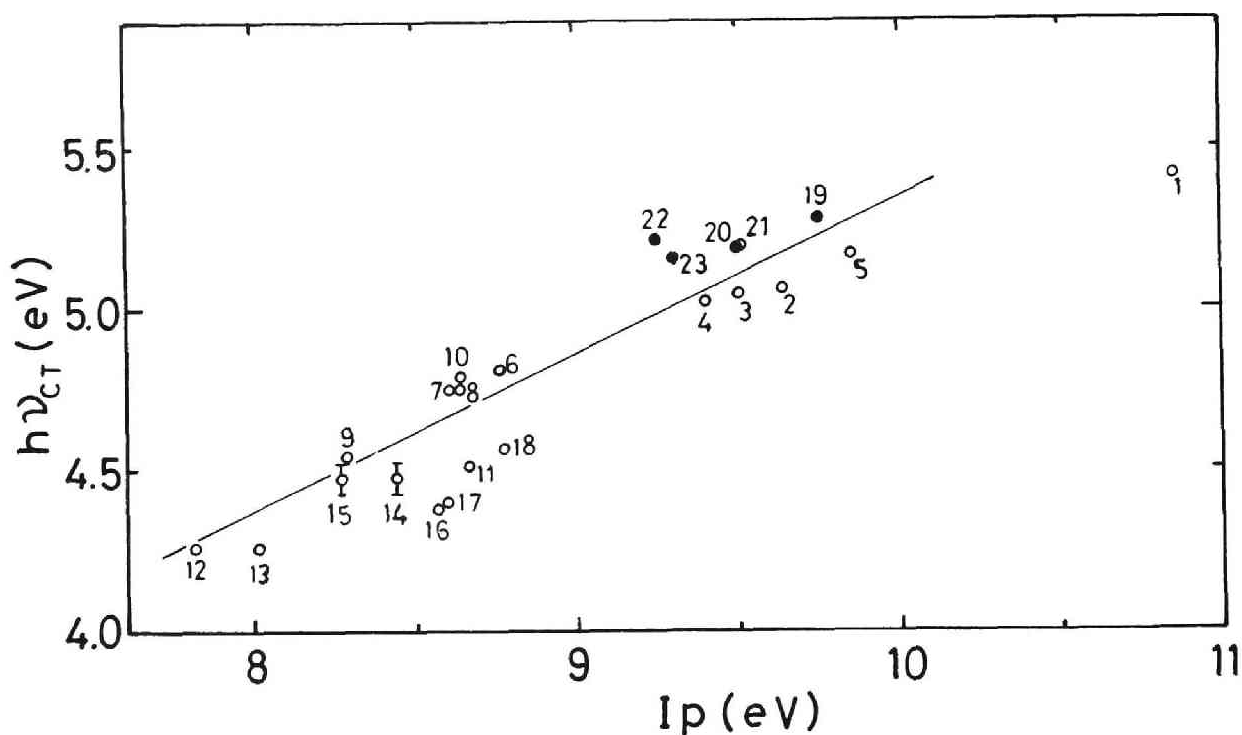
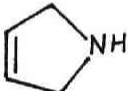
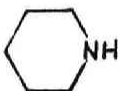
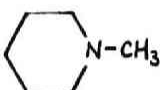
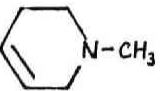
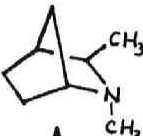
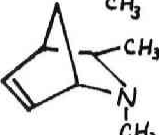
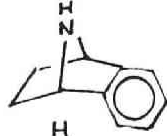
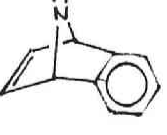
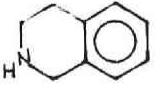
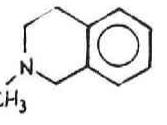


Figure 3. Dependence of the CT transition energy, $h\nu_{CT}$, of iodine complexes upon the ionization potential, IP, of the lone pair in donor amines. Values of IP and $h\nu_{CT}$ are given in Table II. ○ and ● show the first and second ionization potentials, respectively.

