SYNTHETIC AND PHYSICAL-ORGANIC

APPROACH TO CYCLOPHANE CHEMISTRY

Fumio Imashiro

1975

PREFACE

The present thesis is the collection of the studies carried out under the direction of Professor Zen-ichi Yoshida at the Department of Synthetic Chemistry of Kyoto University during 1970-1975. The thesis is concerned with the synthetic and physical-organic aspects of the cyclophane chemistry.

The author wishes to express his gratefull gratitude to Professor Zen-ichi Yoshida. His kind guidance, precious comments and criticisms during the course of this work are sincerely appreciated.

The author further wishes to express his deep thanks to Professor Iwao Tabushi (Kyushu University) for his enthusiastic interest, valuable discussions and encouragement throughout this work.

The author's thanks are also due to Associated Professor Hisanobu Ogoshi and Dr. Shigeo Yoneda for their helpfull discussions and suggestions. The author is also indebted to Dr. Yoshinao Tamaru, Dr. Hidenori Yamada and Dr. Yasuhiro Aoyama and to Messrs. Toshiro Harada, Michio Oda and Toyoshi Iida for their active collaborations. Valuable discussions with the author's colleagues (Dr. S. Kojo, Dr. K. Yamamura, Dr. E. Watanabe, and Messrs. Y. Kuroda, H. Konishi, T. Nakajima and S. Matsumoto) are gratefully acknowledged.

Finally, the author thanks his family for their affectionate encouragement throughout the work.

Fumio Imashiro

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CONTENTS

CHAPTER 1

General Introduction

During over the last two decades remarkable developments of the studies on bridged aromatic compounds, familiarly called the cyclo-phanes, have provided many exciting results which can be associated with the peculiar structures of these compounds.[1,2]

In the cyclophanes containing more than one benzene ring (*e.g.*, $[2^n]$paraxylylenes or [m.n]paracyclophanes), the intramolecular inter-action between the benzene rings, known as the transannular interac-tion (effect), principally consists of a σ type interaction between $2p\pi$ orbitals of the aromatic moieties.[3] Similar σ type interactions of π orbitals play large part in the general intermolecular interac-tions as seen for the π type charge-transfer (CT) interactions[4] or the cycloaddition reactions.[5]
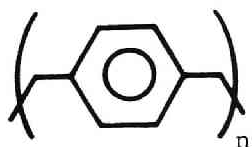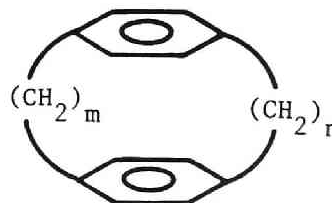
$[2^n]$paraxylylene   [m.n]paracyclophane

[2.2]Paracyclophane, or bis[2.2]paraxylylene, where two benzene rings are mutually linked with only two two-membered methylene bridg-es at *para* positions, is expected to present the large transannular effect on its chemical and physical properties. In fact, many inter-esting spectral characteristics and unusual reaction behaviors are

reported mainly by Cram and his co-workers[6] for this cyclophane and
its derivatives. However, evaluation of the contribution of the
"pure" transannular effect is very difficult, because deformation of
the benzene rings (12.6° from their normal planar state), which is
shown by the X-ray[2b,7] and the thermochemical[8] studies, should con-
taminate the apparent properties.[9]

Thus, interest in the "pure" transannular effect caused by the
normal (undistorted) benzene ring(s) on the spectral and reaction
mechanistic behaviors of the cyclophanes has driven the author to
physical-organic approach to the subjects presented in this thesis.

Recent synthetic[10] and NMR spectral[11] studies on tris[2.2.2]-
paraxylylene suggest that this cyclophane should be one of the most
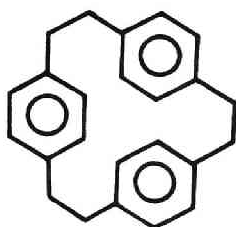
tris[2.2.2]paraxylylene

appropriate compounds for investigation of the "pure" transannular
interaction between the normal benzene rings.

Two benzene rings in tris[2.2.2]paraxylylene can be connected
with one methylene unit at their pseudo-geminal[61] positions to afford
the pseudo-geminal bridged tris[2.2.2]paraxylylene system. This
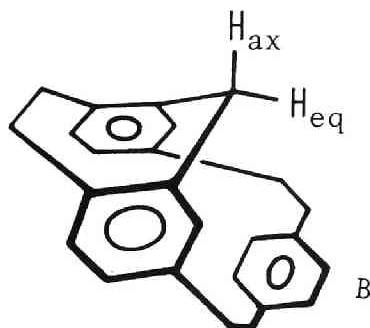
pseudo-geminal methano-
tris[2.2.2]paraxylylene

unique system becomes an excellent model for further investigation

of the transannular effect, since the pseudo-geminal bridge carbon

locates just above (*ca.* 3.5 Å based on Dreiding model) the B benzene

ring of a "face"[12] conformation, and the C-H$_{eq}$ bond is nearly paral-

lel to this B ring, whereas the C-H$_{ax}$ bond is almost perpendicular

to it.

The relative configurations between the reaction site and the

participating π electron cloud is considered to affect the reaction

feature critically. Previous investigations of this field have dealt

almost exclusively with the solvolytic reactions of polycyclic com-

pounds containing the π electrons nearby the reaction center.[13] As

for the cyclophane systems, only small increases of the slovolysis

rates of [9]paracyclophane-n-tosylates (n = 2-5) have been presented.[14]

Taking advantage of the conformational fixation of the pseudo-

geminal bridged tris[2.2.2]paraxylylene system, much more quantita-

tive treatment for the transannular effect due to the normal benzene ring incorporated in the cyclophane becomes possible.

In chapter 2, the electronic spectrum of tris[2.2.2]paraxylylene and the CT spectra between tris[2.2.2]paraxylylene and some electron acceptors are described. The intramolecular transannular interaction among benzene rings is detected as a hypochromic effect in the electronic spectrum and as increase of the equilibrium constant of the CT complex.

Chapter 3 deals with the transannular effect on Friedel-Crafts acetylation of tris[2.2.2]paraxylylenes, where acceleration of the first acetylation and deceleration of the second persist the presence of the significant transannular interaction in the transition state.

Chapter 4 describes preparations of pseudo-geminal ketones of tris[2.2.2]- and tetrakis[2.2.2.2]paraxylylene, and their spectral properties are compared with those of a noncyclic ketone, dibenzosuberone. Both a large high frequency shift of the carbonyl stretching band and a remarkable hypochromic effect in the electronic spectrum observed for pseudo-geminal ketone of tris[2.2.2]paraxylylene present enormous loss of conjugation between carbonyl and aromatics together with considerable angle strain about the carbonyl carbon. Reduction of this ketone gave pseudo-geminal "equatorial" carbinol of tris[2.2.2]paraxylylene stereospecifically, and hydrolysis of the trifluoromethanesulfonate of the "equatorial" alcohol yields stereoisomeric "axial" carbinol again stereospecifically (chapter 5).

The transannular π-participation is appeared conspicuously in the solvolysis of the pseudo-geminal "equatorial" and "axial" systems of tris[2.2.2]paraxylylene (chapter 6). The extremely large difference in the solvolysis rates and the stereochemistry of the product demonstrate importance of the transannular effect on the rate determining and the product determining steps.

Chapter 7 is concerned with syntheses of 2,11-dithiatris[3.3.2]-paracyclophanes as new macrocyclophanes. Chemical shifts of aromatic protons of these compounds markedly depend on the internal rotation of the benzene rings. From these cyclophanes new routes for preparations of tris[2.2.2]paraxylylenes are investigated.

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CHAPTER 2

Electronic Structures and Charge-Transfer Spectra of

Tris[2.2.2]paraxylylene and Related Compounds

2.1 SUMMARY

Electronic spectra of tris[2.2.2]paraxylylene (3°-PX) and some related compounds are measured in order to investigate the electronic interactions (pπ-pπ and pσ-pσ types) between "normal" (undistorted) benzene rings. 3°-PX shows a large hypochromic effect, *i.e.*, its oscillator strength is observed to be 0.61 times of that of the corresponding linear polyparaxylylene. Charge-transfer (CT) spectra between these paraxylylenes and some electron acceptors are also studied. MO calculations (the VI/1, CNDO/2 and CI methods) are carried out in order to elucidate the electronic structure of 3°-PX and also the CT interactions between tetracyanoethylene (TCNE) and 3°-PX, benzene, toluene or *p*-xylene, and reveal the presence of the electronic interaction among the three benzene rings in 3°-PX.

2.2 INTRODUCTION

The electronic interaction between two conjugated molecules, especially for charge-transfer (CT) complexes,[1] or between two conjugated moieties within one molecule, particularly for cyclophanes[2] have been investigated, but the interaction of three conjugated systems has only been studied for trypticene[3] or barrelene.[4] All these compounds as well as janusene[5] have a pσ-pσ type electronic interaction between π orbitals in addition to a common pπ-pπ type interaction. Tris[2.2.2]paraxylylene (abbreviated as 3°-PX)[6] and

tetrakis[2.2.2.2]paraxylylene (4°-PX)[7] seem appropriate to investi-
gate the electronic interaction among three or four "normal" benzene
rings.* In this chapter are described the electronic interaction
in 3°-PX and the CT interactions between 3°-PX and some electron
acceptors. The electronic and CT spectra were measured for p-xylene
and 4,4'-dimethylbibenzyl to compare with those of 3°-PX.

These interactions were also treated with calculations by means
of the variable integrals method 1 (VI/1)[9] or the CNDO/2 method[10]
with the configuration interaction (CI) method. In the VI/1 calcu-
lations for 3°-PX the effects due to methylene bridges were consider-
ed as small perturbations for the orbital energies of the MO's.

2.3   EXPERIMENTAL

Materials.   3°-PX,[6] 4°-PX[7] and 4,4'-dimethylbibenzyl were prepared
by the modified Wurtz coupling of p-xylylene chloride with a sodium-

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* Preliminary experiments of NMR spectra[8] of these paraxylylenes
suggested that benzene rings were statistically facing in each other
(perpendicular to a hypothetical molecular plane) *i.e.,* 3°-PX had a
D_3 and 4°-PX had a D_4 symmetry, respectively. And since several
electronic spectra of mono-substituted 3°-PX or 4°-PX derivatives
displayed that these absorptions consisted of the superpositions of
the components, each benzene ring was considered to be undistorted.

tetraphenylethylene complex, separated through a silica gel column and purified by repeated recrystallizations from n-hexane or a n-hexane–benzene mixture. Commercially available tetracyanoethylene (TCNE) was recrystallized from chloroform and sublimed *in vacuo* (mp 199.5° in a sealed tube, lit.[11] mp 200°). Commercially available chloranil and 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) were re-crystallized from chloroform (mp 292.0–292.5° and 211.0–212.0°, lit.[11] mp 290° and 213°, respectively). Commercially available spectrograde cyclohexane, n-heptane and methylene chloride were used without further purification.

