SYNTHESES AND REACTIONS OF NOVEL FULVENES AND FULVALENES POSSESSING DIAMINOCYCLOPROPENYLIDENE MOIETY

Shuki Araki

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Department of Synthetic Chemistry
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PREFACE

The studies presented in this thesis have been carried out under the direction of Professor Zen-ichi Yoshida at the Department of Synthetic Chemistry of Kyoto University during 1973-1978.

The author wishes to express his grateful gratitude to Professor Zen-ichi Yoshida for his continuous encouragement and partinent advice throughout the work. The auther also wishes to express his sincere thanks to Assistant Professor Hisanobu Ogoshi for his valuable advice and stimulating discussion during the course of this work. Furthermore, the auther is sincerely grateful to Assistant Professor Shigeo Yoneda and Dr. Yoshinao Tamaru for their helpful discussions and comments. The author is also indebted to Messrs. Tatsumi Nakamura, Shuji Kida and Toshio Kakui for their active collaborations. Valuable discussions with the author's colleagues are gratefully acknowledged.

Finally the author thanks his parents for their affectional encouragement throughout the work.

Shuki Araki

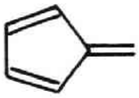
March 1978

CONTENTS

INTRODUCTION

In the last few decades, the chemistry of non-benzenoid aromatic compounds has attracted the interest of chemists to an increasing extent. The synthetic accessibility of numerous new cyclically conjugated π-electron systems and their theoretical understanding has accelerated vigorous development of an interesting field of organic chemistry. Owing to the advancement of quantum chemistry the concept of the aromatic sextet[1] of electrons has been deprived of its leading role and has been replaced by the postulate that planer monocyclic conjugated systems with a $(4n+2)\pi$-electron configuration should in general possess special electronic stability.[2] Besides the well known cyclopentadienyl anion[3] and the tropylium cation[4], the successful syntheses of cyclopropenium cation[5], cyclononatetraenyl anion[6] as well as of the annulenes[7] and bridged annulenes[8] have confirmed these views.

Accompanied with the rapid progress in the chemistry of the monocyclic conjugated π-electron systems, the cross-conjugated π-electron systems, namely fulvenes and fulvalens, have gathered much attention of theoreticians and organic chemists. The participation of the element of cross-conjugation in the π-electron systems of fulvenes and fulvalenes should affect their properties and result in characteristic differences in bonding character and reactivity compared with monocyclic conjugated compounds. Early theoretical calculations[9] predicting the aromaticity of some fulvenes and fulvalenes have prompted the syntheses of these types of cross-conjugated systems. Of these, pentafulvene (1) derivatives were synthesized as early as 1900 by Thiele[3], any other members of this class of compounds had been unknown untill 1959. Since Doering prepared pentafulvalene (2) and heptafulvalene (3) as extremely unstable compounds in 1959,[10] a wide variety of derivatives in this field has been synthesized and studied. Very recently, Neuenschwander ultimately succeeded in the syntheses and isolation of pentafulvene 1[11], heptafulvene (4)[12] and pentaheptafulvalene (sesquifulvalene) (5), and found to be polyolefinic possessing negligible π-delocalization energies. Thus, the chemistry of fulvenes and fulvalenes composed of five- and/or seven-membered ring has been extensively investigated and produced many fruitful results.[13]



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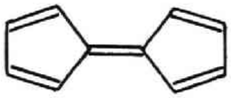

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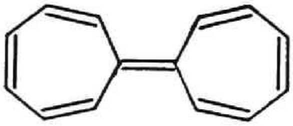

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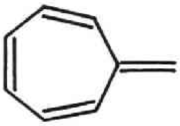

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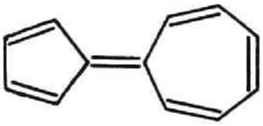

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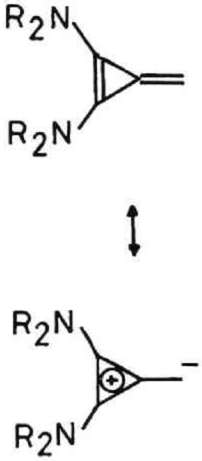
By contrast, the chemistry of the cross-conjugated π-electron systems possessing cyclopropenylidene moiety is rather limitted due to their high reactivities and large strain energies. Cyclopropenium ion, the smallest aromatic system, is of special interest from the viewpoints of aromaticity, bent bonding and unusual hybrization. Yoshida and his coworkers reported[14] that a wide variety of compounds which have cyclopropenylidene moiety was stabilized by the substitution of amino group. Therefore, the strong π-conjugative interaction is reasonably expected between amino group and fulvene and fulvalene systems possessing cyclopropenylidene moiety. In the present thesis are described the syntheses and the reactions of diaminotriafulvene (6), diaminotriapentafulvalene (diaminocalicene) (7) and diaminotrianonafulvalene (8). For this type of cross-conjugated systems, the contribution of the polar canonical structures to the ground state is expected, and amino groups on the three-membered ring should increase the polarity of the triafulvene 6 and the mixed fulvalene systems 7 and 8. It is important to study such compounds in order to clear the relationship between the electronic effect of amino group and π-electron delocalization in respect of the aromaticity of the cross-conjugated π-electron systems.



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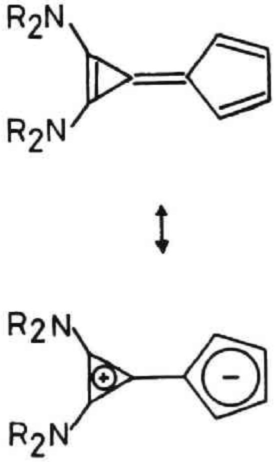

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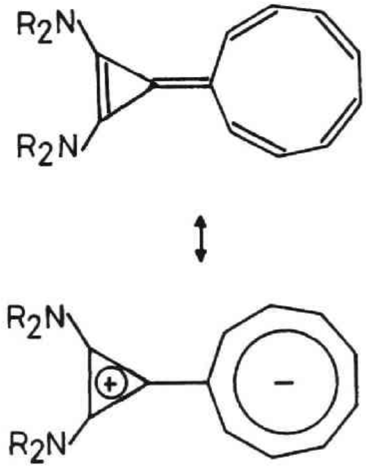

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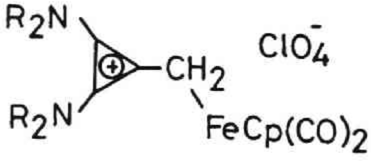
In chapter 1 are described the syntheses and properties of diaminotriafulvene 6 and its transition metal complex (9). Although, triafulvenes possessing substituents on the exocyclic double bond have been prepared so far[15], derivatives without any substituents on the exocyclic carbon have never been reported.[16] The diamino derivative 6 is successfully prepared by the proton abstraction of diaminomethylcyclopropenium ion, and large contribution of polar canonical structures is suggested. The electronic structures as well as the reaction behavior of 6 are in good accord with the results of MO calculation. The iron complex 9 of diaminotriafulvene 6, the first example of triafulvene transition metal complex, is prepared. The spectroscopic data (^{1}H-, ^{13}C-nmr, ir and uv) indicate that 9 is a σ-complex with a σ-bond between the iron atom and the exo-methylene carbon, as is formulated in 9.



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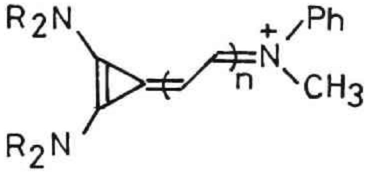
Chapter 2 deals with syntheses and structures of triafulvene immonium salts (10) and vinylogous diaminotriafulvenes (11). The ^{1}H- and ^{13}C-nmr spectra of 10 reveal the delocalization of the positive charge through the polymethine chain. According to the ^{1}H-nmr spectra of 11, significant contribution of polar canonical structures is observed. The immonium salts 10 and the neutral triafulvenes 11 can be regarded as non-benzenoid analogs of cyanine dyes. Electronic spectra of these compounds show regular shifts to longer wave-length with the elongation of the polymethine chain.



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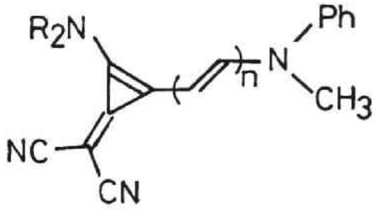

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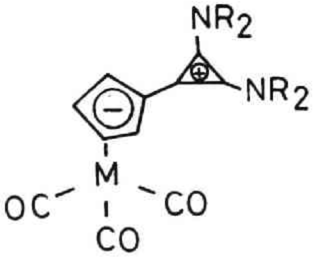
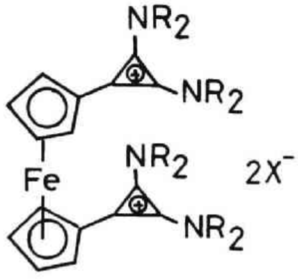
In 1952, Roberts predicted from the results of the HÜckel MO caluculation that calicene has a substantial π-electron delocalization energy and hence to be a stable system with aromatic properties.[17] Although several calicene derivatives have been successfully prepared and discussed about their electronic structures, however, the parent compound and even the simple derivatives without any substituents on the five-membered ring have never been reported.[18] In chapter 3 are described the synthesis and structures of various 5,6-diaminocalicenes. On the basis of the spectral properties, strong π-conjugative interaction between the calicene system and amino group is suggested and the evidences for the aromaticity of 5,6-diaminocalicene are provided.

Chapter 4 concerns with the reaction behavior of 5,6-diaminocalicene 7. Electrophilic substitution of 7 with various electrophiles took place at peripheral positions of the five-membered ring. The reaction with dienophiles gave calicenes substituted at the cyclopentadienyl ring *via* Michael addition. These results clearly indicate that 7 reacted as an aromatic rather than a polyolefin. Present work strongly supports the aromatic character of 5,6-diaminocalicene 7. The reactivity and the reaction position are discussed with the aid of HMO calculations.

Many fulvenes and fulvalenes are not isolable because of their high reactivity toward oxygen or tendency to polymerize, however, in many cases they can be stabilized as ligands in transition metal complexes.[19] It is particularly interesting to study the transition metal complexes of fulvenes and fulvalenes in connection with the structures of fulvenes and fulvalenes. In chapter 5 are described new synthetic methods and structures of the transition metal complexes of 5,6-diaminocalicene 7. In the metaltricarbonyl complexes (12), the polarity of the calicene moiety is found to be more increased than that of 5,6-diaminocalicene itself. The bis-calicene-iron (13) and -cobalt (14) complex can be regarded as a ferrocene and a cobalticinium derivative, respectively. The spectral data of the rhodium complex (15) clearly show the coordination of the rhodium atom to the cyclopentadienyl ring of 7.



12 M = Cr,Mo,W



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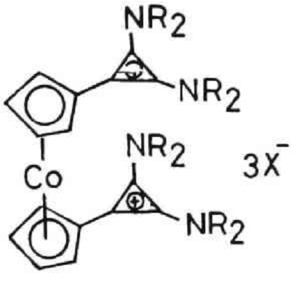

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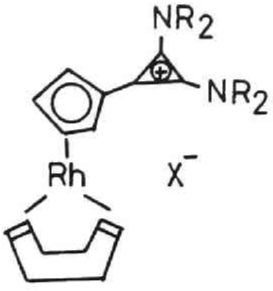

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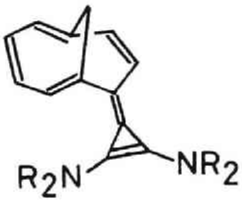
Trianonafulvalene, the higher π-electron analog of calicene, is an important member of cross-conjugated π-electron systems. Many efforts to obtain this molecule have been made, however, no successful results have been reported so far.[20] In chapter 6, the preparation and the characterization of 1,6-methano-9,10-diaminotrianonafulvalene (16), the first derivative of trianonafulvalene, are described. The ^{1}H-nmr spectrum of 16 provides the evidence for the contribution of polar canonical structures to the ground state. The attempt to prepare 9,10-diaminotrianonafulvalene 8 is also described.



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CHAPTER 1

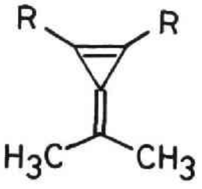
SYNTHESES AND PROPERTIES OF DIAMINOTRIAFULVENE AND ITS IRON COMPLEX

SUMMARY

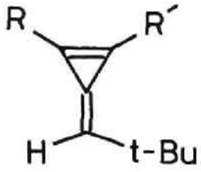
Diaminotriafulvene (4) without any substituents on the exocyclic carbon is synthesized and large contribution of polar canonical structures is suggested. Reaction of 4 with various electrophiles is found to occur at the exocyclic carbon as is expected from the results of HMO calculation. Iron complex of 4, the first transition metal complex of triafulvene, is synthesized and proved to be a σ-complex formulated as 14.

INTRODUCTION

The simplest cross-conjugated system, triafulvene (methylenecyclopropene) 1 has been of special interest to theoreticiansas well as being a synthetic challenge.[1] The first successful synthesis of a triafulvene was a diphenylqinocyclopropene reported by Kende in 1963,[2] and, although a number of triafulvenes with polar substituents on the exocyclic double bond have been reported and some of their chemistry investigated,[3] the parent member has not been isolated.[4] Very recently the syntheses of the simple derivatives without electron withdrawing substituents on the exocyclic double bond, such as 2 and 3, have been reported.[5]



2 R=Me,Et



3 R=t-Bu, R´=Br
R=Br, R´=t-Bu

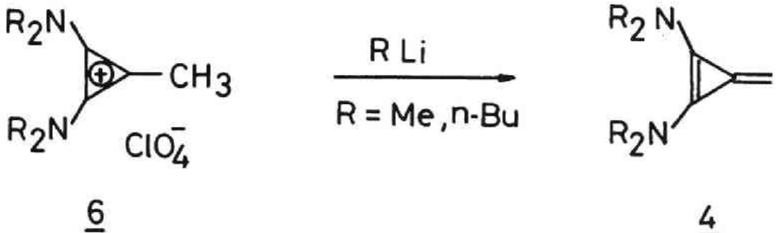
It has been reported that amino group dramatically stabilizes a wide variety of cyclopropenyl compounds,[6] e.g., cyclopropenium, cyclopropenone, cyclopropenethione, and cyclopropeneselone. Although triafulvenes bearing amino groups on the three-membered ring have been reported so far[7], the diaminofulvene without any substituents on the exocyclic double bond is unknown.

In this chapter, the synthesis and properties of diaminotriafulvene (4) are described. Futhermore, the synthesis and structures of the iron complex (5) of 4, the first example of transition metal complex of triafulvene, are described.

RESULTS AND DISCUSSION

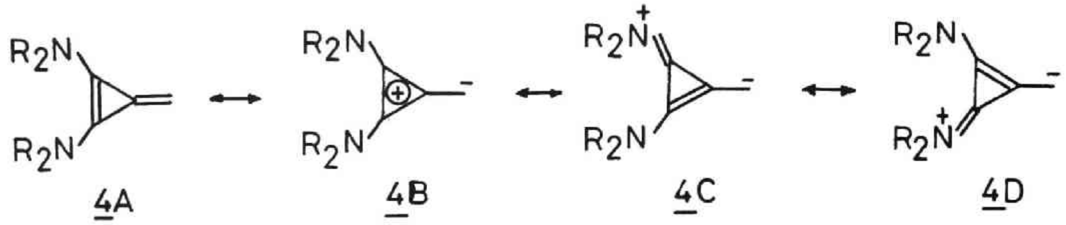
Synthesis and Characterization of Diaminotriafulvene

To a suspension of 1,2-bis(diisopropylamino)-3-methylcyclopropenium perchlorate (6) in dry tetrahydrofuran was added a equimolar amount of n-butyl lithium in n-hexane or methyl lithium in tetrahydrofuran at 0°C under argon atmosphere. After stirring for a few minutes, a transparent homogeneous solution of diaminotriafulvene 4 was obtained. Cooling this solution to -20°- -30°, 4 was obtained as colorless crystals. Diaminotriafulvene 4 is thermally unstable and gradually decomposes even at room temperature under inert atmosphere.



6 4

The ^{1}H-nmr spectrum of 4 obtained from 6 and methyl lithium in tetrahydrofuran-d_8 showed signals at 4.20 (4H, $-C\underline{H}(CH_3)_2$), 2.50 (2H, exo-CH_2-), 1.41 (24H, $-CH(C\underline{H}_3)_2$). The significantly large upfield shift of the exo-methylene protons is most likely due to a large contribution of dipolar form (4B) to the resonance hybrid. In the present system, contribution of immonium structures (4C and 4D) must be large to the ground state. Results of simple Hückel MO calculation in the system 4 support the importance of the polar canonical struc-



tures 4B - 4D.

Charge densities and bond orders calculated by HMO are shown in Figure 1. The charge density on the C_4 carbon was estimated as 1.551 suggesting considerable intramolecular charge transfer from the three-membered ring to this carbon. From the charge density of the nitrogen atom (1.812), electron-donating nature of the amino group was strongly supported. Calculated π-bond order of the exo-cyclic double bond (0.691) clearly shows the decrease of double bond character.

Reaction indices such as the superdelocalizabilities (S_E),[8] the localization energies (L_r)[9] and the free valences (F_r)[10] as well as the charge densities (q_r) are given in Table 1. All the indices in Table 1 predict the high reactivity at the exocyclic carbon (C_4). Indeed, diaminotriafulvene 4 reacts with various electrophiles at the C_4 carbon as is shown in Scheme 1.

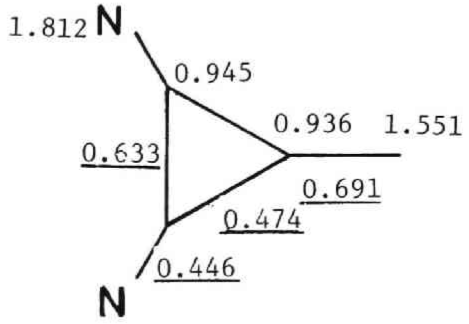
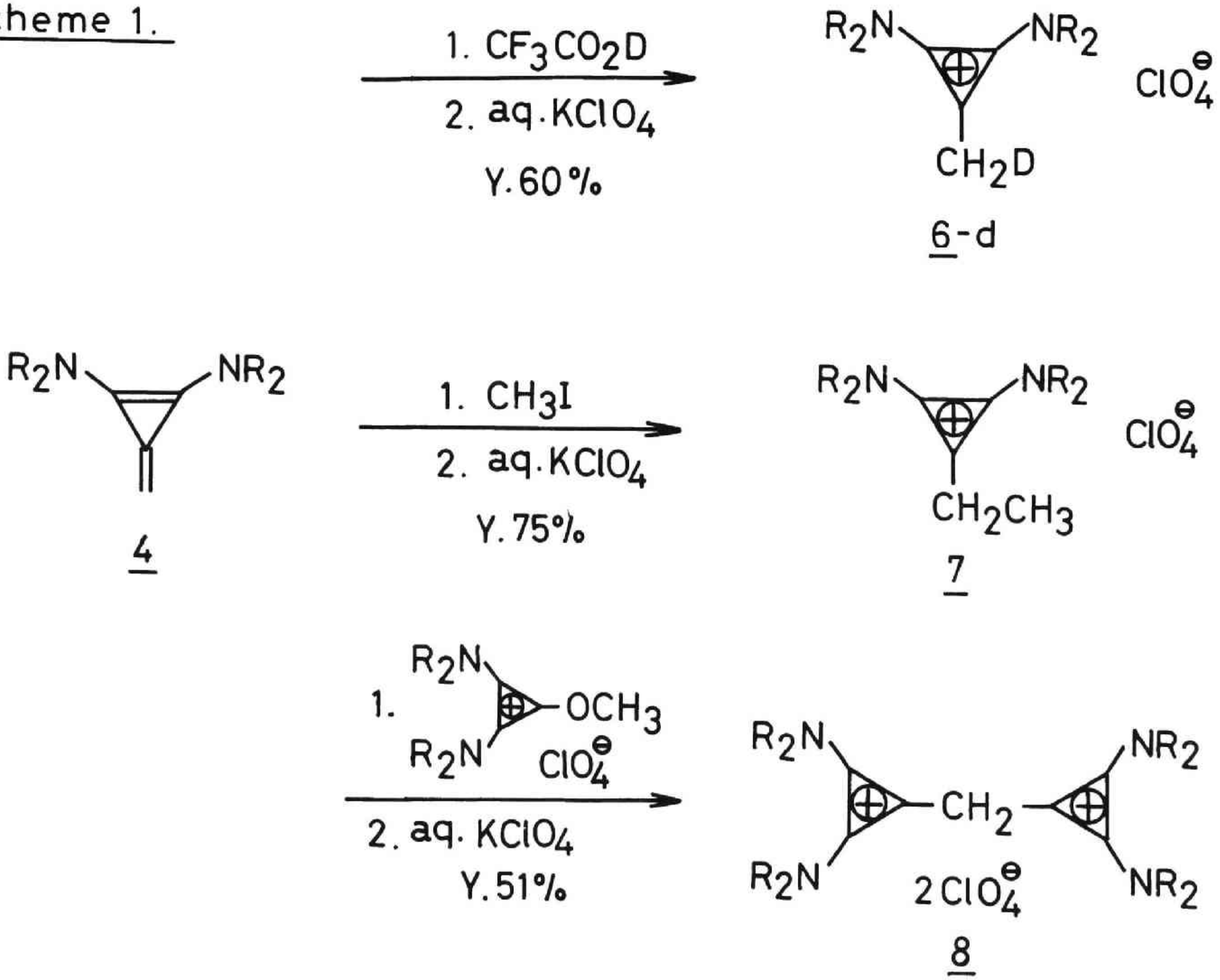


Figure 1. Charge Density and Bond Order in 4 by HMO

Table 1. Reaction Indices in 4

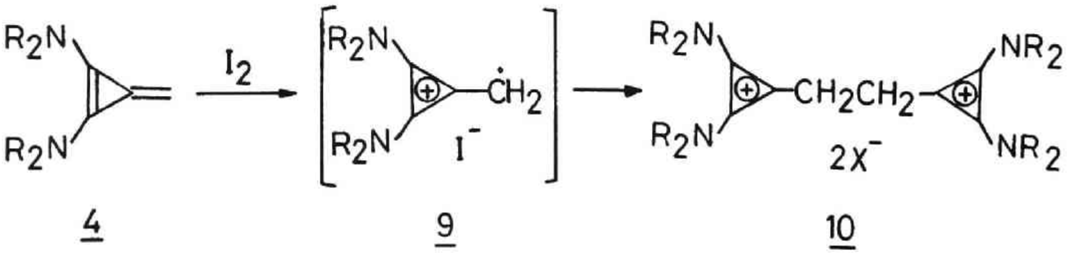
	q_r	S_E	$L(-\beta)$	F_r
C_1	0.936	0.7	3.080	0.093
C_2	0.945	10.2	2.111	0.179
C_4	1.551	40.3	0.813	1.041

Scheme 1.


1. CF_3CO_2D
2. aq. $KClO_4$
Y. 60 %
1. CH_3I
2. aq. $KClO_4$
Y. 75%
1.
OCH_3
2. aq. $KClO_4$
Y. 51%
R_2N
NR_2
$ClO_4^{\ominus}$
CH_2D
CH_2CH_3
CH_2
$2\,ClO_4^{\ominus}$
4
6-d
7
8

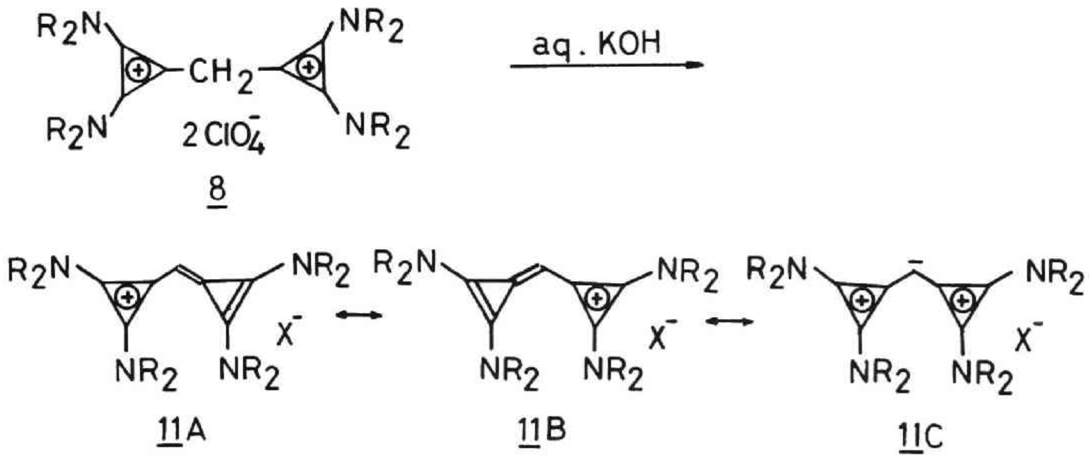
To the solution of 4 prepared from 6 and n-buthyl lithium was added trifluoroacetic acid-d. After treatment with aq. potassium perchlorate, deuterated diaminomethylcyclopropenium perchlorate (6-d) was obtained in 60% yield. The reaction of 4 with methyl iodide followed by treatment with potassium perchlorate gave diaminoethylcyclopropenium perchlorate (7) in 75% yield. Treatment of 4 with diaminomethoxycyclopropenium perchlorate afforded the methylene-bridged dication (8) in 51% yield.

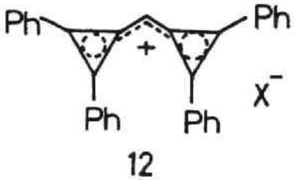
The oxidation reaction of 4 with iodine in tetrahydrofuran gave the ethylene-bridged dication (10) in 86% yield. In this reaction, the cation radical (9) of diaminotriafulvene 4 is considered as a key intermediate, subsequent dimerization of 9 to yield the dication 10. The facile oxidation of 4 observed here is in good agreement with an extremely small value of the calculated ionization potential (-0.0248 β ; 7.12 eV).



These cyclopropenium salts (6-d, 7, 8 and 10) obtained here are all colorless crystals and quite stable to air. Their structures have been confirmed on the basis of ^{1}H-nmr, ir spectra and elemental analyses. The ^{1}H-nmr spectrum of 6-d shows a triplet at δ 2.39 due to $-CH_2D$ group with the coupling constant $J_{H-D}=1.1$ Hz. The cations 6-d, 7, 8 and 10 exhibit characteristic absorptions at ca. 1900 cm^{-1} and ca. 1550 cm^{-1} in the ir spectra. The higher frequency band can be assignable to the framework deformation of the three-membered ring, and lower one to the C(ring)-N stretching mode .

The methylene-bridged dication 8 was easily deprotonated by aqueous potassium hydroxide to afford the interesting mesomeric salt (11). The perchlorate 11 is pale yellow plates and stable to air. The ir spectrum of 11 shows characteristic absorptions at 1900 and 1490 cm^{-1}. In the ^1H-nmr spectrum, the olefinic proton resonates at δ 4.00. This value is shifted to higher magnetic field than that of the corresponding tetraphenyl derivative 12 (δ 6.52)[11], indicating the importance of the tripolar canonical structure (11C).





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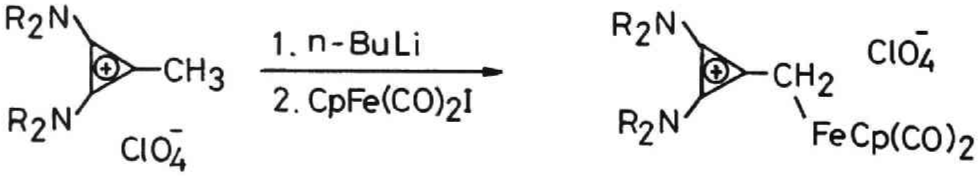
Synthesis and Structures of Triafulvene Iron Complex

Although fulvenes and fulvalenes are generally unstable, in many cases they can be stabilized as ligands in transition metal complexes[12]. A stable iron complex of diaminotriafulvene was synthesized and characterized.

To a solution of diaminotriafulvene in tetrahydrofuran prepared from <u>6</u> and n-butyl lithium was added a solution of cyclopentadienyl-irondicarbonyl iodide (<u>13</u>) in tetrahydrofuran at 0°C under argon atmosphere. The reaction mixture was stirred over night and yellow precipitate which deposited was collected by filtration.



<u>6</u> <u>14</u>

Recrystallization from acetone-ether gave yellow plates of <u>14</u> in 77% yield. The iron complex <u>14</u> is stable in crystalline form, however, the solution is considerably sensitive to air. The ^1H-nmr spectrum (Figure 2) reveals signals at δ 5.07 (s, 5H, Cp), 3.92 (sep, 4H, $-C\underline{H}(CH_3)_2$) and 1.35 (d, 24H, $-CH(C\underline{H}_3)_2$). The ir spectrum (Figure 3) of <u>14</u> shows absorptions at 2002 and 1955 cm^{-1} (CO stretching vibrations) and the characteristic absorptions at 1905 (ring deformation mode) and 1525 cm^{-1} (C-N stretching vibration).

In Table 2 are summarized the data of the carbonyl stretching vibrations as well as the chemical shifts of the cyclopentadienyl

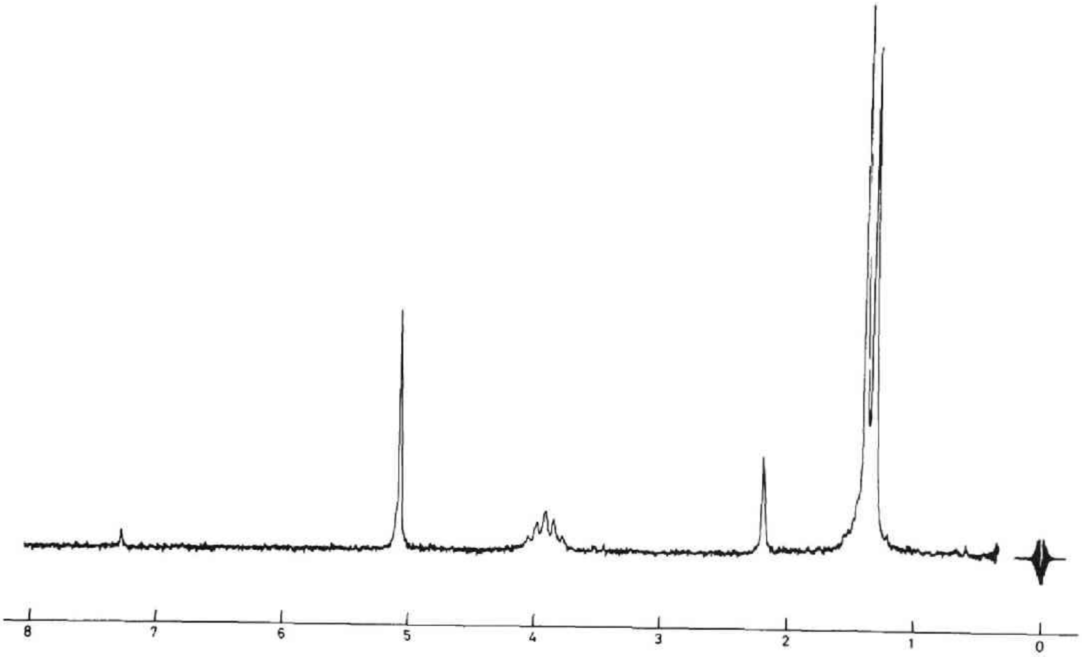


Figure 2. ^{1}H-nmr Spectrum of <u>14</u> in $CDCl_3$

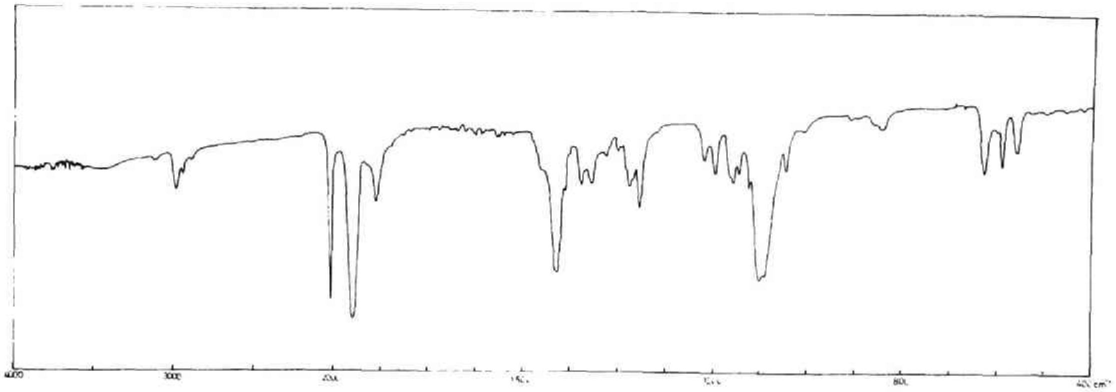


Figure 3. Infrared Spectrum of <u>14</u>

Table 2. Spectroscopic Data of 14 and related complexes

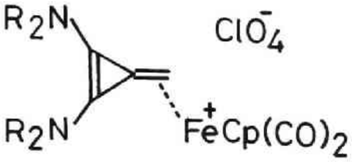
$RFe(CO)_2Cp$ (σ-complex)

R	ν_{CO} (cm^{-1})	Cp (δ)	$-CH_2$ (δ)
$(CH_3)_2CHCH_2-$	2013, 1945	4.64	1.47
$PhCH_2-$	2011, 1952	4.41	2.60
$PhCH_2CH_2-$	2006, 1951	4.56	1.60

alkene-$Fe^+(CO)_2Cp\ X^-$ (π-complex)

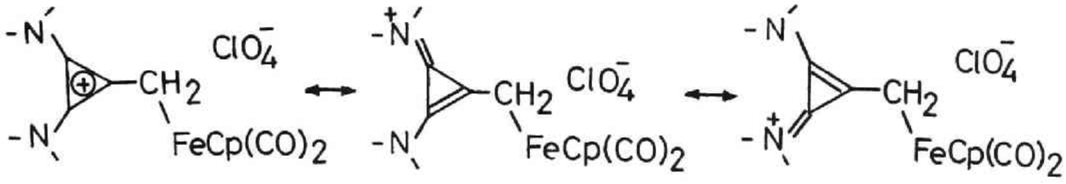
alkene	ν_{CO} (cm^{-1})	Cp (δ)	$-CH_2$ (δ)
$CH_2=CH_2$	2083, 2049	5.63	3.54
$(CH_3)_2C=CH_2$	2090, 2051	5.81	4.02
$PhCH=CH_2$	2082, 2040	5.87	4.4
14	2002, 1955	5.07	2.20
15	2033, 1986	5.27	3.49

protons and the methylene protons in various σ-complexes [$RFe(CO)_2Cp$] and π-complexes [$(alkene)Fe^+(CO)_2Cp\ X^-$][13]. In comparing these spectroscopic data, it is apparent that diaminotriafulvene iron complex 14 can be expressed by the σ-complex structure 14 rather than the π-complex structure (14'). The existence of the σ-bond between the



14'

exocyclic carbon and the iron atom is rationalized by the ^{13}C-nmr spectrum (Figure 4) of 14. The signal of the exo-methylene carbon appears at very high field (-18.8 ppm), clearly indicating 14 to be a σ-complex. The contribution of immonium structure (14B, 14C) is suggested by the high frequency of C-N stretching vibration (1525 cm^{-1}).