Table II. Transition Energies of CT Absorption (λ_{CT}) and Ionization Potentials (IP) in Amines

No of comp.	Compounds	λ_{CT} (nm)	IP (eV)
1.	ammonia	229 ^a	10.85 (n) ^b
2.	MeNH ₂	245 ^a	9.64 (n) ^b
3.	EtNH ₂	246 ^a	9.50 (n) ^b
4.	n-BuNH ₂	247 ^a	9.40 (n) ^b
5.		240	9.85 (n) ^c
6.		258	8.77 (n) ^c
7.		261	8.61 (n) 9.77 (π) ^c
8.		261	8.64 (n) ^c
9.		273	8.29 (n) ^c
10.		259	8.64 (n) 9.33 (π) ^c
11.		275	8.67 (n) 9.37 (π) ^c
12.		291	7.81 (n) ^d
13.		291	8.01 (n) 9.14 (π) ^d

(Table II continued)

14.		275~280	8.44 (n) 9.10 (π) ^c
15.		275~280	8.25 (n) 9.05 (π) 9.97 (π) ^c
16.		283	8.57 (n, π) 9.33 (π) ^c
17.		282	8.60 (n, π) 9.30 (π) ^c
18.	N-methylbenzyl amine	272	8.78 (n) 9.12 (π) ^e
19.	pyridine	235 ^f	9.60 (π) 9.75 (n) ^g
20.	α-picoline	239 ^f	9.20 (π) 9.50 (n) ^g
21.	γ-picoline	239 ^f	9.50 (n) 9.60 (π) ^g
22.	quinoline	238 ^h	8.62 (π) 9.16 (π) 9.2~9.3 (n) ⁱ
23.	isoquinoline	240.5 ^h	8.50 (π) 9.3 (n) 9.41 (π) ⁱ

a. Ref. 13. b. D. W. Turner, "Molecular Photoelectron Spectroscopy," John Wiley & Sons Ltd., 1970. c. Ref. 9. d. Ref. 8. e. K. Yoshikawa and I. Morishima, unpublished result. f. K. R. Bhaskar and S. Singh, Spectrochim. Acta, 23A, 1155(1967). g. E. Heilbronner, V. Hornung, P. H. Pinkerton, and S. F. Thames, Hel. Chim. Acta, 55, 289(1972). h. Ref. 14.

bands are plotted vs. the IP's of n electrons in the donor amines. As is clear from this figure and Table II, the lower the ionization potentials of electron donors are, the smaller the transition energies of the CT bands. This tendency is naturally expected from Mulliken's theory.¹² The linear relation in Figure 3 ensures the assignments of the n orbitals in these amines (1~23). For example, based on the orbital correlation compared with the related compounds, the first IP's (8.44 and 8.25 eV) in 14 and 15 have been attributed to the ionization from the n orbital and the second IP's (9.10 and 9.05 eV) to that from the π orbital. If this is not true, the points of 14 and 15 deviate largely from the linear relationship as is easily recognized. For 22 and 23, the photoelectron spectral assignments of the n orbital were difficult due to the overlap of the bands. Heilbronner et al. estimated that the n IP in quinoline (22) is 9.2~9.3 eV and in isoquinoline (23) is about 9.3 eV, based on the orbital correlation diagram.¹⁴ These bands of n electrons are small and are on the shoulder in π bands. It is apparent that Figure 3 also ascertains their assignments. From the above results and discussion, the measurement of iodine-amine CT absorption is proved to be a useful tool for the assignment of n orbital in the photoelectron spectra of amines.

Then we discuss the deviated points from the linear relationship in Figure 3, such as ammonia (1) which deviates rather largely from the solid line. Nagakura et al. derived a general equation to reproduce observed transition

energies of CT absorptions and fitted separate curves to the data for primary, secondary, and tertiary amines.¹³