Measurements of Electronic and Charge-Transfer Spectra. Electronic spectra were measured by using a Hitachi EPS-3T recording spectro-photometer. CT spectra were recorded immediately after the mixing of the two components dissolved in an appropriate solvent and kept at *ca.* 25°. The concentration of 3°-PX or 4,4'-dimethylbibenzyl was adjusted to be from 1.33×10^{-2} to 24.9×10^{-2} M, and from 1.19×10^{-2} to 74.3×10^{-2} M, respectively, while the concentration of TCNE was taken to be 0.1×10^{-2} M. Equilibrium constants and molar extinction coefficients of the TCNE complexes were estimated by means of the Benesi-Hildebrand's equation.[12]

2.4 CALCULATION

Calculation Procedure for Electronic Structure of 3°-PX. In the present calculations, 3°-PX was treated to be composed of mutually
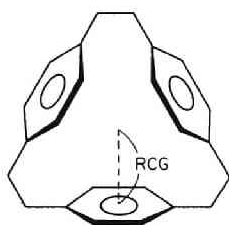
3° - PX
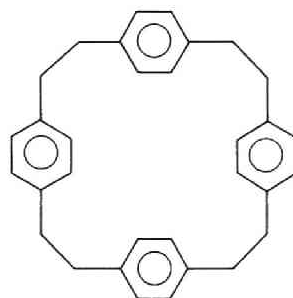
4° - PX

interacting three "normal" benzene rings. Calculations were carried

out using the VI/1 method which treated π electrons only. The de-

tails of this method were described elsewhere.[9] As previously men-

tioned for polyparaxylylenes and/or janusene, two types of electronic

interactions ($p\pi$-$p\pi$ and $p\sigma$-$p\sigma$) of π orbitals should be considered.

Thus, for 3°-PX resonance integrals and electron repulsion integrals

were evaluated with the similar equations described in the original

VI/1 method.[9] However, a parameter, k, was newly added to the orig-

inal parametrization in the resonance integral, which was put equal

to 0.92442.* Transition energies were calculated by means of the

CI method restricted to the 36 singly excited configurations. For

the present study, the author assumed that 3°-PX had a D_{3h} symmetry

* This value was taken so that the calculated lowest singlet transi-

tion energy of benzene should be 4.88 eV. see ref. 9.

and that for each benzene, C-C bond length was 1.397 Å and C-C-C bond angle was 120°.

Calculation Procedure for Electronic Structures of Benzene, Toluene, p-Xylene and TCNE. These four compounds were calculated using the CNDO/2 method according to the Del Bene and Jaffe's parametrizations.[10] On calculating these compounds, reasonable assumption was made for their symmetry being D_{6h} for benzene, C_s for toluene, C_{2v} for p-xylene and D_{2h} for TCNE. For benzene, toluene and p-xylene, C-C (aromatic ring), C-C (single bond) and C-H bond lengths were taken to be 1.40, 1.52 and 1.08 Å, respectively, and bond angles in a benzene ring and a methyl group (∠CCH) were taken to be 120° and 109.5°, respectively. The geometry of TCNE was assumed to be the same as Wold's.[13] The transition energies were calculated by means of the CI method restricted to the 30 singly excited configurations.

Stabilization Energy and Transition Energy of CT-Complex with TCNE.

Stabilization energies due to the CT interaction between benzene, toluene, p-xylene or 3°-PX and TCNE and transition energies of each CT-complex thus formed were calculated by means of the CI method, where the ground, the CT and the locally excited (LE) configurations were taken into account. A wave function of a CT-complex was usually represented as a linear combination of these configurations. But in the present calculations the back CT configurations (charge-transfer from TCNE to aromatics) and the LE configurations in TCNE were neglected.[**] For the CT-complex between benzene, toluene or p-xylene and TCNE, two CT configurations and four lowest LE configurations in

donors were cosidered, where the CT configurations corresponded to one-electron transfer configurations from the two highest π-type occupied orbitals of TCNE, whereas for the CT-complex between 3°-PX and TCNE, six CT configurations and six lowest LE configurations were considered.

The energies of the CT configurations were evaluated as follows,

$$E_{i \to j}^{CT} = I(i) - A(j) - C_{ij} \tag{1}$$

where $I(i)$ was the ionization potential of the i th MO of donors, $A(j)$ was the electron affinity of the j th MO of TCNE, and C_{ij} was the Coulomb integral between these two orbitals. The Coulomb integral was calculated according to the point-charge approximation.

The off-diagonal elements were taken to be proportional to the overlap integrals between the two related MO's as shown in equation (2).[14,15]

$$\langle \Psi_0 | H | \Psi_{i \to j}^{CT} \rangle = - c \cdot S_{ij} \tag{2}$$

where c was a constant and Ψ_0 was the wave function of the ground configuration etc.

Geometries of a CT-complex were so taken as one of benzene planes of the donor molecule and TCNE plane to be parallel and to

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** In the present cases, the overlap integrals between the ground configurations and the back CT configurations is very small because of the shapes of the MO's in question, see ref. 14.

keep axial symmetry (mostly C_{2v}) on varying intermolecular distance,

R, from 3.2 to 3.6 Å * (Fig. 1) where at each distance, TCNE was

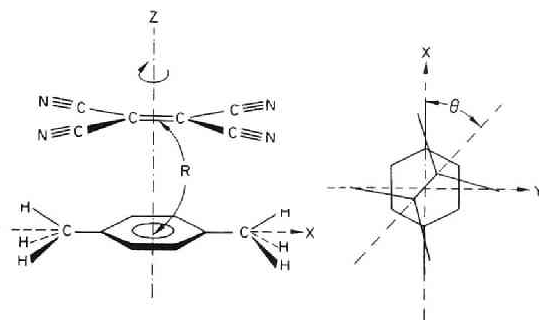treated to rotate around the axis by 10° from 0° to 180°. In the

Fig. 1 Assumed geometry of the p-xylene-TCNE

complex. (model I).

case of toluene and p-xylene, two conformations about the methyl

substituents were considered as shown in Fig. 1. Model I correspon-

ded to a geometry where one hydrogen of the methyl group on the plane

of symmetry of the donor placed toward TCNE, while model II corre-

sponded to the reverse geometry.

All of the calculations in this study were carried out by using

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* In crystalline states of the TCNE complexes with aromatic compounds

without methyl substituent, these distances were observed to be 3.2-

3.3 Å, see ref 1a p 234.

the FACOM 230 60 computer at the Data Processing Center of Kyoto University.

2.5   RESULTS AND DISCUSSION

Electronic Structure of 3°-PX.   In Fig. 2 are shown electronic spectra of 3°-PX, 4,4'-dimethylbibenzyl and bis(p-xylyl)-p-xylene measured in cyclohexane. Calculated singlet-singlet transition energies of the mutually or transannularly interacting three benzene rings are illustrated in Fig. 3. According to the present calculation, a splitting of the original lowest excited state ($^1B_{2u}$) of each benzene ring into two *via* the transannular electronic interaction is not large on varying RCG (a radius of an inscribed circle of the three benzene rings). However the next higher excited states arisen from the penultimate excited state of benzene ($^1B_{1u}$) show a remarkable splitting. The difference in the directions of the transition moments may be responsible for this difference in the splitting.

Ionization potentials and singlet-singlet transition energies of benzene, toluene and p-xylene calculated using the CNDO/2 method are summerized in Table 1 and 2, respectively. Ionization potentials are obtained by the Koopmans' theorem and corrected so as the first ionization potential of benzene to be 9.40 eV. Results of the calculations suggest that "methyl effect" is larger for the ionization potential than for the transition energy, *i.e.*, the methyl substituents affect the orbital energies of the MO's more directly. Thus
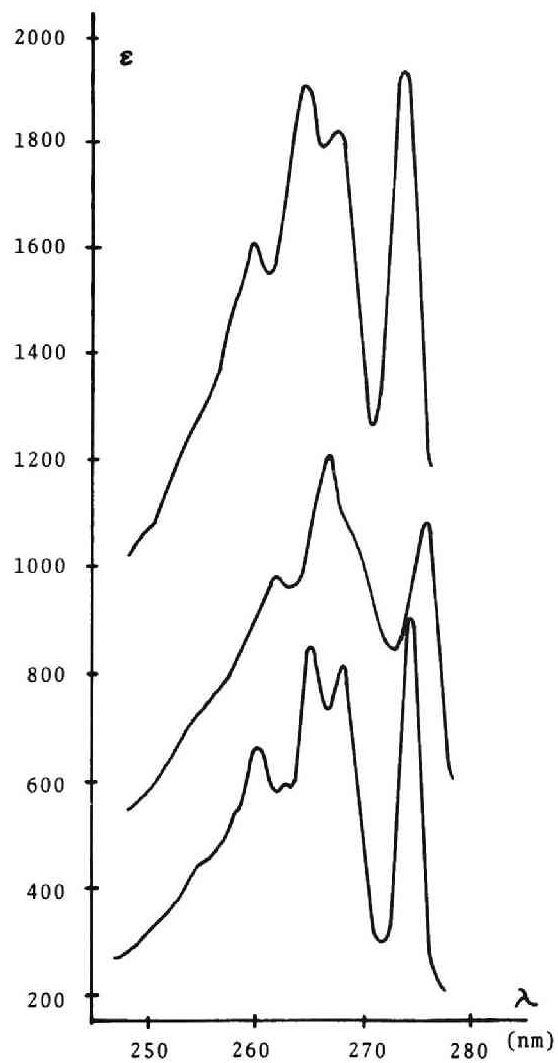
Fig. 2   Electronic spectra of 3°-PX (a),
4,4'-dimethylbibenzyl (b) and bis(p-xylyl)-
p-xylene (c).   All curves except the low-
est are displaced upword by 300 unit from
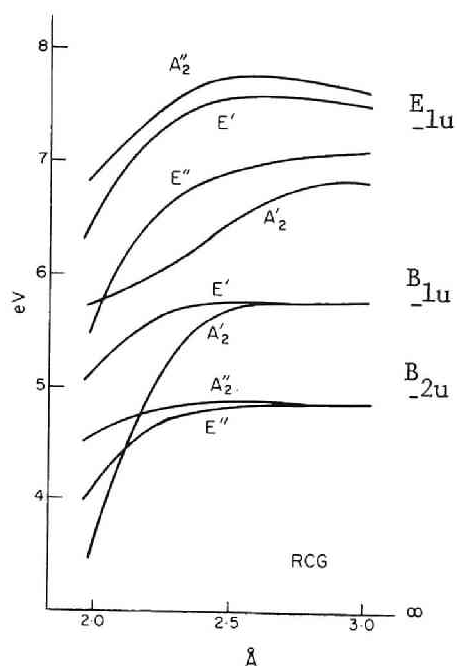the curve immediately below.

Fig. 3 Singly excited states of mutually or trans-
annularly interacting three benzene rings. RCG means
a radius of an inscribed circle of the three rings.

Table 1. Ionization potentials (eV)

	Benzene	Toluene	p-Xylene	$3°$-PX^c
Calc.^{a}	9·40	9·03	8·70	8·14
		9·37	9·35	8·94
				9·27
				9·50
Obs.^{b}	9·40	8·9	8·71	
		9·13	9·21	

^{a}Calculated by assuming $I_p = -\epsilon_i - 1·367$ eV, where ϵ_i
is the ith orbital energy.

^{b}By photoelectronspectroscopic study, A. D. Baker,
D. P. May and D. W. Turner, J. Chem. Soc., (B) 22 (1968).

^{c}Calculated by assuming $I_p = -\epsilon_i - 0·944$ eV $- \Delta$,
where ϵ_i is the ith orbital energy and Δ is estimated as a
perturbation, loc. cit.