14A 14B 14C

It is notable that the heptafulvene iron complex synthesized by Kerber and Ehntholt[14] is reported to be represented as a resonance hybrid of the π-complex structure (15A) and the σ-complex structure (15B), the two structures contributing about equally.

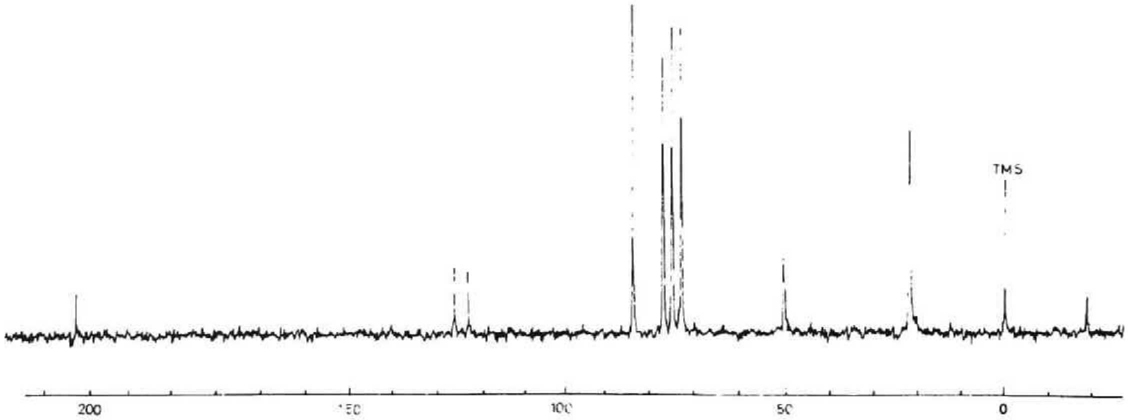


Figure 4. ^{13}C-nmr Spectrum of 14 in $CDCl_3$

In the diaminotriafulvene iron complex 14, it is doubtless that the dominant contribution of the σ-complex structure (14) can be attributable to the strong electron-donating effect of the amino groups.

15A 15B

EXPERIMENTAL

Bis(diisopropylamino)triafulvene (4)

To a suspension of 1,2-bis(diisopropylamino)-3-methylcyclopropenium perchlorate (6) 350 mg (1 mmol) in 3 ml of tetrahydrofuran was added n-butyl lithium (1.1 mmol) in hexane at 0°C under argon. After stirring for a few minutes, the suspension turned homogeneous. Cooling this solution to -20° - -30°C, colorless crystals of 4 are obtained.

1,2-Bis(diisopropylamino)-3-monodeuteriomethylcyclopropenium perchlorate (6-d)

To a solution of 4 prepared from 6 175 mg (0.5 mmol) and n-butyl lithium (0.55 mmol) in 3 ml of tetrahydrofuran was added trifluoroacetic acid-d at 0°C under argon. After stirring for 1 min, the reaction mixture was poured into aq. potassium perchlorate and extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was recrystallized from dichloromethane-ether to give the perchloric salt (6 + 6-d) 131 mg (80%) as colorless crystals. The ^{1}H-nmr spectrum of the product in $CDCl_3$ showed a triplet at δ 2.38 ($-CH_2D$, J_{H-D}=1.1 Hz). The deuteration is estimated as 80% based on the integral of this signal.

1,2-Bis(diisopropylamino)-3-ethylcyclopropenium perchlorate (7)

To a solution of 4 prepared from 6 350 mg (1 mmol) and n-butyl lithium (1.1 mmol) in 5 ml of tetrahydrofuran was added methyl iodide 0.5 ml (7.5 mmol) at 0°C under argon. After stirring for 30 min, the reaction mixture was poured into aq. potassium perchlorate and extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was recrystallized from dichloromethane-ether to afford 7 273 mg (75%) as colorless crystals; mp 107°C; ir (KBr, cm^{-1}) 1910, 1548, 1470, 1342, 1090, 623; uv (CH_3CN) λ_{max} 225 (sh, log ε 4.02); ^{1}H-nmr ($CDCl_3$) δ 3.96(m,4H,$-C\underline{H}(CH_3)_2$), 2.78(q,2H,$-CH_2-$), 1.38(d,24H, $-CH(C\underline{H}_3)_2$), 1.33(t,3H,$-CH_3$),

Anal. Calcd for $C_{17}H_{33}N_2ClO_4$: C, 55.95; H, 9.11; N, 7.68.
Found : C, 55.76; H, 8.89; N, 7.62.

1,2-Bis(diisopropylamino)-3-(diisopropylaminocyclopropenylio)cyclopropenium perchlorate (8)

To a solution of 4 prepared from 6 175 mg (0.5 mmol) and n-butyl lithium (0.55 mmol) in 3 ml of tetrahydrofuran was added 1,2-bis(diisopropylamino)-3-methoxycyclopropenium perchlorate 366 mg (1 mmol) in 3 ml of dichloromethane at 0°C under argon. After stirring over night, the reaction mixture was poured into aq. potassium perchlorate and extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was recrystallized from dichloromethane-ether to afford 8 349 mg (51%) as colorless crystals ; mp >300°C; ir (KBr, cm^{-1}) 1900, 1560, 1545, 1377,1355,1095,623; uv (CH_3CN) λ_{max} 242 (log ε 4.41); ^{1}H-nmr (CF_3CO_2H) δ 4.50 (s,2H,$-CH_2-$), 4.26 (sep, 4H, $-C\underline{H}(CH_3)_2$), 4.02 (sep, 4H,-C$\underline{H}$(CH$_3$)$_2$), 1.47 (d, 24H, -CH(C$\underline{H}_3$)$_2$), 1.44 (d, 24H, -CH (C$\underline{H}_3$)$_2$).

Anal. Calcd for $C_{31}H_{58}N_4Cl_2O_8$:

C, 54.30; H, 8.52; N, 8.17; Cl, 10.34; O, 18.67.

Found; C, 54.15; H, 8.58; N; 8.26; Cl, 10.53; O, 19.25.

1,2-Bis(diisopropylamino)-3-(diisopropylaminocyclopropenylioethyl)-cyclopropenium perchlorate (10)

To a suspension of 4 prepared from 6 350 mg (1 mmol) and n-butyl lithium (1.1 mmol) in 5 ml of tetrahydrofuran was added iodine 127 mg (0.5 mmol) in 2 ml of tetrahydrofuran. After stirring for 15 min, the reaction mixture was poured into aq. potassium perchlorate and extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was recrystallized from dichloromethane-ether to afford 10 303 mg (86%) as colorless crystals ; mp 298°C(dec) ;ir (KBr, cm^{-1}) 1906, 1555, 1463, 1375, 1353, 1095, 623; uv (CH_3CN) λ_{max} 239 (log ε 4.25) ; ^{1}H-nmr (CF_3CO_2H) δ 4.20 (sep,4H,-C$\underline{H}$(CH$_3$)$_2$), 4.02 (sep,4H, -C$\underline{H}$ (CH$_3$)$_2$), 3.30 (s,4H,-CH$_2$-), 1.50 (d,24H,-CH(C$\underline{H}_3$)$_2$), 1.47 (d,24H,-CH (C$\underline{H}_3$)$_2$).

Anal. Calcd for $C_{32}H_{60}N_4Cl_2O_8$: C, 54.93; H, 8.64; N, 8.01.

Found : C, 55.04; H, 8.72, N, 8.07.

1,2-Bis(diisopropylamino)-4-(diisopropylaminocyclopropenylio)triafulvene perchlorate (11)

A solution of the dication 8 120 mg (0.17 mmol) in 10 ml of dichloromethane was poured into aq. potassium hydroxide (450 mg in

50 ml of water) and stirred vigorously for 5 min at room temperature. The organic layer was separated, washed with water, and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue was crystallized from dichloromethane-ether to give 11 82 mg (82%) as pale yellow plates; mp 185°C; ir (KBr, cm^{-1}) 1900, 1490, 1442, 1339, 1215, 1155, 1093 ; ^1H-nmr ($CDCl_3$) δ 4.00 (s, 1H, olefin), 3.85 (sep, 4H, $-C\underline{H}(CH_3)_2$), 1.30 (d, 24H, $-CH(C\underline{H}_3)_2$).

Anal. Calcd for $C_{31}H_{57}N_4ClO_4$: C, 63.62; H, 9.82; N, 9.57.

Found: C, 63.85; H, 9.97; N, 9.43.

Diaminotriafulvene iron complex (14)

To a solution of 4 prepared from 6 200 mg (0.57 mmol) and n-butyl lithium (0.57 mmol) in 5 ml of tetrahydrofuran was added cyclopentadienylirondicarbonyl iodide (13) 173 mg (0.57 mmol) in 2 ml of tetrahydrofuran at 0°C under argon. After stirring over night, yellow precipitate which deposited was collected by filtration, washed with tetrahydrofuran and dried. Recrystallization from acetone-ether afforded 14 230 mg (77%) as yellow plates ; mp 189°C(dec) ; ir (KBr, cm^{-1}) 2002, 1955, 1905, 1525, 1351, 1095, 622, 587, 554 ; uv (CH_3CN) λ_{max} 340 (log ε 3.98); ^1H-nmr ($CDCl_3$) δ 5.08 (s, 5H, Cp), 3.92 (sep, 4H, $-C\underline{H}(CH_3)_2$), 2.20 (s, 2H, $-CH_2-$), 1.35 (d, 24H, $-CH(C\underline{H}_3)_2$) ; ^{13}C-nmr ($CDCl_3$) 215.4(CO), 127.8($C_{1,2}$), 124.6(C_3), 86.2(Cp), 51.2($-C\underline{H}(CH_3)_2$), 22.1($-CH(C\underline{H}_3)_2$), -18.8($-CH_2-$).

Anal. Calcd for $C_{23}H_{35}N_2ClO_6Fe$: C, 52.43; H, 6.70; N, 5.32.

Found: C, 52.30; H, 6.91; N, 5.40.

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CHAPTER 2

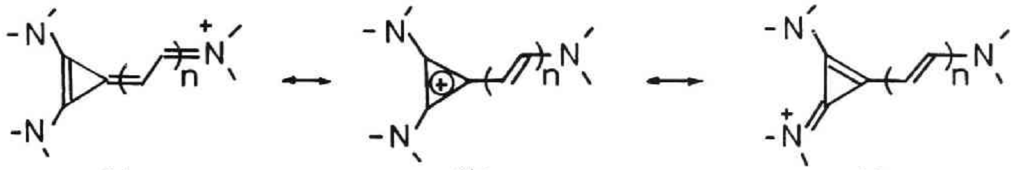
SYNTHESES AND STRUCTURES OF TRIAFULVENE IMMONIUM SALTS AND VINYLOGOUS DIAMINOTRIAFULVENES

SUMMARY

Triafulvene immonium salts (1, n=1,2) and vinylogous diaminotriafulvenes (5, n=1,2) are synthesized and characterized. The ^{1}H-nmr and ^{13}C-nmr spectra of 1 show delocalization of positive charge through the polymethine chain. According to the ^{1}H-nmr spectra of 5, polar canonical structures contribute markedly to the electronic structure at the ground state. Electronic spectra of these compounds exhibit large bathochromic shifts with the elongation of the polymethine chain.

INTRODUCTION

Triafulvene immonium salts (1, n=1,2) can be regarded as a kind of triafulvenes stabilized by immoniomethyl (n=1) or immoniopropenyl (n=2) group at the exo-methylene carbon. These salts are considered to be the resonance hybrid of triafulvene structure (1A), cyclopropenium structure (1B) and immonium structure (1C).


1A 1B 1C

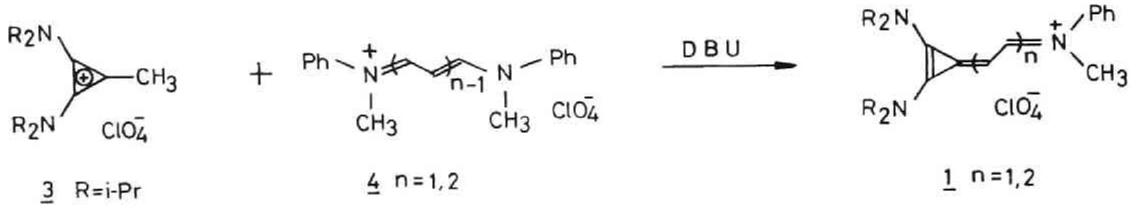

2A 2B

Jutz has been reported heptafulvene immonium salts (2, n=1,2), the higher π-electron homolog of 1, as deep colored materials[1]. This type of compounds is of interest as the non-benzenoid analog of cyanine dyes. In thischapter, the synthesis of 1 is described and the properties are discussed from the spectroscopic data. Futhermore, the preparation and characterization of vinylogous triafulvenes 5 (n=1,2), obtained from the reaction of 1 and malononitrile in the presence of diazabicycloundecene (DBU) are described.

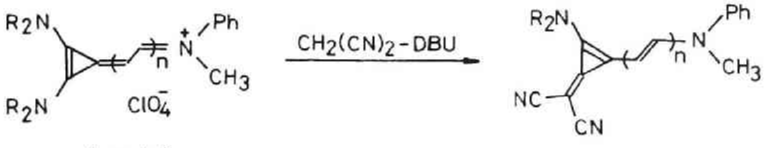
RESULTS AND DISCUSSION

Syntheses

Triafulvene immonium salts (1, n=1,2) were synthesized from the reaction of 1,2-bis(diisopropylamino)-3-metylcyclopropenium perchlorate (3) and polymethinium perchlorates[2] (4, n=1,2) in the presence of diazabicycloundecene (DBU). The products (1, n=1,2) were isolated as stable crystalline solid: 1 (n=1), 33% yield, pale yellow prisms, mp 113°C ; 1 (n=2), 65% yield, brilliant yellow plates, mp 201°C (dec).

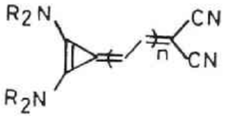


2,3-Diamino-4,4-dicyanotriafulvenes (5, n=0) have been synthesized as stable colorless crystals from the reaction of diaminochlorocyclopropenium ion and malononitrile in the presence of DBU. Treatment of the salts (1, n=1,2) with malononitrile in the presence of DBU gave vinylogous diaminotriafulvenes (5, n=1,2) : 5 (n=1), 7% yield, pale yellow prisms, mp 118°C; 5 (n=2), 5% yield, orange prisms, mp 161°C. The triafulvenes (5, n=1,2) are apparently the reaction products *via* the nucleophilic attack of the conjugated base of malononitrile o. at three-membered ring carbons. No products of type 6 *via* the attack at the side-chain carbon were obtained.



1 n=1,2

5 n=1,2



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Spectral Properties

^{1}H-nmr spectra

In the table 1 are summarized the ^{1}H-nmr parameters of the immonium salts (1, n=1,2) and the neutral triafulvenes (5, n=1,2). The ^{1}H-nmr spectrum of 1 (n=1) shows a pair of doublets (J=13.7 Hz) due to the olefinic protons (H_1 and H_2) at δ 7.67 and 5.10, respectively (Figure 1). In the ^{1}H-nmr spectrum of 1 (n=2), two olefinic protons appear at δ 5.87 and 5.68 as a doublet and doublets of doublet, respectively (Figure 2). The protons H_2 and H_4 resonate in aromatic region and are not assigned The vicinal coupling constants were estimated as $J_{1,2}$=15.0 Hz, $J_{2,3}$=11.0 and $J_{3,4}$=12.8. The relatively large values of the coupling constants $J_{1,2}$ and $J_{3,4}$ indicate the considerable double bond character for the C_1- C_2 bond and C_3- C_4 bond. This trend is best expressed by the canonical structures 1B and 1C. The transoid conformation of the side-chain has been confirmed from the values of the vicinal coupling constants. The similar phenomena were also observed in the series of 5 (n=1,2), indicating the importance of the structures 5A and 5B in the ground state. The ^{1}H-nmr

Table 1. ^1H-Nmr parameters of 1(n=1,2) and 5(n=1,2) in $CDCl_3$

1(n=1)	7.67(d,1H,H_2,J=13.7Hz),7.5-7.0(m,5H,Ph),5.10(d,1H,H_1,J=13.7),3.94(sep,4H,$-C\underline{H}(CH_3)_2$),3.37(s,3H,$N-CH_3$),1.37(d,24H,$-CH(C\underline{H}_3)_2$)
1(n=2)	7.5-7.0(m,7H,Ph+H_2+H_4),5.87(d,1H,H_1,J=15.0),5.68(dd,1H,H_3,J=12.8,11.0),4.00(sep,4H,$-C\underline{H}(CH_3)_2$),3.34(s,3H,$N-CH_3$),1.41(d,24H,$-CH(C\underline{H}_3)_2$)
5(n=1)	8.00(d,1H,H_2,J=12.9),7.5-7.0(m,5H,Ph),5.04(d,1H,H_1,J=12.9),4.03(sep,1H,$-C\underline{H}(CH_3)_2$),3.70(sep,1H,$-C\underline{H}(CH_3)_2$),3.33(s,3H,$N-CH_3$) 1.32(d,12H,$-CH(C\underline{H}_3)_2$)
5(n=2)	7.5-7.0(m,7H,Ph+H_2+H_4),5.78(d,1H,H_1,J=15.0),5.59(dd,1H,H_3,J=11.3,12.9),4.10(sep,1H,$-C\underline{H}(CH_3)_2$),3.70(sep,1H,$-C\underline{H}(CH_3)_2$),3.28(s,3H,$N-CH_3$),1.33(d,6H,$-CH(C\underline{H}_3)_2$),1.29(d,6H,$-CH(C\underline{H}_3)_2$)

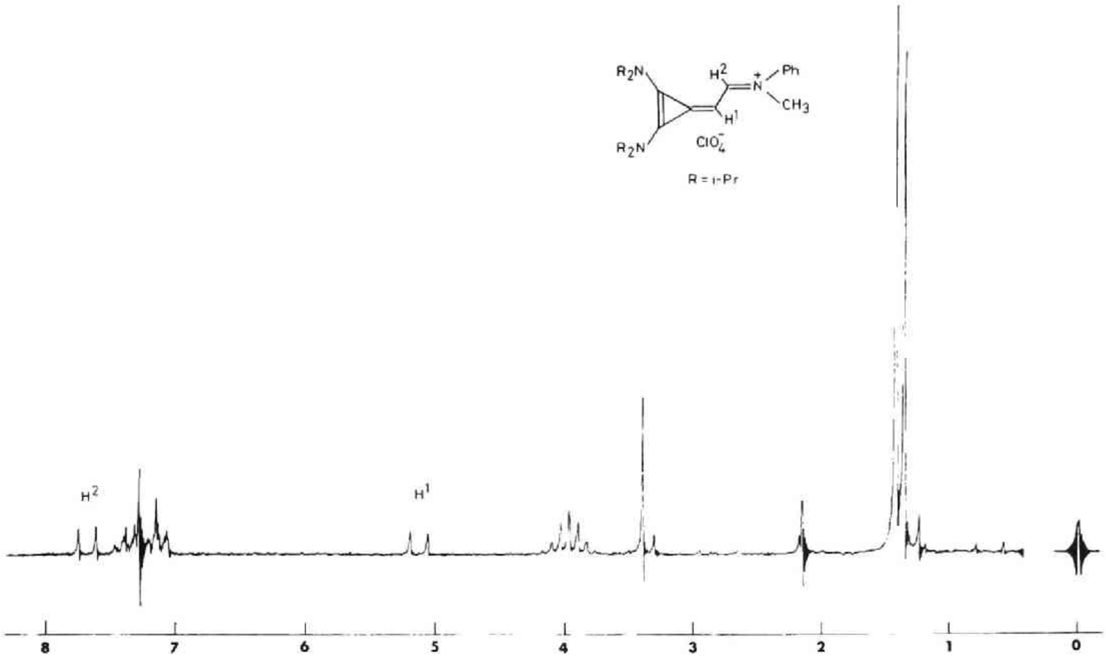


Figure 1. ^{1}H-nmr Spectrum of 1 (n=1) in $CDCl_3$

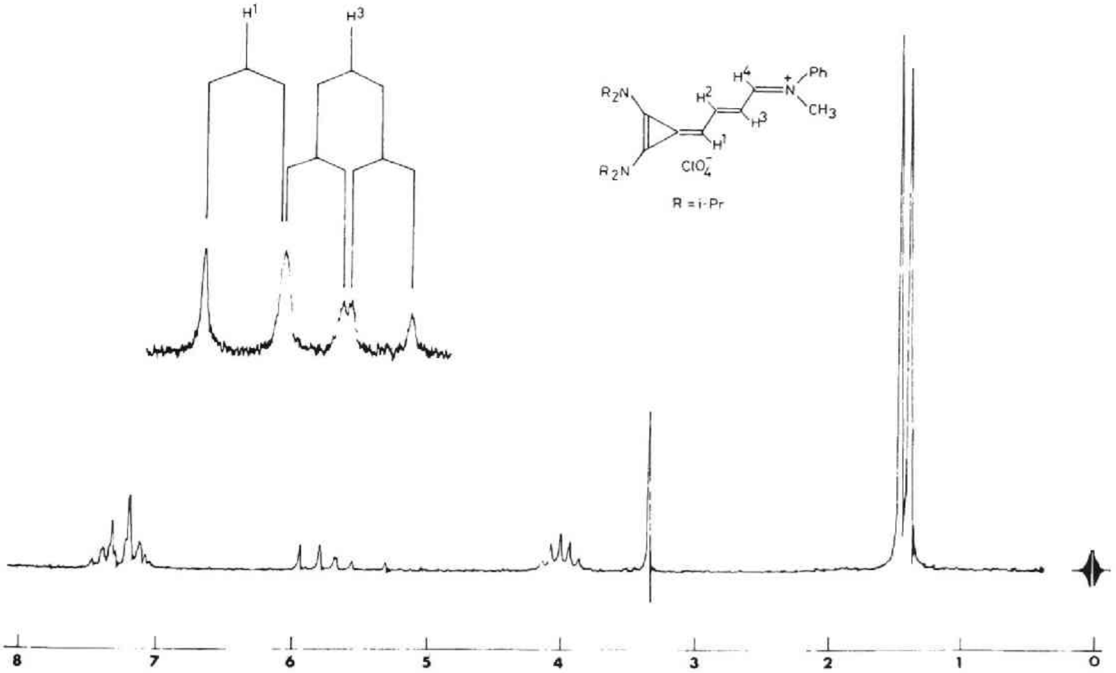


Figure 2. ^{1}H-nmr Spectrum of 1 (n=2) in $CDCl_3$

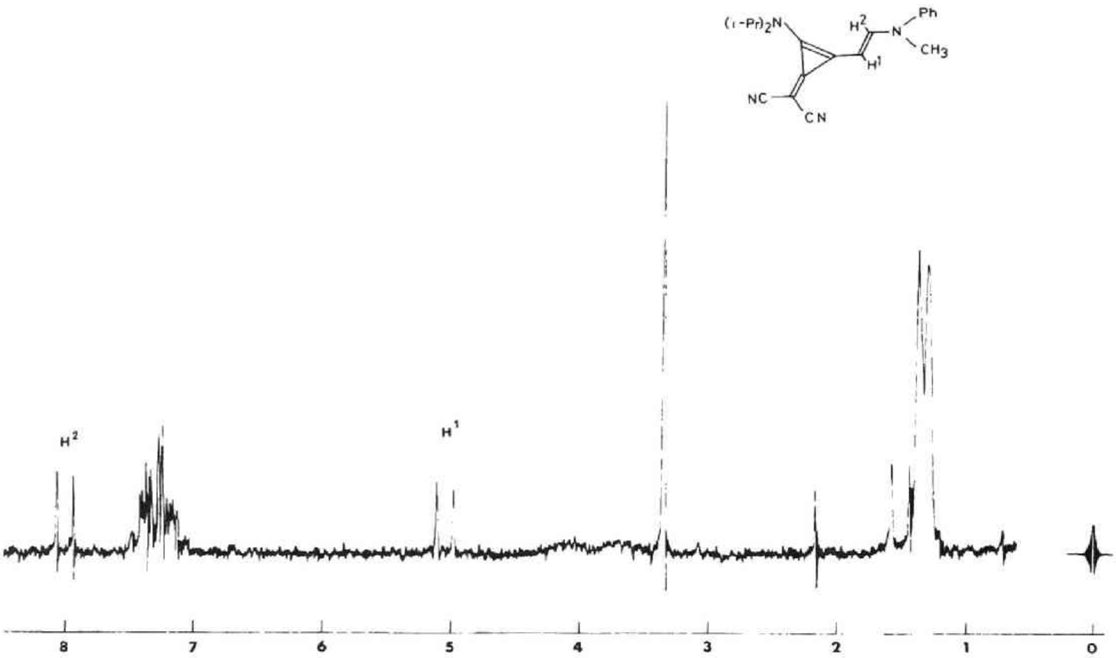


Figure 3. ^{1}H-nmr Spectrum of $\underline{5}$ (n=1) in $CDCl_3$

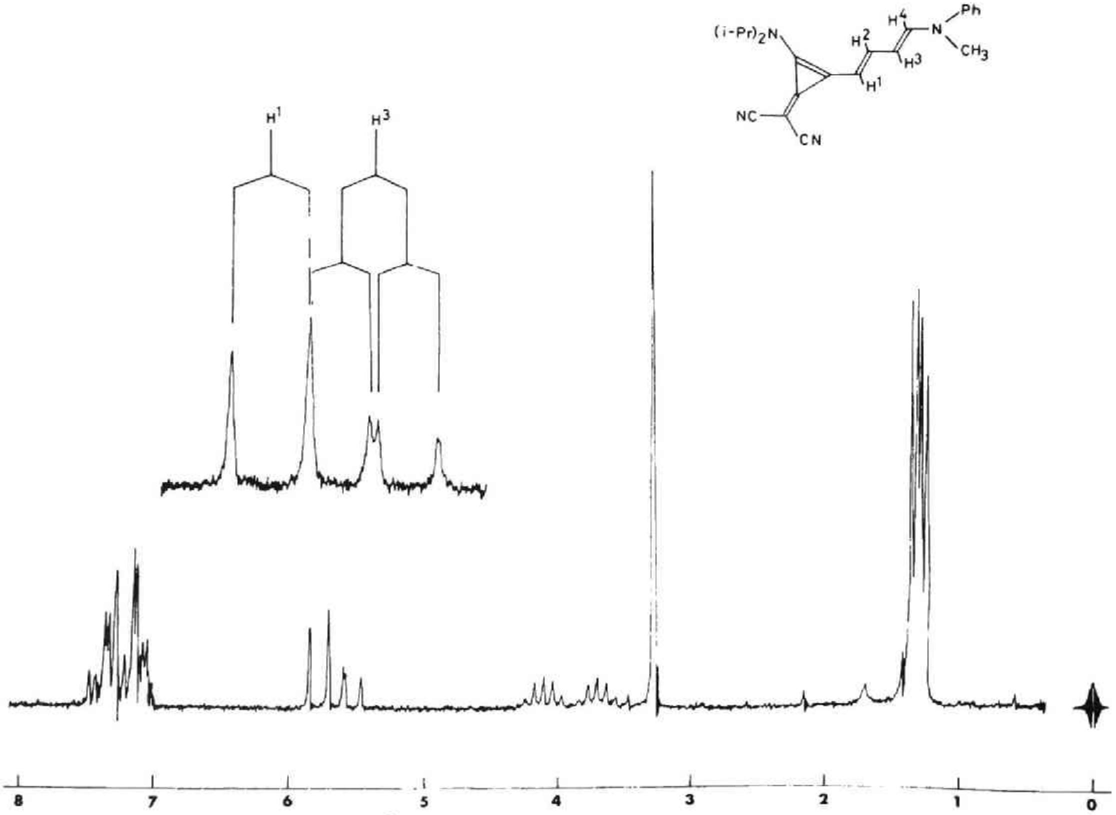
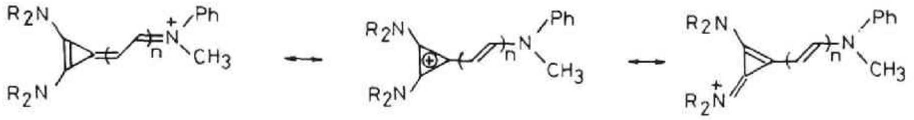
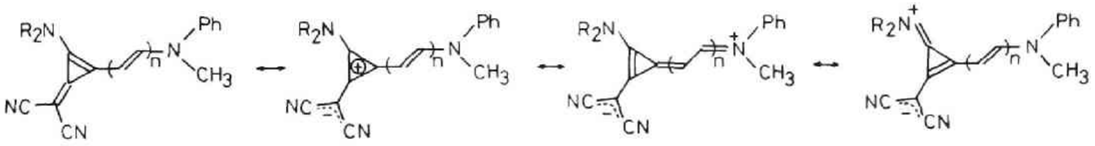


Figure 4. ^{1}H-nmr Spectrum of $\underline{5}$ (n=2) in $CDCl_3$

spectra of 5 (n=1,2) show two different sets of isopropyl groups (Figure 3,4), suggesting the non-equivalence of the isopropyl groups. This fact is interpreted in terms of the rotation barrier around the carbon (ring) - nitrogen bond, expressed by the canonical structure 5D.