$$h\nu_{CT} = \sqrt{(IP-A)^2 - 4S\beta(IP-A) + 4\beta^2} / (1-S^2) \quad (1)$$

They used different parameters (overlap integral (S), exchange integral (β) and effective electron density (A)) for these three kinds of amines. The values of these parameters, S, $|\beta|$, and A, decrease in the order of primary amine > secondary amine > tertiary amine. This may imply that other physical factors beside IP values should be considered to interpret the intrinsic nature of lone pair electrons. That is, the "size" of the lone pair electrons or penetration of the n orbital into the σ and π orbitals, or some other steric effects may be important. These factors may influence the manner of CT interaction of iodine with primary, secondary and tertiary amines. The negative deviation of ammonia in Figure 2 is thus attributable to such effects. It is also interesting in Figure 2 that the amines having homoallyl (11,13) or homobenzyl (16, 17,18) n, π interaction, deviate negative from the linear relationship. In contrast to this, the bishomoallyl (7) and bishomobenzyl (14,15) n, π interacting amines show no apparent deviation from the solid line. It has been indicated that in homoallyl and homobenzyl interacting systems the n orbital could mix with π and π^* orbitals, whereas in bishomoallyl and bishomobenzyl systems the n orbital interacts only with π orbitals. This suggests that the n orbital takes in the π and π^* orbitals effectively in the former

systems, which may result in the decrease of "size" in the front side of the lone pair electrons in the homoally and homobenzyl n, π interacting molecules. This will cause the decrease of overlap integral (S) and exchange integral ($|S|$) in the iodine-amine complexes. Consequently the $h\nu_{CT}$ values decrease as is clear from equation (1). The deviation of $\tilde{\nu}_7$, $\tilde{\nu}_{14}$, and $\tilde{\nu}_{15}$ may be thus explained.

Intrinsic Nature of the Nitrogen Lone Pair Electrons.

Based on the above results and discussion, let us discuss the intrinsic nature of the nitrogen lone pair electrons of amines in connection with the structural effect. Accompanied with the recent development of ion cyclotron spectroscopy, gas-phase basicities of alkylamines have been reported.^{15,16} It has been recognized that the basicity order of simple aliphatic amines in aqueous solution at 25°C (NH_3 < primary < secondary < tertiary) cannot be explained by any single cumulative substituent factor such as the inductive effect.¹⁷ In contrast to this, it has been established^{15,16} that gas-phase basicity follows the order, NH_3 < primary < secondary < tertiary, which corresponds well the decreasing order of IP values of the lone pair electrons. This ordering of gas-phase basicity was attributed mainly to polarization effect of the amines. This large polarization effect in gas-phase was estimated to be masked almost completely in aqueous solution basicities by nearly compensating effects, that is, hydrogen bonding contributions ($NH^+ \cdots OH_2$), hydrophobic interactions and possibly some other effects. While the hybridization effect (the s character of

the lone pair electrons) does not attenuate in solution phases. As a result, in aqueous solution the hybridization effect becomes important together with hydrogen bonding contributions and hydrophobic interactions of alkyl groups. Related to this, for strained cyclic amines the important role of lone pair hybridization on IP values and basicities has been indicated.^{15,18} It is also interesting that steric hindrance is considered not to be a major factor to determine basicities both in gas and solution phases.¹⁵

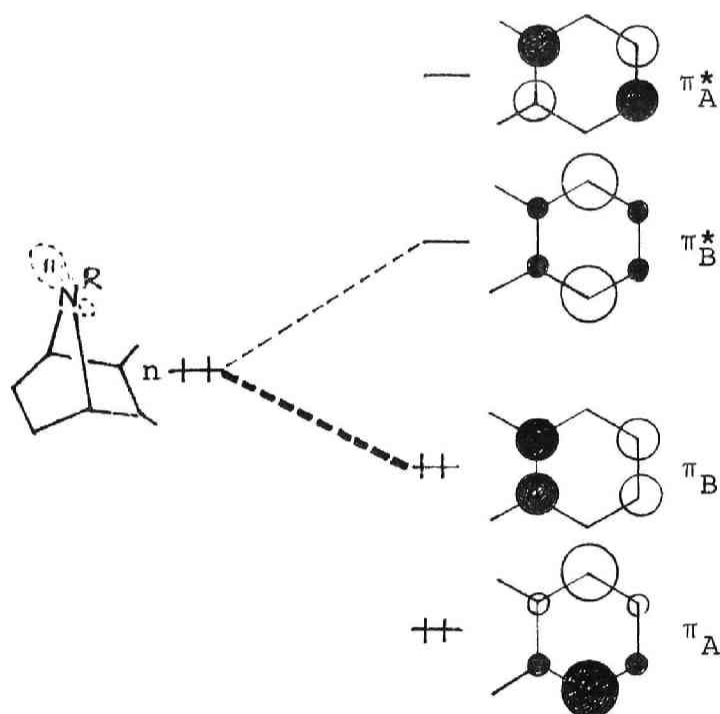
As polarizability of a molecule or a bond connects with both energies and coefficients of molecular orbital, the polarization effects are expected to be combined with the extent of penetration of the lone pair electrons into the skeleton. It may be proper to consider that the extent of orbital penetration into the skeleton increases in the order, primary < secondary < tertiary amines. The different features in the iodine complexes with primary, secondary, tertiary amines is thus attributable to these effects. The negative deviation of the homoallyl and homobenzyl n, π interacting molecules in Figure 2 may be also due to such effects, hence the n orbital mixed considerably with the π and π^* orbitals in these dis-symmetrical systems. In order to delineate further the intrinsic nature of lone pair electrons, theoretical study including the concept of orbital penetration of lone pair into the skeleton may be awaited.