Table 2. Singlet-singlet transition energies of benzene, toluene and p-xylene.

| Benzene | | | | Toluene | | | | p-Xylene | | | |
| Calc. | | Obs. | | Calc. | | Obs. | | Calc. | | Obs. | |
eV	(f)	eV	(ε)	eV	(f)	eV	(ε)	eV	(f)	eV	(ε)
4.71	(0.0)	4.75[a]	(160)	4.63	(0.004)	4.62[a]	(230)	4.53	(0.016)	4.52[a]	(620)
5.04	(0.0)	6.11[b]	(7400)	4.95	(0.006)	6.02[b]	(7000)	4.84	(0.022)	5.74[b]	(7500)
6.75	(1.85)	6.40[b]	(55000)	6.65	(0.886)			6.53	(0.786)		
				6.67	(0.972)			6.63	(1.01)		

a. "Organic Electronic Spectral Data," M. J. Kamlet Ed., Volume I 1946-1952, Interscience, New York, N. Y. (1960).

b. E. S. Stern and C. J. Timmons, "Electronic Absorption Spectroscopy in Organic Chemistry," 3rd Edition, London (1970).

a tentative conclusion is drawn that "methyl effect" is regarded to be a small modification for calculation of the orbital energy. Such modification is extended to other π-type orbitals and applies to the MO's of benzene and the three interacting benzene system in order to calculate the transition energies of p-xylene and 3°-PX. The unperturbed MO's of 3°-PX are obtained by the above calculation at RCG = 2.5 Å (Fig. 3), where the calculated energy difference between the lowest allowed transition of the system of the three interacting benzenes and the lowest transition of benzene itself is in accord with the observed energy difference in the lowest transitions of 3°-PX and p-xylene.

Resultes of these CI calculations are shown in Table 3. Oscillator strengths of the lowest allowed transitions for p-xylene and 3°-PX are calculated to be 0.0193 and 0.0412, respectively.[*] Observed oscillator strengths of these lowest transitions of linear p-xylene analogues are approximately proportional to the number of the benzene rings in a molecule, $i.e.$, 0.006 for p-xylene, 0.012 for 4,4'-dimethylbibenzyl and 0.019 for bis(p-xylyl)-p-xylene. Since 3°-PX has three benzene rings in itself, the oscillator strength of 3°-PX should be compared with three times of that of p-xylene by assuming the similar linearity. On this ground, the ratio of the calculated value to three times that of p-xylene (0.0412:0.0579) is

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[*] These values are estimated with the equation, $f = 4.32 \times 10^{-9} \times \varepsilon_{max} \times \Delta\nu_{1/2}$.

Table 3. Calculated singlet-singlet transition

energies of p xylene and 3°-PX.[a]

| p-Xylene | | 3°-PX | |
eV	(f)	eV	(f)
4.593	(0.0193)	4.496	(0.0)
		4.538	(0.0413)
5.460	(0.0184)	5.223	(0.0)
		5.432	(0.0648)
7.100	(1.17)	6.307	(0.0)
		6.803	(0.0)
7.113	(1.20)	7.249	(2.85)
		7.439	(0.851)

a. CI calculations using the VI/1 MO's considering
"methyl effect".

0.710, in good agreement with the observed ratio, 0.61 (0.011:0.018)

Such a large hypochromic effect has not been observed in [n.n]para-

cyclophanes (n $\geq$ 4) which are considered to have undistorted benzene

rings.[16]

Bathochromic shift and loss of fine structure, by which is char-

acterized the electronic spectrum of [2.2]paracyclophane,[16] have been

interpreted with the large electronic interaction between two dis-

torted benzene rings involving the intramolecular CT interactions.[2,17]

The similar characteristics are anticipated according to the present

results (Fig. 3), when RCG is smaller than 2.5 Å. However observed

remarkable hypochromic effect is clearly related to the electronic

transannular interaction among three benzene rings in 3°-PX.

Charge-Transfer Spectra. Absorption maxima of CT spectra of the complexes of p-xylene, 4,4'-dimethylbibenzyl, 3°-PX or 4°-PX with TCNE, chloranil or DDQ measured in methylene chloride are shown in Table 4, and the shapes of the CT spectra of TCNE complexes are illustrated in Fig. 4.[*] Equilibrium constants and molar extinction coefficients of the TCNE complexes in the same solvent are summerized in Table 5. Table 4 shows qualitatively that the absorption maximum of a CT complex with a cyclic polyparaxylylene (3°-PX or 4°-PX) locates in longer wavelength region than that of a CT complex with a linear polyparaxylylene (p-xylene or 4,4'-dimethylbibenzyl). To be noted for the TCNE complex with 3°-PX is that its equilibrium constant is much larger than the complexes with other donors. Another characteristic of this complex is that only a single broad detectable absorption maximum is seen for this complex, whereas two distinguishable absorption maxima are observed for other TCNE complexes, though superposed considerably. The latter characteristics in the shape of the CT spectra are often observed for the CT spectra of the TCNE complexes with benzene derivatives. One possible interpretation for these characteristics is that the two maxima are attributed to the two CT configurations from the two highest occupied MO's of the

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* The CT spectrum of the TCNE complex with bis(p-xylyl)-p-xylene is also measured , but its absorption is very similar to that of p-xylene.
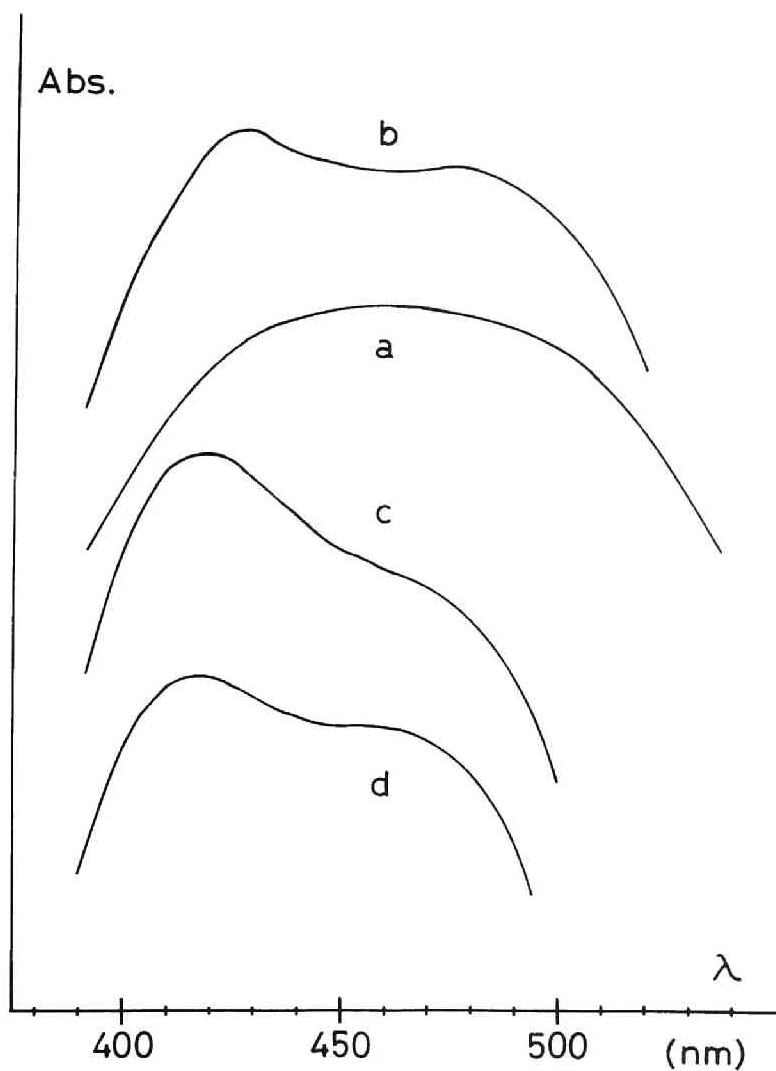
Fig. 4 CT spectra of TCNE complexes in methylene chloride. Curves are separated on vertical axis so they can be distinguished, and are identified by the paraxylylene of the complex as follows: a, 3°-PX; b, 4°-PX; c, 4,4'-dimethylbibenzyl; d, p-xylene.

Table 4. Absorption maxima of the CT spectra measured in methylene chloride

Acceptor Donor	TCNE (eV) (eV)	Chloranil (eV)	DDQ[a] (eV)
p-xylene	2·95 2·65	3·02	2·38
4,4'-dimethyl-bibenzyl	2·95 2·65	—[b]	2·37
3°-PX	2·70	2·76	2·26
4°-PX	2·90 2·58	2·88	2·27

[a]2,3-Dichloro-5,6-dicyano-p-benzoquinone
[b]Superposed

Table 5. Equilibrium constants (K's) and molar extinction coefficients (ε's) of the TCNE complexes[a]

Donor	λ mμ	K l/mol	ε l/mol·cm
p-Xylene[b]	415	0·489	2650
4,4'-Dimethyl-bibenzyl	420	0·35	3000
	474	0·22	4300
3°-PX	460	2·5	2000
4°-PX	428	(K · ε = 2300)[c]	
	480	(K · ε = 2200)[c]	

[a]Measured in methylene chloride at room temperature (ca. 25°).
[b]At 22°, R. E. Merrifield and W. D. Phillips, J. Am. Chem. Soc., 80, 2778 (1968), see ref. 14 (b), p. 184.
[c]Only products of K and ε were obtained.

donors to the one lowest unoccupied MO of TCNE.[1a] An alternative interpretation is that the two maxima are attributed to the two geometrically different orientations of the donor and the acceptor of different energies originated from the single electronic CT configuration.[1a,18,*] Calculated results for the CT complexes are shown in

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* For toluene- or p-xylene-TCNE complex, the present calculations show that there is one rotationally most stable isomer for model I or model II, respectively, however the rotational barriers are considerably small as shown later. And for the transition probability of two CT transitions at each most stable configuration, both transitions are allowed for model I, although only one is permitted for model II.

in Table 6, where an electron affinity of TCNE is taken to be 2.10

eV,* which is obtained by means of the present CNDO/2 calculation,

and the constant, c, in Eq (2) is assumed to be equal to 25 eV.[14,15]

Table 6. Calculated stabilization energies due to the CT interaction and the two lowest transition energies of the TCNE complexes at $R = 3 \cdot 4$ Å

| | Benzene | Toluene | | p-Xylene | | 3°-PX |
		model I	model II	model I	model II	
ΔE_{ST} max (kcal/mol)	$-2 \cdot 39$	$-2 \cdot 44$	$-2 \cdot 41$	$-2 \cdot 54$	$-2 \cdot 42$	$-2 \cdot 92$
$\theta(°)$	30 (90)	50	90	50	90	0
barrier (kcal/mol)	$0 \cdot 04$	$0 \cdot 31$	$0 \cdot 15$	$0 \cdot 56$	$0 \cdot 21$	$0 \cdot 50$
$h\nu_{CT_1}(eV)^b$	$3 \cdot 79$	$3 \cdot 48$	$3 \cdot 49$	$3 \cdot 17$	$3 \cdot 19$	$3 \cdot 04$
$h\nu_{CT_2}(eV)^c$	$3 \cdot 89$	$3 \cdot 82$	$3 \cdot 81$	$3 \cdot 80$	$3 \cdot 79$	$3 \cdot 80$

$^a\theta$ means that the stabilization energy is maximum at this degree. See Fig 1.
^{b}An average value about the first lowest transition energies is shown.
^{c}An average value about the second lowest transition energies is shown.

Since the calculated stabilization energy, ΔE_{st}, due to the CT inter-

action displays only minor change on varying the angle θ (Fig. 1),

the two lowest transition energies, $h\nu_{CT_1}$ and $h\nu_{CT_2}$, are approxi-

mated to the average values of the rotational isomers (θ from 0° to

180°) at R = 3.4 Å (Fig. 1) in the present calculation. The calcu-

lated stabilization energies and the rotational barriers of the TCNE

complexes with benzene, toluene and p-xylene increase in this order.