1A 1B 1C



5A 5B 5C 5D

^{13}C-nmr spectra

The ^{13}C-nmr chemical shifts of the triafulvene immonium salts 1 (n=1,2) are summarized in Figure 5. In the compound 1 (n=1), the signal due to C_1 carbon appears at very high field (81.9 ppm), on the contrary C_2 carbon resonates at very lower field (147.1 ppm). These ^{13}C-nmr chemical shifts are in good agreement with the corresponding proton chemical shifts, H_1 (δ 7.67), H_2 (δ 5.10). The simmilar tendecy was observed in the case of 1 (n=2). The carbon C_1 and C_3 in 1 (n=2) resonate at much higher field (103.0 and 99.9 ppm respectively) than C_2 and C_4 (146.1 ppm). The shielding effect observed

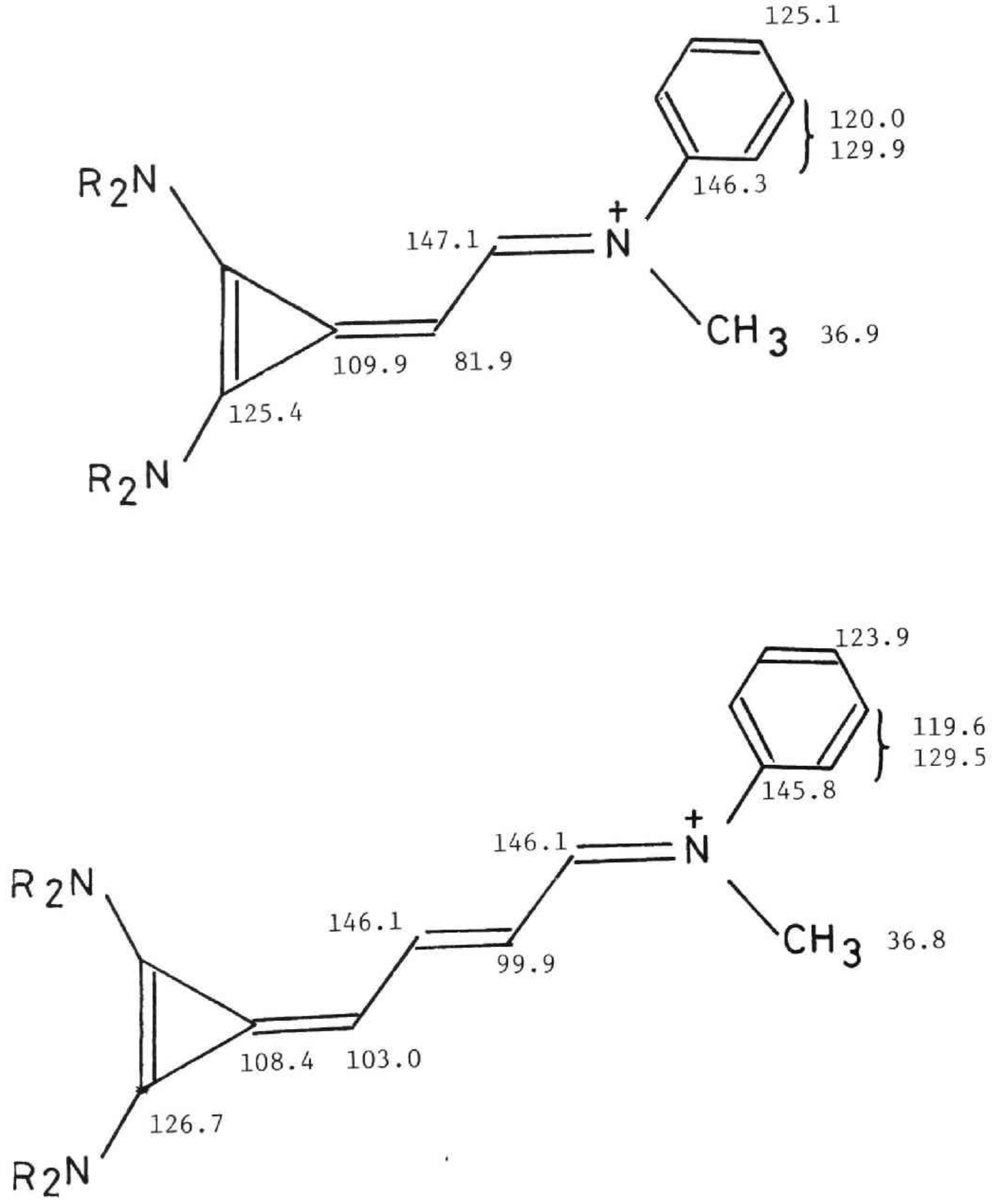
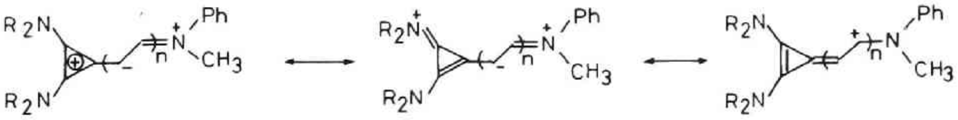


Figure 5. ^{13}C-Nmr Chemical Shifts of 1(n=1) (top) in $CDCl_3$ and 1(n=2) (bottom) in $CDCl_3$

on the C_1 and C_3 carbons suggests the higher electron densities on these carbons. On this basis, the charge separated structures (1D and 1E) are considered to play an important role for the stability of these triafulvene immonium salts. The low chemical shifts observed on the carbons C_2 and C_4 are rationalized by the inductive effect of the immonium group and by the contribution of the canonical structure 1F.



1D 1E 1F

Electronic spectra

The electronic spectra of the triafulvene immonium salts (1, n=1,2) and the triaminocyclopropenium ion[3] (1, n=0) are shown in Table 2 and Figure 6. Each compound showed two absorption maxima, and the shorter wave-length maximum showed small bathochromic shifts going from 1 (n=0) to 1 (n=2). On the contrary, the longer wave-length one exhibited large bathchromic shifts (ca. 50-60 nm per one vinyl group) with the elongation of the polymethine chain. It is noteworthy that the corresponding heptafulvene analogs[1] (2, n=1,2,3) have electronic absorptions at longer wave-length than 1 (n=0,1,2). For example, the heptafulvene immonium perchlorate 2 (n=2) is blue-black needles having the longest wave-length absorption at 560 nm[1], while the corresponding triafulvene derivative 1 (n=2) is brilliant yellow

Table 2. Electronic Spectra of 1(n=0,1,2) and 5(n=0,1,2) in CH_3OH

	λ_{max} (log ε)
1(n=0)	230 (4.18), 279 (4.45)
1(n=1)	234 (3.85), 342 (4.18)
1(n=2)	264 (3.52), 392 (4.09)
5(n=0)	241 (3.67), 282 (4.30)
5(n=1)	266 (4.46), 371 (4.42)
5(n=2)	280 (4.35), 410 (sh), 428 (4.62), 450 (sh)

crystals with the absorption maximum at 392 nm (Table 3). In the series of the neutral triafulvenes 5 (n=0,1,2)[4], the large bathochromic shifts and the increase of the intensities of the longer wavelength maxima were also observed with the extention of the π-delocalization area (Table 2 and Figure 7).

Ir spectra

In Table 3 are shown the ir spectra of the immonium salts 1 (n=0,1,2) and triafulvenes 5 (n=0,1,2). The bands at ca. 1900 cm^{-1} are considered to be due to the cyclopropenium ring deformation, and this band is infra-red inactive for the triaminocyclopropeninm ion 1 (n=0)[5]. In the ir spectra of 5 (n=0,1,2), two characteristic absorptions due to $C\equiv N$ stretching vibrations appear at ca. 2000 cm^{-1} (Table 3). The wave-numbers of these absorptions increase in the order of 5 (n=0) < 5 (n=1) < 5 (n=2). This fact indicates that the contribution of the polar canonical structures (5B, 5C and 5D) decreases accompanied with the elongation of the polymethine chain: 5 (n=0) > 5 (n=1) > 5 (n=2).

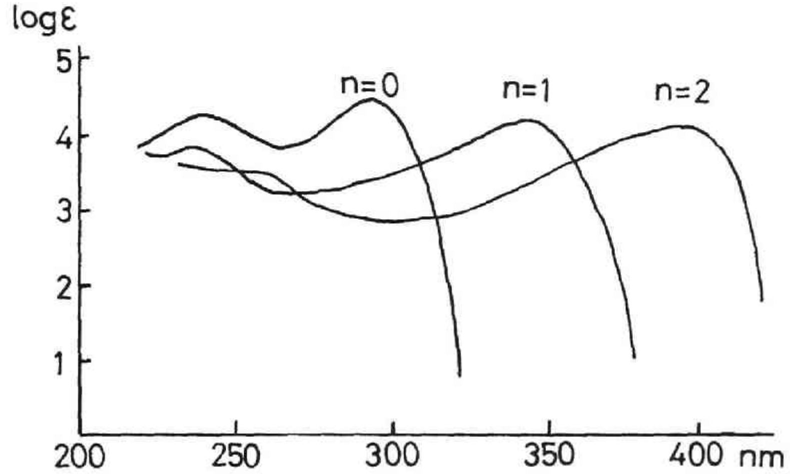


Figure 6. Electronic Spectra of 1 (n=0,1,2) in CH_3CN

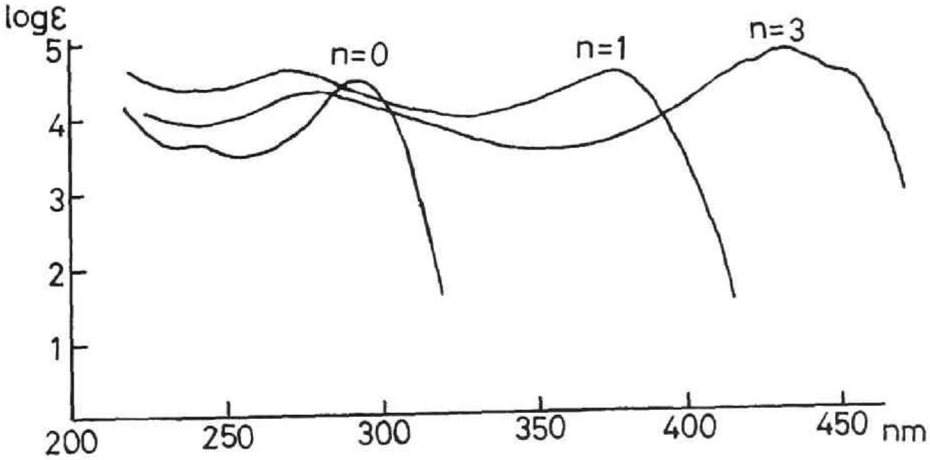


Figure 7. Electronic Spectra of 5 (n=0,1,2) in CH_3CN

Table 3. Infrared Spectra of 1(n=0,1,2) and 5(n=0,1,2) (KBr, cm^{-1})

1(n=0)	1530, 1512, 1492, 1411, 1404, 1100
1(n=1)	1910, 1617, 1594, 1530, 1456, 1354, 1097
1(n=2)	1903, 1620, 1578, 1537, 1447, 1338, 1097
5(n=0)	2188, 2163, 1922, 1505, 1440, 1350
5(n=1)	2198, 2170, 1906, 1616, 1591, 1500, 1450, 1355, 1328, 1311
5(n=2)	2198, 2177, 1882, 1615, 1592, 1577, 1497, 1436, 1418, 1347

EXPERIMENTAL

1,2 -Bis(diisopropylamino)-4-(methyl-phenyl-immoniomethyl)-triafulvene perchlorate 1 *(n=1)*

To a solution of 1,2-bis(diisopropylamino)-3-methylcyclopropenium perchlorate 3 350 mg(1 mmol) and bis(N-methylanilino)carbonium perchlorate 4 (n=1) 425 mg (1 mmol) in 5 ml of dichloromethane was added 0.5 ml of diazabicycloundecene (DBU) and stirred at room temperature for 2 days. The mixture was poured into water and extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel with benzene-acetone (7:3) as eluent. Crystallization of pale yellow band from acetone-ether gave 156 mg (33%) of 1 (n=1) as pale yellow prisms; mp 113°C.

Anal. Calcd for $C_{24}H_{38}N_3ClO_4$: C, 61.59; H, 8.18; N, 8.98.

Found : C, 61.86; H, 7.92; N, 8.89.

1,2-Bis(diisopropylamino)-4-[3-(methyl-phenyl-immonio)-Δ^1-propenyl]-triafulvene perchlorate 1 *(n=2)*

To a mixture of 3 1.00 gr (2.86 mmol) and 1,3-bis(N-methylanilino)-propenium perchlorate 4 (n=2) 1.10 gr (3.14 mmol) in 5 ml of dichloromethane was added 1 ml of DBU and stirred at room temperature for 3 days. The reaction mixture was poured into water and extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel using benzene-acetone (7:3) as eluent. Crystallization of yellow band from acetone-ether gave 918 mg (65%) of 1(n=2) as brilliant yellow plates; mp 201°C(dec).

Anal. Calcd for $C_{26}H_{40}N_3O_4Cl$: C, 63.20; H, 8.16; N, 8.50.
Found : C, 63.37, H, 8.28; N, 8.57.

1-Diisopropylamino-2-(2-N-methylanilinovinyl)-4,4-dicyanotriafulvene 5 (n=1)

To a mixture of the triafulvene immonium salt (1, n=1) 300 mg (0.67 mmol) and malononitrile 81 mg (1.23 mmol) in 3 ml of dichloromethane was added 0.3 ml of DBU and stirred at room temperature for 4 days. The mixture was poured into water and extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel using benzene-acetone (8:2) as eluent. Crystallization from ether-cyclohexane gave 16 mg (7%) of 5 (n=1) as pale yellow prisms; mp 118°C.

Anal. Calcd for $C_{21}H_{24}N_4$: C, 75.87; H, 7.28; N, 16.85.
Found : C, 76.07, H, 7.32; N, 17.06.

1-Diisopropylamino-2-(4-N-methylanilino-$\Delta^{1,3}$-butadienyl)-4,4-dicyanotriafulvene 5 (n=2)

To a mixture of the triafulvene immonium salt (1, n=2) 918 mg (1.86 mmol) and malononitrile 130 mg (2.00 mmol) in 3 ml of dichloromethane was added 0.3 ml of DBU and stirred at room temperature for 3 days. The mixture was poured into water and extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel using benzene-acetone (8:2) as eluent. Crystallization from ether-cyclohexane gave 30 mg (5%) of 5 (n=2) as orange prisms; mp 161°C.

Anal. Calcd for $C_{23}H_{26}N_4$: C, 77.06; H, 7.31; N, 15.63.
Found: C, 77.27; H, 7.36; N, 15.71.

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CHAPTER 3

SYNTHESIS AND STRUCTURES OF 5,6-DIAMINOCALICENES

SUMMARY

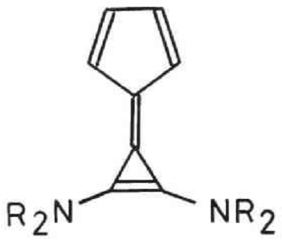
Various 5,6-diaminocalicenes are prepared from the reaction between diaminochlorocyclopropenium and cyclopentadienides, and their physical properties are characterized by ir, uv, ^{1}H-nmr and ^{13}C-nmr spectra. The strong interaction between amino group and calicene system is suggested and the evidence for the aromaticity of the diaminocalicene is provided.

INTRODUCTION

The calicene (cyclopropenylidenecyclopentadiene) system (1) could be of interest from the theoretical and organic point of view, because a significant contribution of resonance form (1B) would be expected to the ground state. Roberts and Streitwieser[1] have

1A 1B

predicted from the results of the simple Hückel MO calculation that calicene has a substantial π-electron delocalization energy and hence to be a reasonably stable system with aromatic properties. Recent calculations[2], however, have led to the conclusion that calicene is essentially a polyolefin possessing negligible resonance energy. Several calicene derivatives have been successfully prepared and discussed about their electronic structures[3]. Nevertheless, the parent calicene and even the simple derivatives with any substituent on the five-membered ring have never been reported[4]. Recently, it has been reported[5] that amino group dramatically stabilizes a wide variety of cyclopropenyl compounds. Thus, 5,6-diaminocalicene (2) is expected to be stable from the striking electronic effect of amino



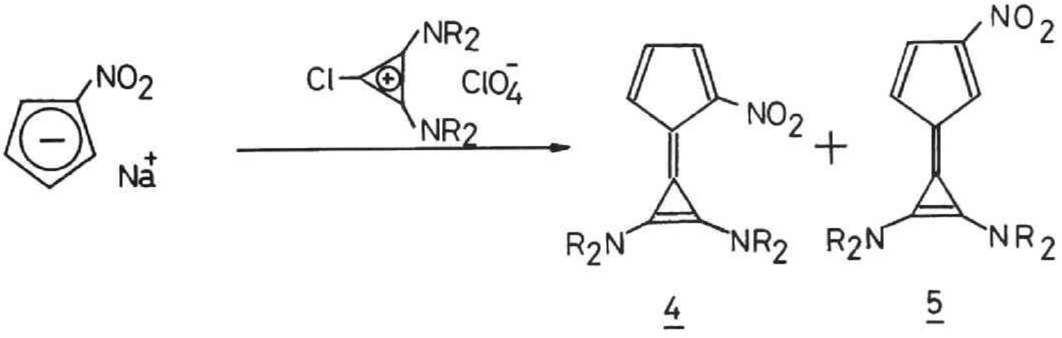
2

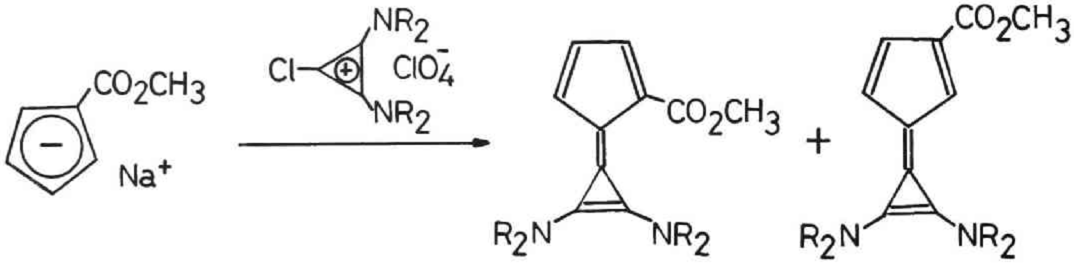
groups. In this chapter, the synthesis and structures of various 5,6-diaminocalicene are described and the aromaticity of the diaminocalicene system 2 is discussed from the spectroscopic data.

RESULTS AND DISCUSSION

Synthesis

Five-membered ring substituted diaminocalicenes were synthesized from the reaction of the corresponding cyclopentadienide and diaminochlorocyclopropenium. The mixture of sodium nitrocyclopentadienide and 1,2-bis(diisopropylamino)-3-chlorocyclopropenium perchlorate (3) was stirred in ethanol at room temperature. 1-Nitro-5,6-diaminocalicene (4) and 2-nitro-5,6-diaminocalicene (5) were separated from the reaction mixture as yellow crystals in 32 and 15% yield, respectively. The reaction of sodium methoxycarbonylcyclopentadienide and 3 gave pink crystals of 1-methoxycarbonyl- and 2-methoxycarbonyl derivatives (6 and 7) in 2 and 60% yield, respectively. Dicyano derivatives (8, 9) were obtained from the reaction of tetramethylammonium 1,2-dicyanocyclopentadienide and 3 as colorless crystals in 23 and 12% yield, respectively. Thus obtained 5,6-diaminocalicenes are quite stable in air without decomposition in several months.





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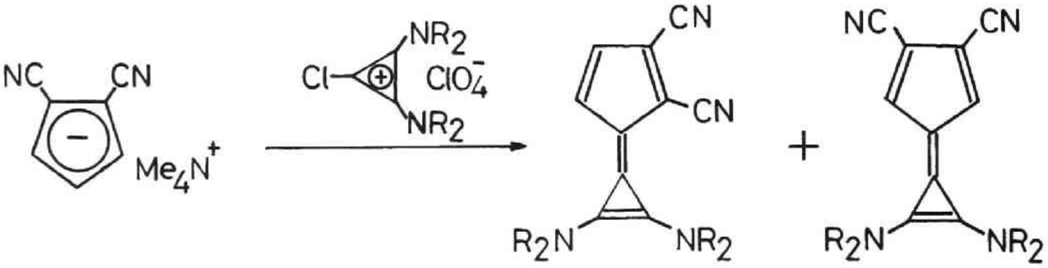
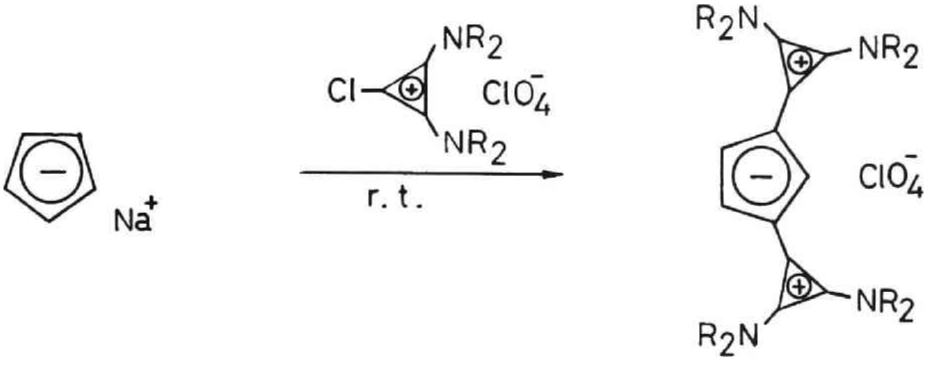


8 9

An attempt to prepare a 5,6-diaminocalicene which has no substituent on the five-membered ring from the reaction of unsubstituted cyclopetadienide and diaminochlorocyclopropenium 3 at room temperature gave a tripolar mesomeric salt (10)[6]. Treatment of sodium cyclopentadienide and diaminochlorocyclopropenium 3 at room temperature gave 1,3-bis(diaminocyclopropenilio)cyclopentadienide perchlorate 10 as pale green crystals in 54% yield. No other isolable products were obtained. The formation of the tripolar compound 10 strongly suggests the existence of the 5,6-diaminocalicene as a reaction intermediate. High reactivity of the diaminocalicene accelerates the introduction of the second diaminocyclopropenium ion to the electron-rich five-membered ring at ambient temperature. It has been found that the second substitution with diaminocyclopropenium group



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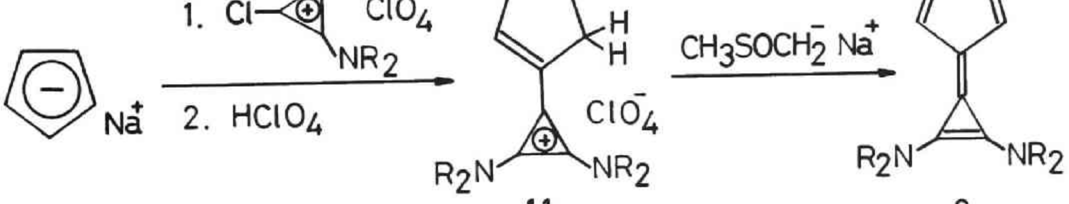
can be avoided by carring out the reaction at lower temperature. To a tetrahydrofuran **solution** of sodium cyclopentadienide was added 3 in dichloromethane at -70°. The mixture was stirred at -30° for 1 hr and then treated with dilute perchloric acid. Extraction with dichloromethane followed by recrystallization gave pale yellow needles of the protonated calicene (11) in 93% yield. The structure of 11 was confirmed by the spectral data and the elemental analysis. Deprotonation of 11 by using dimethylsulfinyl anion in dimethylsulfoxide gave the 5,6-diaminocalicene (2) in 82% yield. The calicene 2 is colorless crystals and fairly stable in air in crystalline form, however, 2 is rapidly oxidized in the solution.



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Spectra

In the infrared spectra, 5,6-diaminocalicenes show two bands in the regions 1910 - 1890 and 1480 - 1530 cm^{-1}(Table 1 and Figure 1-4). These bands are characteristic of calicene system. It has been considered that the higher wave-number band is due to the stretching of the cyclopropene double bond and the lower one to the stretching of the pivotal bond. S.Andreades[7] reported, however, that these two modes are strongly coupled on the basis of normal coordinate analysis. Futhermore, the lower band is considered to be strongly coupled with the C-N stretching vibrations. The nitro derivatives <u>4</u> and <u>5</u> show signals due to the symmetric stretching vibration of nitro group at 1373 and 1351 cm^{-1} respectively. The carbonyl stretching vibrations of <u>6</u> and <u>7</u> were found at 1658 and 1662 cm^{-1} respectively. These shifts to lower wave numbers are attributed to the conjugation of carbonyl group with calicene system. In the spectrum of the 1,2-dicyano derivative <u>8</u>, the C≡N stretching bands appeared at 2190 and 2180 cm^{-1}, while the symmetrical isomer <u>9</u> showed only one signal at 2190 cm^{-1}.

The electronic spectrum of unsubstituted diaminocalicene <u>2</u> shows strong absorption at 338 nm (log ε 4.58) with shoulders at 255 and 222 nm (Table 2). This absorption can be assigned to a transition involving intramolecular charge transfer. The absorption maximum shifts to longer wave-length with decrease in polarity of solvent : 336 (EtOH), 338 (CH_3CN), 340 (CH_2Cl_2), 342(C_6H_{12}) and 345 (C_6H_6). A solvent effect of this type can be interpreted as resulting

Table 1. Characteristic Infrared Absorption of 5,6-Diaminocalicenes (cm^{-1}, KBr disk)

compound	substituent	absorptions			
2	none	1900,	1490		
4	1-NO_2	1904,	1525,		1375 (ν_{s-NO_2})
5	2-NO_2	1895,	1513,		1351 (ν_{s-NO_2})
6	1-CO_2CH_3	1895,	1504,		1658 (ν_{CO})
7	2-CO_2CH_3	1897,	1500,		1662 (ν_{CO})
8	1,2-$(CN)_2$	1900,	1520,	1502,	2190, 2180 (ν_{CN})
9	2,3-$(CN)_2$	1905,	1523,	1502,	2190 (ν_{CN})
10	2-$C_3^+(NR_2)_2$	1895,	1510,	1480	

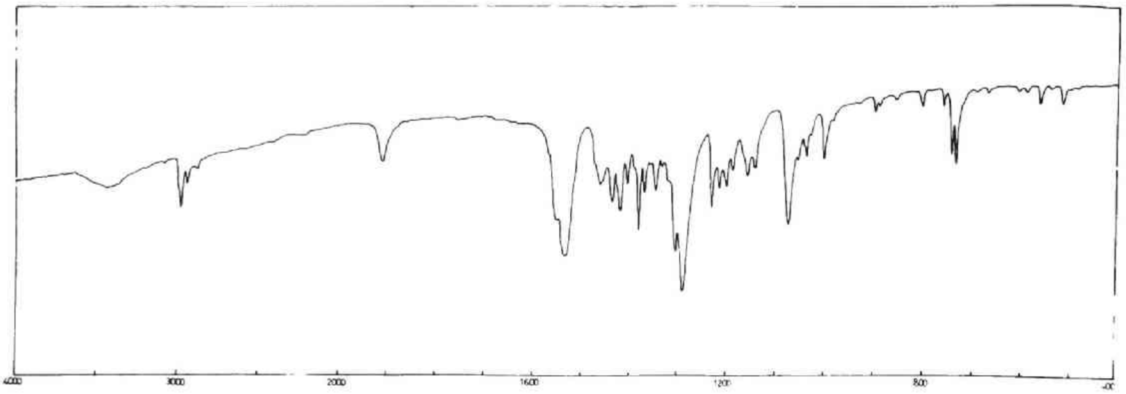


Figure 1. Infrared Spectrum of 4

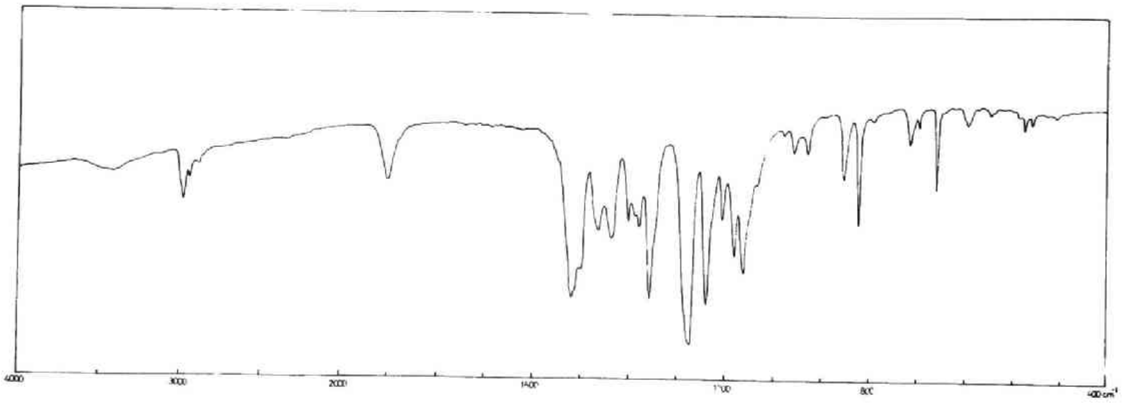


Figure 2. Infrared Spectrum of 5

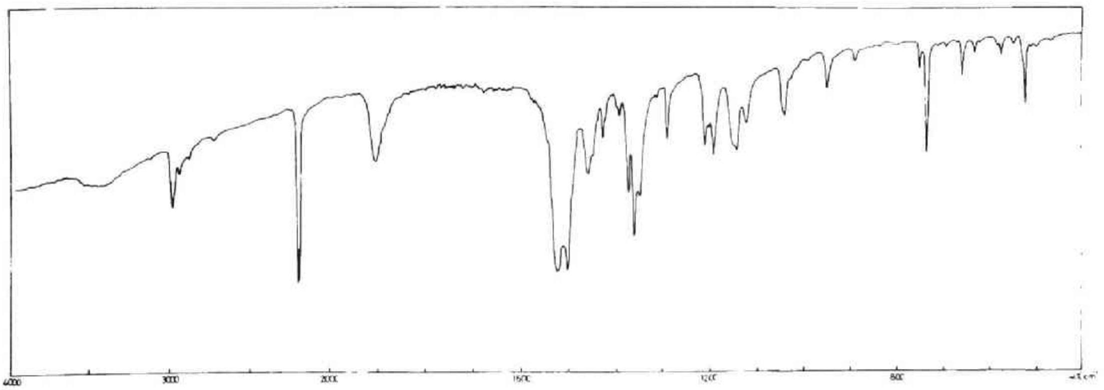


Figure 3. Infrared Spectrum of 8

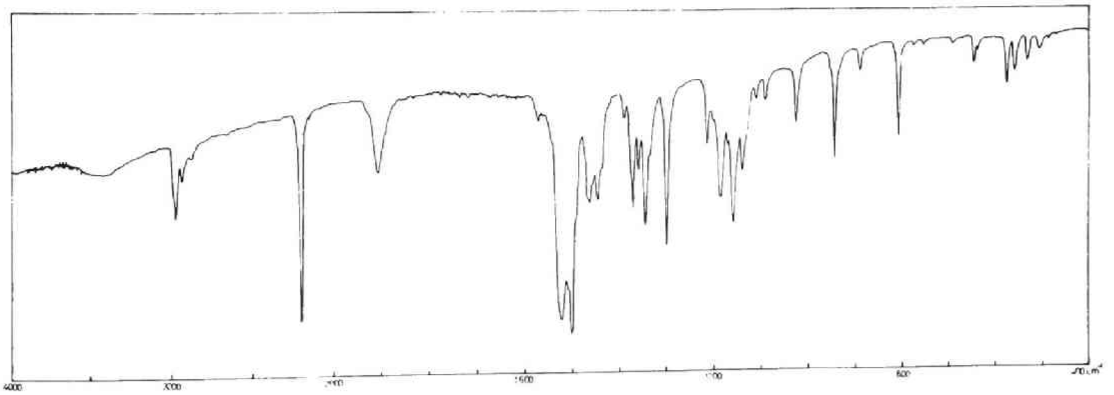
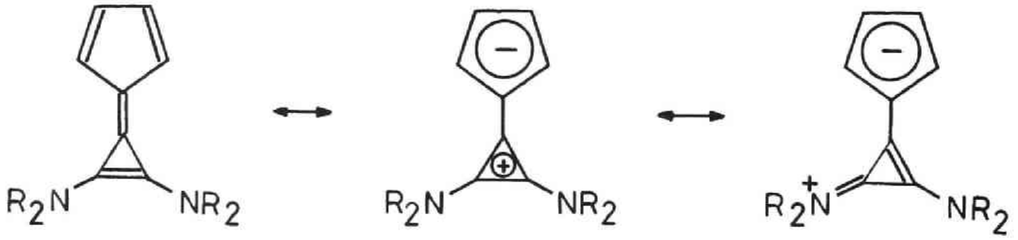


Figure 4. Infrared Spectrum of 9

from a transition to an exited state which is less polar than the ground state[8]. This result suggests that the contribution of polar canonical structures (2B and 2C) are important in the ground state.