On Homoconjugation. Recently there have been considerable interest about homoconjugation or homoaromaticity.^{19,20,21} The concept of homoconjugation has been discussed in connection

with molecular symmetry, topology and the numbers of π electrons ($2n$ or $2(n+1)\pi$ electrons). However the studies on homoconjugation and homoaromaticity seem to be speculative yet. In this section, we want to discuss on homoconjugation in connection with our experimental results. In our recent photoelectron and nmr spectroscopic studies,^{6,7,8,9} we reported that homoallyl systems tend to be stabilized by the interaction between n and π electrons, while bishomoallyl systems are destabilized. In other words, n and π electrons are repulsive in bishomoallyl interacting systems. On the contrary, these electrons are rather attractive in homoallyl interacting systems. These experimental trends were interpreted as follows.^{6,7,8,9} In the bishomoallyl interacting system the through-space interaction between n and π^* orbitals is symmetry forbidden and, therefore, the direct $n-\pi$ interaction is significantly important. This results in destabilization of the system, because of the electronic repulsion between doubly occupied orbitals. In contrast to this, in the homoallyl interacting system the molecular dissymmetry allows both $n-\pi$ and $n-\pi^*$ interactions. Thus, the $n-\pi^*$ interaction may become relatively important, which results in stabilization or no apparent change of the total energy in the interacting system.

Similar experimental trends are also encountered for homobenzyl and bishomobenzyl n,π interacting systems. It has been reported that the homobenzyl and bishomobenzyl interactions lead the interacting systems stabilization and destabilization, respectively.⁹ Such a feature is explained

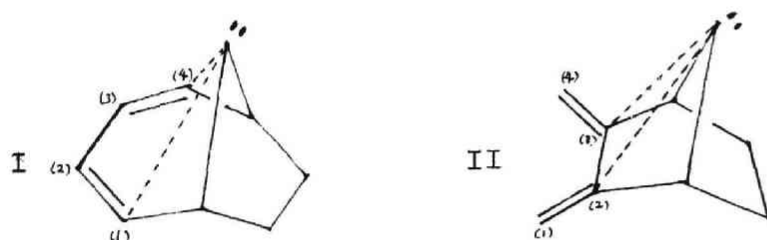
in the following manner ⁹ It has been pointed out that the degeneracy of the highest occupied orbitals in benzene is removed by the presence of two ortho disubstituents, and that the π_B orbital lies above the π_A orbital in benzocycloalkene derivatives ¹⁹ and benzonorbornene derivatives. ⁹ Similarly the π_A^* orbital may lie above the π_B^* orbital in benzonorbornene derivatives. Consequently, the ordering of the π orbitals becomes as follows (for simplification, we omitted the lowest occupied and highest unoccupied π orbitals). From this scheme, one can easily recognize



that the n orbital can interact only with π_B and π_B^* orbitals in bishomobenzyl interacting systems. As the π electron densities on the junction carbons in the π_B orbital are much larger than those in the π_A orbital, the n orbital preferentially interacts with the π_B orbital. Consequently, this destabilizes the bishomobenzyl n, π interacting system.