Each of the three complexes has two CT transition energies of similar

magnitude, and the difference in the two CT transition energies also

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* Electron affinity of TCNE is estimated to be 2.2 eV from CT spectra

of the complexes with several electron donors, see ref. 1a p 387.

increase in the same order (*ca.* 0.1, 0.3 and 0.7 eV, respectively).

This difference varies with changing the distance, R. From these cal-

culations the lowest energy differences are evaluated to be 0.05 eV

for benzene, 0.16 eV for toluene, 0.44 eV for *p*-xylene and 0.60 eV

for 3°-PX. These results suggest that the two maxima in the CT

spectra are difficult to distinguish for benzene and toluene.

Observed widths of the absorptions at half maximum intensity of the

CT spectra also supported this suggestion, *i.e.*, 6200 cm^{-1} (0.77 eV)

for benzene, 6700 cm^{-1} (0.83 eV) for toluene and 8900 cm^{-1} (1.1 eV)

for *p*-xylene.

Table 7. Comparison of the calculated CT transition energies with the observed
CT transition energies of TCNE complexes[a]

	Benzene	Toluene	*p*-Xylene[b]	4.4′ Dimethyl-[b] bibenzyl	3°-PX
Calc. (av.)[c]	3·84	3·65	3·49	—	3·42
gas phase[d]	3·67	3·35	3·12	—	—
n-heptane solution	3·29[d]	3·10[d]	2·91[d]	2·86	2·88
methylene chloride solution	3·19	3·02	2·80	2·80	2·70
Δ[e]	0·65	0·63	0·69	—	0·72

[a]Energies in eV. Calculations were carried out at R = 3·4 Å.
[b]Observed value is average one of two maxima.
[c]An average value of the two lowest transition energies is shown.
[d]M. Kroll, *J. Am. Chem. Soc.* **90**, 1097 (1968).
[e]Difference between calculated and observed (in methylene chloride) value.

Comparison of the calculated CT transition energies with the

observed absorption maxima of the CT spectra in gas phase and in so-

lutions are summerized in Table 7. On investigation of Table 6 and 7

a conclusion may be drwan that the transition energy of the TCNE

complex with toluene or *p*-xylene is in better agreement with the cor-

responding observed energy by taking the average value of the two
transition energies than taking the lowest value. As shown in
Table 7, the differences between the calculated and observed transi-
tion energies are nearly constant for the donors used (by 0.63-0.72
eV higher than in methylene chloride). According to the present
calculation for the TCNE complex with 3°-PX, double maxima should be
observed because of the considerably large difference between the two
calculated transition energies (it amounts to be at least 0.60 eV),
in a contrast to the observed absorption shape of single broad maxi-
mum (the width of the absorption at half maximum intensity is observ-
ed to be 8200 cm^{-1} or 1.0 eV). Observed free energy difference
between the TCNE complex with 3°-PX and that with p-xylene estimated
from K values listed in Table 5 is $ca.$ 1 kcal/mol, while the calcu-
lated difference is $ca.$ 0.5 kcal/mol. Both results, however, demon-
strate that the complex with 3°-PX is more stable than that with
p-xylene.

Eventually it should be better noted that the observed CT spec-
tra of the TCNE complexes with the donors presented here consist of
two CT transitions, in which mainly two for simple aromatics (six for
3°-PX) CT configurations are mixed in each other.

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CHAPTER 3

Transannular Effect on Friedel-Crafts Acetylation

of Tris[2.2.2]paraxylylenes

3.1   SUMMARY

Friedel-Crafts acetylations of tris[2.2.2]paraxylylenes have been investigated. The first acetylation of tris[2.2.2]paraxylylene (I) proceeds easily at $-70 \sim -40°$, while the second or the third acetylation of acetyltris[2.2.2]paraxylylene (II) undergoes at $2°$. The second acetyl group does not substitute the benzene ring having the first group, and no ring-fused product is detected under the present conditions. Rates of the acetylations of I, II and 4,4'-dimethylbibenzyl (V) relative to p-xylene (VI) are determined by competitive experiments, being 2.6, 0.041, 1.41 and 1. These results are interpreted by the transannular effect mainly attributed to charge-transfer (CT) interaction among π systems of the compounds and/or repulsion between positive charges developing in a transition state and an aluminum chloride complex of acetylparaxylylene.

3.2   INTRODUCTION

Acetylation of tris[2.2.2]paraxylylene (I) using acetyl chloride instead of acetic anhydride[1] as an acetylating reagent gave acetyltris[2.2.2]paraxylylene (II) as a sole product. This result suggests that further acetylation should be very slow. Similar monoacetylation of [m.n]paracyclophanes, where m and n were smaller than or equal to 4 was reported by Cram,[2] and the rate retardation of the second acetylation was attributed to a transannular effect of another benzene

ring existing parallel to the reacting benzene ring. To account for the electronic spectrum of I and the intermolecular charge-transfer (CT) interaction between I and electron acceptors, the transannular effect in the benzene rings of I was considered.[3] Therefore, the rates of the Friedel-Crafts acetylations of tris[2.2.2]paraxylylenes become much interesting and important for clarification of the trans-annular effect on the transition state of the reaction.

3.3   RESULTS AND DISCUSSION

Acetylation of Tris[2.2.2]paraxylylenes.   Aluminum chloride catalized

Table 1.   Acetylation of Tris[2.2.2]paraxylylenes
and Related Compounds.[a]

| Substrate | Concentration, M | | | Time | Products |
| | | | | hr | $\%^b$ |
	AcCl	AlCl$_3$			
I[c]	0.10	0.20	0.30	20	I(5), II(94)
II	0.13	0.13	0.38	1	II(10), III(74), IV(8)
V	0.10	0.10	0.13	0.5	V(31),[d] acetyl-V(64)[d]
VI	0.10	0.10	0.13	0.5	VI(34),[d] acetyl-VI(66)[d]

a. In methylene chloride at 2° unless specified.   b. Based on the amounts after isolation.   c. Carried out at $-70 \sim -40°$.   d. Based on gas-liquid chromatographic analysis.
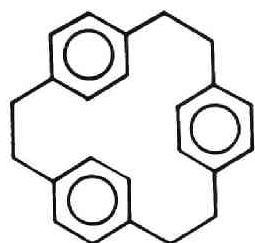
I
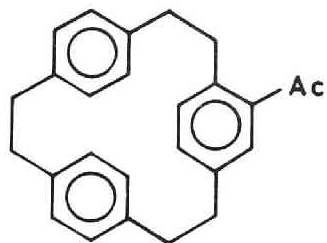
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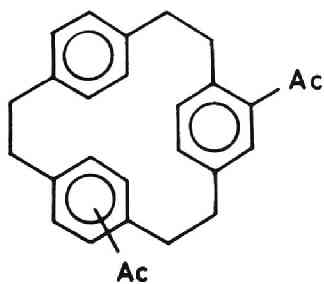
III
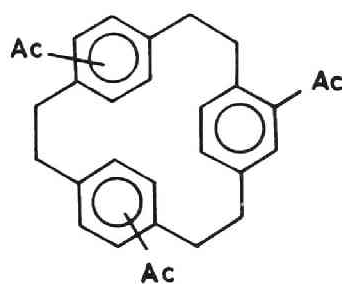
IV

acetylation of I with 2 moles of acetyl chloride in methylene chloride at low temperature (-70~-40°) gave II[1] in nearly quantitative (94 %) yield together with 5 % of the recovered starting material. Neither di- or triacetylated compound nor rearranged (ring-fused) product could be detected under the present condition. However, at 2° II was moderately acetylated to afford 74 % of diacetyltris-[2.2.2]paraxylylene (III),* 8 % of triacetyltris[2.2.2]paraxylylene (IV)* and 10 % of recovered II. Table 1 summerizes the yields of

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* Many positional isomers are possible for di- or triacetylated compounds.

the products together with those for the acetylations of 4,4'-di-
methylbibenzyl (V) and *p*-xylene (VI).
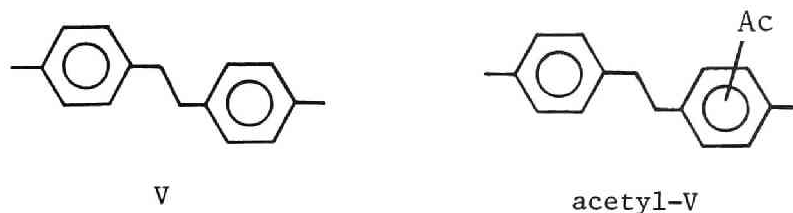
V   acetyl-V

NMR spectra of III and IV show absence of di- or triacetylated

benzene rings and absence of vinylic protons, indicating that no ring

fusion took place.[*] As shown in Fig. 1, mass spectra of II, III and

IV at 70 eV are also in accord with the idea that only one acetyl

group is introduced into one paraxylylene unit, *i.e.*, fragment ions

of II, III and IV mainly consist of combinations of paraxylylene

(*m/e* 104) and acetylparaxylylene (*m/e* 146) moieties.[**]

Relative Rate of Acetylation.   The relative rates of acetylation

were determined by competitive reactions, where I, II and V competed

with VI (standard), respectively. The results thus obtained are

summerized in Table 2.

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* Ring-fused products have been frequently obtained in electrophilic

substitutions of [2.2]metacyclophanes.[4]

** Mass spectra of $[2^n]$paraxylylenes and their derivatives have been

reported to show predominant fragmentation to substituted para-

xylylene (or methylenetropylium) ion radicals.[1,5,6]
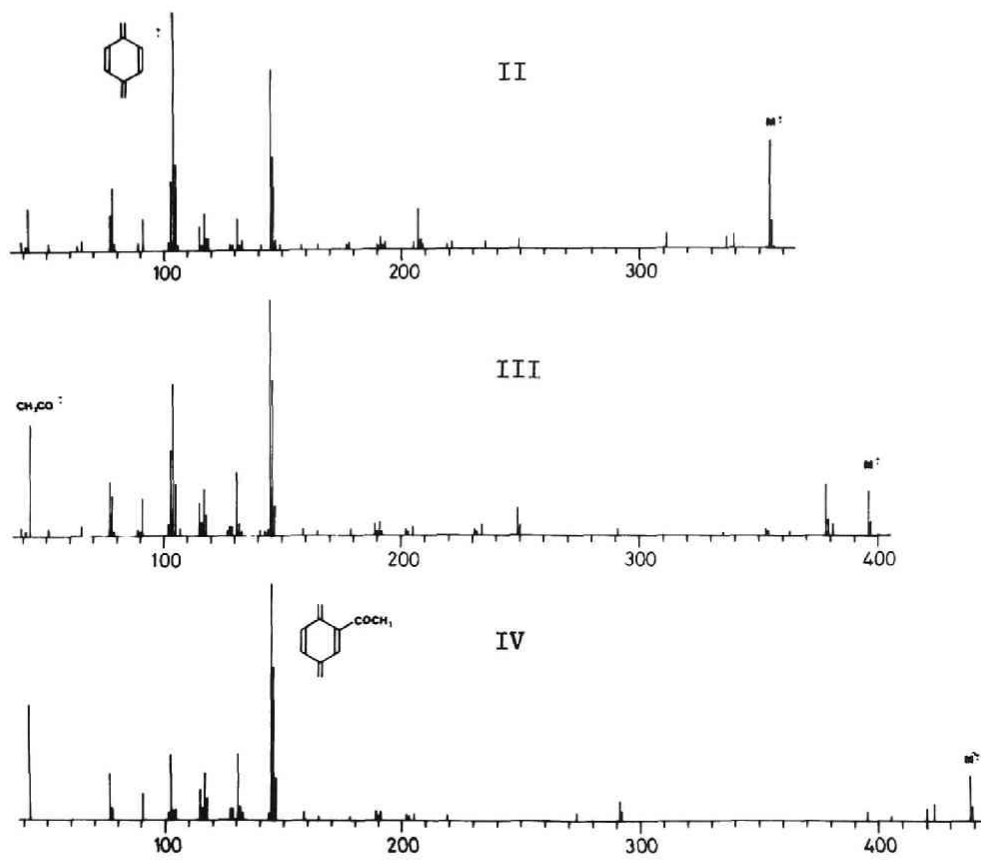
Fig. 1   Mass spectra of acetylated tris[2.2.2]-

paraxylylenes: II, top; III, middle; IV, bottom.