2A 2B 2C

Similar solvent effect was also observed for the substituted diaminocalicenes. In Table 3 is shown the result of 2,3-dicyano-5,6-diaminocalicene 9 with that of 2,3-dicyano-5,6-diphenylcalicene (12)[9]. The degree of the shift is larger in the diaminocalicene 9 compared with that of the diphenyl derivative 12. This fact provides the evidence of the strong π-conjugative interaction between the amino group and the calicene system.

Table 3.

Solvent Effect of the Absorption Maxima of 9 and 12

	C_6H_6	$CHCl_3$	CH_2Cl_2	EtOH	CH_3CN
9	335	329	325	320	314 nm
12	358	354	352	349	347 nm

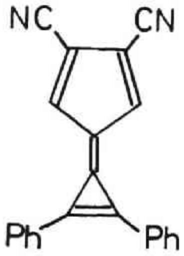

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Table 2. Electronic Spectra of 5,6-Diaminocalicenes (nm, CH_3CN)

compound	substituent	λ_{max} (log ε)
2	none	222 (sh), 255 (sh), 338 (4.58)
4	1-NO_2	275 (4.05), 387 (4.40)
5	2-NO_2	236 (4.26), 294 (4.33), 414 (4.55)
6	1-CO_2CH_3	228 (sh), 299 (4.03), 342 (3.99)
7	2-CO_2CH_3	225 (sh), 245 (4.29), 341 (4.59)
8	1,2-$(CN)_2$	256 (sh), 295 (4.18), 325 (sh)
9	2,3-$(CN)_2$	223 (4.30), 254 (4.39), 259 (sh), 314 (4.47), 323 (sh)
10	2-$C_3^+(NR_2)_2$	245 (4.34), 275 (sh), 367 (4.70), 384 (4.73)

The ^1H-nmr spectral data were summarized in Table 4. 5,6-Diaminocalicene 2 showed signals at δ 1.42 (d, 24H, $-CH(CH_3)_2$), 4.04 (sep, 4H, $-CH(CH_3)_2$), 6.22 (m, 2H, H_2 and H_3) and 6.62 (m, 2H, H_1 and H_4) (Figure 5). The latter two signals assigned to the ring protons were analysed as an AA'BB' type. The spectrum in Figure 5 was satisfactorily reproduced using computer simulation technique with coupling constants $J_{1,2}$= 4.0, $J_{2,3}$= 2.8, $J_{1,3}$= 1.9 and $J_{1,4}$= 2.1 Hz. The simulated spectrum is given in Figure 6. According to the relationship[10] between the π-bond order ($p_{r,s}$) and the vicinal coupling constant : $J_{vic} = 7.12\ p_{r,s} - 1.18$, $p_{1,2}$ and $p_{2,3}$ were estimated as 0.73 and 0.56 respectively. The π-bond orders calculated by the Hückel MO method were found to be $p_{1,2}$= 0.67 and $p_{2,3}$= 0.63 (Figure 4).

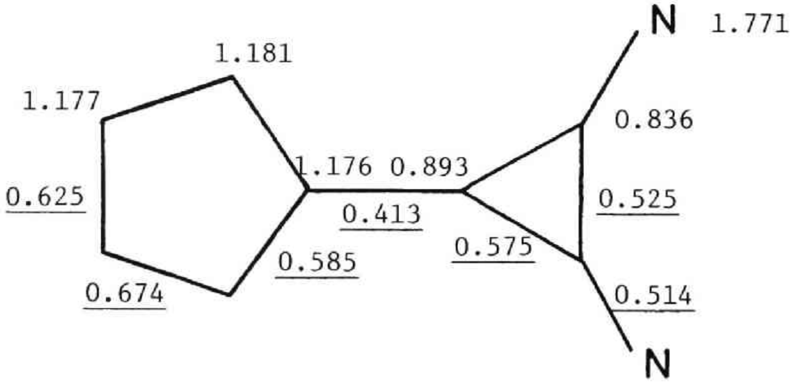


Figure 4. π-Bond Order and π-Electron Density in 2 by HMO

Table 4. ^{1}H-nmr Parameters of 5,6-Diaminocalicenes in $CDCl_3$ (δ values)

	$-C\underline{H}_3$	$-C\underline{H}$	five-membered ring protons	others
2	1.41	4.04	6.22(AA'BB',$H_{2,3}$),6.62(AA'BB',$H_{1,4}$)	
4	1.34	3.93	6.01(dd,H_3,J=4.4,3.3),6.15(dd,H_4,J=3.3,2.2),6.94(dd,H_2,J=4.4,2.2)	
5	1.43	4.06	6.34(dd,H_4,J=4.8,2.5),6.79(dd,H_3,J=4.8,2.2),7.25(dd,H_1,J=2.5,2.2)	
6	1.26	3.98	5.72(dd,H_3,J=3.8,3.4),6.03(dd,H_4,J=3.4,2.0),6.36(dd,H_2,J=3.8,2.0)	3.50(CO_2CH_3)
7	1.42	4.06	6.49(dd,H_4,J=4.4,2.3),6.69(dd,H_3,J=4.4,2.0),7.24(dd,H_2,J=2.3,2.0)	3.76(CO_2CH_3)
8	1.30	4.07	6.03(d,H_3,J=3.9),6.34(d,H_4,J=3.9)	
9	1.41	4.07	6.80(s,$H_{1,4}$)	
10	1.46	4.10	6.67(d,$H_{3,4}$,J=2.2),7.18(t,H_1,J=2.2)	

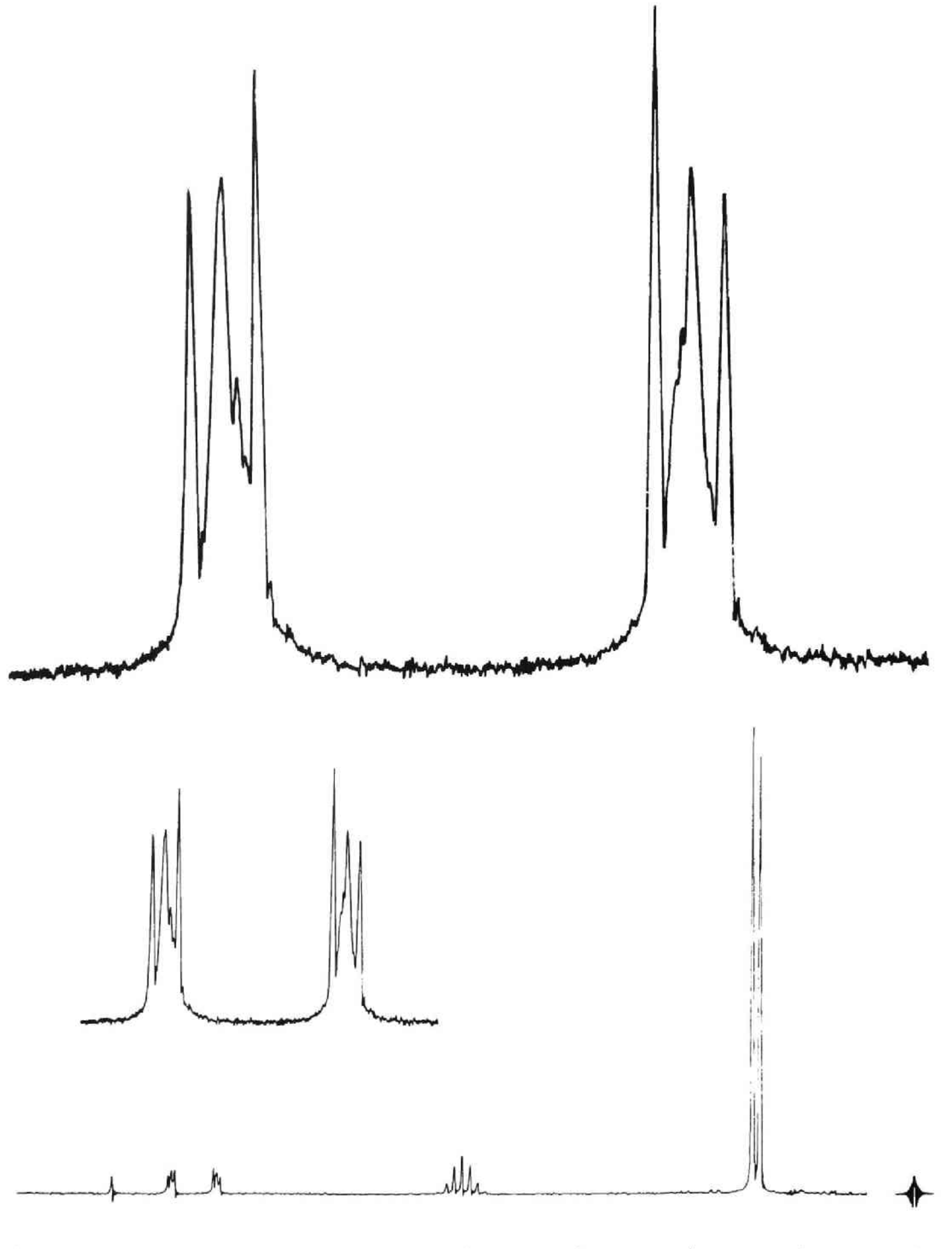


Figure 5. ^{1}H-nmr Spectrum of 2 in $CDCl_3$

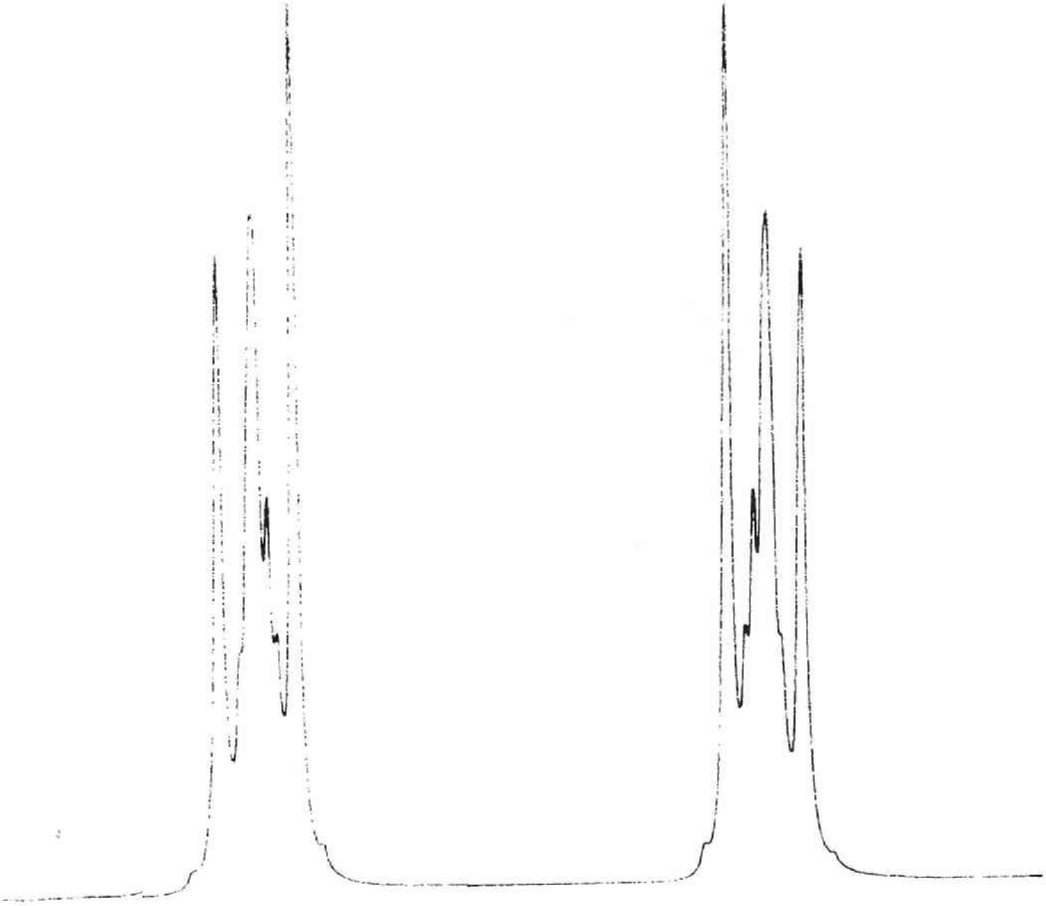


Figure 6. Computer Simulated Spectrum of 2

Both results obtained here show that although $p_{1,2}$ is somewhat larger than $p_{2,3}$, both values are not very different from each other. The π-bond orders of 2 are in the aromatic range on the basis of Streitwieser's proposal[11]: single bond $p_{r,s} < 0.4$, aromatic bond $p_{r,s} = 0.5 - 0.7$, double bond $p_{r,s} > 0.8$. From the π-electron density calculated by HMO, the π-electron of 2 is shown to migrate from the three-membered ring and the nitrogen atoms to the five-membered ring, suggesting the large contribution of the dipolar structure 2B and the immonium structure 2C to the ground state. The aromaticity of the 5,6-diaminocalicene is doubtless due to large electron donation from the amino group. In the ^{1}H-nmr of 4, three sets of doublet of doublets due to the five-membered ring protons appeared at δ 6.94 (J=4.4, 2.2 Hz) 6.15 (J=3.3, 2.2) and 6.01 (J=4.4, 3.3) (Table 4). The signal at the lowest magnetic field (δ 6.94) can be assigned as H_2, because the large magnetic anisotropy of the nitro group should strongly deshield the adjacent H_2 proton. The signal at the highest magnetic field (δ 6.01) could be assigned to H_3, and the signal at δ 6.15 to H_4 which is somewhat deshielded than H_3 due to the influence of the cyclopropenium group. The coupling constant $J_{2,3}$ (4.4 Hz) is larger than $J_{3,4}$ (3.3 Hz), indicating the larger double bond character of $C_2 - C_3$ bond compared with that of C_3-C_4 bond. This fact strongly suggests the importance of the canonical structures 4D and 4E at the ground state. The similar tendency was also observed in the case of the 1-methoxycarbonyl derivative 6 ($J_{2,3}$=3.8, $J_{3,4}$=3.4 Hz) (Figure 8). In the 2-substituted derivatives (5, 7 and 10), the H_1 proton resonates

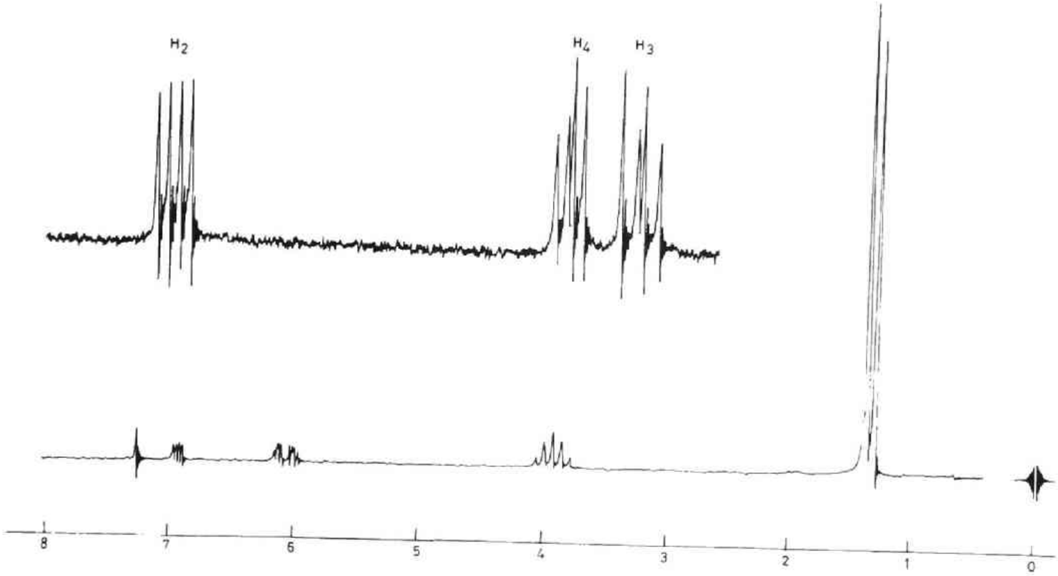


Figure 7. ^{1}H-nmr Spectrum of 4 in CDCl$_3$

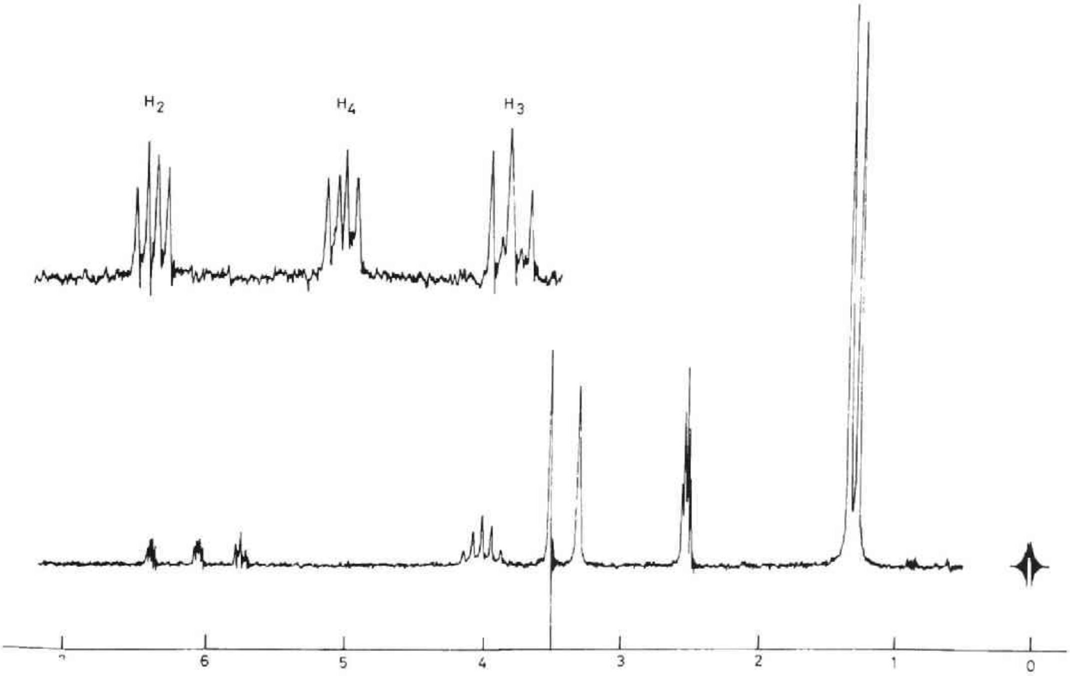


Figure 8. ^{1}H-nmr Spectrum of 6 in DMSO-d$_6$

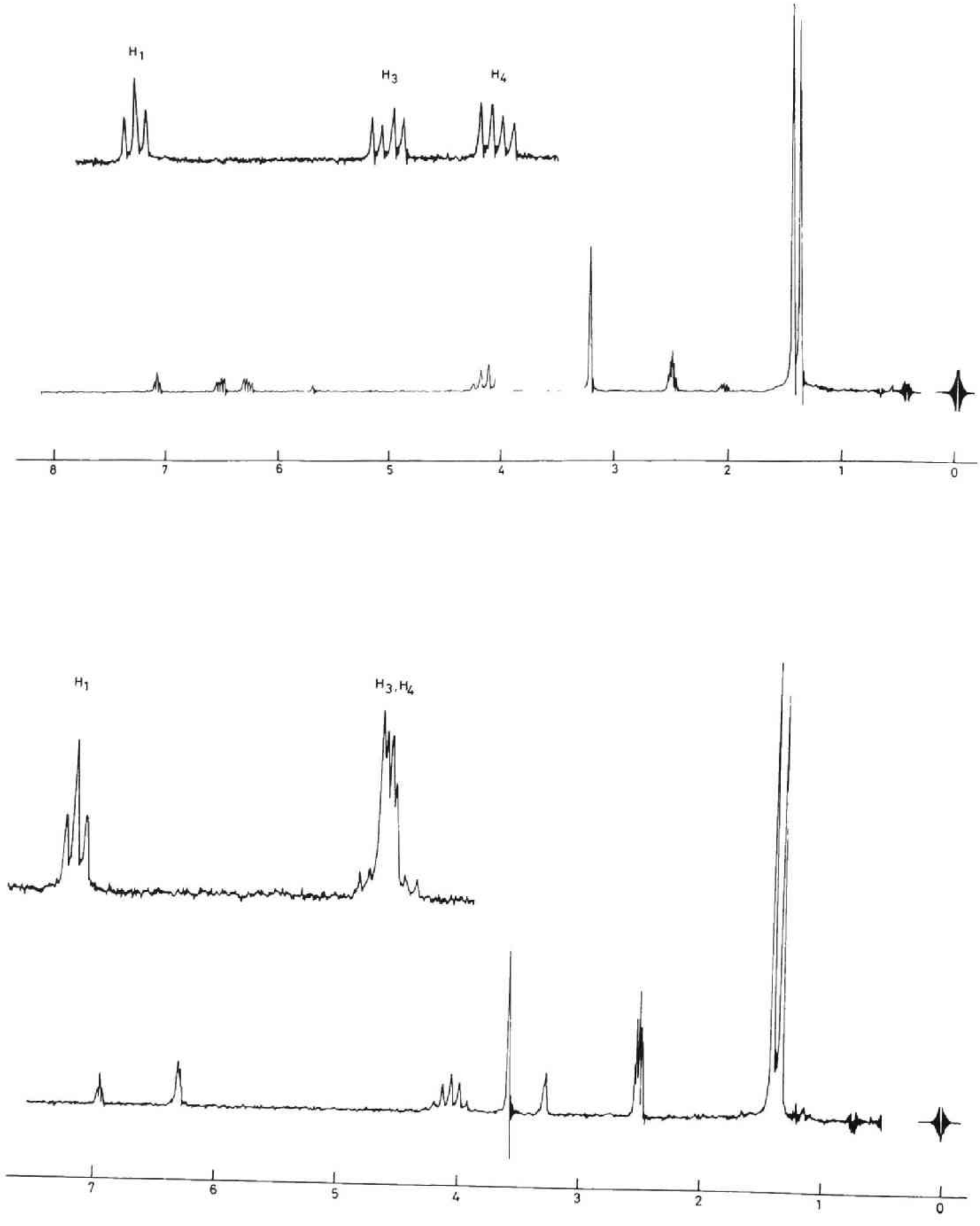
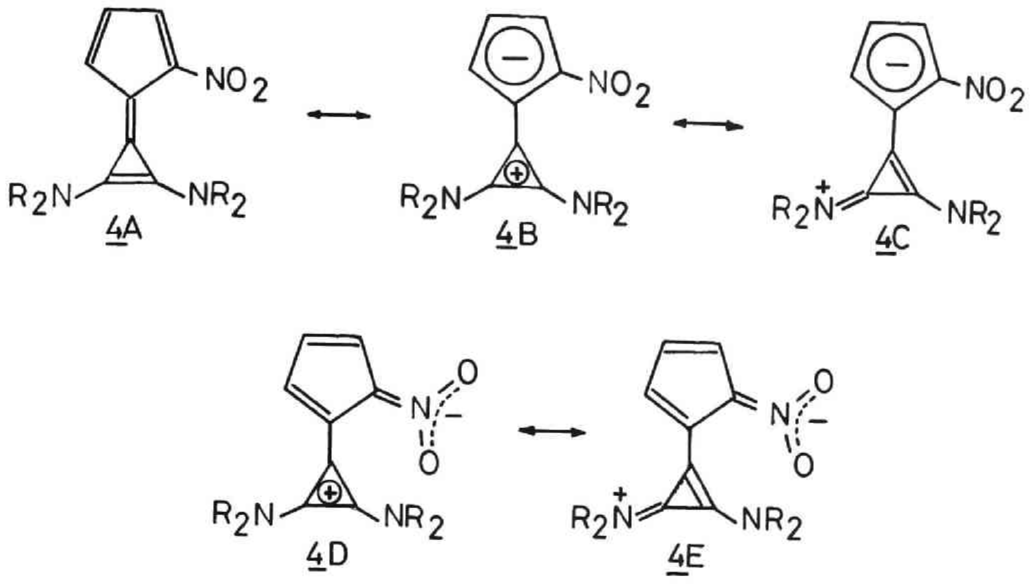


Figure 9. ^{1}H-nmr Spectra of 5 (top) in DMSO-d_6 and 7 (bottom) in DMSO-d_6



at very low field (δ 7.25 in 5, 7.24 in 7 and 7.18 in 10) due to the electronic effects of the two electron-withdrawing substituents (cyclopropenium and nitro or methoxycarbonyl) (Figure 9). The ring protons of the dicyanodiaminocalicene 8 and 9 appear at higher magnetic field than those of the corresponding dicyanodiphenyl derivatives 12 and 13[9] (Figure 10). This indicates the higher electron density of the five-membered ring of the diaminocalicene. Futhermore, the smaller coupling constant $J_{3,4}$ (3.9 Hz) in 8 compared with that ($J_{3,4}$= 4.7 Hz) in 13 is in good agreement with the strong π-conjugative effect of the amino groups.

The ^{13}C-nmr data are summarized in Table 5. Assignments for the carbon chemical shifts were made with the aid of off-resonance technique. Poor solubility makes it difficult to determine the carbon chemical shifts of the dicyano derivatives 8 and 9. The five-membered ring

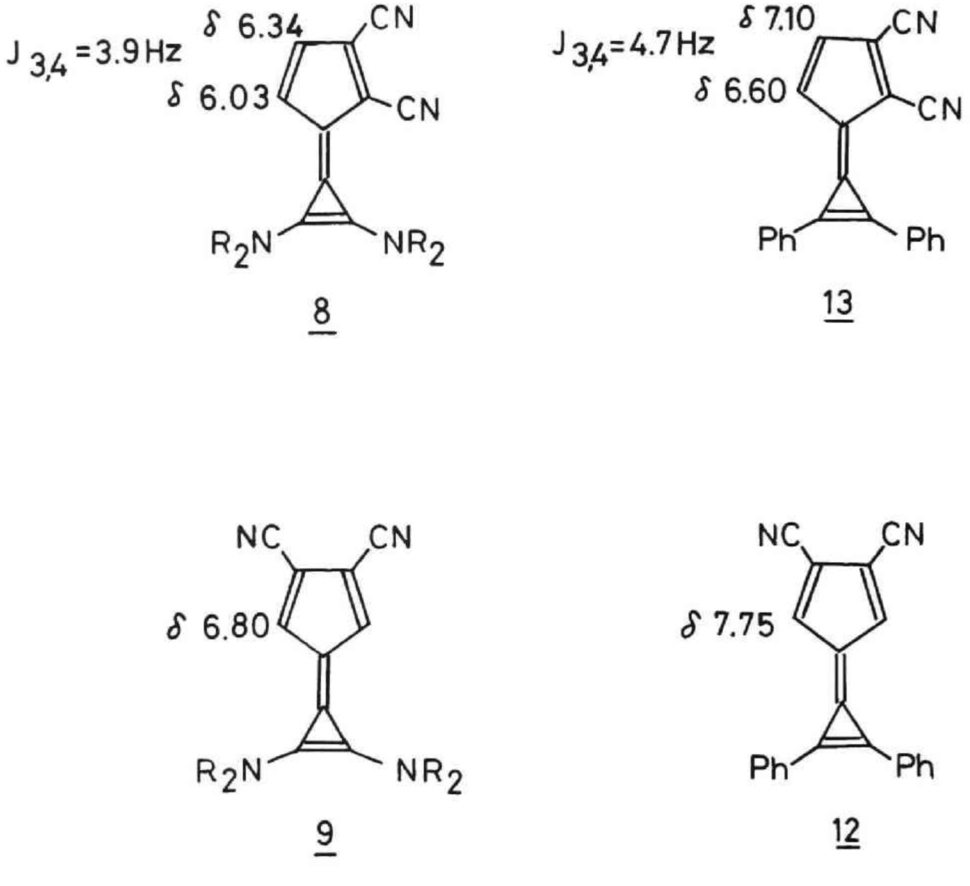


Figure 10. Chemical Shifts and Coupling Constants($J_{3,4}$) of Diaminodicyanocalicene 8, 9 and Diphenyldicyanocalicene 12, 13

carbons of the unsubstituted 5,6-diaminocalicene 2 appeared at 113.7 ($C_{1,4}$), 112.7 ($C_{2,3}$) and 98.2 (C_8) (Figure 11). It is reported that the sp^2 carbons of cyclopentadiene resonate at 132.2 and 132.8[12], while, cyclopentadienide anion at 102.1 ppm[13]. In comparing these chemical shifts, the high electron densities on the cyclopentadienyl ring carbons of the diaminocalicene 2 are made clear . Again, this is in good agreement with the expected large contribution of the polar structures 2B and 2C to the ground state. The five-membered ring carbons of the substituted 5,6-diaminocalicenes are somewhat deshielded than those of the unsubstituted derivative 2 due to the electron-withdrawing nature of the substituents. The electronic structure of the tripolar mesomeric salt 10 is considered to be the resonance hybrid of formulae 10A, 10B and 10C. Its ^{13}C-chemical shifts of the five-membered ring carbons show the high electron density of the cyclopentadienyl ring, that is , the tripolar structure 10C is considered to be dominant in the ground state. It might be considered that

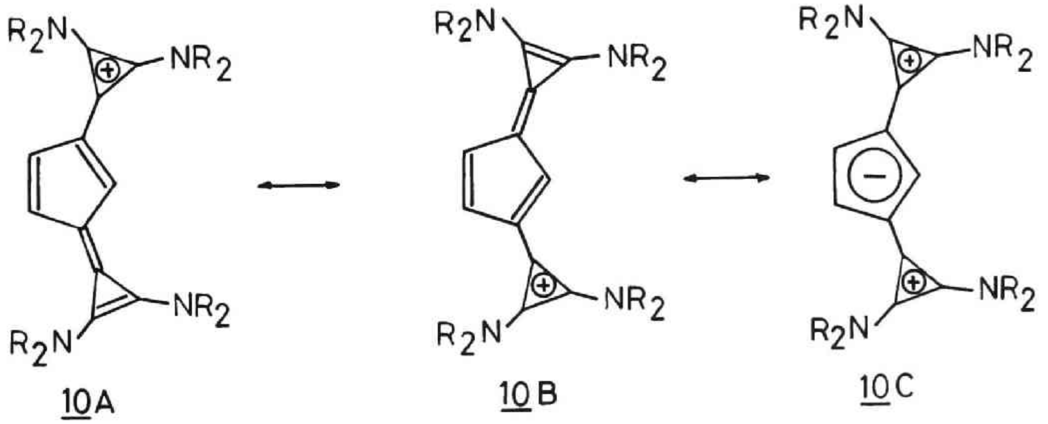


Table 5. ^{13}C-nmr Chemical Shifts of 5,6-Diaminocalicene in $CDCl_3$

	$-\underline{C}H_3$	$-\underline{C}H$	five-membered ring carbons	three-membered ring carbons
2	22.3	50.2	113.7($C_{1,4}$),112.7($C_{2,3}$),98.2(C_8)	115.0(C_7),120.3($C_{5,6}$)
4	21.6	51.6	133.0(C_1),113.4,114.1,117.8($C_{2,3,4}$),101.7(C_8)	113.8(C_7),131.4($C_{5,6}$)
5	22.1	51.4	111.6(C_1),137.6(C_2),114.6($C_{3,4}$),103.7(C_8)	111.8(C_7),124.7($C_{5,6}$)
6*	21.9	50.9	116.4(C_1),111.1,115.9,116.6($C_{2,3,4}$),103.0(C_8)	111.9(C_7),129.3($C_{5,6}$)
7**	22.3	50.8	119.5(C_1),117.0(C_2),114.4,115.2($C_{3,4}$),101.7(C_8)	114.0(C_7),122.7($C_{5,6}$)
10	22.2	51.2	118.4(C_1),116.3($C_{3,4}$),104.8($C_{2,8}$)	111.4(C_7),124.1($C_{5,6}$)