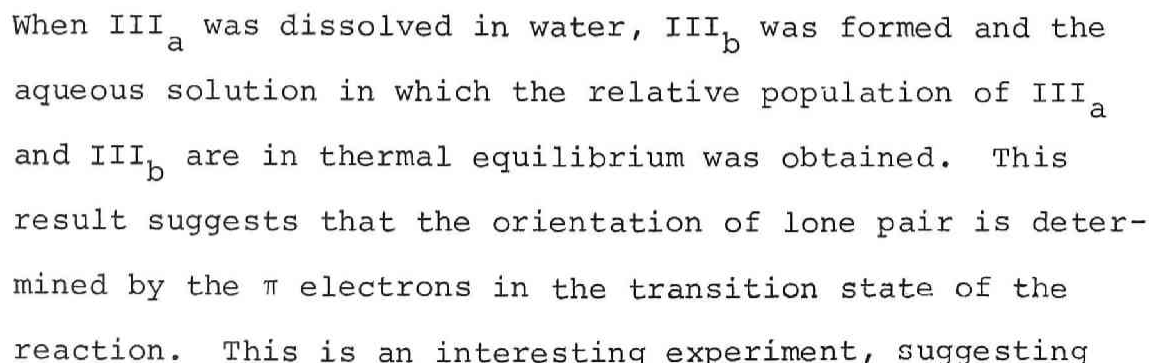
On the other hand, the homobenzyl n, π interacting system is electronically rather stabilized similar to the case of the homoallyl interacting system because of the interaction between n and π^* orbitals.

Keeping the above discussion in mind, we then briefly discuss on homoconjugation and homoaromaticity. Many chemists have been discussed about homoconjugation or homoaromaticity mainly by the way of using the idea of molecular symmetry.^{20,21,22} If one stands other point of view, one will notice that homoconjugation connects with the concept, how effectively π^* orbitals are taken in the occupied orbitals, which results in stabilization of the interacting systems. The idea of bicycloaromaticity and bicycloantiaromaticity²¹ may also concerns to such stabilization and destabilization of the π electron systems. As an example, let us discuss the n, π interacting systems, anions I and II shown below. Both I and II include the π



conjugative system of 1,3-butadiene. In these systems, the nonbonded orbital mainly interacts with the lowest unoccupied orbital, because the interaction with the highest occupied orbital is symmetry forbidden. However, the π atomic orbital coefficients of the 1,4-carbons in the butadiene skeleton fairly smaller than those of the 2,3-carbons. Consequently, the greater stabilization due to the

Finally, we discuss about stereospecific lone pair orientation in a reaction which is controlled by nonbonded π electrons. In the Dieles-Alder type reaction to prepare N-methyl-7-azanorbornadiene-2,3-dicarboxylic acid (III), the lone pair anti conformer (III_a) with respect to the dicarboxyl group was preferentially obtained.²³



the homoconjugation is also connect with chemical reactivity or stereo-selectivity in chemical reactions. Experimental details and further theoretical treatments will appear in a separate manuscript.

References and Notes

- (1) See e.g.; M. J. Goldstein and R. Hoffmann, J. Amer. Chem. Soc., 93, 6193(1971).
- (2) See e.g.; S. Winstein and C. Ordronneau, J. Amer. Chem. Soc., 82, 2085(1960), S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, 77, 4183(1955).
- (3) J. K. Stille and K. N. Sannes, J. Amer. Chem. Soc., 94, 8489(1972).
- (4) C. C. Levin, R. Hoffmann, W. J. Hehre, and J. Hudec, J. Chem. Soc. Perkin II, 210(1973).
- (5) T. Yonezawa, I. Morishima, and Y. Ohmori, J. Amer. Chem. Soc., 92, 1267(1970). I. Morishima, K. Okada, T. Yonezawa, J. Chem. Soc. Chem. Commun., 33(1971). I. Morishima, K. Okada, T. Yonezawa, and K. Goto, J. Amer. Chem. Soc., 93, 3922(1971).
- (6) I. Morishima and K. Yoshikawa, J. Amer. Chem. Soc., 97, 2950(1975).
- (7) K. Yoshikawa, K. Bekki, M. Karatsu, T. Kamio, and I. Morishima, J. Amer. Chem. Soc., in press.
- (8) I. Morishima, K. Yoshikawa, K. Toyoda, M. Karatsu, T. Yonezawa, S. Sakata, and S. Ikegami, submitted for publication.
- (9) I. Morishima, K. Yoshikawa, M. Hashimoto, and K. Bekki, J. Amer. Chem. Soc., 97, 4283(1975).
- (10) L. A. Carpino and D. E. Barr, J. Org. Chem., 31, 764 (1966).
- (11) H. T. Clarke, H. B. Gillespie, and S. Z. Weiss Haus, J. Amer. Chem. Soc., 55, 4571(1933).