Table 2. Relative Rate of Acetylation.[a]

Compound	k_{rel}[b]	k_{corr}[c]	n[d]
I	7.8 ± 0.5	2.6 ± 0.2	12
II	0.081 ± 0.004	0.041 ± 0.002	8
V	2.8 ± 0.1	1.4 ± 0.1	8
VI	1.0[e]	1.0[e]	4

a. At $2 \pm 0.5°$. Details of the procedures are found in the EXPERIMENTAL. b. Relative rate in mole unit. c. Relative rate corrected statistically with n. d. Number of reaction sites. For II and III, each benzene ring substituted with an acetyl group is not accounted. e. Taken as a standard.

Rate enhancement in the first acetylation of I compared with acyclic paraxylylenes (V and VI) is relatively small (1.9 and 2.6 times at 2°, respectively). A transition state in the usual Friedel-Crafts acetylation of the present type is considered to resemble a σ complex or a Wheland intermediate, because substantial isotope effects are observed for the reactions and the acetyl cation is regarded as a weak electrophile.[7] Molecular orbital (CNDO/2) calculation also supports this consideration.[8] The small rate enhancement in the first acetylation of I, therefore, is considered to be attributable to transannular stabilization of the σ complex by other

benzene rings. The transannular stabilization[2,9] in the present case

mainly consists of the CT interaction between the σ complex of react-

ing benzene (c in Fig. 2) and the other benzenes (a and b in Fig. 2).

(a)   (b)   (c)
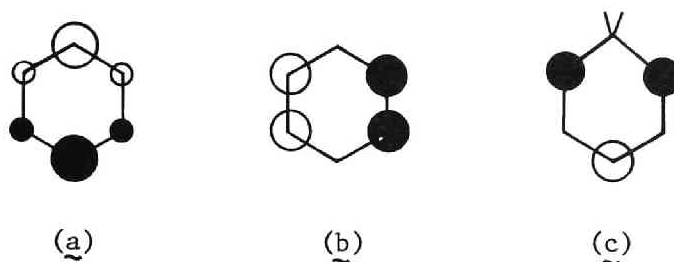
Fig. 2   The highest occupied MO's of benzene, (a) and (b),

and the lowest unoccupied π type MO of the σ complex, (c).

This consideration is in agreement with the reported relative rates

of the acetylation of [m.n]paracyclophanes, where the rate of the

first acetylation increases as two benzene rings come closer.[2c]

A large depletion (63 times at 2°)[*] of the rate is observed for

the second acetylation of II relative to the first of I. The decel-

erated second acetylation of [4.4]paracyclophane was reported,[2b]

where the rate ratio (the second acetylation to the first) was found

to be *ca.* 1/20 at room temperature after the statistical correction

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* Based on the yield data listed in Table 1, the rate difference at

low temperature (-70∼ -40°) is evaluated[2b] to be more than 130 after

the statistical correction.

was made for the number of the reaction sites. If the similar estimation is applied to the acetylation of [3.4]paracyclophane[2c] by our hands, the corresponding rate ratio now becomes only *ca.* 1/10 at room temperature.

Based on the similarity between the lowest unoccupied π orbital of the acetylparaxylylene complexed with aluminum chloride and that of the σ complex shown as $\underset{\sim}{c}$ in Fig. 2, the aluminum chloride complex should be stabilized by the CT type interaction, which reduces reactivity of the benzene ring of II in the second acetylation. Since one more paraxylylene unit exists in II compared with acetyl[3.4]- or acetyl[4.4]paracyclophane, and as shown in Table 3 acetylparaxylylene complexed with aluminum chloride in II is inclined about 60° ($\theta = 30°$) from parallel to the reacting benzene ring, decrease of the rate of the second acetylation should be smaller for II than for acetyl[3.4]- or acetyl[4.4]paracyclophane from view point of expected interactions in Table 3. The present result, just contrary to the such simple prediction as above, seems to be very interesting. This abnormal behavior may be interpreted with the following consideration; a rigid structure of II prevents the relief of the CT interaction and the reduction of the repulsion between the positive charges, while the benzene rings in [3.4]- or [4.4]paracyclophane have more freedom of intramolecular motion to separate the two benzene moieties, *e.g.*, by internal rotation of the benzene rings.[*]

The rate of the third acetylation of III is approximately estimated by Cram's treatment to be *ca.* 1/9 relative to that of the

Table 3. Interactions between Benzene Rings of Cyclophanes.
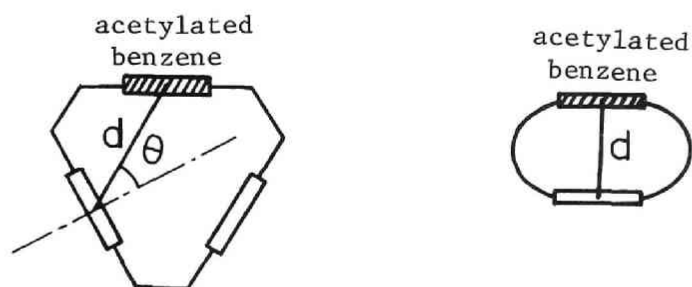
Interaction		II	[4.4]para-cyclophane	[3.4]para-cyclophane
Distance[a]	(d, Å)	4.2	3.8	3.1
Angle	(θ, °)	30	0	10
Interaction Expected	(A)[b]	0.005	0.012	0.047
	(B, eV)[c]	3.4	3.8	4.7
Interaction Observed[e]	($\Delta G^{\ddagger}$, kcal/mol)	2.26[e]	1.77[2b,f]	1.36[2c,f]

a. Estimated based on Dreiding model.   b. Overlap integral between $2p\pi$ orbitals located imaginarly at the center of the two benzene rings, respectively.   c. Qoulomb repulsion energy between the two benzene rings estimated by use of point-charge approximation.   d. Evaluated from the relative rates (the first acetylation to the second).   e. At 2°.   f. At room temperature.

second. This relatively small reduction of the rate may be attribut-
able to the smallness of deactivation of the benzene ring due to the
additional second acetyl group compared with that due to the first.

Finally it is noted that an expected rate enhancement (Table 2),
though small, is observed for the acetylation of V, which suggests
that the transannular stabilization in the transition state as de-
scribed above is present even for the acyclic paraxylylene such as V.

3.4   EXPERIMENTAL

Melting points were uncorrected. NMR spectra were recorded with
a Varian HA-100 spectrometer. Mass spectra were determined by a
Hitachi RMU-6C or RMS-4 mass spectrometer.

Materials.   Commercially available methylene chloride was dried over
calcium chloride and distilled before use. Commercially available
acetyl chloride was also distilled before use. Commercially avail-
able *p*-xylene (Guaranteed Reagent, Nakarai Chemicals) was used
directly without further purification. 4,4'-Dimethylbibenzyl was
prepared by the Wurtz reaction of *p*-methylbenzyl chloride with iron
in dimethylformamide and purified with recrystallization from ethanol
(mp 80.5-81.0°, lit.[10] mp 81-81.5°). Tris[2.2.2]paraxylylene (I) was

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* Carboxyl derivatives of [3.4]- and [4.4]paracyclophanes have been
reported to undergo racemization at relatively low temperatures.[2c]

prepared by the reported procedure[1] (mp 168°, lit.[1] mp 168°).

Acetylation of I. To a stirred mixture of 0.82 ml (11.6 mmol) of acetyl chloride, 2.3 g (17 mmol) of aluminum chloride in 25 ml of methylene chloride was added a solution of 1.8 g (5.8 mmol) of I in 33 ml of methylene chloride dropwise for 15 min keeping the temper- ature of the mixture at -70°. Stirring was continued for 20 hr till the temperature rose to -40°. Then the reaction mixture was poured into a mixture of ice and hydrochloric acid, and extracted with methylene chloride. The methylene chloride extract was washed with saturated aqueous sodium chloride, with aqueous sodium bicarbonate, and with saturated aqueous sodium chloride. The solution was dried over anhydrous sodium sulfate and the solvent was evaporated. The residue was chromatographed on a silica gel column. The first elution with petroleum ether gave 93 mg (5 %) of recovered I, and the second fraction eluted with benzene gave 1.9 g (94 %) of acetyltris- [2.2.2]paraxylylene (II). Recrystallization of II from petroleum ether gave colorless columns: mp 85.5-86.5° (lit.[1] mp 80-81°).

Acetylation of II. To a stirred mixture of 36 μl (0.50 mmol) of acetyl chloride, 200 mg (1.5 mmol) of aluminum chloride and 4 ml of methylene chloride was added 177 mg (0.50 mmol) of II. Stirring for 1 hr, a mixture of ice-water and hydrochloric acid was added into the mixture, and whole was extracted with chloroform. The organic layer was washed with aqueous sodium bicarbonate and with aqueous sodium

chloride, and dried over anhydrous sodium sulfate. The solvent was
evaporated and the residue was chromatographed on a silica gel (TLC
20 × 20 × 0.2 cm) with benzene-ether (95:5) to give 18 mg (10 %) of II,
145 mg (74 %) of diacetyltris[2.2.2]paraxylylene (III) as a colorless
paste and 17 mg (8 %) of triacetyltris[2.2.2]paraxylylene (IV) as a
colorless paste.

III: nmr δ (CCl$_4$, TMS) 2.37-2.40 (6H, m, acetyl), 2.7-3.9 (12H,
m, methylene), 6.4-6.7 (8H, m, aromatic), 7.0-7.1 (3H, m, aromatic,
ortho to carbonyl).

IV: nmr δ (CCl$_4$, TMS) 2.38-2.41 (9H, m, acetyl), 2.7-3.9 (12H,
m, methylene), 6.4-6.8 (6H, m, aromatic), 7.0-7.1 (3H, m, aromatic,
ortho to carbonyl).