* 49.9($CO_2\underline{C}H_3$),166.3($\underline{C}O_2CH_3$)

** 50.2($CO_2\underline{C}H_3$),167.3($\underline{C}O_2CH_3$)

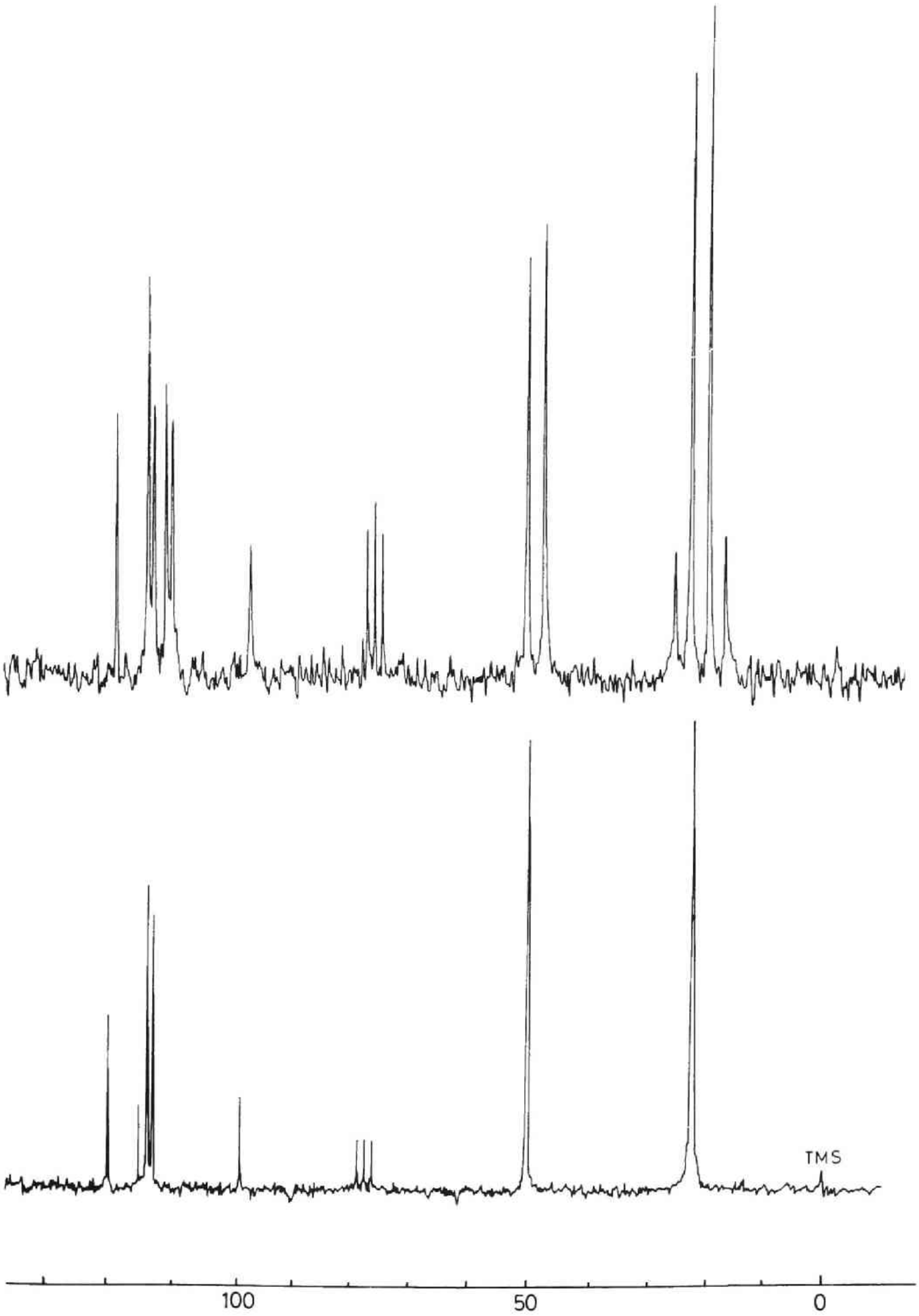


Figure 11. ^{13}C-nmr spectrum of $\underline{2}$ in $CDCl_3$

the chemical shifts of the three-membered ring carbons ($C_{5,6}$) bonded to the nitrogen atom reflect the contribution of cyclopropenium ion character of the three-membered ring. The electron-withdrawing substituent on the five-membered ring apparently increases the cyclopropenium character. The lower chemical shifts of the carbons $C_{5,6}$ in the 1-substituted derivatives 4 and 6 are considered to be due to the magnetic anisotropy of the substituents.

EXPERIMENTAL

1-Nitro-5,6-bis(diisopropylamino)calicene (4) and 2-Nitro-5,6-bis(diisopropylamino)calicene (5)

The mixture of sodium nitrocyclopentadienide 708 mg (5.32 mmol) and 1,2-bis(diisopropylamino)-3-chlorocyclopropenium perchlorate (3) 962 mg (2.59 mmol) in 30 ml of absolute ethanol was stirred for 41 hr at room temperature. The reaction mixture was poured into water and extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate and the solvent was evaporated under reduced pressure. The residue was chromatographed on thin layer of silica gel to afford 286 mg (32 %) of 4 and 135 mg (15 %) of 5 as yellow crystals (from dicloromethane-n-pentane).

4: mp 197°(dec); ir (KBr, cm^{-1}) 2975, 1904, 1525, 1375, 1300, 1286, 1068, 735 and 727; mass m/e 345 (M^+).

Anal. Calcd for $C_{20}H_{31}N_3O_2$: C, 69.53; H, 9.05; N, 12.16.
Found: C, 69.69; H, 9.13; N, 12.00.

5: mp 265°(dec); ir (KBr, cm^{-1}) 2975, 1895, 1513, 1351, 1268, 1235, 918 and 756; mass m/e 345 (M^+).

Anal. Calcd for $C_{20}H_{31}N_3O_2$: C, 69.53; H, 9.05; N, 12.16.
Found: C, 69.43; H, 8.87; N, 12.34.

1-Methoxycarbonyl-5,6-bis(diisopropylamino)calicene (6) and 2-Methoxycarbonyl-5,6-bis(diisopropylamino)calicene (7)

To a suspension of sodium hydride (in 50% mineral oil, 1.33 gr, 27 mmol) in 40 ml of tetrahydrofuran was added cyclopentadiene 0.85 ml

(9 mmol) in 10 ml of tetrahydrofuran at 0°C. The mixture stirred at 0°C for 30 min. and then methyl chloroformate 0.64 ml(9 mmol) in 10 ml of tetrahydrofuran was added dropwisely at -30° and warmed gradually to room temperature. To this solution of sodium methoxycarbonylcyclopentadienide was added 3 2.23 gr (6 mmol) in 30 ml of dichloromethane and stirred over night at room temperature. The reaction mixture was poured into water and extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was chromatographed on thin layer of silica gel to afford 6 43 mg (2%) and 7 1.29gr (60%) as pink crystals.

6: mp 187°(dec); ir (KBr, cm^{-1}) 2975, 1895, 1658, 1504, 1356, 1155 and 1065; mass m/e 358 (M^+).

Anal. Calcd for $C_{22}H_{34}N_2O_2$: C, 73.70; H, 9.56; N, 7.81.
Found: C, 73.83; H, 9.61; N, 7.59.

7: mp 187°(dec); ir (KBr, cm^{-1}) 2965, 1897, 1662, 1500, 1468, 1298 and 1157; mass m/e 358 (M^+).

Anal. Calcd for $C_{22}H_{34}N_2O_2$: C, 73.70; H, 9.56; N, 7.81.
Found: C, 73.82; H, 9.55; N, 8.07.

1,2-Dicyano-5,6-bis(diisopropylamino)calicene (8) and 2,3-Dicyano-5,6-bis(diisopropylamino)calicene (9)

A solution of tetramethylammonium dicyanocyclopentadienide 1.997 gr (8.15 mmol) and 3 750 mg (2.02 mmol) in 10 ml of dichloromethane was refluxed for 40 hr. The reaction mixture was poured into water and extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was chromatographed on alumina using benzene-acetone (8 : 2) as eluent. Crystallization from acetone – n-pentane gave 163 mg (23%) of 8 and 85 mg (12%) of 9 as colorless crystals.

8: mp 233°(dec); ir (KBr, cm^{-1}) 2970, 2190, 2180, 1900, 1520, 1502, 1360 and 737; mass m/e 350 (M^+).

Anal. Calcd for $C_{22}H_{30}N_4$: C, 75.39; H, 8.63; N, 15.99.
Found: C, 75.23; H, 8.62; N, 16.12.

9: mp >300°; ir (KBr, cm^{-1}) 2970, 2190, 1905, 1523, 1502, 1300, 943 and 808; mass m/e 350 (M^+).

Anal. Calcd for $C_{22}H_{30}N_4$: C, 75.39; H, 8.63; N, 15.99.
Found: C, 75.19; H, 8.47; N, 16.03.

1,3-Bis(diaminocyclopropenilio)cyclopentadienide Perchlorate (10)

To a solution of sodium cyclopentadienide (2 mmol) in 10 ml of tetrahydrofuran was added 3 371 mg (1 mmol) in 5 ml of dichloromethane at room temperature under argon atmosphere. After stirring for 1hr, the reaction mixture was poured into water and extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was crystallized from dichloromethane-ether gave 10 as pale green crystals in 54% yield; mp 207°(dec); ir (KBr, cm^{-1}) 2970, 1895, 1510, 1480, 1338 and 1095.

Anal. Calcd for $C_{35}H_{59}N_4ClO_4$: C, 66.16; H, 9.37; N, 8.82.
Found : C, 66.34; H, 9.50; N, 8.77.

1.2-Bis(diisopropylamino)-3-cyclopentadienylcyclopropenium Perchlo-

rate (11)

To a solution of sodium cyclopentadienide in 10 ml of tetrahydrofuran prepared from sodium hydride 214 mg (in 50% mineral oil, 4.2 mmol) and cyclopentadiene 0.036 ml (4.2 mmol) was added 3 742 mg (2.0 mmol) in 4 ml of dichloromethane at -70°. The mixture was stirred at -30° for 1 hr, poured into cold 3% perchloric acid and extracted with dichloromethane. The extract was condensed into small portion under reduced pressure at 0° and the residue was dissolved into cold ether. Resulting pale yellow crystals (11) was collected and dried, 746 mg (93%): mp 238°(dec); ir (KBr, cm^{-1}) 2975, 1900, 1545, 1350 and 1095; UV (CH_3CN) λ_{max} 326(logε 4.09); ^1H-nmr ($CDCl_3$) δ 7.25 (m, 1H, H_4), 6.70 (m, 2H, H_2 and H_3), 4.08 (sep, 2H, $-C\underline{H}(CH_3)_2$), 3.49 (m, 2H, $-CH_2-$) and 1.41 (d, 24H, $-CH(C\underline{H}_3)_2$); ^{13}C-nmr ($CDCl_3$) 141.5, 138.8, 132.8 ($C'_{2,}{}'_{3,}{}'_{4}$), 126.7 (C'_1), 44.7 (C'_4), 129.5 ($C_{1,2}$), 104.7 (C_3), 50.3, 54.6 ($-\underline{C}H(CH_3)_2$), 21.6 ($-CH(\underline{C}H_3)_2$).

Anal. Calcd for $C_{20}H_{33}N_2O_4Cl$: C, 59.91; H, 8.30; N, 6.99.

Found: C, 59.82; H, 8.28; N, 7.11.

5,6-Bis(diisopropylamino)calicene (2)

To a solution of dimethylsulfinyl sodium (1.93 mmol) in 30 ml of dimethylsulfoxide was added 11 746 mg (1.85 mmol) in 15 ml of dimethylsulfoxide. The reaction mixture was stirred at room temperature for 1 min. and poured into water. Thus obtained white precipitate was collected and washed with n-pentane. Recrystallization from dichloromethane-n-pentane gave 2 , 448 mg (82%) as colorless crystals, mp 159°, ir (KBr, cm^{-1}) 2975, 1900, 1490, 1340, 1330, 903 and 705;

mass m/e (rel. intensity) 300 (M^+, 25), 257 (M - i-Pr, 100), 131 (25), 104 (71).

Anal. Calcd for $C_{20}H_{32}N_2$: C, 79.94; H, 10.74; N, 9.32.

Found: C, 79.72, H, 10.86; N, 9.15.

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CHAPTER 4

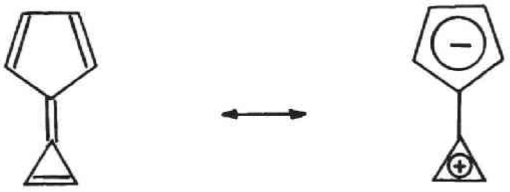
REACTIONS OF 5,6-DIAMINOCALICENE WITH ELECTROPHILES AND DIENOPHILES

SUMMARY

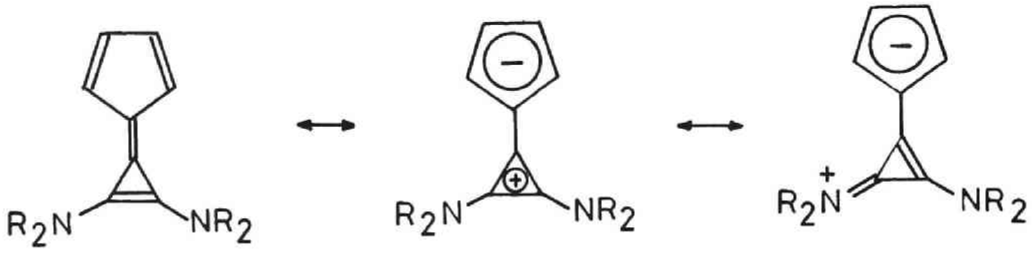
The reaction of 5,6-bis(diisopropylamino)calicene (2) with various electrophiles and dienophiles have been investigated. Electrophilic substitution takes place at peripheral positions of the five-membered ring. The reaction with dienophiles gives the calicenes substituted at the cyclopentadienyl ring *via* Michael addition. Aromatic character of 2 has been proposed on the basis of these reaction behaviors. The reactivity and the reaction position are discussed with the aid of Hückel MO calculations.

INTRODUCTION

Calicene (1) is a member of mixed-fulvalene system and caracterized by the resonance hybrid of covalent structure (1A) and dipolar structure (1B)[1]. Although the attempt to prepare the parent compound has been unsuccessful[2], some derivatives have been synthesized by several groups. Aromatic character of the calicenes has been argued from structural studies and reaction behaviors. Kende and his coworkers reported[4] that diacylcalicenes (8 and 9) undergo substitution reaction on the five-membered ring. This trend seems to give an evidence for their aromatic character in the substitution reactions. While, Prinzbach and Fischer reported[5] cycloaddition reaction of dibenzo- and tetraphenylcalicene (13 and 14) with dienes, dienophiles and diazo compound. Such variety of reaction behavior seems to be derived from the electronic effect of the substituents. In the previous chapter, aromaticity of 5,6-diaminocalicene (2) has been proposed on the basis of the spectroscopic properties. It is particularly interesting to examine the reaction behavior of 2 to elucidate the



1A 1B



2A 2B 2C

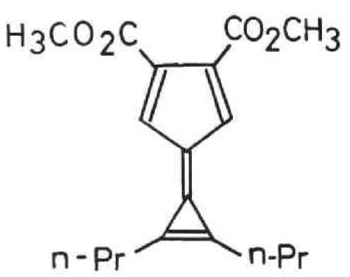
importance of the canonical structures (2A, 2B and 2C) in the reaction, that is, to evaluate the aromatic character of the new calicene. In this chapter, the reactions of 2 with various electrophiles and dienophiles are described. The reactivity of 2 is also discussed in terms of the ionization potentials estimated by Hückel MO calculation, and the position of substitution reaction predicted from electron transfer theory, superdelocalizabilities and localization energies are compared with the experimental results.

RESULTS AND DISCUSSION

Reaction of 2 with Electrophiles

The reaction of 2 with methylchloroformate in the presence of potassium carbonate gave 2-methoxycarbonyl-5,6-diaminocalicene (2) as stable pink crystals in 53% yield. The physical properties (mp, ir, uv, ^{1}H-nmr and ^{13}C-nmr)of 3 were completely in accord with those of the authentic sample prepared from the reaction of methoxycarbonylcyclopentadienide and diaminochlorocyclopropenium (see chapter 3). The position of substitution was confirmed to be the 2-position and the 1-substituted derivative was not found in the present reaction. The reaction of 2 with cupric nitrate in acetic anhydride gave 2-nitro-5,6-diaminocalicene (4) in 14% yield. ^{1}H-Nmr data of 4 support the introduction of the nitro group to the 2-position. The product 4 is brilliant yellow crystals and show absorption maxima at 236, 294 and 414 nm in the electronic spectra. Low excitation band at 414 nm shows the large bathochromic shift compared with that of the starting calicene 2 (338 nm). This fact supports the introduction of the chromopher (nitro group) to the calicene skelton. The ir spectrum shows the absorption at 1351 cm^{-1} due to the asymmetric N-O stretching vibration of the nitro group. A tripolar mesomeric salt (5) was obtained from the reaction of 2 and diaminochlorocyclopropenium perchlorate in good yield. The diaminocalicene 2 also reacted with 1-methy-2-iodopyridinium iodide to afford an orange mesomeric salt (6). The compound isolated as a perchlorate salt is quite stable in air. The long wave-length maximum (384 nm for 5, 444 nm for 6) in the electronic spectrum shows bathochromic shift relative to that of the parent diaminocalicene 2 (388 nm), in good agreement with the expanded π-electron system. Treatment of 2 with 4 mol of N-chlorosuccinimide and N-bromosuccinimide in acetonitrile gave tetrachloro- and tetrabromocalicene (7, 8) respectively. No other halogenated calicenes were detected.

The electrophilic substitution reaction of 2 described above strongly suggests the aromatic character of the diaminocalicene. Kende and his co-workers reported[4] that some calicene derivatives such as 2,3-dimethoxycarbonyl-5,6-di-n-propylcalicene (9) and 1,2-benzo-3-methoxycarbonyl-5,6-di-n-propylcalicene (10) undergo substitution reaction (nitration, bromination, acylation, formylation reaction and diazo-coupling) on the five-membered ring. In these derivatives, it is considered that the electron-withdrawing substituent (methoxycarbonyl group) on the five-membered ring should strongly affect the electronic structure and increase cyclopentadienide ion character (6π) of the five-membered ring. In these cases, the reaction



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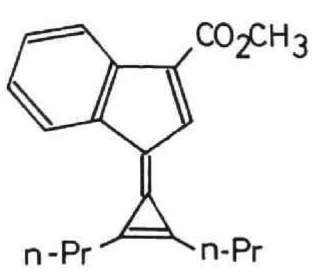

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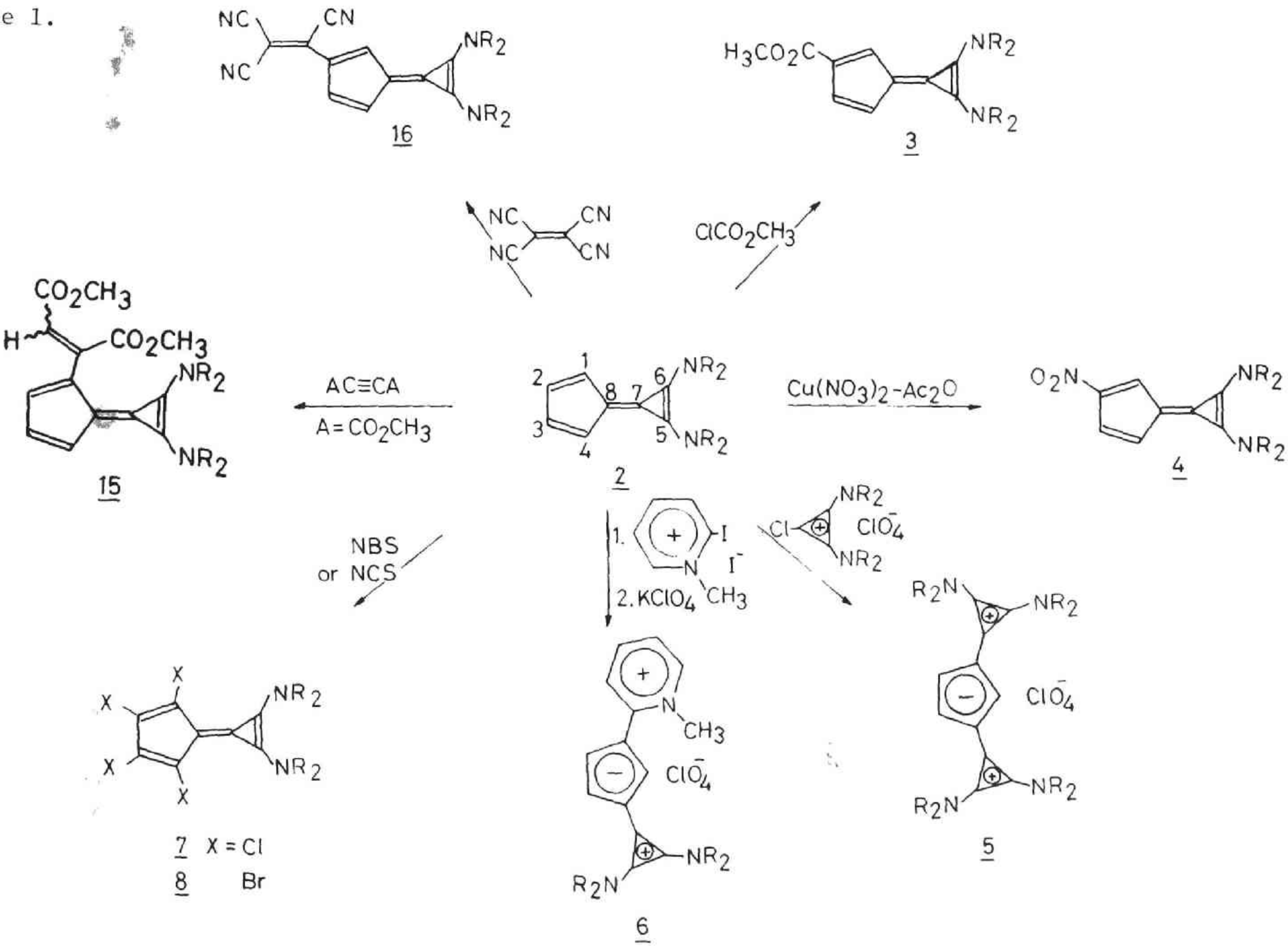
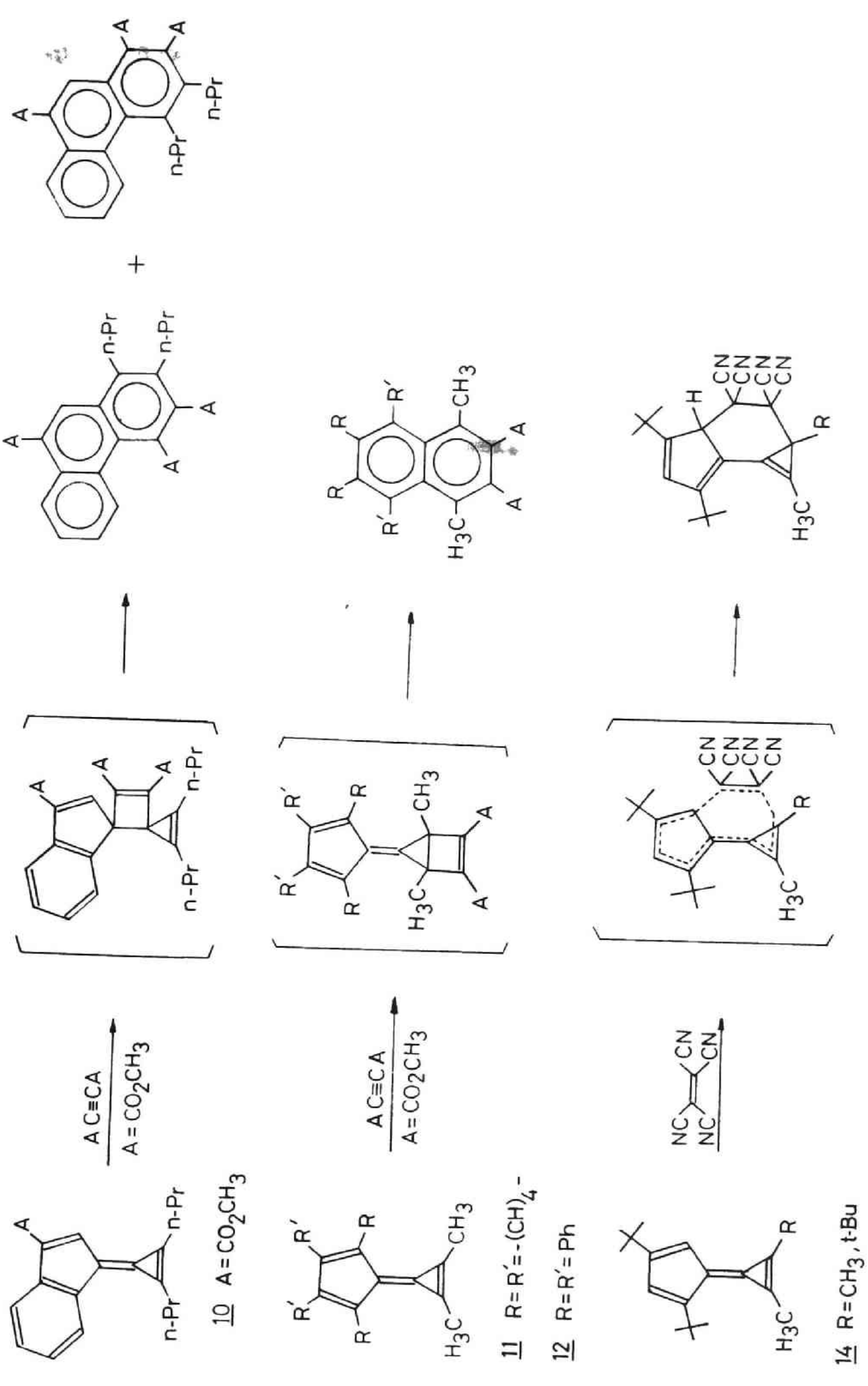
Scheme 1.


NC
CN
NC
NR2
NR2
16
H3CO2C
NR2
NR2
3
NC
CN
NC
CN
ClCO2CH3
CO2CH3
H
CO2CH3
NR2
NR2
15
AC≡CA
A = CO2CH3
2
1
6
NR2
8
7
3
4
5
NR2
2
Cu(NO3)2-Ac2O
O2N
NR2
NR2
4
NBS
or NCS
1.
+
I
N
I⁻
CH3
2. KClO4
NR2
Cl
+
ClO4⁻
NR2
R2N
+
NR2
−
ClO4⁻
+
R2N
NR2
5
X
X
X
X
NR2
NR2
7 X = Cl
8 Br
+
N
CH3
−
ClO4⁻
+
NR2
R2N
6

is allowed only at the 1-position. The aromatic character of 2 shown by a wide variety of substitution reaction seems to be compatible with considerable contribution of the polar structures 2B and 2C to the ground state.

Reaction of 2 with Dienophiles

Kende and his co-workers reported[4] that the reaction of 10 with dimethylacatylenecarboxylate to afford the mixture of phenanthrene derivatives. The cycloaddition reaction of dibenzo- and tetraphenylcalicene (11, 12) with dimethylacetylenedicarboxylate has been also reported[5] to give naphthalene derivatives in good yield. Prinzbach reported[6] that the calicene (13) substituted by t-butyl groups reacted with tetracyanoethylene to give a 1 : 1 adduct. In this case, an [8 + 2] cycloaddition mechanism is proposed and the calicene 13 is considered to react as a conjugated tetraene. Thus, the reaction of calicene with dienes or dienophiles is rather complicated and the diversity of the reaction is considered to be derived from the variety of the substituents. The investigation of reaction behavior of 2 toward dienophiles is another useful examination for determination whether 2 behave as an aromatic or not. Tetracyanoethylene and dimethyl acetylene dicarboxylate are knoun as reactive dienophiles[7] known as well as weak electrophiles[8]. In order to investigate whether 2 undergoes Diels-Alder reaction or electrophilic reaction, the reaction of 2 with tetracyanoethylene and dimethyl acetylene dicarboxylate was carried out.



10 A=CO$_2$CH$_3$

11 R=R'=-(CH)$_4$-

12 R=R'=Ph

14 R=CH$_3$, t-Bu

To a solution of 2 in chloroform was added dimethylacetylenecarboxylate at room temperature. The color of the reaction mixture turned immediately to orange. After stirring for 5 min., the reaction mixture was chromatographed on silica gel to afford 15 as brown crystals in 68% yield. The structure of 15 was confirmed by microanalysis and spectral data. The elemental analysis ($C_{26}H_{38}N_2O_4$) as well as the mass spectrum (m/e 442 as a parent peak) indicates 15 to be a 1 : 1 adduct of 2 and the acetylene. The ir spectrum of 15 shows an existence of two strong carbonyl stretching absorptions at 1739 and 1688 cm^{-1} (Figure 1). The ^1H-nmr of 15 (Figure 2) shows three cyclopentadienyl ring protons at δ 6.49 (dd, 1H, H_2 or H_4, J=1.8, 3.6 Hz), 6.36 (dd, 1H, H_4 or H_2, J=1.8, 3.6) and 6.18 (t, 1H, H_3, J=3.6 Hz), a vinyl proton at δ 4.29 (s, 1H), two methoxy protons at δ 3.90 (s, 3H) and 3.64 (s, 3H) as well as isopropyl protons at δ 4.05 (sep, 4H, $-C\underline{H}(CH_3)_2$) and 1.39 (d, 24H, $-CH(C\underline{H}_3)_2$). These data indicate that 15 is a 1,2-dicarbomethoxyvinyl substituted diaminocalicene. The position of the substituent is confirmed to be the 1-position on the basis of the chemical shifts and the coupling constants of the five-membered ring protons (H_2, H_3 and H_4). Present result is a striking contrast to the case of various electrophiles described above and the case of tetracyanoethylene (*vide infra*). Discussion about the reaction position will be described latter. The product 15 is not a Diels-Alder reaction product but a Michael addition product. No evidence for Diels-Alder reaction was observed.