- (12) R. S. Mulliken and W. B. Person, "Molecular Complexes," John Wiley & Sons, Inc., 1969.
- (13) H. Yada, J. Tanaka, and S. Nagakura, Bull. Chem. Soc. Japan, 33, 1660 (1960).
- (14) F. Brogli, E. Heilbronner, and T. Kobayashi, Helv. Chim. Acta, 55, 274 (1972).
- (15) M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, Jr., J. Amer. Chem. Soc., 93, 4314 (1971). D. H. Aue, H. M. Webb, and M. T. Bowers, *ibid.*, 94, 4726 (1972), *ibid.*, 97, 4136, 4137 (1975).
- (16) E. M. Arnett, F. M. Jones, III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, J. Amer. Chem. Soc., 94, 4726 (1972). W. G. Henderson, M. Taagepera, D. Holtz, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *ibid.*, 94, 4728 (1972). R. W. Taft, M. Taagepera, K. D. Summerhays, and J. Mitsky, *ibid.*, 95, 3811 (1973).
- (17) For example, N. F. Hall and M. R. Sprinkle, J. Amer. Chem. Soc., 54, 3469 (1932).
- (18) K. Yoshikawa, M. Hashimoto, and I. Morishima, J. Amer. Chem. Soc., 96, 288 (1974).
- (19) P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, Helv. Chim. Acta, 52, 1745 (1969).
- (20) S. Winstein, Quart. Rev. (London), 23, 141 (1969).
- (21) M. J. Goldstein, J. Amer. Chem. Soc., 89, 6357 (1967).
- (22) Ref. 1.
- (23) M. Karatsu, K. Yoshikawa, and I. Morishima, to be submitted for publication.

CHAPTER 11

CONCLUSION

In Part II, the author aimed to elucidate the structural effects on the nature of lone pair or half-occupied orbital (Chapters 2,3,4,10) and intramolecular n,π interaction (Chapters 4,5,6,7,8,9,10) in N-heterocyclic compounds, by using various spectroscopic techniques and MO calculations.

In Chapter 2, it was shown that the IP's of lone pair electrons in cyclic amines are well correlated linearly with their s-character. The gas-phase basicities of these amines were found to be closely connected with the hybridization of the nitrogen lone pair electrons.

In Chapters 3 and 4, stable dialkyl nitroxides were studied by use of photoelectron spectroscopy (Chapter 3) and electron spin resonance spectroscopy (Chapter 4). The adiabatic first ionization potentials were found to be 6.77 and 6.73 eV for di-tert-butyl nitroxide and 2,2,6,6-tetramethylpiperidine-N-oxyl. Doublet splitting of the oxygen lone pair electrons with different peak intensity was quantitatively interpreted in terms of triplet and singlet states of the photoionized cation.

From the esr study in Chapter 4, the nitroxide hyperfine coupling constants of 22.6 and 23.1 G were obtained for 7-azabenzanorbornadiene-7-oxyl and 7-azabenzonorbornene-7-oxyl, respectively. These values are the largest for dialkyl nitroxide radicals so far reported¹ and suggest strongly pyramidal structure around the nitrogen atom.