Acetylation of 4,4'-Dimethylbibenzyl (V). A solution of 424 mg (2.0
mmol) of V and 145 µl (2.0 mmol) of acetyl chloride in 20 ml of
methylene chloride was stirred in an ice bath. Into the solution was
added 350 mg (2.6 mmol)of aluminum chloride, and stirring was con-
tinued for 30 min. The mixture was poured onto a mixture of ice-
water and hydrochloric acid, and extracted with chloroform. The
organic layer was separated, washed with aqueous sodium bicarbonate,
aqueous sodium chloride, and dried over anhydrous sodium sulfate.
The solvent was evaporated and the residue was chromatographed on a
silica gel column. The first fraction eluted with *n*-hexane-benzene
(1:1) gave 131 mg (31 %) of recovered V. The second fraction eluted
with benzene gave 325 mg (64 %, or 92 % based on consumed V) of two

isomers (1:2.6 by NMR spectrum and 1:2.7 by gas-liquid chromato-graphy) of acetyl-4,4'-dimethylbibenzyl (acetyl-V) as a colorless paste: mass spectrum m/e (rel intensity) 253 (M+1, 9), 252 (M^+, 45), 237 (17), 149 (19), 147 (67), 106 (26), 105 (100), 79 (19), 77 (24), 43 (20); nmr δ ($CDCl_3$, TMS) 2.29 and 2.34 (3H, two s's, acetyl), 2.45 (6H, s, methyl), 2.7–3.2 (4H, m, methylene), 7.0–7.2 (6H, m, aromatic), 7.27 and 7.31 (1H, two m's, aromatic, *ortho* to carbonyl).

Acetylation of p-Xylene (VI).   Acetylation of VI was carried out in the same manner as described for the acetylation of V. Products were analyzed by gas-liquid chromatography using appropriate standards.

Competitive Acetylation, General Prcedure.   Each competitive acetylation was carried out for 5 min at $2 \pm 0.5°$ till addition of a mixture of ice-water and hydrochloric acid into the reaction mixture. Adequate quantities of internal standards and 1 ml of chloroform were added into the mixture. The organic layer was sep-arated, neutralized with sodium bicarbonate, dried over anhydrous sodium sulfate, carefully condensed, and analyzed. Quantitative determination of the products was made with peak area intensity of gas-liquid chromatography on a Simadzu GC-6A instrument. Calibration was made by use of internal standards. Each competitive runs was repeated at least twice.

Individual Reaction Conditions. *(a) I and VI.* To a solution of
10 μl (0.14 mmol) of acetyl chloride in 2 ml of methylene chloride
was added 30 mg (0.23 mmol) of aluminum chloride in a 10 ml reaction
flask equipped with a thermometer. The reaction flask was placed in
a thermostated bath to keep the temperature of the solution at 2 ±
0.5°. Then a precooled (at 2°) solution of 169 mg (1.6 mmol) of VI
and 26.7 mg (0.087 mmol) of I in 2 ml of methylene chloride was added
into the solution with vigorous stirring.

(b) II and VI. To a solution of 39 mg (0.11 mmol) of II and 12.1 mg
(0.11 mmol) of VI in 1 ml of methylene chloride was added 8 μl (0.11
mmol) of acetyl chloride in a 10 ml reaction flask equipped with a
thermometer. The reaction flask was placed in a thermostated bath
to keep the temperature of the solution at 2 ± 0.5°. Then 100 mg
(0.75 mmol) of aluminum chloride was added with vigorous stirring.

(c) V and VI. The reaction procedure was similar to *(b)* except the
quantities of VI (48.4 mg, 0.46 mmol) and V (32.4 mg, 0.15 mmol)
instead of II.

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CHAPTER 4

Preparations and Properties of Pseudo-Geminal Ketones

of Tris[2.2.2]- and Tetrakis[2.2.2.2]paraxylylene

4.1   SUMMARY

Pseudo-geminal ketone of tris[2.2.2]paraxylylene (I) and that of tetrakis[2.2.2.2]paraxylylene (II) are prepared and their spectral properties are investigated in comparison with those of dibenzo-suberone (III). The carbonyl stretching band of I is observed at abnormally high frequency region (by *ca.* 50 cm^{-1}) compared with that of III, while that of II is at a position similar to that of III. The electronic spectrum of I shows that I has enormous loss of conjugation due to lack of coplanarity between carbonyl and aromatics. The chemical shift of H$_o$ (*ortho* to carbonyl) of I, shown at by 1.8 ppm higher field than that of the corresponding proton of III, also supports this structural characteristic.

4.2   INTRODUCTION

Although two aromatic rings of lower paraxylylenes lie close, little attempt has been made to link these two aromatic rings with one more carbon bridge probably because of difficulties associated with their preparations due to the rigidity of the parent hydro-carbons (*e.g.*,[2.2]paracyclophane). The author has found that carboxytris[2.2.2]- or carboxytetrakis[2.2.2.2]paraxylylene underwent quite easily an intramolecular cyclization reaction, giving the corresponding cyclized product, respectively, *i.e.*, the corresponding ketone linked at pseudo-geminal position, in excellent yield.

In this chapter, the preparations and some interesting spectral properties of I and the pseudo-geminal ketone of tetrakis[2.2.2.2]-paraxylylene (II) are described.

4.3   RESULTS AND DISCUSSION

Preparation.   I was prepared by the intramolecular cyclization reaction of carboxytris[2.2.2]paraxylylene[1] and was obtained as colorless prisms, mp 215.0-215.5°, in 84 % yield.   Similarly II was synthesized from carboxytetrakis[2.2.2.2]paraxylylene,[2] as slightly pale yellow prisms, mp 195-203°,* in 93 % yield.

I   II   III
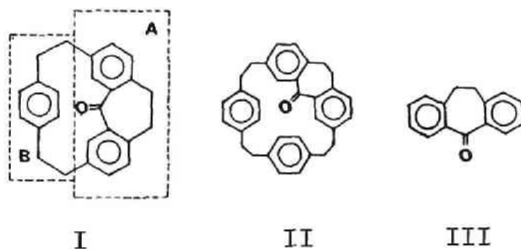
IR Spectrum.   Carbonyl stretching, $\nu_{C=O}$, is one of the most sensitive vibrations to structural change.[3] The $\nu_{C=O}$ values of I, II and dibenzosuberone (III)[4] measured in carbon tetrachloride are shown in Table 1.   An abnormally large high frequency shift (*ca.* 50 cm^{-1}) of $\nu_{C=O}$ was observed for I compared with the reference compound III, whereas $\nu_{C=O}$ of II showed only a slight migration (*ca.* 7 cm^{-1} up-

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*   Namely, II seemed to change its crystal structure from prisms and melted completely at 203°.

Table 1. Carbonyl Stretching Band ($\nu_{C=O}$) of the Ketones.[a]

Ketone	$\nu_{C=O}$ (cm^{-1})	
I	1701sh[b]	1698
II	1664sh	1656
III	1654	1649

a. ca. 10^{-2} M Solution of CCl_4.

b. Shoulder.

ward). The high frequency shift of $\nu_{C=O}$ observed for some of the formally conjugated aryl or diaryl ketone is mainly ascribed to loss of conjugation due to lack of coplanarity between carbonyl and aromatic moiety in a sterically hindered situation.[3] However, aromatic ketones which seem to have normal internal C-C-C bond angles and to have little or poor conjugation were reported to have unexpectedly small high frequency shifts. Thus, only a +9 cm^{-1} shift was observed for the $\nu_{C=O}$ value of acetomesitylene compared with that of acetophenone,[3] or an 18 cm^{-1} difference was reported for the $\nu_{C=O}$ value of 1-keto[2.2]paracyclophane relative to that of p-methylacetophenone.[6,*] Therefore in the present ketone, some additional effects which cause high frequency shift should be operative as well as loss of conjugation. One possibility is an angle strain at a small internal C-C-C bond angle which brings about the $\nu_{C=O}$ toward high

frequency effectively as seen in a series of alkanones.[7] Halford has

given a formula for the $\nu_{C=O}$ values of aliphatic ketones as a function

of the internal bond angle ψ

$$\nu_{C=O}(cm^{-1}) = 1278 + 68\,k - 2.2\psi(degrees)$$

where k was the carbonyl stretching force constant for an aliphatic

ketone. It was shown that k was equal to $(10.2 \pm 0.3) \times 10^{-5}$ dynes/

cm and was almost independent of the internal bond angle ψ.[7]

Schleyer and Nicholas used this equation for evaluation of internal

bond angles of cyclic alkanones with slight modification (*i.e.*, k =

10.244 instead of k = 10.2).[8] Using the Schleyer's equation and the

estimated difference (8.5°) between the internal bond angle of I and

of III based on Dreiding models, the high frequency shift due to

angle strain is calculated to be 19 cm^{-1} which is still small to

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* A statistical correction for the $\nu_{C=O}$ values because of a rotation

about the single bond was not considered. Probably this rotation

should be one of the reasons which do not expand the difference

of the $\nu_{C=O}$ values remarkably. For example, more sterically hindered

aromatic ketone such as 2,4,6,-tri-*tert*-butylacetophenone was

reported to show $\nu_{C=O}$ at about 1700 cm^{-1} (by *ca.* 10 cm^{-1} higher

frequency than acetomesitylene) in carbon tetrachloride.[5]

account for the large observed high frequency shift.* Thus the both

effects, loss of conjugation and bond angle strain, must be

responsible for the high frequency shift observed for I because of

the rigidity of its structure.

NMR Spectrum. Observed chemical shifts and spin-spin coupling

constants of I-III are listed in Table 2, and especially aromatic

regions of the spectra of I and II are shown in Fig. 1. Assignments

of aromatic protons were made on the spin decoupling experiments.

Since two protons, H_a's, of I locate just above (3.1 Å) the

"face" ** benzene ring (A) in a Dreiding model, protons at δ 5.51 were
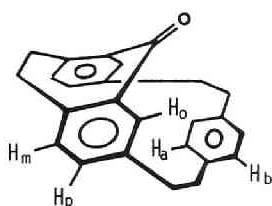
assigned as H_a's. This absorption is considerably shifted to high

field (by 1.09 ppm) compared with the aromatic protons of the parent

tris[2.2.2]paraxylylene (sharp singlet at δ 6.62 in carbon tetra-

---

* From recent studies on some cycloalkanones,[9] it seems that such a

simple linear relation among the $\nu_{C=O}$ values and the internal C-C-C

bond angles is not existed exactly.

** Terminology of "face" and "lateral" were used for janusene by

Cristol.[10] The author wishes to use these terminology to distinguish

two limiting conformations of aromatic rings of higher paraxylylenes.

chloride),[1] and is similar to aromatic protons observed at δ 5.50

which locate just above (3.0 Å) aromatic rings of 4,5:7,8-dibenzo-

[2.2]paracyclophane.[11] While H_a and H_b of I had no *ortho* coupling,

those of II showed a normal *ortho* coupling (by 8.5 Hz), though their

coupling pattern was an AA'BB' type in an accurate sense. Thus

relative positions of H_a and H_b of II should be *ortho* to each other.

The chemical shift of H_o, *ortho* proton to carbonyl, of I or II

appears (a) in higher field than that of H_m (by 0.79 ppm for I) or H_p

(by 0.95 ppm for I or by 0.18 ppm for II) and (b) in surprisingly

higher field than that of H_o of III (by *ca.* 1.8 ppm for I or by *ca.*

0.9 ppm for II). In contrast to the observation (a), H_o of III or

ortho protons of simple carbonyl derivatives of tris[2.2.2]- or
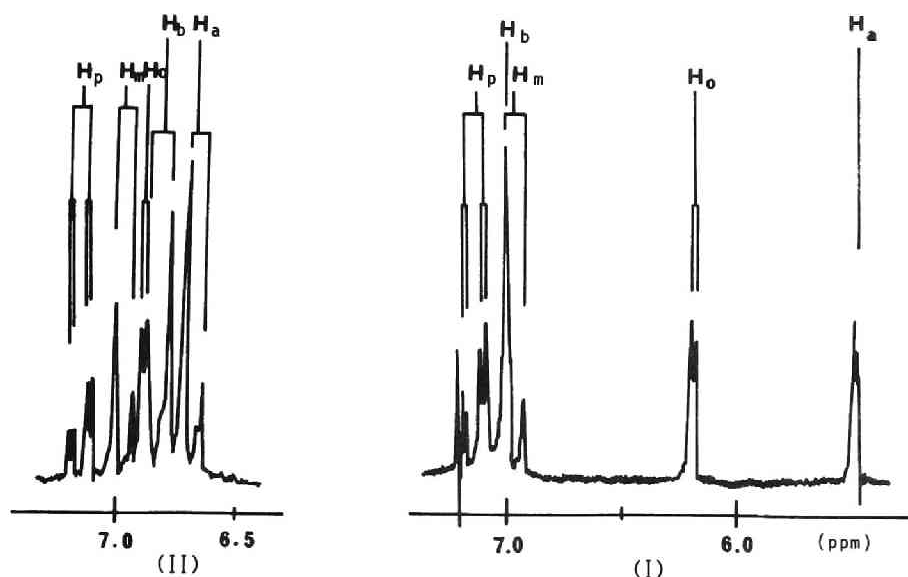
Fig. 1 Aromatic regions of NMR spectra of
I (in CDCl$_3$) and II (in CS$_2$) at 31.5°.