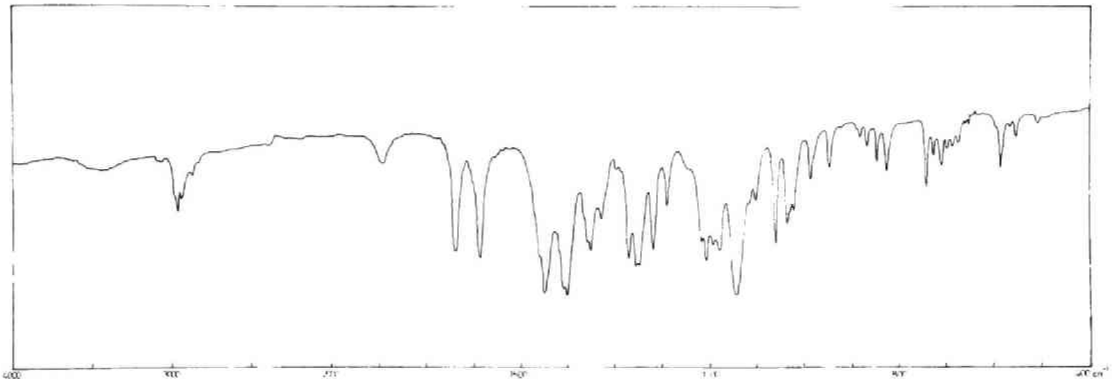


Figure 1. Infrared Spectrum of 15

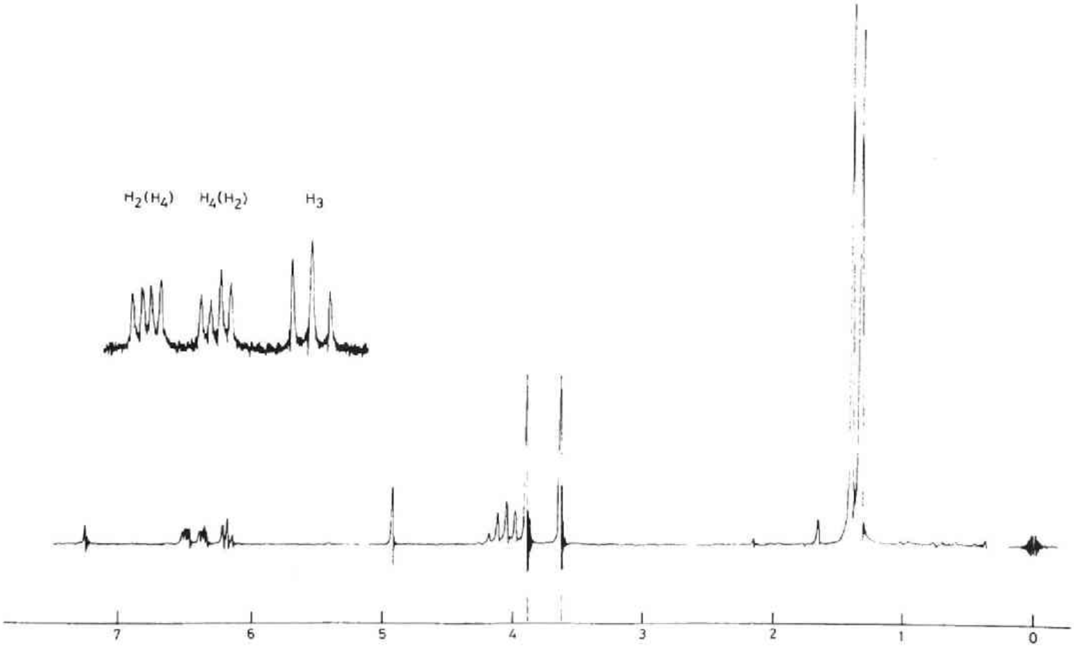
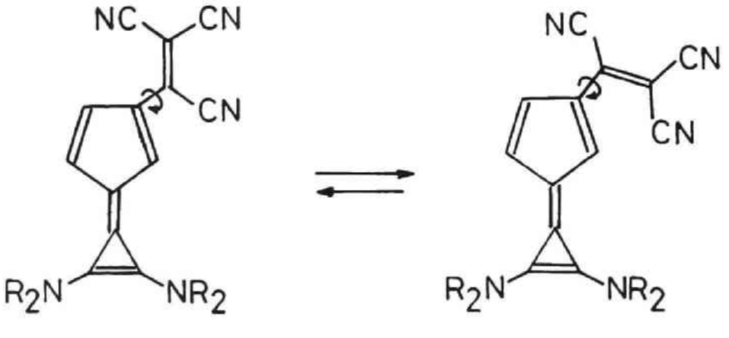


Figure 2. ^{1}H-nmr Spectrum of 15 in $CDCl_3$

When 2 was treated with tetracyanoethylene, purple-red crystals of 16 was obtaind. Elemental analysis and spectral data support the proposed structure 16. In the ir spectrum (Figure 3), a strong C≡N stretching vibration appeared at 2190 cm^{-1}. The ^1H-nmr spectrum (in CD_2Cl_2, at room temperature) shows signals at δ 4.06 (sep, 4H) and 1.43 (d, 24H) due to the isopropyl protons. Cyclopentadienyl ring protons appear at δ 7.80, 7.15 and 6.60 as broad multiplets with nonintegral area. At elevated temperature (in 1,1,2,2-tetrachloroethane-d_2, 130°C), the ring proton signals sharpened and appeared at δ 7.40 (H_1), 6.76 (H_3 or H_4) and 6.40 (H_4 or H_3) with equal area (Figure 4). This phenomenon is well interpreted in terms of the restricted rotation around the bond between the five-membered ring and the tricyanovinyl group. As described in chapter 3, these chemical shifts suggest the product 16 to be a 2-substituted derivative. The 1-substituted calicene was not detected. The tricyanovinyl calicene 16 is undoubtedly formed *via* the Michael addition, then subsequent elimination of hydrogene cyanide.



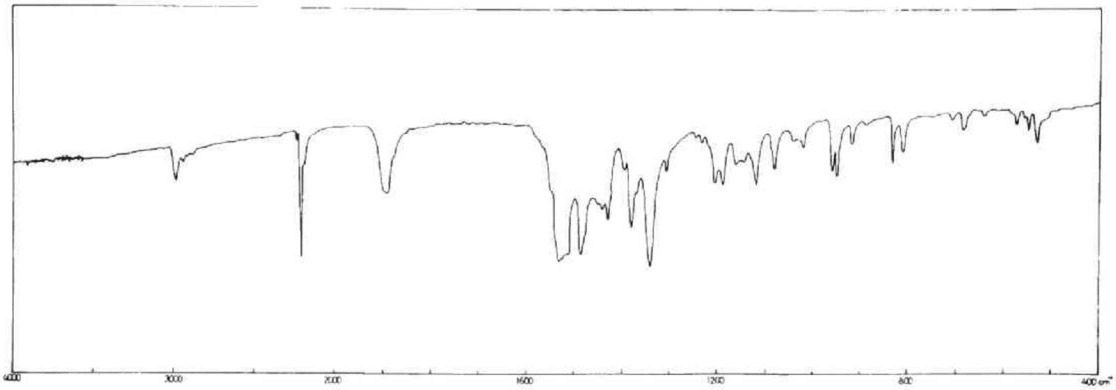


Figure 3. Infrared Spectrum of 16

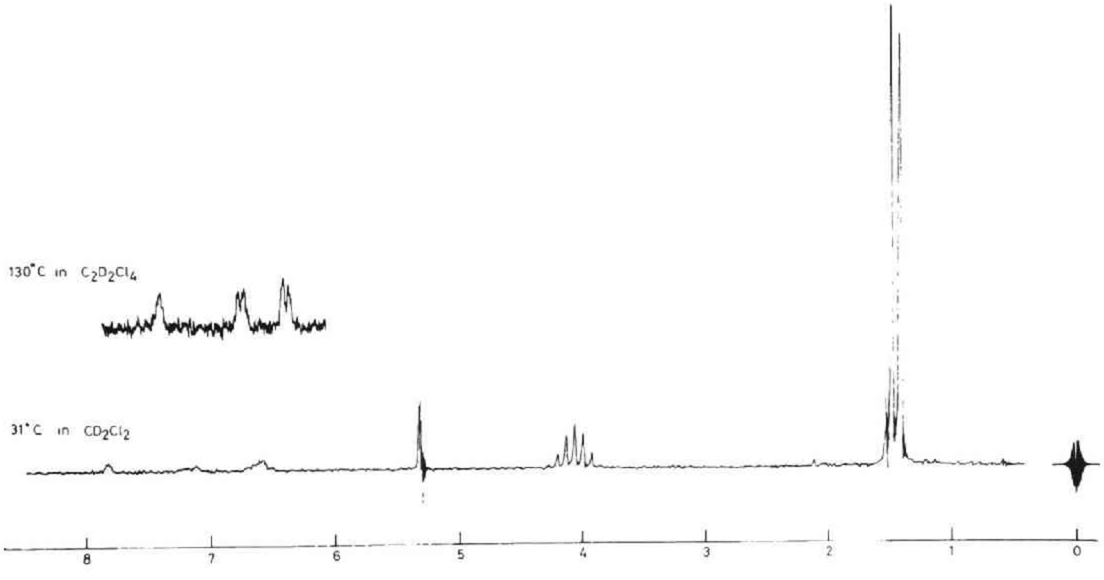


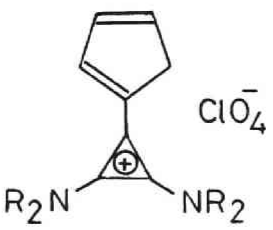
Figure 4. ^{1}H-nmr Spectrum of 16

All the **reactions** of 2 with electrophiles and dienophiles are summarized in Scheme 1. From these result, it is concluded that 2 has an aromatic character and dipolar structure (2B) and immonium structure (2C) play an important role in the reaction of 2.

The reaction of the diaminocalicene 2 with dienophiles gave no Diels-Alder reaction products, but afforded Michael addition products 15 and 16, by the electrophilic attack of the electron-deficient unsaturated compounds. This reaction **behavior** of 2 toward the dienophiles stongly suggests the cyclopentadienide ion character of the five-membered ring of the diaminocalicene (canonical structures 2B and 2C). The amino groups on the three-membered ring strongly stabilize the present system.

Hückel MO Treatment

In order to interpret the reaction position of 2, the Hückel MO calculation was carried out in the diaminocalicene system. The π-electron densities (q_r) and the reaction indices such as the superdelocalizabilities (S_E)[9], the localization energies (L_r)[10] and the free valences (F_r) were evaluated and are given in Table 1. The π-electron densities and the reaction indices in Table 1 suggest that the electrophilic attack should take place at the 1-position rather than the 2-position, however, the differences of the electron densities and the reaction indices on the C_1 carbon and the C_2 carbon are quite small. The calculated results are in good accord with the case of dimethyl **acetylene** dicarboxylate. However, the reaction position of the other electrophiles and tetracyanoethylene described above cannot be interpreted by the reaction indices. In these cases, it is considered that the large steric hindrance, which is not taken into account in the HMO caluculation, of the bulky diisopropylamino groups prevents the approach of electrophiles to the C_1 carbon. According to molecular model (CPK and dreiding), the C_1 and C_4 carbons are almost covered with the isopropyl groups and protected from the attack of the reagent. It seems that less bulky electrophiles such as proton should attack the C_1 carbon. Indeed, protonation of 2 with perchloric acid gave the protonated calicene (17) almost quantitatively with a small amount (< 5%) of the isomer (18)(monitered by the ^{1}H-nmr spectrum). In this case, the high reactivity of the C_1 carbon as well as the stability of the product seems to be an important factor.



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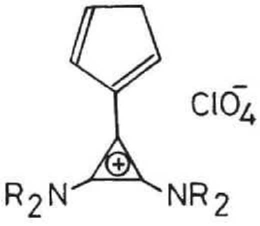

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The fact that the reaction of 2 with most electrophilic reagents such as NO_2^+, etc., gave monosubstituted derivatives of 2 (only the halogenation afford tetrasubstituted ones) can be rationalized by ionization potentials calculated from Hückel MO method. The calculated ionization potentials (E_{ho}, energy of the highest occupied MO) of several substituted derivatives are listed in Table 2. In the case of attack by NO_2^+, the ionization potentials are shown to increase with increasing substitution. This indicates that the subsequent electrophilic substitution becomes difficult. On the other hand, the ionization potentials decrease with halogen substitution and this accounts for the fact that the tetrahalo derivative is exclusively obtained in the halogenation.

Table 1. π-Electron Densities and Reaction Indices of 2

	q_r	S_E	Fr	L(- β)
C_1	1.181	1.558	0.473	1.946
C_2	1.177	1.508	0.433	2.029
C_5	0.836	1.419	0.049	2.432
C_7	0.893	0.648	0.118	2.820
C_8	1.176	0.790	0.169	2.796

Table 2. Ionization Potentials of the Derivatives of 2

substituent	NO_2	Cl	Br
none	0.395	0.395	0.395
2	0.429	0.350	0.349
2,3	0.463	0.328	0.311
1,2,3		0.318	0.299
1,2,3,4		0.316	0.298

EXPERIMENTAL

2-Methoxycarbonyl-5,6-diaminocalicene (3)

Methyl chloroformate (95 mg, 0.1 mmol) was added to a mixture of 5,6-bis(diisopropylamino)calicene 2 (253 mg, 0.84 mmol) and potassium carbonate (138 mg, 1 mmol) in 5 ml of dichloromethane under argon atmosphere. The mixture was stirred at room temperature for 24 hr and the solvent was removed under reduced pressure. The residue was chromatographed on alumina (Merk II-III) using benzene-acetone (8:2) as eluent. Recrystallization from ether-n-pentane gave 3 (160 mg, 53%) as pink crystals. The physical properties (mp, ir, uv, ^{1}H-nmr and ^{13}C-nmr) of the product 3 were completely in accord with those of the authentic sample (see Chapter 3).

2-Nitro-5,6-diaminocalicene (4)

Cuplic nitrate trihydrate $Cu(NO_3)_2 \cdot 3H_2O$ (170 mg, 0.70 mmol) was added to a solution of 2 (100 mg, 0.33 mmol) in 20 ml of acetic anhydride under argon atmosphere. The mixture was stirred for 3.5 hr at room temperature, poured into water and extracted with dichloromethane. The extract was washed with water and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel (Wakogel C-200). Recrystallization from dichloromethane-n-pentane gave 4 (16 mg, 14%) as yellow crystals. The physical properties of the product 4 were completely in accord with those of the authentic sample (see Chapter 3).

1,3-Bis(diaminocyclopropenylio)cyclopentadienide perchlorate (5)

A mixture of 2 (30 mg,0.1 mmol) and 1,2-bis(diisopropylamino)-3-chlorocyclopropenium perchlorate (37 mg, 0.1 mmol) in 2 ml of dichloromethane containing triethylamine (0.0137 ml, 0.1 mmol) were stirred under argon atmosphere. After stirring for 2 hr at room temperature, the reaction mixture was poured into aq. potassium perchlorate and extracted with dichloromethane. The solvent was removed under reduced pressure, and the residue was crystallized from dichloromethane-ether to give 5 (57 mg, 90%) as pale green crystals. The physical properties of the product 5 were in accord with those of the authentic sample (see Chapter 3).

1-(1-Methyl-2-pyridino)-3-(diaminocyclopropenilio)cyclopentadienide perchlorate (6)

A mixture of 2 (300mg, 1 mmol) and 1-methyl-2-lodopyridinium iodide (297 mg, 1 mmol) in 15 ml of N,N-dimethylformamide in the presence of potassium carbonate (264 mg, 1.8 mmol) are stirred at room temperature for 20 hr under argon atmosphere. The reaction mixture was poured into aq. potassium prechlorate and extracted with dichloromethane. The solvent was removed under reduced pressure, and the residue was chromatographed on alumina (Merk II-III). Crystallization of the yellow band from dichloromethane-ether gave 6 as orange needles: mp 204°(dec); ir (KBr, cm^{-1}) 1901, 1631, 1531, 1517, 1493, 1350 and 1092; uv (CH_3CN) λ_{max} 238($\log\varepsilon$ 4.03), 293 (4.17), 300 (sh), 360 (4.05) and 444 (4.47); ^1H-nmr ($CDCl_3$) δ 8.22 (broad d, 1H, J=6.5Hz), 7.80 (m, 2H), 6.67 (dq, 2H, H_4 and H_5, $J_{2,4}$=$J_{2,5}$=2.2, $J_{4,5}$= 4.6), 4.30 (s, 3H, N-CH_3), 4.10 (sep, 4H, methine), 1.47 (d, 24H, methyl).

Anal. Calcd for $C_{26}H_{38}N_3ClO_4$: C, 63.46; H, 7.78; N, 8.54.
Found: C, 63.67; H, 8.02; N, 8.53.

1,2,3,4-Tetrachloro-5,6-diaminocalicene (7)

Under argon atmosphere, 2 (50 mg, 0.17 mmol) in 1 ml of acetonitrile was added to a solution of N-chlorosuccinimide (88 mg, 0.66 mmol) in 1 ml of acetonitrile at -25° and the mixture was gradually warmed to room temperature. After stirring for 1 hr, white precipitate which deposited was collected by filtration, washed with acetonitrile, and dried in vacuo. Tetrachloro derivative 7 (39 mg, 53%) was obtained as white powder: mp ca. 240°(dec); ir (KBr, cm^{-1}) 1905, 1537, 1375 and 1338; uv (CH_3CN) 228 (sh), 308 (sh) and 321 (logε 3.57); mass m/e 438 (M^+).

Anal. Calcd for $C_{20}H_{28}N_2Cl_4$: C, 54.81; H, 6.44; N, 6.39.
Found: C, 54.83; H, 6.38; N, 6.52.

1,2,3,4-Tetrabromo-5,6-diaminocalicene (8)

Under argon atmosphere, 2 (50 mg, 0.17 mmol) in 1 ml of acetonitrile was added to a solution of N-bromosuccinimide 118 mg (0.66 mmol) in 1 ml of acetonitrile at room temperature. After stirring for 1 hr, white precipitate which deposited was collected by filtration, washed with acetonitrile, and dried in vacuo. Tetrabromo derivative 8 (86 mg, 84%) was obtained as white powder: mp ca. 220° (dec); ir (KBr, cm^{-1}) 1905, 1540, 1374, 1338 and 1163; uv (CH_3CN)

231 (sh), 310 (logε 3.43).

Anal. Calcd for $C_{20}H_{28}N_2Br_4$: C, 38.99; H, 4.58; N, 4.55.
Found: C, 39.18; H, 4.45; N, 4.61.

1-(1,2-Dimethoxycarbonylvinyl)-5,6-diaminocalicene (15)

To a solution of 2 (100 mg, 0.33 mmol) in 3 ml of chloroform was added dimethylacethylenedicarboxylate (48 mg, 0.33 mmol) in 20 ml of chloroform. The reaction mixture was stirred for 3 min at room temperature under argon atmosphere. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel (Wakogel C-200) using benzene-acetone (8 : 2) as eluent. Crystallization of the yellow band from acetone-petroleum ether gave 15 (98 mg, 68%) as brown crystals: mp 157°(dec); ir (KBr, cm^{-1}) 2970, 1894, 1739, 1688, 1553, 1504, 1455, 1359, 1209 and 1146; uv (CH_3CN) 299 (logε 4.20), 412 (4.29); ^{1}H-nmr ($CDCl_3$) δ 6.49 (dd, 1H, H_2 or H_4, J=1.8, 3.6Hz), 6.36 (dd, 1H, H_4 or H_2, J=1.8, 3.6Hz), 6.18 (t, 1H, H_3, J=3.6), 4.92 (s, 1H, vinyl), 4.05 (sep, 4H, methine), 3.90 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3), 1.36 (d, 24H, methyl); mass m/e 442 (M^+).

Anal. Calcd for $C_{26}H_{38}N_2O_4$: C, 70.56; H, 8.65; N, 6.33.
Found: C, 70.02; H, 8.62; N, 6.22.

2-Tricyanovinyl-5,6-diaminocalicene (16)

To a solution of 2 (150 mg, 0.5 mmol) in 20 ml of methanol was added tetracyanoethylene (64 mg, 0.5 mmol) in 10 ml of methanol. The reaction mixture was stirred for 5 min at room temperature under argon atmosphere. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel (Wakogel C-200) using benzene-acetone (8 : 2) as eluent. Crystallization of the red band from dichloromethane-ether gave 12 (51 mg, 25%) as purple-red crystals: mp >280°; ir (KBr, cm^{-1}) 2190, 1890, 1532, 1485, 1427, 1378 and 1339; uv (CH_3CN) 225 (logε 4.29), 280 (4.11), 294 (4.13), 500 (4.54); ^{1}H-nmr (CD_2Cl_2, r.t.) δ 7.80 (m), 7.15 (m), 6.60 (m), 4.06 (sep, 4H, methine), 1.43 (d, 24H, methyl), at 130° in 1,1,2,2-tetrachloroethane-d_2, the cyclopentadienyl ring signals appeared at 7.40 (m, 1H, H_1), 6.76 (m, 1H, H_3 or H_4) and 6.40 (m, 1H, H_4 or H_3); mass m/e 401 (M^+).

Anal. Calcd for $C_{25}H_{31}N_5$: C, 74.78; H, 7.78; N, 17.44.

Found: C, 74.58; H, 7.85; N, 17.30.

Protonation of 2

A solution of 2 (100 mg, 0.33 mmol) in 10 ml of dichloromethane was poured into cold diluted perchloric acid (5%, 20 ml) and shaked vigorously. The organic layer was separated, washed with water and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was recrystallized from dichloromethane-ether to give pale yellow crystals of 17 in almost quantitative yield: mp 238°(dec); ir (KBr, cm^{-1}) 2975, 1900, 1545, 1350 and 1095; uv (CH_3CN) 326 (logε 4.09); ^{1}H-nmr ($CDCl_3$) δ 7.25 (m, 1H, H_4), 6.70 (m,2H, H_2 and H_3), 4.08 (sep, 2H, methine), 3.49 (m, 2H, methylene), 1.41 (d, 24H, methyl), a signal at δ 3.40 due to the methylene protons of the isomer (18) was observed. The integral of the signal was less than 5% of that of the methylene signal of 15 at δ 3.49. When the signal at δ 3.49 was irradiated, the spectral pattern of the olefinic protons changed as follows: δ 7.25 (q, 1H, H_4, $J_{2,4}$=1.3,$J_{3,4}$=

2.2Hz), 6.72 (dd, 1H, H_2, $J_{2,3}$=5.4,$J_{2,4}$=1.3), 6.68 (dd, 1H, H_3, $J_{2,3}$= 5.4,$J_{3,4}$=2.2).

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CHAPTER 5

SYNTHESIS AND STRUCTURES OF TRANSITION METAL COMPLEXES OF 5,6-DIAMINOCALICENE

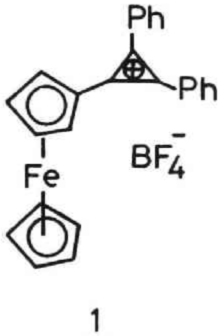
SUMMARY

Six transition metal complexes of 5,6-diaminocalicene (3) are synthesized directly from 3 and various metal sources. In the all complexes obtained here, each transition metal coordinates to the electron-rich five-membered ring of 3, and the contribution of the dipolar structure of the diaminocalicene moiety in the complexes is found to increase than that in the ligand 3. According to the C-N stretching vibrations in the ir spectra, the order of the polarity of the ligand is following: 10 (Co^{III} complex) > 8 (Fe^{II}) > 13 (Rh^{I}) > 4 (Cr^{0}) $\sim$ 5 (Mo^{0}) $\sim$ 6 (W^{0}).

INTRODUCTION

Calicene is one of a group of unsaturated hydrocarbons known as fulvalenes, many of which are not isolable because of their high reactivity toward oxygen or tendency to polymerize.[1] In many cases, however, fulvalenes can be stabilized as ligands in transition metal complexes.[2] Cais and Eisenstadt reported[3] the first example (1) of the transition metal complex of calicene prepared from the reaction of ferrocene with 3,3-dichloro-1,2-diphenylcyclopropene in the presence of borontrifluoride etherate. It has been reported that the reaction of 6,6'-diaminofulvene and ferrous chloride gave a stable ferrocene derivative (2) in good yield.[4] This result prompted to prepare the transition metal complexes of the electron-rich diaminocalicene (3).

In this chapter, are described new synthetic methods and structure of the transition metal complexes of 5,6-diaminocalicene 3.



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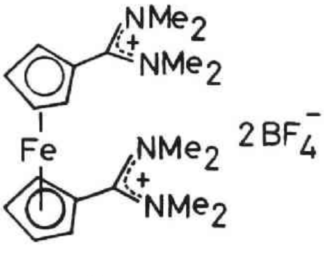
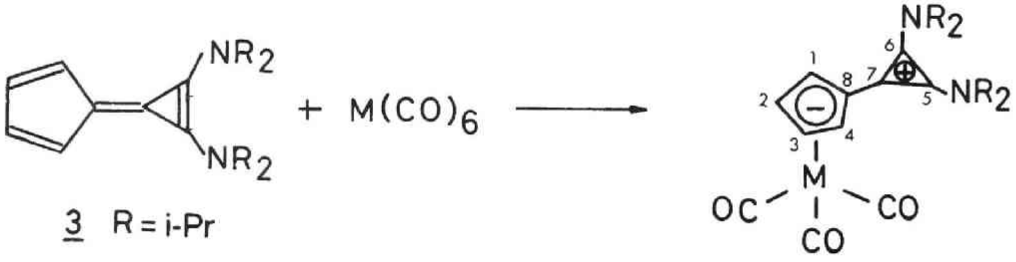


2

RESULTS AND DISCUSSION

Synthesis and Properties of Calicene-Metaltricarbonyls (4 - 6): Metal = Cr^0, Mo^0 and W^0

5,6-Bis(diisopropylamino)calicene 3 and chromiumtricarbonyl were refluxed in dry dioxane under argon atmosphere. Column chromatography of the reaction mixture on alumina followed by recrystallization gave orange crystals of calicene-chromiumtricarbonyl (4) in 20% yield. The molybdenum and tungsten complexes (5 and 6) were also obtained in the similar manner.



3 R = i-Pr

4 M = Cr^0
5 Mo^0
6 W^0

The calicene-metaltricarbonyls (4, 5 and 6) are separated as orange to yellow needles and gradually decomposed on exposure to air. These complexes are insoluble in non-polar organic solvents (e.g. pentane, hexane and petroleum ether), freely soluble in polar solvents (e.g. methanol, ethanol, acetone and acetonitrile). The solution of these neutral complexes is very sensitive to air and dark material was deposited on standing in air. The mass spectra of 4 - 6 revealed the molecular ion peak of calicene-$M(CO)_3$: M = Cr, Mo and W, indicating the complexes to be monomeric.

The ^1H- and ^{13}C-nmr spectra of the diaminocalicene-metaltricarbonyls 4 - 6 (Table 1 and 2) provide the evidence for the suggested structures. The ^1H-nmr spectra showed signals of the isopropyl groups at δ 1.39 - 1.40 (doublet) and 4.05 - 4.06 (septet) as well as the five-membered ring protons at 4.72 -5.84 (AA'BB' pattern). The ring protons of the complexes resonate at higher magnetic field than those of the diaminocalicene 3 (δ 6.22 and 6.62). This result clearly indicates that the metal is coordinated to the five-membered ring of 3. The ^{13}C-nmr spectra also support the structures 4 - 6. The cyclopentadienyl carbons (C_1-C_4 and C_8) of the complexes resonate at 75.6 - 92.5 ppm, while the five-membered ring carbons of the free diaminocalicene 3 resonate at 99.6 - 114.6 ppm. The values of ^{13}C-nmr chemical shifts indicate the increase of the electron density on the cyclopentadienyl ring of the calicene-metalcarbonyls compared with that of the calicene itself.

In the ir spectra of 4 - 6 (Figure 2) three carbonyl stretching vibrations appear in the region 1918 - 1780 cm^{-1}. The band in the region 1910 - 1905 cm^{-1} is characteristic ring deformation of diaminocyclopropenyl compounds and the band in the region 1530 - 1525 cm^{-1} is assignable to the three-membered ring carbon-nitrogen stretching vibration.[5] The corresponding bands of the free diaminocalicene 3 appear at 1900 and 1490 cm^{-1} respectively. Higher frequencies of the

Table 1. ^{1}H-nmr Parameters of Diaminocalicene 3 and its Transition Metal Complexes in CD_3CN (δ values)

compound	$-CH(C\underline{H}_3)_2$	$-C\underline{H}(CH_3)_2$	ring protons	others
3	1.41 (d)	4.04 (sep)	6.22, 6.62 (AA'BB')	
4	1.39 (d)	4.06 (sep)	4.72, 5.17 (AA'BB')	
5	1.40 (d)	4.05 (sep)	5.31, 5.84 (AA'BB')	
6	1.39 (d)	4.05 (sep)	5.30, 5.80 (AA'BB')	
8	1.45 (d)	4.12 (sep)	4.80, 4.95 (AA'BB')	
10	1.42 (d), 1.50 (d)	4.16 (sep), 4.24 (sep)	6.16, 6.30 (AA'BB')	
13	1.48 (d)	4.12 (sep)	5.52, 5.59 (AA'BB')	2.00 (m,COD CH_2) 4.12 (m,COD olefin)

Table 2. ^{13}C-nmr Chemical Shifts of Diaminocalicene 3 and its Transition Metal Complexes in CD_3CN

	$-CH(C\underline{H}_3)_2$	$-C\underline{H}(CH_3)_2$	$C_{2,3}$	$C_{1,4}$	$C_{5,6}$	C_7	C_8	others
3	22.7	51.4	113.1	114.6	121.5	115.4	99.6	
4	21.6	51.9	84.9	87.2	126.1	110.1	75.6	243.0 (CO)
5	22.0	52.1	89.3	92.5	125.5	108.3	80.6	232.6 (CO)
6	22.0	52.1	87.1	89.7	125.9	107.7	78.9	223.0 (CO)
8	21.6, 22.6	50.3, 55.8	72.7	74.9	130.4	107.4	67.5	
10	19.7, 21.2	50.7, 55.6	84.1	87.7	131.3	112.7	73.9	
13	22.1	52.4	88.6 (d,J=3.9Hz)	91.0 (d,J=2.9Hz)	126.4	105.1	85.7 (d,J=2.9Hz)	31.9 (COD CH_2) 67.5 (d,J=14.7Hz COD olefin)

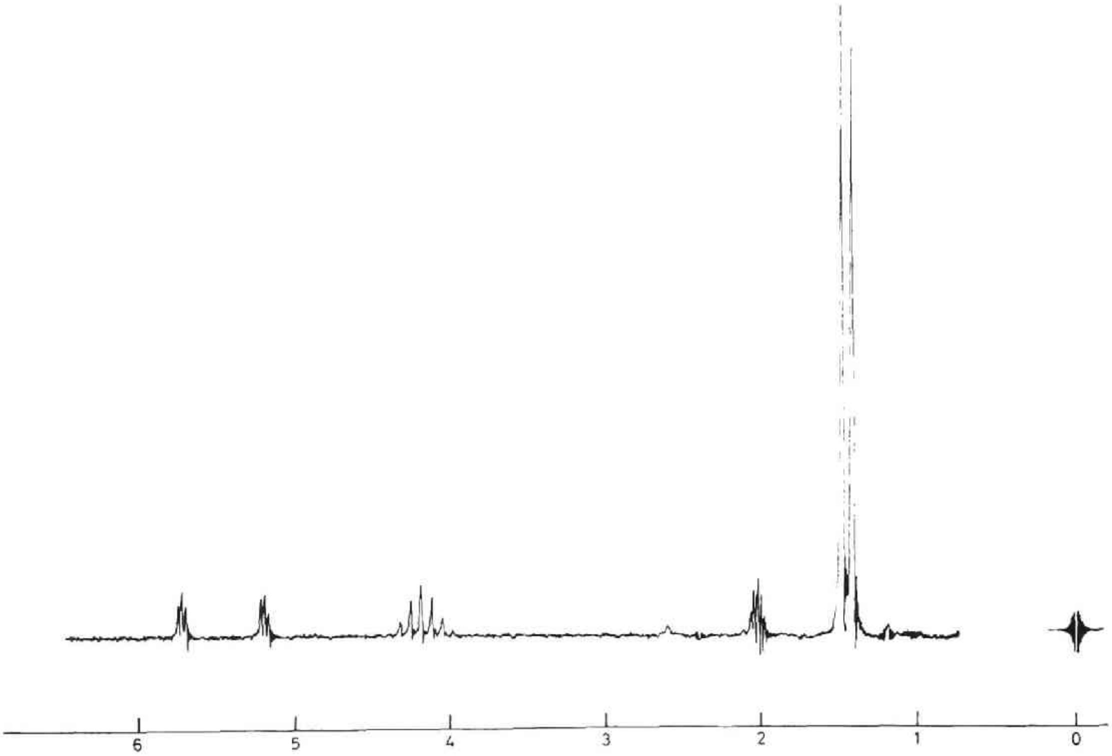
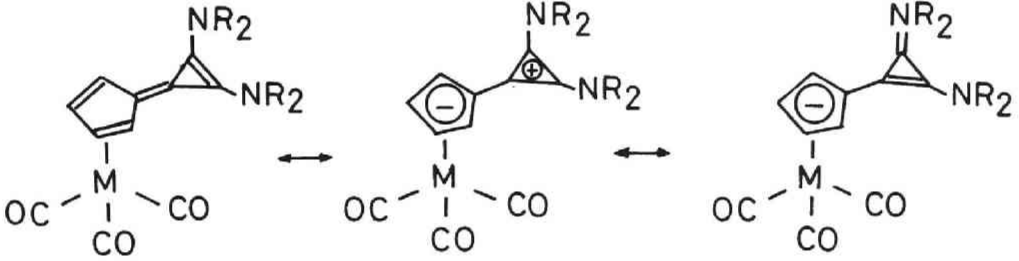


Figure 1. ^{1}H-nmr Spectrum of $\underline{5}$ (Mo^0 complex) in acetone-d_6

C-N stretching of the complexes compared with that of 3 indicate a strong π-conjugative interaction between amino groups and cyclopropenium ring.