Appreciable temperature dependence of proton hyperfine coupling constants for the vinylidene proton in 7-azabenzonorbornadiene-7-oxyl were observed. The observed proton hyperfine coupling constants and their temperature dependence were interpreted in term of specific orientation of the N-O bond in these nitroxide radicals with the aid of INDO UHF MO calculations. It was concluded that the N-O bond tilts toward the vinylidene group in 7-azabenzonorbornadiene-7-oxyl, while toward the benzene ring in 7-azabenzonorbornene-7-oxyl.

In Chapter 5, it was found that perturbation of nitrogen lone pair IP's induced by the interaction with nonadjacent carbon-carbon double bond is quite different in β,γ -unsaturated five-membered cyclic amines and β,γ -unsaturated six-membered cyclic amines. These results were explained as follows. The bishomoallyl-type homoconjugation in the five-membered amines favors the through-space interaction between doubly occupied n and π orbitals with destabilization of the lone pair orbital, and homoconjugation in the five-membered amines involves n,π and n,π^* orbital interactions with a little stabilization or no apparent variation of the lone pair orbital energy. It was also found that lone pair IP's in N-H and N-methyl derivatives of six-membered cyclic amines are differently perturbed by the nonadjacent π group. This was attributed to the difference of the relative importance of n,π and n,π^* orbital interactions which depend on n and π orbital energy levels and orientation of the lone pair electrons.

From the study in Chapter 6, it was concluded that the nitrogen lone pair in N-methyl-2-azabicyclo[2.2.2]oct-5-ene is preferentially orientated at the exo position while the exo and endo positions are equally favored in the N-H derivative. With the aid of MO calculations, it was indicated that steric repulsion and n, π homoconjugative electronic stabilization are essentially important to determine the lone pair orientation in this system.

In Chapter 7, it was concluded that the 2- and 3-methyl carbons occupy the endo and exo positions, respectively, in 2,3-dimethyl-2-aza-5-norbornene studied here. Magnetic anisotropic shielding effect of the nitrogen lone pair electrons was also discussed. It was concluded that the transverse susceptibility of the lone pair is negative and therefore the proton located perpendicular to the lone pair orientation is deshielded. From the photoelectron spectra of 2-aza-5-norbornene derivatives, it was suggested that homoallyl n, π interaction stabilizes the interacting system electronically.

In Chapter 8, it was concluded that in N-methyl-7-azanorbornadiene-2,3-dicarboxylic acid the lone pair electrons preferentially occupy an anti position with respect to the electron rich π bond. It was also found that the lone pair electrons of N-methyl-7-azabenzonorbornene and N-methyl-7-azabenzonorbornadiene preferentially occupy the anti position with respect to the benzene ring.

Similar trend of stereospecific lone pair orientation was also encountered for their N-H derivatives. From these experimental results, it was concluded that n and π electrons are repulsive in bishomoallyl and bishomobenzyl interacting systems involved in the five membered cyclic and bicyclic amines and that the nitrogen lone pair electrons prefer an anti position with respect to the π bond or π electron rich group so as to avoid the repulsive interaction. It was also indicated that pK value of the lone pair anti conformer (with respect to the π electrons or π electron rich group) is smaller than that of the syn conformer in these 7-azanorbornenyl derivatives.

In Chapter 9, the manners of electron spin transmission onto the benzene ring in the $\text{Ni}(\text{AA})_2$ -complexes of benzylamines and 1,2,3,4-tetrahydroisoquinolines (homobenzyl n,π interacting system) were found to be quite different each other. Such an experimental trend was attributed to the different lone pair- $\text{N}-\text{C}_\alpha-\text{C}_\beta$ arrangement in these two types of compounds. In the former case, hyperconjugative spin delocalization is the main mechanism of electron spin distribution. On the contrary, spin transmission through the σ -skeleton becomes relatively important in the latter system.

In Chapter 10, it was found that UV spectra are apparently different between bishomobenzyl (7-azabenzonorborene derivatives) and homobenzyl (1,2,3,4-tetrahydroisoquinoline derivatives) n,π interacting systems. From the measurement of CT absorption of iodine complexes with

various amines, the n IP's of these amines obtained from their photoelectron spectra were assigned definitely. Based on these results and the previous studies in this thesis, it was indicated that orbital penetration of lone pair into the skeleton is an important factor upon the intrinsic nature of lone pair electrons. It was also generally suggested that the concept of homoaromaticity or homoconjugation² is connected with the stabilization due to the mixing of π^* orbital into the occupied π orbitals.