Table 2. The NMR Data of the Ketones in $CDCl_3$

at 31.5° (δ from internal TMS).[a]

Ketone	H_o	H_m	H_p	H_a	H_b	$-CH_2-$
I[b]	6.21(d)	7.00(d)	7.16(dd)	5.51(m)	7.03(m)	2.2-3.4(m)
II[c]	7.08(d)	7.08(d)	7.26(dd)	6.86(AA'BB')		2.94(br.s) 2.96(br.s) 3.08(br.s)
III	8.0(m)	7.1-7.4(m)				3.10(br.s)

a. Abbriviations are: br.s, broad singlet; d, doublet; dd, doublet of doublet; m, multiplet.   b. $J(H_m-H_p)$= 8.0 Hz, $J(H_o-H_p)$= 2.0 Hz. c. $J(H_m-H_p)$= 7.5 Hz, $J(H_o-H_p)$= 2.0 Hz, apparent J_{AB}= 8.5 Hz, $\Delta\nu_{AB}$= 13 Hz.

tetrakis[2.2.2.2]paraxylylene such as acetyltris[2.2.2]paraxylylene were observed at lower field (by 0.5-1.2 ppm)[1,2] than H_m or H_p. These upfield shifts of H_o's of I and II, therefore, are attributable (*a*) mainly to the shielding effect of the "face" benzene ring, (*b*) particularly for I to elimination or considerable reduction of the anisotropic deshielding effect of the carbonyl[12] because of non-planarity between carbonyl and aromatic rings discussed in the IR spectrum,[*] and (*c*) slightly to the inductive effect of the *meta* substituted methylene bridges. Assuming a conformational similarity between III and the *A* moiety of I, the effect due to (*a*) is approximately evaluated by use of the Johnson-Bovey's method[13] to be *ca.*

1.0 ppm upfield for H_o of I compared with H_o of III. At most 0.2 ppm

upfield shift might be responsible for the effect due to (c).** Thus

this simple calculation suggests that the upfield shift attributed to

(b) amounts ca. 0.5 ppm.***

An extra effect to cause the upfield shift of H_o, one might

consider the deformation of the benzene rings. This seems, however,

not to be important, since even [6]paracyclophane which has an

apparently very deformed benzene ring, has been reported to show

its aromatic protons at δ 7.17,[15] i.e., in the normal aromatic re-

gion. That H_m and H_p of I and II also appear in the normal aromatic

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* Being described in chapter 4, NMR measurements for pseudo-geminal

methanotris[2.2.2]paraxylylene (IV) and dibenzosuberane (V) show no

remarkable change of the chemical shift difference between H_m or H_p

of I and that of IV, (-0.12 or -0.28 ppm, respectively) compared with

the corresponding protons of III and those of V (-0.2 ppm).

** Aromatic protons of 1,2,4-trimethylbenzene absorbed at by 0.15 ppm

higher field than those of p-xylene.[14]

*** Aromatic protons of a conjugated benzene ring of 1-keto[2.2]-

paracyclophane was reported to absorb as a singlet at δ 6.63,[6] i.e.,

by 1.28 ppm higher field than ortho protons of acetophenone (δ 7.91)[16]

According to the present discussion, the upfield shift attributed to

(b) for this ketone is estimated to be ca. 0.4 ppm (0.4 $\fallingdotseq$ 7.91-6.63

-0.68[6] (due to a) -0.2 (due to c)).

region (δ 7.00-7.16) affords additional support for the negligible contribution of benzene deformation to the upfield shift of the H_o of I.

Electronic Spectrum.   Electronic spectra of I-III recorded in methylene chloride, cyclohexane and ethanol are shown in Table 3.

Table 3. Electronic Spectra of the Ketones

Ketone	methylene chloride		cyclohexane	ethanol
	λ(nm)	ε(1/mol·cm)	λ(nm)	λ(nm)
I	276	4380	271	275
	281sh[a]	4240		280sh
	322sh	280	330	
II	271sh	11600	268	271sh
	275	11700		275
	303sh	4090	295	303sh
	348sh	520	351	
III	270	12900	266	270
	296sh	3740	293sh	
	344	410	351	342sh

a. Shoulder.

According to the low temperature absorption, phosphorescence and degree of polarization spectra of III,[17] an absorption at 270 nm is assigned as intramolecular charge-transfer (CT) transition between carbonyl and aromatics, that near 300 nm as the Lb band, and that at 344 nm as the $n\pi^*$ transition in carbonyl. These assignments seem to be valid to the spectra of I and II considering the wave length and the intensity of the absorptions together with the solvent effects, $i.e.$, the bathochromic shifts were observed for the CT and the Lb bands and the hypsochromic shift for the $n\pi^*$ band in ethanol or methylene chloride solution, though the Lb band of I was not clearly observed.

A large hypochromic effect in the CT band and a remarkable hypsochromic shift (21 nm in cyclohexane) of the $n\pi^*$ band are observed for I compared with III. These characteristics in the electronic spectra are probably connected with the lack of coplanarity of "conjugated" carbonyl[6,18] mentioned above, and indicate again that deformation of the benzene rings is not important, since remarkable bathochromic shifts have often been observed for electronic spectra of cyclophanes containing deformed benzene rings such as [n]paracyclophanes.[15,19]

Both the wavelength and the intensity of λ_{max} of II are very similar to those of III, though a slight bathochromic shift due to $meta$ methylene bridges is seen for the CT or the Lb band. Thus, similarity between strucural environment of a carbonyl in II and in III is again indicated in the electronic spectra, in accord with the IR

spectra.

4.4   EXPERIMENTAL

All melting points were uncorrected. Commercially available
spectrograde carbon tetrachloride, cyclohexane, ethanol, methylene
chloride and deuteriochloroform were used directly for the spectral
measurements. IR spectra were taken on a Hitachi EPI-G3 grating
infrared spectrophotometer. NMR spectra were recorded with a Varian
HA-100 spectrometer, and electronic spectra were measured with a
Hitachi EPS-3T spectrometer. Mass spectra were determined by a
Hitachi RMU-6C mass spectrometer with ionization current 70 eV.

Pseudo-Geminal Ketone of Tris[2.2.2]paraxylylene (I).   To a solution
of 744 mg (2.1 mmol) carboxytris[2.2.2]paraxylylene in 40 ml of
phosphorous oxychloride were added 4 g of freshly powdered zinc
chloride. The mixture was stirred at 60° untill the yellow color of
the solution changed to orange (1 hr). Then the reaction mixture was
poured onto ice with careful stirring and extracted with ether-
benzene (1:1). The ether-benzene extract was washed with aqueous
hydrochloric acid, with aqueous sodium bicarbonate and saturated
aqueous sodium chloride. The solution was dried over anhydrous
sodium sulfate and the solvent was evaporated. The residue was
recrystallized with benzene-*n*-hexane (4:1) and gave 575 mg (1.7 mmol,

84 % yield) of I as prisms. Recrystallization of a small sample

from n-hexane gave colorless prisms: mp 215.0–215.5°; mass spectrum

m/e (rel intensity) 338 (M$^+$, 100), 234 (21), 233 (27), 219 (12), 206

(28), 205 (57), 191 (15), 189(19), 119 (20), 104 (13); ir (KBr) 2920,

1695, 1610, 1500, 1440, 1290, 1170, 900, 810, 800, 785, 610 cm^{-1}.

Anal. Calcd for $C_{25}H_{22}O$: C, 88.72; H, 6.55.

Found   : C, 88.73; H, 6.76.

Pseudo-Geminal Ketone of Tetrakis[2.2.2.2]paraxylylene (II).   To a

solution of 67 mg (0.15 mmol) of carboxytetrakis[2.2.2.2]paraxylylene

in 50 ml of chloroform were added 20 mg of freshly powdered zinc

chloride and 45 mg of phosphorous oxychloride. The mixture was

stirred at 60° and a small amount of zinc chloride was further added

after one day. After 2 days, the mixture was poured onto ice and

extracted with chloroform. The chloroform extract was washed with

diluted hydrochloric acid, aqueous sodium bicarbonate and saturated

aqueous sodium chloride. The solution was dried over anhydrous

sodium sulfate and the solvent was evaporated. The residue was

chromatographed on a silica gel column with n-hexane-chloroform (1:1).

The eluted materials were recrystallized from n-hexane to give 60 mg

(0.14 mmol, 93 % yield) of II as pale yellow prisms: mp 195–203°;

mass spectrum m/e (rel intensity) 442 (M$^+$, 16), 209 (13), 168 (15),

167 (90), 165 (22), 149 (41), 119 (19), 105 (100); ir (KBr) 2920,

1650, 1605, 1510, 1435, 1415, 1300, 1275, 1180, 815, 620, 590 cm^{-1}.

Anal. Calcd for $C_{33}H_{30}O$: C, 89.55; H, 6.83.

Found   : C, 89.51; H, 6.54.

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CHAPTER 5

Preparations and Properties of Some Derivatives of

Pseudo-Geminal Ketone of Tris[2.2.2]paraxylylene

5.1 SUMMARY

Some derivatives of pseudo-geminal ketone of tris[2.2.2]para-
xylylene (I) are prepared and their spectral properties are investi-
gated in connection with their structural characteristics. Thus,
borohydride or alkaline zinc reduction of I gives pseudo-geminal
"equatorial" carbinol (III) stereospecifically, and hydrolysis of the
trifluoromethanesulfonate of III (IV) yields pseudo-geminal "axial"
carbinol (V) again stereospecifically. The stereochemistry of III
and V is determined on the basis of chemical shifts of benzhydryl
and H_o (*ortho* to carbonyl) protons in NMR spectra. The difference in
chemical shifts of H_p protons of the two alcohols is explained with
the change in electron densities of *para* carbon atoms.

5.2 INTRODUCTION

In the preceding chapter, the author described the high yield
preparation of pseudo-geminal ketone of tris[2.2.2]paraxylylene (I)
and its spectral properties connected with its structure. The re-
markable high frequency shift of $\nu_{C=O}$ band in IR spectrum and the
large hypochromic effect of intramolecular charge-transfer ab-
sorption on electronic spectrum of I compared with the corresponding
spectral characteristics of dibenzosuberone (VI) demonstrated the
lack of coplanarity between carbonyl and benzene planes, and the
presence of angle strain about the carbonyl.[1]

Taking advantage of these characteristics in the structure, some derivatives of I were prepared in order to elucidate relationships between structure and spectral properties. In this chapter are also described some interesting NMR spectral characteristics of the pseudo-geminal tris[2.2.2]paraxylylene derivatives.