These spectroscopic data strongly suggest the larger contribution of dipolar structures (B and C) in the complexes 4 - 6 compared with that in the diaminocalicene 3. In the complexes, the calicene behaves as a 6π-electron ligand (cyclopentadienide) expressed by the canonical structures B and C, and the contribution of covalent structure A is considered to be small.



A B C

The electronic spectra of the three complexes exhibited two maxima in analogous positions (Table 3). Quantitative determination of the absorption intensities was difficult due to the rapid decomposition of the complexes in solution. Hypsochromic shift of the absorption maxima of the diaminocalicene complexes 4-6 was observed compared with that of the corresponding diaminofulvene complex 7.[6]

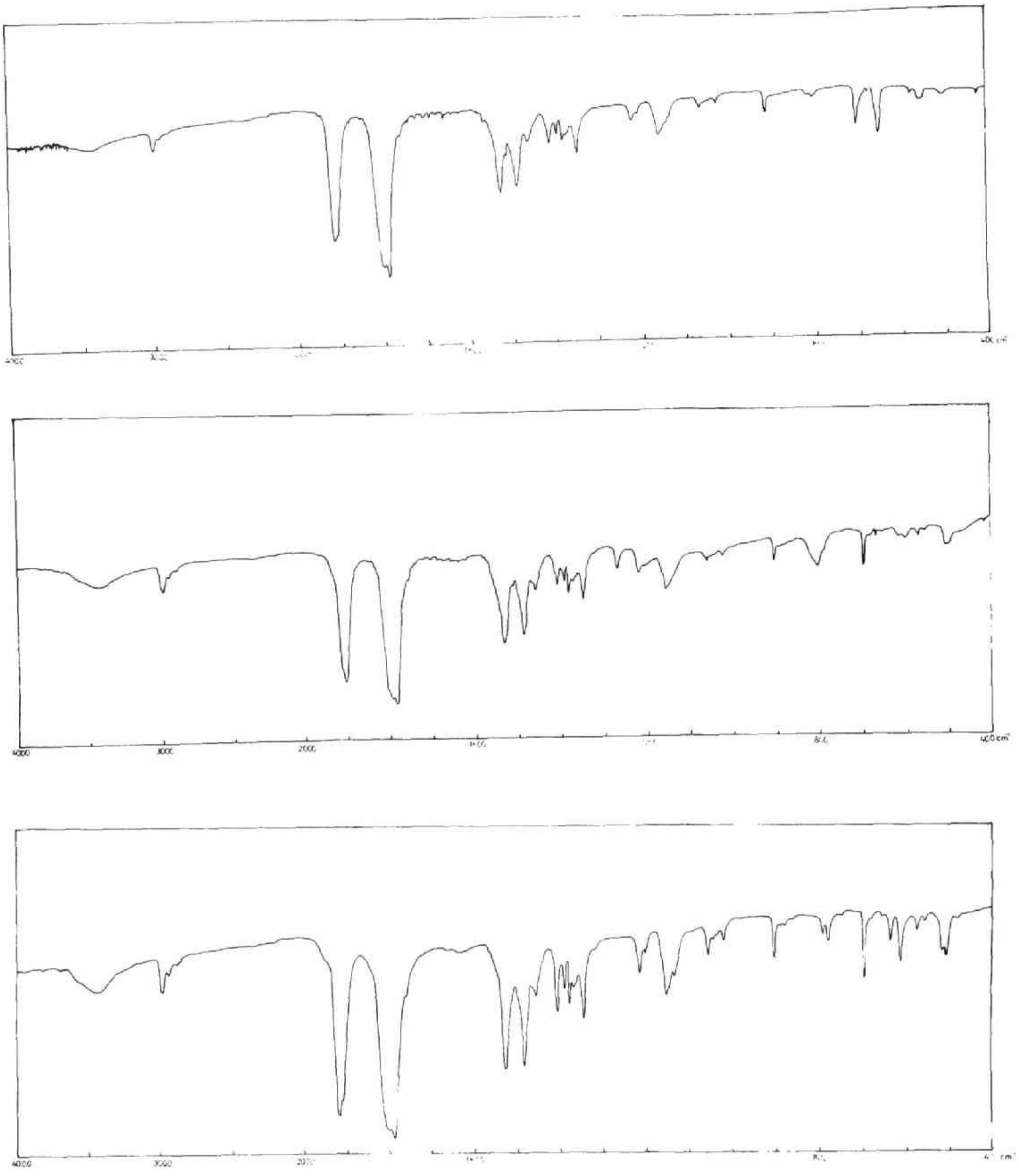
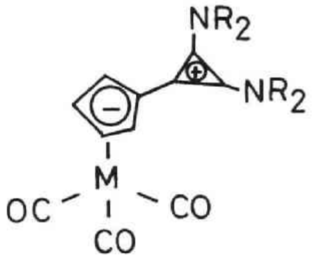


Figure 2. Infrared Spectra of 4 (Cr^0 complex) (top), 5 (Mo^0 complex) (middle) and 6 (W^0 complex) (bottom)

Table 3. Electronic Spectra of Diaminocalicene- and Diaminofulvene-metaltricarbonyl (4 - 6, 7)

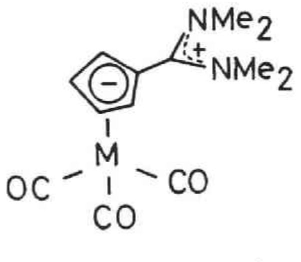
compound		maxima (nm)
calicene-$Cr(CO)_3$	4	278, 416
-$Mo(CO)_3$	5	274, 388
-$W(CO)_3$	6	268, 388
fulvene-$Cr(CO)_3$	7	220, 269, 343, 512



4 M= Cr^{0}

5 Mo^{0}

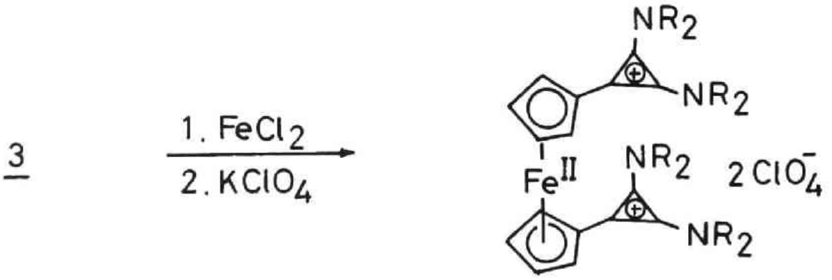
6 W^{0}



7 M= Cr^{0}

Synthesis and Properties of Bis(calicene)metal Complexes (8,10): Metal = Fe^{II} and Co^{II}

The diaminocalicene 3 was treated with an excess molar amount of ferrous chloride in tetrahydrofuran under argon atmosphere. After the reaction was completed, the mixture was treated with aq.$KClO_4$ solution and extracted with dichloromethane. Purification by column chromatography and recrystallization gave stable brick-red needles of bis(calicene)iron complex 8 in 25% yield. The structure of 8 was confirmed by microanalysis and spectral data. Elemental analysis showed that the iron complex was constituted of two calicenes and two perchlorate anions formulated as bis(calicene)iron diperchlorate 8. The complex 8 is diamagnetic and in the ^1H-nmr spectrum (Table 1, Figure 3) The five-membered ring protons show signals of AA'BB' pattern at δ 4.80 ($H_{2',3'}$) and 4.95 ($H_{1',4'}$). These values are at lower magnetic field than that of ferrocene (δ 4.13). Observed deshielding effect is probably attributed to the inductive effect and the large magnetic anisotropy of the diaminocyclopropenium ions. These chemical shifts are comparable to those of the corresponding diaminofulvene complex 2 (δ 4.92 and 5.07).[4]



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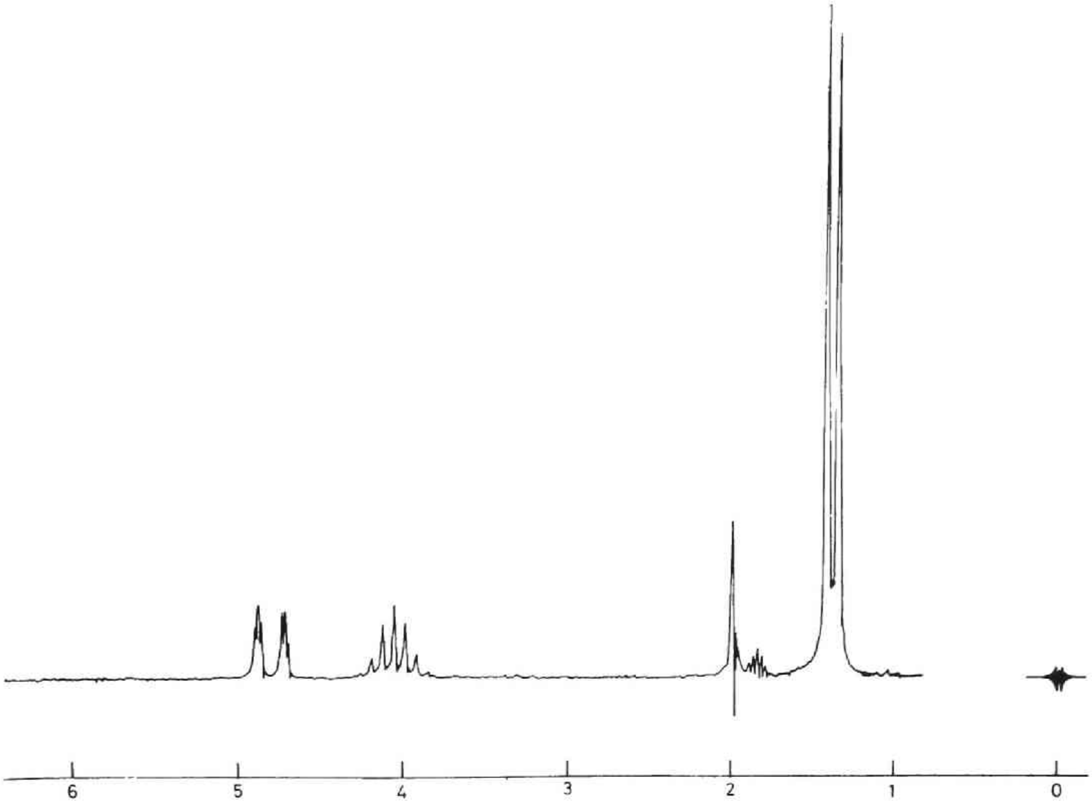


Figure 3. ^{1}H-nmr Spectrum of 8 (Fe^{II} complex) in CD_3CN

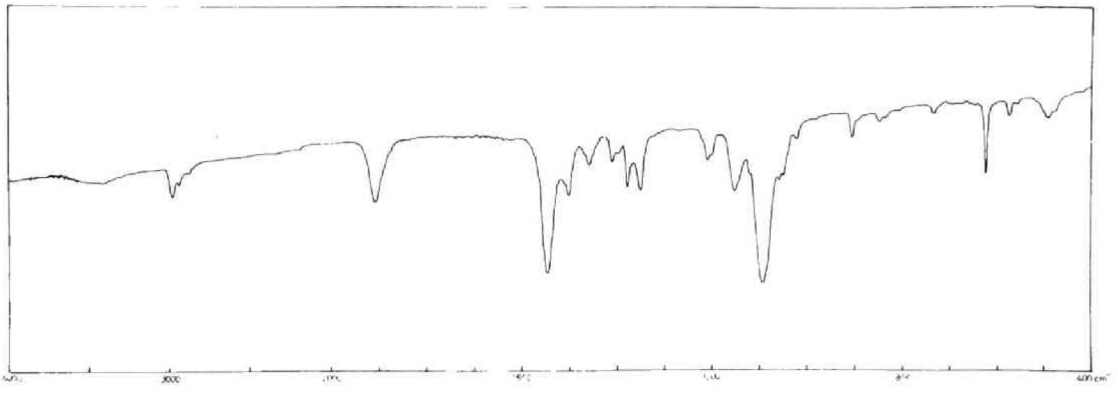
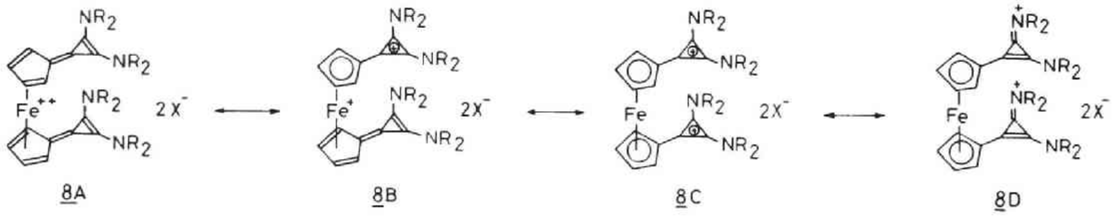


Figure 4. Infrared Spectrum of 8 (Fe^{II} complex)

In the ^{13}C-nmr spectrum of 8 (Table 2), the five-membered ring carbons (C_1- C_4 and C_8) show signals at 74.9,72.7 and 67.5 ppm, which appear at lower field than that of ferrocene (68.1 ppm). This trend is explainable by electronic effect of diaminocyclopropenium groups. The three-membered ring carbons (C_{5},$_{6}$ and C_7) resonate at 130.4 and 107.4 ppm, respectively. These values are very similar to those of 1,2-bis(diisopropylamino)-3-phenylcyclopropenium perchlorate (9) (133.0 and 107.1 ppm, respectively). These chemical shifts indicate that the iron complex 8 is a 1,1'-bis(diaminocyclopropenium)substituted ferrocene derivative and two positive charges in 8 are mainly localized on the two diaminocyclopropenium moieties.



Large contribution of the immonium structure (8D) is also rationalized by the ^{13}C-nmr signals. The methine and methyl carbon signals of isopropyl groups exhibit two pairs of singlets assigned to two non-equivalent isopropyl groups. This result can be explained in terms of the rotational barrier around the C-N bond between the three-membered ring and the amino group.

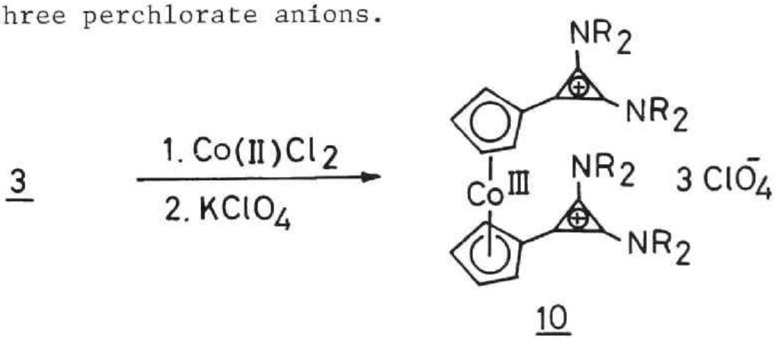
The ir spectrum of 8 (Figure 4) shows a strong band at 1548cm^{-1} which is comparable to that of the diaminocyclopropenium ion 9 (1553

cm^{-1}). High frequency of the C-N stretching vibration suggests the increase in the double bond character of the carbon-nitrogen bond (structure <u>8D</u>). It is noteworthy that comparison of the stretching vibration of <u>8</u> with that of the free diaminocalicene <u>3</u> ($1490cm^{-1}$) also indicates the preference of the ionic structures (<u>8C</u> and <u>8D</u>) at the ground state.

The electronic spectrum of <u>8</u> exhibites absorptions at 322 and 466 nm with shoulder at 245 nm. Low excitation band at 466 nm shows bathochromic shift relative to that of parent ferrocene (440 nm).

An attempt to prepare <u>8</u> from the reaction with diaminochlorocyclopropenium ion and ferrocene or 1,1'-dilithioferrocene was failed. Present synthetic method seemed to provide a facile pathway to prepare the type of the sandwich compound of calicene like <u>8</u>.

The successful synthesis of <u>8</u> prompted to carry out the attempt to replace the central atom of the sandwich compound from iron to other transition metals. The reaction of the calicene with cobalt(II) chloride in tetrahydrofuran at room temperature afforded stable orange powder of the cobalt(III) complex (<u>10</u>). Elemental analysis and spectroscopic properties are compatible to bis-calicene complex with three perchlorate anions.



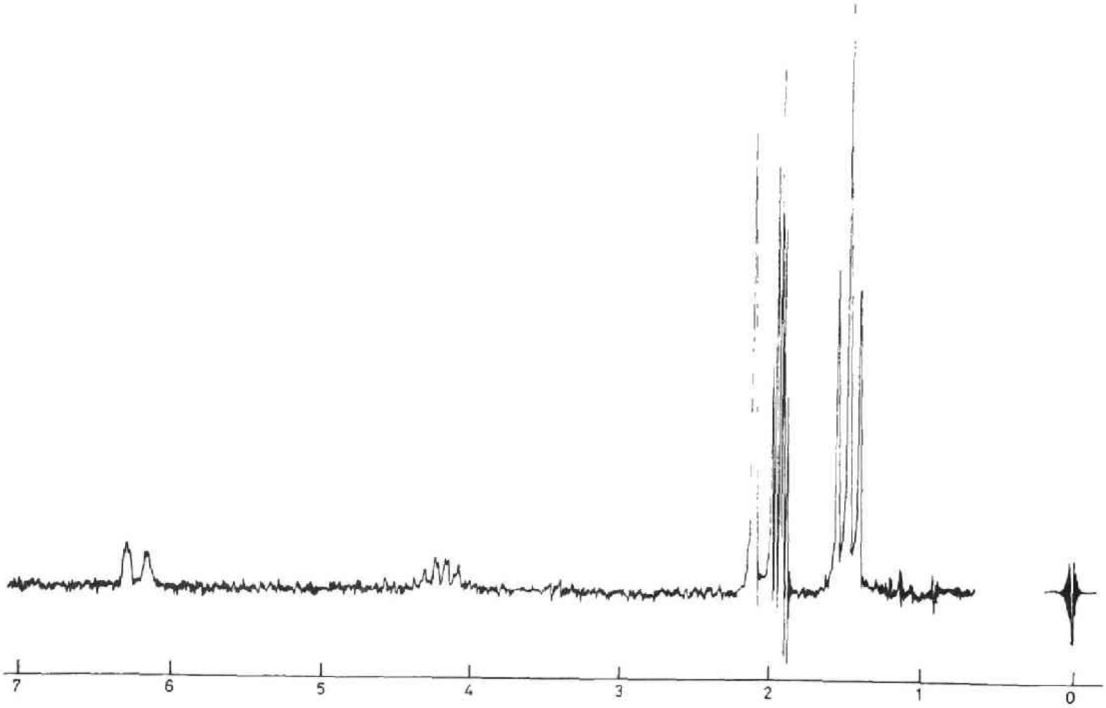


Figure 5. ^{1}H-nmr spectrum of 10 (Co^{III} complex) in CD_3CN

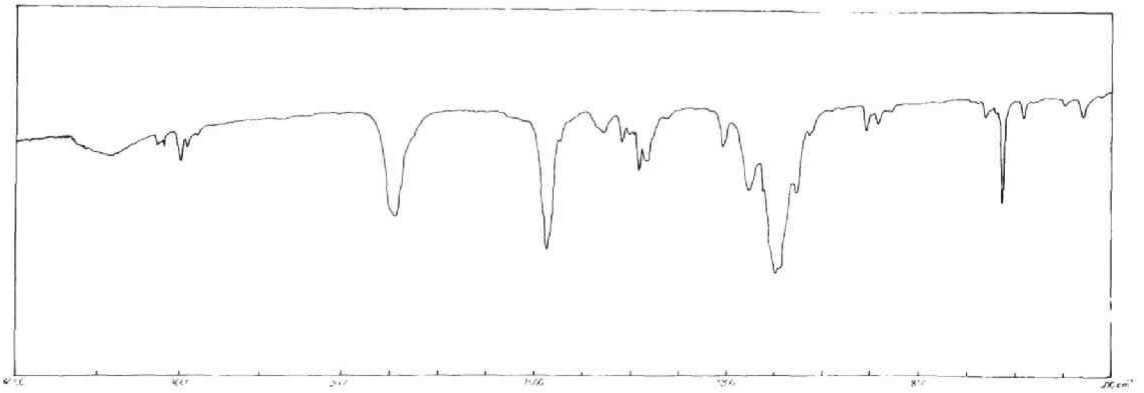
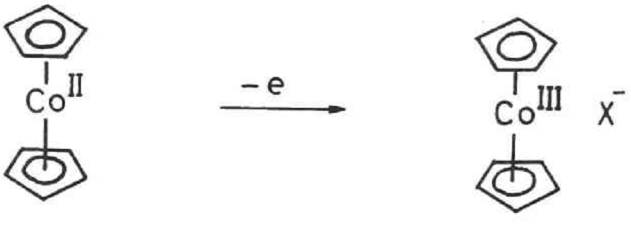


Figure 6. Infrared spectrum of 10 (Co^{III} complex)

The complex 10 is a diamagnetic and the central cobalt atom was found to be trivalent. It was reported that cobaltcene (Co^{II}) (11) was readily oxidized in atmosphere to give stable cobalticinium (Co^{III}) cation (12)[7,8].



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12

The cobalticinium derivative 10 seems to be a oxidation product of the cobaltcene derivative which is generated initially from the reaction of 3 and cobalt(II) chloride.

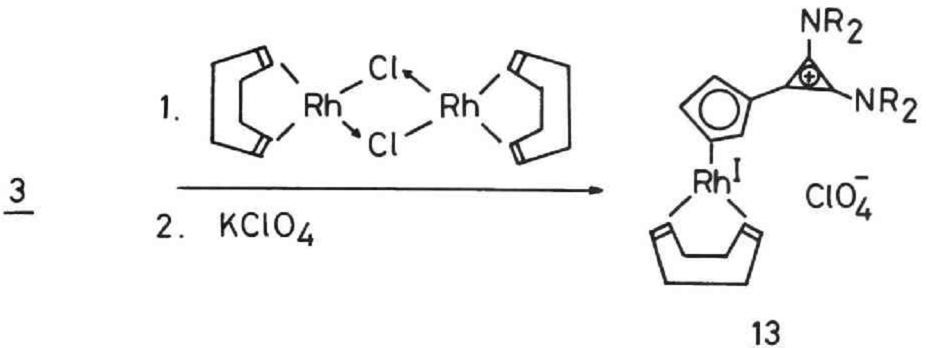
In the ^1H-nmr spectrum (Table 1,Figure 5), the five-membered ring protons show signals at δ 6.16 and 6.30 as an AA'BB' pattern. The chemical shifts of the ring protons are shifted to lower field than that of cobalticinium cation 12 (δ 5.76) due to the electronic effect of the diaminocyclopropenium groups. The ^{13}C-nmr spectrum (Table 2) of 10 reveals signals of cyclopentadienyl ring carbons (C_1-C_4 and C_8) at 87.7, 84.1 and 73.9 ppm,which appear essentially in the same region of that of 12 (85.0 ppm). The three-membered ring carbons ($C_{5,6}$ and C_7) resonate at 131.3 and 112.7 ppm,respectively. Again, these chemical shifts are very similar to those of diaminocyclopropenium 9 (133.0 and 107.1). The spectroscopic data clearly indicate that the complex 10 is a cobalticinium derivative substituted with two diaminocyclopropenium groups. Large contribution of immonium structure to the ground state is supported by the feature of the isopropyl signals in the ^{1}H-nmr and ^{13}C-nmr spectra. The isopropyl groups show two different sets of signals in both ^{1}H- and ^{13}C-nmr spectra, indicating restricted rotation around the C-N bond.

In the ir spectrum of 10 (Figure 6), a strong band of the C-N stretching vibration appears at 1575 cm^{-1}. Very high frequency of the band also rationalizes large contribution of the immonium structure. In the cobalt complex 10, the polalization of the ligand (diaminocalicene) is extremely large and the cyclopropenium ion is stabilized by the amino group.

The cobalt(III) complex 10 is isoelectric to the iron(II) complex 8, showing absorptions at 272 nm (log ε 4.46) and 482 (4.19) in the electronic spectrum. The long wavelength absorption (482 nm) of 10 lies at lower energy of 8 (458 nm).

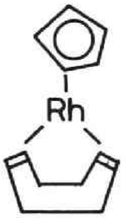
Synthesis and Properties of Calicene-rhodium-cycloocta-1,5-diene Complex (13)

The rhodium complex 13 was synthesized from 3 and bis(cycloocta-1,5-diene)dichlorodirhodium. Its elemental analysis and spectral properties are consistent with the structure formulated as 13. The complex 13 is air-stable yellow plates, insoluble in non-polar solvents but freely soluble in polar organic solvents.



13

The ^{13}C-nmr spectrum of 13 (Figure 7) shows three doublets at 91.0, 88.6 and 85.7 ppm due to the cyclopropenium carbons ($C_{1,4}$, $C_{2,3}$ and C_8 respectively) with $^{13}C-^{107}Rh$ coupling constants 2.9 - 3.9 Hz. This fact indicates the coordination of the rhodium atom to the cyclopentadienyl ring of the diaminocalicene 3. The values of the chemical shifts and coupling constants of 13 are identical with those of cyclopentadienylrhodiumcycloocta-1,5-diene (14) (86.4 ppm and 3.7 Hz, respectively)^9. The cyclopropenium carbons ($C_{5,6}$ and C_7) resonate at



14

126.4 and 105.1 ppm, showing considerable contribution of ionic structures (13B and 13C) of the ligand to the ground state.

The ^{1}H-nmr spectrum (Figure 8), cyclopentadienyl protons appear at δ 5.52 and 5.59 as an AA'BB' pattern, slightly low field compared with those of 14 due to the influence of the diaminocyclopropenium

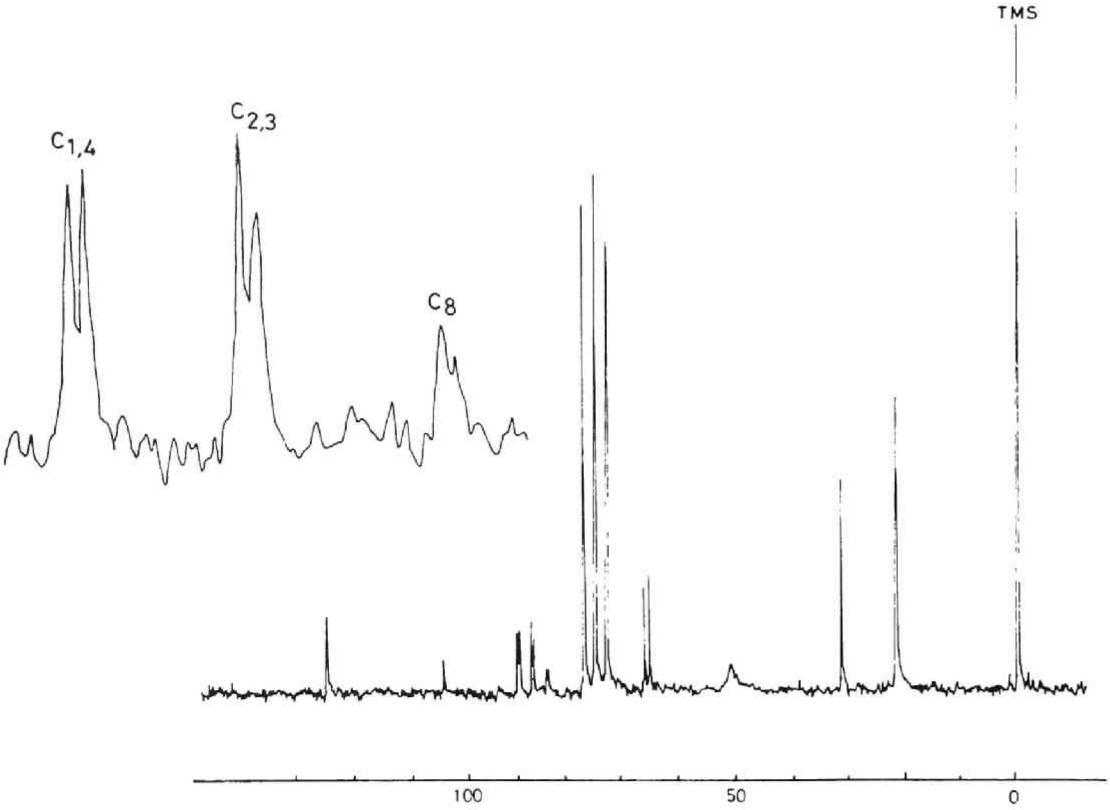


Figure 7. ^{13}C-nmr Spectrum of 13 (Rh^{I} complex) in $CDCl_3$

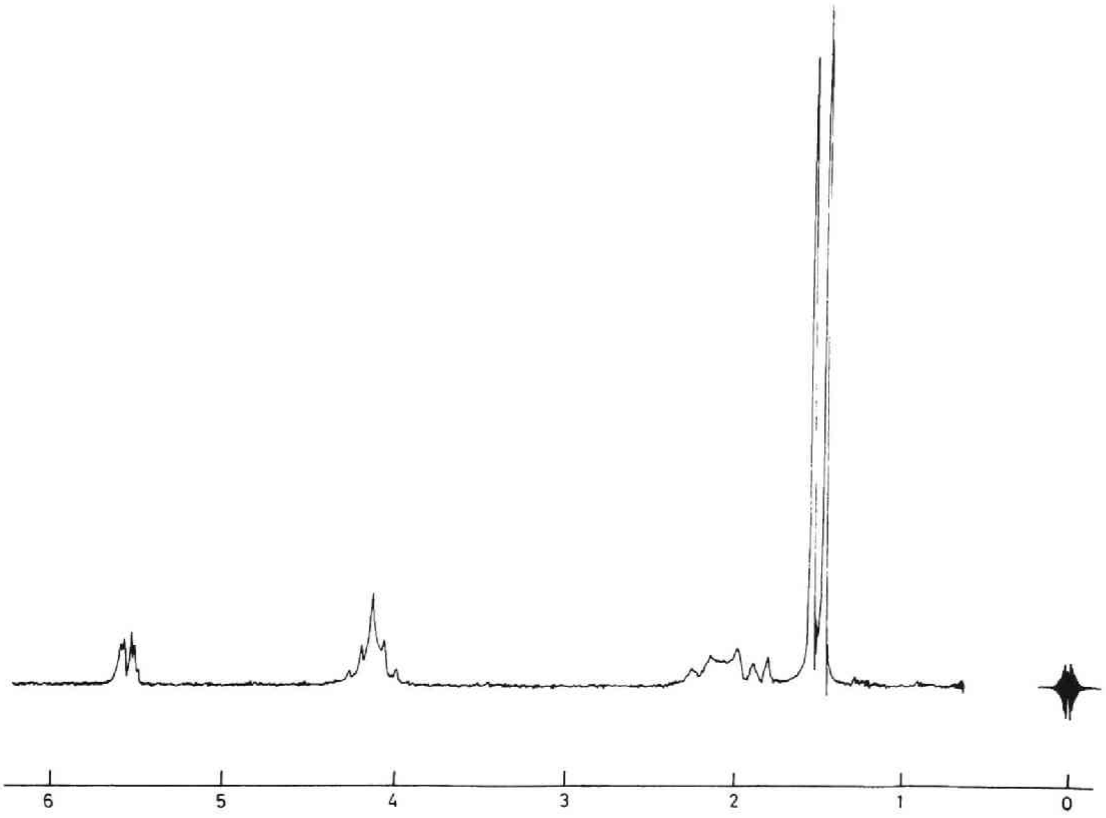


Figure 8. ^{1}H-nmr Spectrum of 13 (Rh^{I} complex) in COCl$_3$

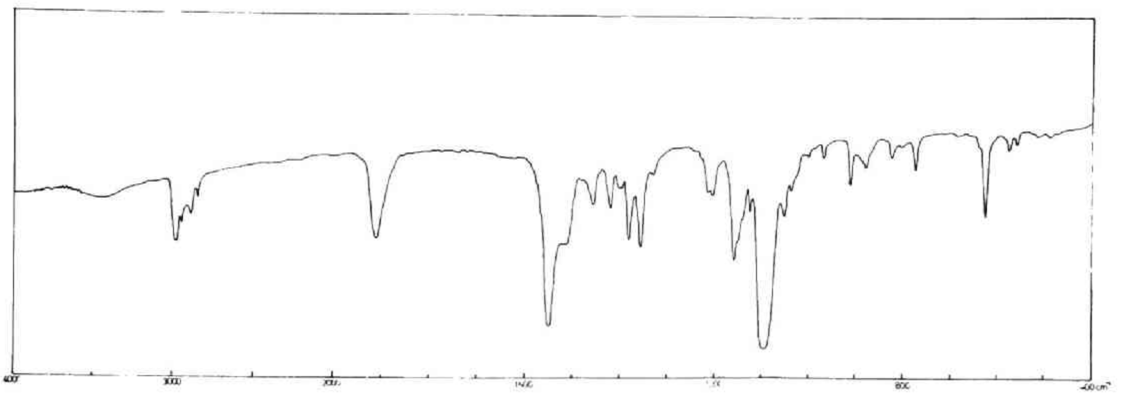
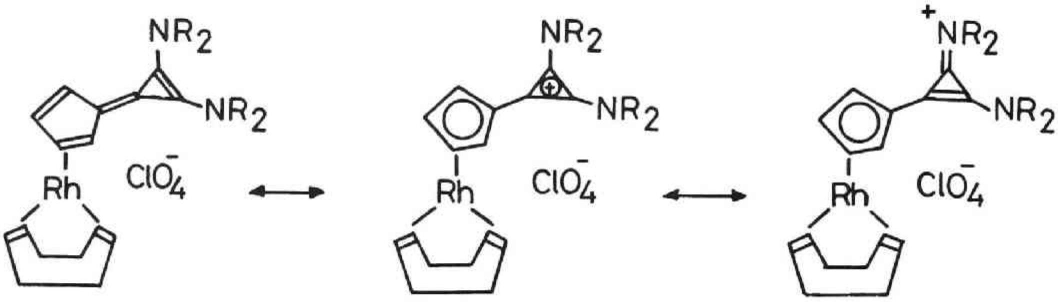


Figure 9. Infrared Spectrum of 13 (Rh^{I} complex)

group. While, the chemical shifts of the cycloocta-1,5-diene moiety of 13 are quite similar to those of 14. In the ir spectrum (Figure 9) of 13, the C-N stretching vibration appeared at 1545 cm^{-1} indicating considerable double bond character. These spectral data clearly show that the rhodium complex 13 can be represented by ionic structures (13B and 13C).