Summarizing the results and discussion in Chapters 5~10, it is concluded that n and π electrons are repulsive in the bishomoallyl and bishomobenzyl interacting systems, while these electrons are electronically rather attractive in the homoallyl and homobenzyl interacting systems. The lone pair electrons prefer the orientation in which the interacting system is more stabilized.

It may be of value that some new experimental methods were used in these studies to investigate the lone pair orientation in various cyclic and bicyclic amines. It has been one of the difficult problems in stereochemistry to determine the lone pair orientation. For example, the conformational equilibrium of piperidine has been the subject of prolonged controversy.³ Some claimed for the lone pair preferentially equatorial, the lone pair axial, and the lone pair equally oriented. The author has elucidated the lone pair orientation in several cyclic and bicyclic amines by the measurements of Ni(AA)₂-induced ¹H and ¹³C nmr shifts, of magnetic anisotropic effect of the nitrogen

lone pair electrons in ^1H nmr, of stereospecific ^{13}C nmr shifts, and of Eu-induced shifts and Gd-induced line broadening in ^1H nmr. These results and the experimental techniques used in these studies are expected to serve as an aid in the progress of stereochemistry in heterocyclic compounds.

References

- (1) M. J. Goldstein and R. Hoffmann, J. Amer. Chem. Soc., 93, 6193(1971).
- (2) See ref. 24,25,26,27 in Part II, Chapter 5.
- (3) See ref. 15,16,23,24 in Part II, Chapter 4.

GENERAL CONCLUSION

The major concern of chemistry is the interpretation of the structures of molecules and the chemical reactions they undergo. Developments of molecular orbital (MO) theories including all valence electrons have provided quantitative description of the structure of organic molecules and their chemical properties with the assistance of some powerful spectroscopic methods. In the last twenty or thirty years, the application of quantum mechanics to chemistry has many times been stimulated by the development and improvement of various physical tools, e.g., X-ray diffraction, UV, IR, NMR, ESR spectroscopies. These spectroscopies afford us a great deal of important informations concerning the steric and electronic structures of a molecule. Theoretical chemists have tried and are trying to calculate precisely the physico-chemical properties measured by these spectroscopic methods.

In this thesis, the author aimed to study the conformational or geometrical dependence of electronic structures in N-heterocyclic molecules. New physical instruments, ^{13}C nmr and photoelectron spectroscopies, have been applied to these studies as the main experimental tools. MO calculations were also carried out in order to interpret the experimental results theoretically.

In Part I, it was emphasized that alternating nature is generally important in the manner of electron charge and spin distributions in σ -electron system. It was also

found that the charge and spin distributions in σ -skeleton exhibit marked conformational and geometrical dependence.

In Part II, it was shown that molecular strain affects the nature of lone pair or half-occupied orbitals remarkably. From the studies of nonbonded n, π interactions, it was concluded that n and π electrons are repulsive in the bishomoallyl and bishomobenzyl interacting systems, while these electrons are rather attractive in the homoallyl and homobenzyl interacting systems. The lone pair electrons thus prefer the orientation in which the interacting system is more stabilized. The results and conclusions obtained in these studies are expected to serve as an aid in the progress in physical and organic chemistry.

Lastly, the author wishes to mention briefly about the relation of chemistry with human life. Nowadays mankind is faced to serious problems, e.g., environmental pollution, food crisis, energy problem, cancer, etc. These problems should be tackled by chemists, because chemistry is concerned closely with all of these problems. Through the long evolutionary process, living organisms have gradually obtained functions and characters to live. One can say that environment, including living things and their products, has evolved itself along with the progress of living organisms. Accordingly, we should scrutinize nature more thoroughly and more widely in order to solve these serious problems. In this sense, it is important for chemists to develop chemistry, as well as other area of science, and to increase

chemical knowledge. The primary concern to interpret precisely the molecular properties is still a problem at the present stage in chemistry. Further development in fundamental research of chemistry and its positive application to human life are awaited.