13A 13B 13C

EXPERIMENTAL

Diaminocalicene-chromiumtricalbonyl (4)

A mixture of 5,6-bis(diisopropylamino)calicene 3 300 mg (1 mmol) and chromiumhexacarbonyl 220 mg (1 mmol) were refluxed for 5 hr in 5 ml of dioxane under argon atmosphere. The solvent was removed under reduced pressure and the residue was chromatographed on alumina (Merk II-III). Yellow band eluted by pentane-acetone mixture (6:4) was collected and the solvent was evaporated under reduced pressure. Crystallization of the residue from hexane-acetone gave 87 mg (20%) of 4 as air-unstable orange needles; mp 196°C(dec).

Anal. Calcd for $C_{23}H_{32}N_2O_3Cr$: C, 63.28; H, 7.39: N, 6.42.
Found : C, 63.18; H, 7.50; N, 6.60.

Diaminocalicene-molybdenumtricarbonyl (5)

Diaminocalicene 3 300 mg (1 mmol) and molybdenumhexacarbonyl 264 mg (1 mmol) were refluxed for 1.5 hr in 10 ml of tetrahydrofuran. The mixture was treated in an analogous manner as described above and 150 mg (31%) of 5 was obtained as air-unstable yellow needles; mp 148° C(dec).

Anal. Calcd for $C_{23}H_{32}N_2O_3Mo$: C, 57.49; H, 6.71; N, 5.83.
Found : C, 55.09; H, 6.80; N, 5.63.

Diaminocalicene-tungstentricarbonyl (6)

A mixture of diaminocalicene 3 300 mg (1 mmol) and tungstenhexacarbonyl 352 mg (1 mmol) were refluxed for 5 hr in 5 ml of dioxane under argon atmosphere as described above and 160 mg (28%) of 6 was obtained as air-sensitive yellow needles;mp i48°C(dec).

Anal. Calcd for $C_{23}H_{32}N_2O_3W$: C, 48.60; H, 5.67; N, 4.93.
Found; C, 47.32; H, 5.82; N, 4.72.

Bis(diaminocalicene)iron diperchlorate (8)

To 45 mmol of anhydrous ferrous chloride in 40 ml of tetrahydrofuran was added diaminocalicene 3 900 mg (3 mmol) in 13 ml of tetrahydrofuran. The mixture was stirred at room temperature for 6 hr and then refluxed for 2.5 hr. After cooling to room temperature, the reaction mixture was poured into aq. potassium perchlorate and extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was crystallized from acetone-ether to give 321 mg (25%) of 8 as stable brick-red needles; mp 220°(dec); ir (KBr, cm^{-1}) 1908, 1548, 1502, 1410, 1380, 1351, 1092, 623 ; uv (CH_3CN, nm) 245 (sh), 322 (log ε 4.32), 466 (3.08).

Anal. Calcd for $C_{40}H_{64}N_4O_8Cl_2Fe$: C, 56.14; H, 7.54; N, 6.55.
Found : C, 56.44, H, 7.74, N, 6.56.

Bis(diaminocalicene)cobalt triperchlorate (10)

Diaminocalicene 3 300 mg (1 mmol) and anhydrous cobalt(II) chloride 155 mg (1.2 mmol) were stirred in 15 ml of tetrahydrofuran for 18 hr at room temperature under argon atmosphere. The mixture was poured into aq. potassium perchlorate and extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was crystallized from acetonitrile-ether to give 133 mg (25%) of 10 as stable orange powder; mp > 300°C; ir (KBr, cm^{-1}) 1887, 1575, 1453, 1416, 1380, 1365, 1098,625; uv (CH_3CN, nm) 272 (log ε 4.46), 303 (sh), 385 (sh), 482 (4.19).

Anal. Calcd for $C_{40}H_{64}N_4O_{12}Cl_3Co$

C, 50.14; H, 6.73; N, 5.85; Cl, 11.10.

Found C, 49.99; H, 6.79; N, 6.00; Cl, 10.84.

Diaminocalicene-rhodium-cycloocta-1,5-diene perchlorate (13)

Diaminocalicene 3 150 mg (0.5 mmol) and bis(cycloocta-1,5-diene)-dichlorodirhodium 123 mg (0.25 mmol) were refluxed for 2 hr in 8 ml of benzene. The reaction mixture was poured into aq.potassium perchlorate, extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate and the solvent was evaporated under reduced pressure. The residue was chromatographed on silica gel using benzene-acetone (7:3) as eluent. Crystallization from dichloromethane-ether gave 62 mg (20%) of 13 as yellow plates, mp 220°C (dec); ir (KBr, cm^{-1}) 1907, 1545, 1453, 1415, 1376, 1352, 1095,623; uv (CH_3CN, nm) 222(sh), 264(sh), 332(log ε 4.05).

Anal. Calcd for $C_{28}H_{44}N_2O_4ClRh$: C, 55.04; H, 7.26, N, 4.58.

Found: C, 55.00; H, 7.34; N, 4.71.

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CHAPER 6

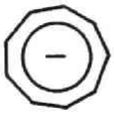
PREPARATION AND STRUCTURES OF 1,6-METHANO-9,10-DIAMINOTRIANONAFULVALENE

SUMMARY

1,6-Methano-9,10-diaminotrianonafulvalene (13), the first example of trianonafulvalene, are prepared and characterized. The ^{1}H-nmr spectrum of 13 provides the evidence of the contribution of polar canonical structures to some extent. An attempt to prepare 9,10-diaminotrianonafulvalene 7 is also described.

INTRODUCTION

Cyclononatetraenide anion (1) was prepared in 1963 and proved to be a aromatic 10π electron system[1]. The finding of the aromaticity of this carbanion has prompted the syntheses of a series of cross-conjugated systems possessing cyclononatetraenilidene moiety, e.g., nonafulvene, pentanonafulvalene and heptanonafulvalene. Nonafulvene (2) has been prepared recently and found to be polyolefinic[2]. A diamino derivative (3) has been isolated as unstable yellow crystals[3]. Benzo analogs of pentanonafulvalene and heptanonafulvalene such as 4 and 5 have been synthesized and suggested to be nonplaner, non-aromatic molecules, the dipolar forms making little contribution to the structures[4]. The smallest nonafulvalene, trianonafulvalene (6),



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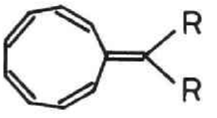
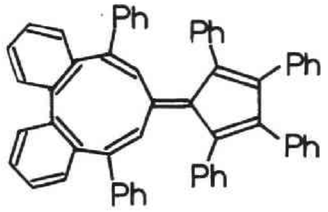


2 R=H

3 =NMe$_2$



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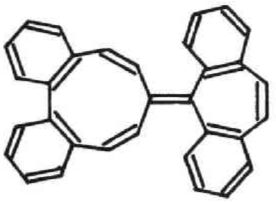

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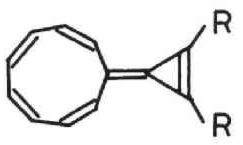


6 R = H

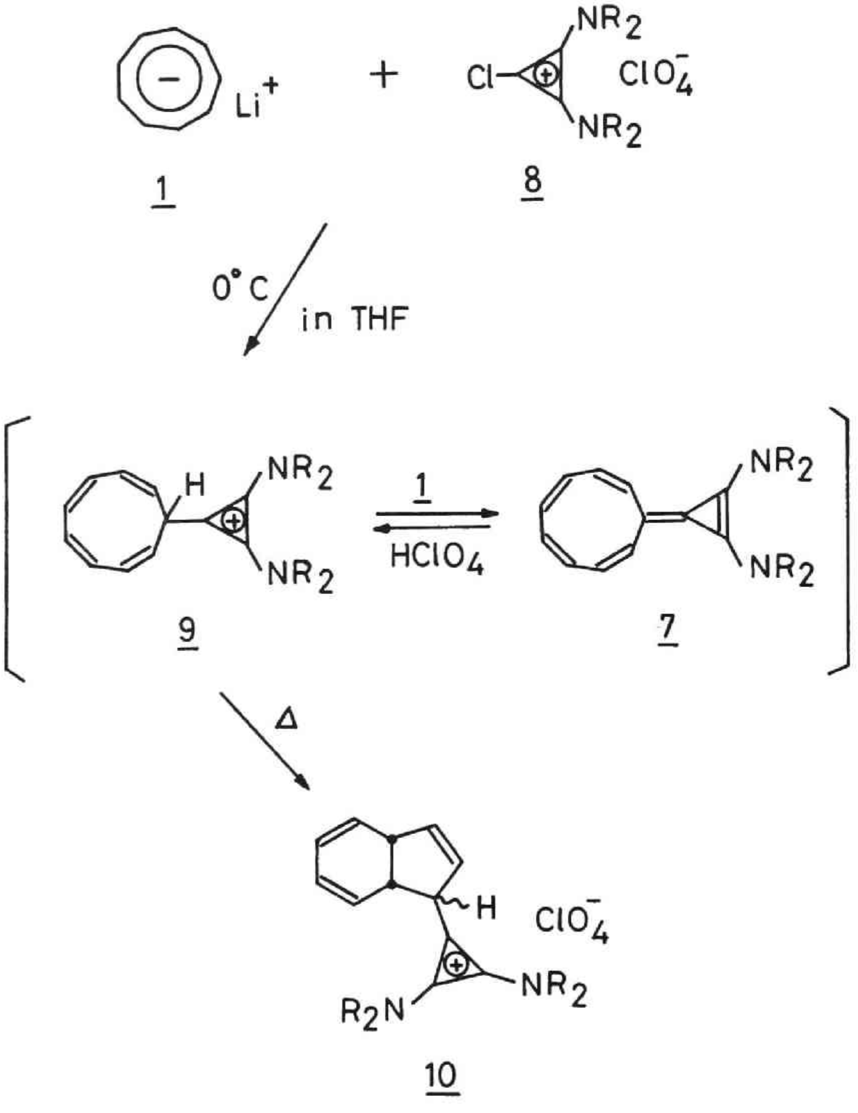
7 = NR$_2$

has never been prepared so far[5]. It is considered that the striking electron-donating effect of amino group described in the previous chapters should also stabilize the electronic system of trianonafulvalene 6. In this chapter, synthesis and characterization of diaminotrianonafulvalene derivative are described.

RESULTS AND DISCUSSION

Reaction of Lithium Cyclononatetraenide and Diaminochlorocyclopropenium Perchlorate

To a suspension of diaminochlorocyclopropenium perchlorate (8) in tetrahydrofuran was added a two molar amount of lithium cyclononatetraenide (1) in tetrahydrofuran at 0°C under argon atmosphere. The reaction mixture turned to deep yellow in color and the suspended cyclopropenium ion 8 has gone into the solution. The reaction mixture was acidified with diluted perchloric acid and chromatographed on silica gel to affored 10 as pale yellow powder. The structure of the product was confirmed as an 8,9-dihydroindene derivative based on the elemental analysis and the spectral data. It has been reported[1] that cyclononatetraene derivatives rapidly undergo electrocyclic ring closure to afford 8,9-dihydroindene derivatives even at room temperature. Therefore, the reaction mechanism is considered as illustrated in Scheme 1. The addition product (9) of the cyclononatetraenide 1 and the cyclopropenium 8 was deprotonated by the action of the excess cyclononatetraenide 1 to yield diaminotrianonafulvalene (7). The fulvalene 7 was protonated by the addition of perchloric acid to reproduce the cyclopropenium cation 9 which rearranged to the isolated product 10. The work up of the reaction mixture without the addition of perchloric acid gave a trace of 10 as a isolable product. These experimental results suggest that diaminotrianonafulvalene 7 is extremely sensitive to air. The main obstacle to the synthesis of diamino-

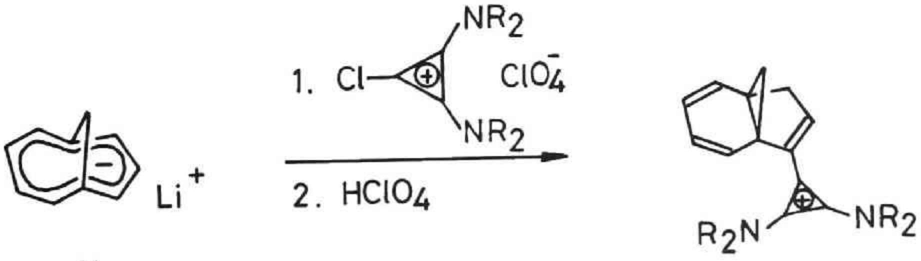


Scheme 1. Reaction of Lithium Cyclononatetraenide 1 and Diaminochlorocyclopropenium Perchlorate 8

trianonafulvalene is considered to be the high reactivity toward oxygen and facile rearrangement to 8,9-dihydroindene derivative.

Reaction of Lithium 1,5-Methanocyclononatetraenide and Diaminochlorocycloprepenium Perchlorate

A wide variety of bridged annulenes has been prepared and the chemistry of this area is extensively studied[6]. The methano bridged aromatic anion, 1,5-methanocyclononatetraenide (11), has been found to be stable even at room temperature[7]. A thermally stable diaminotrianonafulvalene derivative (13) was prepared from the reaction of 1,5-methanocyclononatetraenide 11 and diaminochlorocyclopropenium 8. To a suspension of 1,2-bis(diisopropylamino)-3-chlorocyclopropenium perchlorate 8 in tetrahydrofuran was added the solution of lithium 1,5-methanocyclononatetraenide 11 in tetrahydrofuran at room temperature under argon atmosphere. After the treatment of diluted perchloric acid, pale yellow crystals of 12 were obtained in 33% yield.



11

12

The cyclopropenium salt 12 is quite stable in air at room temperature. The structure was confirmed by the spectral data and the microanalysis. The ^{1}H-nmr spectrum (Figure 1) of 12 shows signals at δ 6.20 (m, 2H, olefin), 5.89 (m, 3H, olefin), 4.13 (sep, 2H, $-C\underline{H}(CH_3)_2$), 3.87 (sep, 2H, $-CH(CH_3)_2$), 2.85 (dq, 2H, $-CH_2-$ in the five-membered ring, J= 18.4 and 2.4 Hz), 1.44 (d, 18H, $-CH(C\underline{H}_3)_2$) and 1.29 (d, 6H, $-CH(C\underline{H}_3)_2$). The methylene protons in the three-membered ring show a pair of doublets at δ 1.59 (1H) and 0.22 (1H) with the coupling constant J_{gem} 3.5 Hz. The value of the small coupling constant give the proof to the proposed norcaradiene structure 12.

Deprotonation of 12 was performed by the use of dimethylsulfinyl anion. Addition of dimethylsulfinyl sodium in dimethylsulfoxide (DMSO) to the solution of 12 in DMSO immedeately gave a orange-red solution. The ^{1}H-nmr spectrum (Figure 2) provides direct evidence for the formation of 1,6-methano-9,10-diaminotrianonafulvalene (13) : 6.60 (m, 3H, olefin), 6.29 (m, 2H, olefin), 5.86 (m, 1H, olefin), 4.16 (sep, 4H, $-C\underline{H}(CH_3)_2$), 1.27 (a pair of d, 24H, $-CH(C\underline{H}_3)_2$), 1.14 (d, 1H, $-CH_2-$, J= 7.0 Hz), -0.60 (d, 1H, $-CH_2-$, J= 7.0 Hz). The increase in the *gem*-coupling constant from 3.5 to 7.0 Hz in 12 and 13, respectively, is consistent with the change from cyclopropane to methylene bridge type protons[8], e.g., the equiliblium between the cycloheptatriene form (13) and the norcaradiene form (13') lies far to 13 at room temperature. It must be noted that in the corresponding nonafulvene system (14)[9], the equiliblium between 14 and 14' lies far to the norcaradiene form (14'), in quite contrast to the present system,

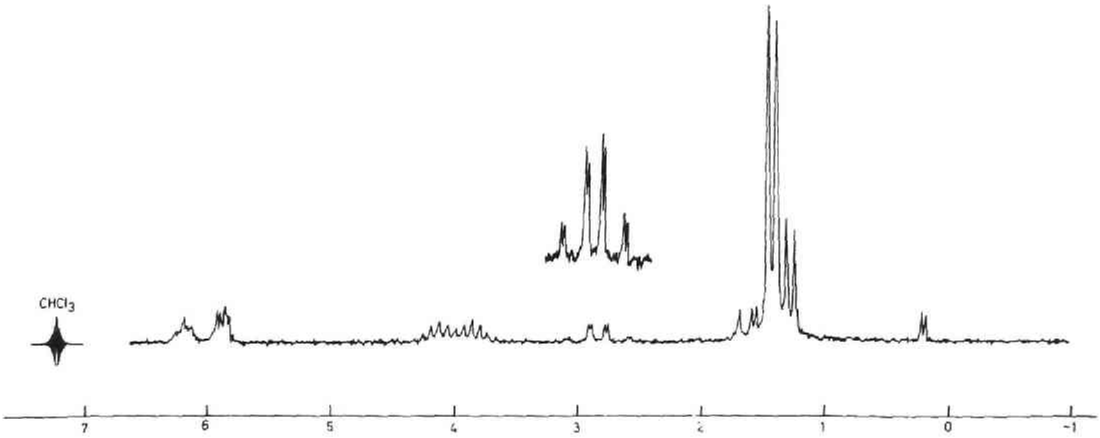


Figure 1. ^{1}H-nmr Spectrum of <u>12</u> in $CDCl_3$

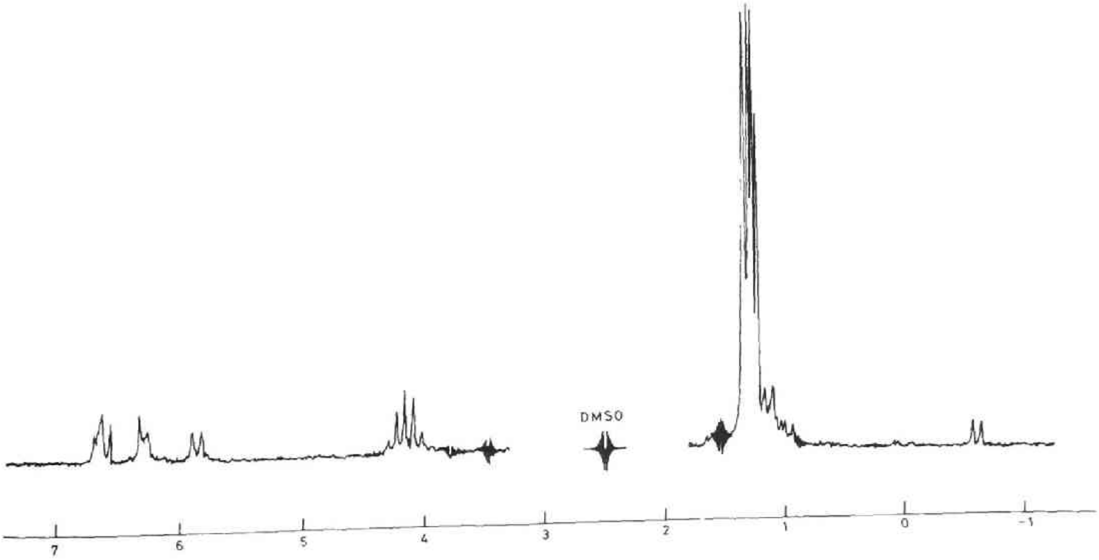
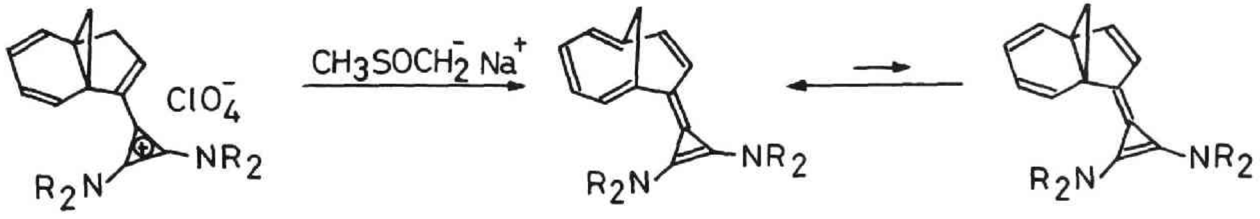


Figure 2. ^{1}H-nmr Spectrum of <u>13</u> in DMSO-d_6



12 13 13'

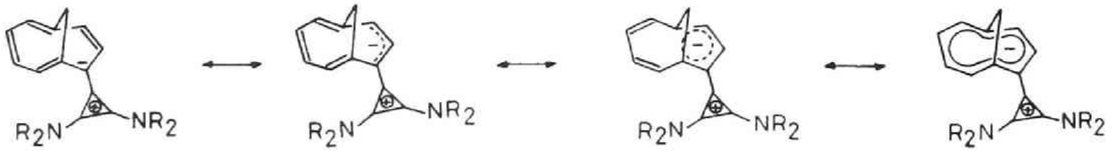
14 14'

R = H
= SMe
= NMe_2

Table 1. Chemical Shifts and Coupling Constants of the Bridge-methylene protons

compound		δ ($-CH_2-$, ppm)	Δ δ	J_{gem} (Hz)
<u>12</u>		1.59, 0.22	1.37	3.5
<u>15</u>		1.47, 0.10	1.37	3.5
<u>14</u>	R = H	1.65, 0.19	1.46	2.5
	SCH_3	1.89, 0.30	1.59	2.9
	$N(CH_3)_2$	1.71, 0.13	1.58	3.0
<u>13</u>		1.14,-0.60	1.74	7.0
<u>11</u>		-0.45,-0.95	0.50	7.5

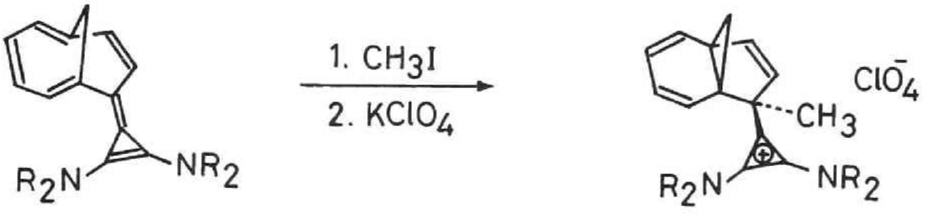
diaminotrianonafulvalene 13. In Table 1 are summarized the values of the chemical shifts and the *gem*-coupling constants of the bridge-methylene protons in the diaminotrianonafulvalene 13 and related compounds. In comparing the chemical shifts of the bridge-methylene protons in the trianonafulvalene 13 and those of the related norcaradiene compounds 12, 15 and 14, the protons in 13 are more shielded than those in 12, 15 and 14. This fact suggests the contribution of the polar canonical structures (13A - 13D) to the ground state of 13. On the other hand, the bridge-methylene protons of the 10π aromatic anion 11 resonate at higher magnetic field than those of 13, indicating the contribution of the 10π aromatic structure 13D is not dominant.



13A 13B 13C 13D

It is important to note that the difference of the chemical shifts between the two bridge-methylene protons ($\Delta\delta$) in 13 (1.74 ppm) is very large comparing that in the aromatic anion 11 (0.50 ppm). If the 10π aromatic structure 13D is important to the electronic structure of 13, the diamagnetic ring current on the nine-membered ring should shift the two bridge-methylene protons almost equally to higher field. Observed large value of $\Delta\delta$ in 13 suggests the contribution of the ionic structures (13A, 13B) as well as the 6π homocyclopentadienide structure (13C) rather than the 10π cyclononatetraenide structure (13D).

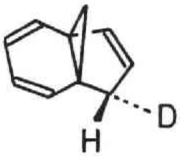
The generation of 1,6-methano-9,10-diaminotrianonafulvalene 13 was also confirmed by the reaction of 13 with methyl iodide. To the solution of 13 in DMSO was added methyl iodide in DMSO. The color of the mixture turned from orange-red to light brown. After the treatment of potassium perchlorate, the methylated compound (16) was obtained in 65% yield.



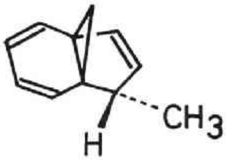
13

16

The position of methylation was confirmed by the ^{1}H-nmr spectrum: 6.20 (m, 2H, olefin), 5.95 (m, 3H, olefin), 5.50 (d, 1H, J= 6 Hz, olefin), 3.90 (m, 4H, $-C\underline{H}(CH_3)_2$), 1.84 (d, 1H, J= 3.8, $-CH_2-$), 1.81 (s, 3H, $-CH_3$), 1.47 (d, 24H, $-CH(C\underline{H}_3)_2$), 0.09 (d, 1H, J=3.8, $-CH_2-$). The exclusive formation of 16 is in good agreement the high electron density on the C_{12} carbon of 13 calculated by simple HMO. The sharp singlet at δ 1.81 due to the methyl protons suggests the stereospecific introduction of methyl group at C_{12} of 13. A remarkable stereospecificity has been reported for the electrophilic attack of the parent aromatic anion 11 by deuterium oxide and methyl iodide to afford 17 and 18, respectively.[10] The stereochemistry of the methyl group in 16



17



18

could not be rigorously determined, however, in analogy to the case of 11, attack by methyl iodide must occur from the side opposite the methylene bridge.

EXPERIMENTAL

1,2-Bis(diisopropylamino)-3-(8,9-dihydroindenyl)cyclopropenium perchlorate (10)

To a suspension of 1,2-bis(diisopropylamino)-3-chlorocyclopropenium perchlorate (8) 742 mg (8 mmol) in 1 ml of tetrahydrofuran was added a solution of lithium cyclononatetraenide (1)(8 mmol) in 15 ml of tetrahydrofuran at 0°C under argon atmosphere. The color of the reaction mixture was turned to deep yellow. After stirring over night at 0°C, the mixture was poured into dil. perchloric acid and extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel using benzene-acetone (7:3) as eluent. Crystallization from dichloromethane-ether gave pale yellow powder of 10 335 mg (37%): mp 240°C (dec); ir (KBr, cm^{-1}) 2980, 1905, 1545, 1346, 1093, 625: ^{1}H-nmr (CD_2Cl_2) δ 6.5-5.5(m,6H, olefin), 4.0(m,4H,$-C\underline{H}(CH_3)_2$), 4.0-2.0(m,3H,methine), 1.39(d,12H, $-CH(C\underline{H}_3)_2$), 1.37(d,12H,$-CH(C\underline{H}_3)_2$).

Anal. Calcd for $C_{24}H_{37}N_2ClO_4$: C, 63.63; H, 8.23; N, 6.19.
Found : C, 63.66; H, 8.04; N, 6.18.

1,2-Bis(diisopropylamino)-3-(7-tricyclo[4.3.1.0^{1,6}]-deca-2,4,7-trienyl)-cyclopropenium perchlorate (12)

To a suspension of 8 742 mg(2 mmol) in 12 ml of tetrahydrofuran was added a solution of lithium 1,6-methanocyclononatetraenide (11) prepared from tricyclo[4.3.1.0^{1,6}]-deca-2,4,7-triene (15) 520 mg (4 mmol) and n-butyl lithium (4 mmol) in 16 ml of tetrahydrofuran in the presence of N,N,N',N'-tetramethylethylenediamine (2 ml). The reaction mixture was stirred for 30 min at room temperature under argon and poured into dil. perchloric acid, and then extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel using benzene-acetone (8:2) as eluent. Crystallization from acetone-ether gave pale yellow crystals of 12 307 mg (33%): mp 220°C(dec); ir (KBr, cm^{-1}) 2975, 1910, 1557, 1457, 1353, 1092, 624; uv (CH_3CN) λ_{max} 245 (log ε 3.95), 264 (sh).

Anal. Calcd for $C_{25}H_{37}N_2ClO_4$: C, 64.57; H, 8.02; N, 6.03.

Found : C, 64.34; H, 8.21; N, 5.88.

1,6-Methano-9,10-bis(diisopropylamino)trianonafulvalene (13)

^{1}H-Nmr measurement

To a solution of dimethylsulfinyl-d_5 sodium prepared from sodium hydride 5 mg (0.2 mmol) and 0.3 ml of dimethylsulfoxide-d_6 was added a solution of 12 47 mg (0.1 mmol) in 0.2 ml of dimethylsulfoxide-d_6. The resulting orange-red solution revealed the spectrum shown in Figure 2.

1,2-Bis(diisopropylamino)-3-[9-(9-methyltricyclo[4.3.1.0^{1,6}]-deca-2,4,7-trienyl)]cyclopropenium perchlorate (16)

To a solution of 1,6-methano-9,10-diaminotrianonafulvalene 13 (0.1 mmol) in 3 ml of dimethylsulfoxide (DMSO) was added methyl iodide 0.05 ml (0.75 mmol) in 1 ml of DMSO at room temperature under argon.

After stirring for 1 hr, the reaction mixture was poured into aq. potassium perchlorate and extracted with dichloromethane. The extract was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel using benzene-acetone (8:2) as eluent. Crystallization from acetone-ether gave pale yellow crystals of 16 31 mg (65%): mp 206°C; ir (KBr, cm^{-1}) 2975, 1881, 1533, 1450, 1376, 1357, 1093; uv (CH_3CN) λ_{max} 243 (log ε 4.05), 280 (sh).

Anal. Calcd for $C_{26}H_{39}N_2ClO_4$: C, 65.19; H, 8.21: N, 5.85.

Found : C, 65.20; H, 8.43: N, 5.65.

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4. Synthesis and Structures of 5,6-Diaminocalicenes
   Z. Yoshida, S. Araki and H. Ogoshi
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5. Reactions of 5,6-Diaminocalicene with Electrophiles and Dienophiles
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6. Synthesis and Structures of Transition Metal Complexes of 5,6-Diaminocalicene
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7. Preparation and Structures of 1,6-Methano-9,10-diaminotriananonafulvalene

   Z. Yoshida, S. Araki and H. Ogoshi

   submitted to *J. Am. Chem. Soc.*

ORAL PRESENTATION LIST

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3. Preparations and Structures of 5,6-Diaminocalicenes
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4. 9,10-Diaminotrianonafulvalenes
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