5.3 RESULTS AND DISCUSSION

Preparation. From tris[2.2.2]paraxylylene, pseudo-geminal ketone (I) was prepared as described elsewhere.[1] Reduction of I with sodium borohydride in dioxane or zinc powder in alkaline aqueous ethanol gave 92 % or 71 % yield, respectively, of "equatorial" alcohol (III), mp 181.0°, exclusively. The Wolff-Kishner reduction of I with aqueous hydrazine and sodium hydroxide at 195° yielded 44 % of pseudo-geminal methanotris[2.2.2]paraxylylene (II) and 46 % of III. III was converted to the corresponding trifluoromethanesulfonate (IV) on treatment with *n*-butyllithium and trifluoromethanesulfonyl chloride in ether. IV was hydrolyzed in aqueous dioxane to give the stereo-isomeric "axial" alcohol (V), mp > 300°, in quantitative yield. The *p*-nitrobenzoates of III and V (IX and X, respectively) were prepared by the usual method.

Determination of Stereochemistry of Pseudo-Geminal Carbinols of Tris[2.2.2]paraxylylene. Based on molecular model (Dreiding and CPK), the pseudo-geminal bridged tris[2.2.2]paraxylylenes are regarded to have appreciably rigid structures, where conformation
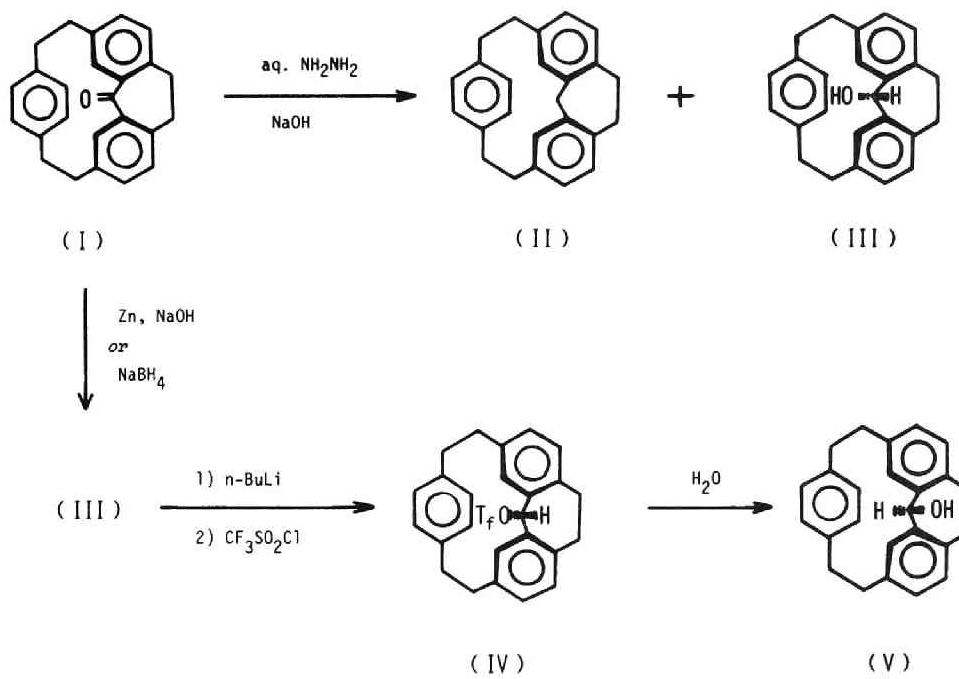
change between "equatorial" and "axial" positions about pseudo-geminal carbon atom seems to be difficult and environments of these positions seem to be remarkably different in each other. The stereochemistry of the two isomeric alcohols (III and V) was investigated mostly based on NMR spectra. The NMR spectral data of the two alcohols are shown in Table 1 along with those of the related compounds. Absorptions of the aromatic and benzhydryl protons are recorded in Fig. 1.

The seven membered ring of II (shown in Fig. 2 by bold line) is forced to be in a boat conformation due to the remarkably large

Table 1. The NMR Data of Pseudo-Geminal Bridged Tris[2.2.2]paraxylylene

and Related Compounds in $CDCl_3$ at 31.5° (δ from internal TMS)[a].

Compound	H_o	H_m	H_p	H_a	H_b	H_{ax}	H_{eq}	$-CH_2-$	OH
I[b]	6.21(d)	7.00(d)	7.16(dd)	5.51(m)	7.03(m)			2.2-3.4(m)	
II[c]	6.12(m)	6.88(d)	6.88(d)	5.57(m)	7.07(m)	4.12(d)	2.88(d)	2.4-3.5(m)	
III[d]	6.52(m)	6.87(d)	6.91(dd)	5.56(m)	7.07(m)	6.07(s)		2.3-3.4(m)	1.60(br.s)
V[e]	6.11(m)	6.94(d)	6.97(dd)	5.52(m)	7.05(m)		5.01(s)	2.3-3.2(m)	2.00(br.s)
								3.7-3.9(m)	
VI[b]	8.0(m)	7.1-7.4(m)						3.10(br.s)	
VII		7.09(s)				4.10(s)		3.16(s)	
VIII		7.0-7.5(m)				5.91(s)		2.9-3.4(m)	2.22(br.s)

a. Abbreviations are: s, singlet; br.s, broad singlet; d, doublet; dd, doublet of doublet; m, multiplet.   b. Ref. 1.   c. $J(H_o-H_p)=J(H_o-H_m)=$ 1.2 Hz, $J(H_{ax}-H_{eq})=$ 12.4 Hz.   d. $J(H_m-H_p)=$ 8.0 Hz, $J(H_o-H_p)=$ 1.5 Hz.   e. $J(H_m-H_p)=$ 8.0 Hz, $J(H_o-H_p)=$ 1.5 Hz.
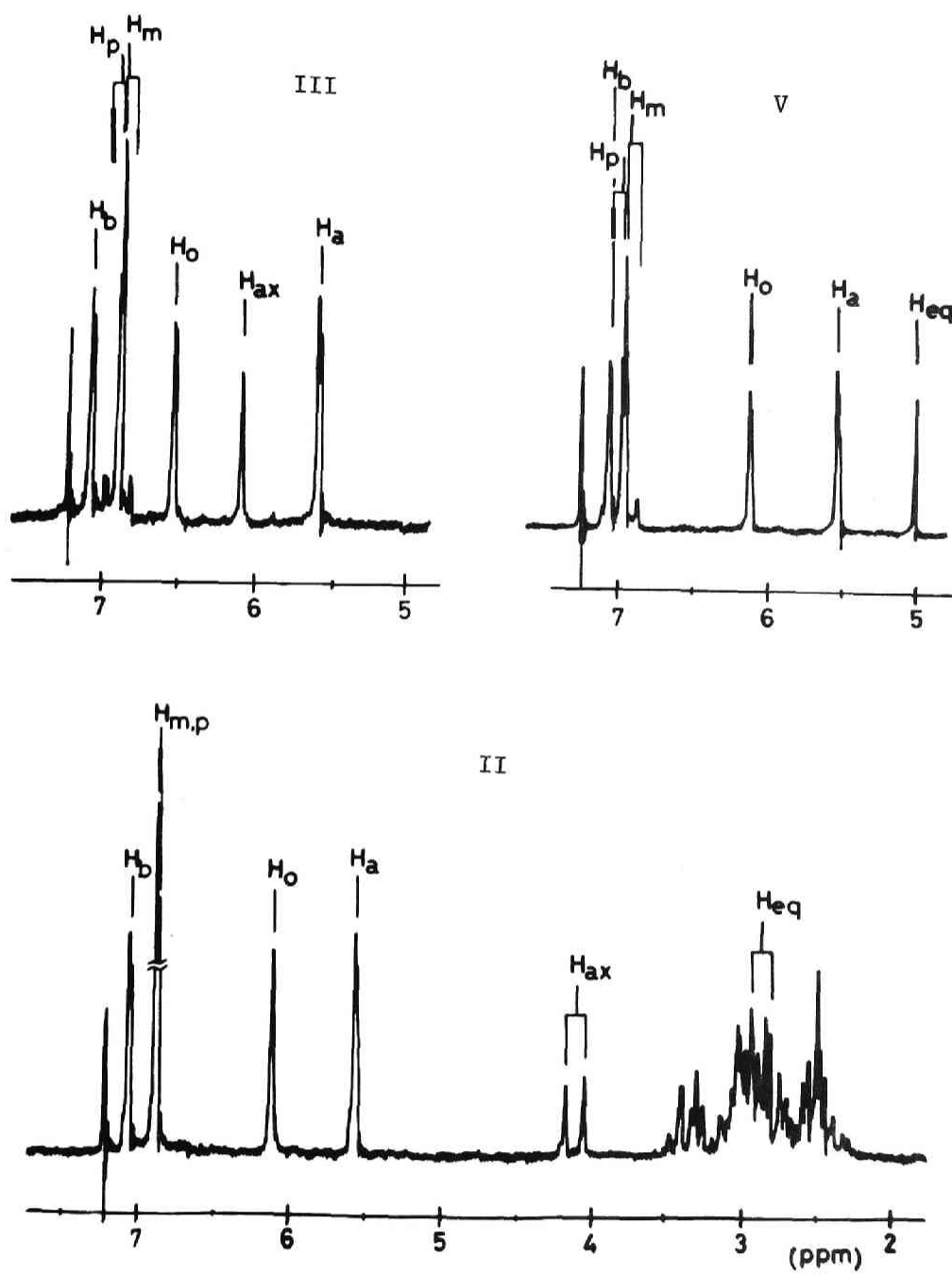
Fig. 1 Aromatic and benzhydryl regions of NMR

spectra of II, III and V in CDCl$_3$ at 31.5°

(VI)   X = CO
(VII) X = CH₂
(VIII) X = CHOH

(II)
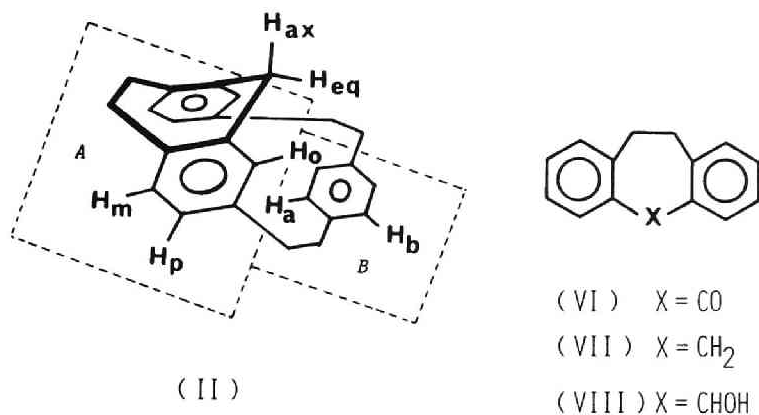
Fig. 2

barrier to the expected conformation change, as shown by the NMR
spectrum of II in hexachlorobutadiene which shows no substantial
temperature dependence up to 180°. Irradiation at δ 2.88 caused
increase in area intensity of the H_o signal (δ 6.12) of II by 22 ± 1
%, whereas only a very small increase (2.7 ± 0.1 %) was observed
uppon irradiation at δ 4.12. From this nuclear Overhauser effect[2]
the higher field signal (δ 2.88) was determined to H_{eq}, "equatorial"
about the pseudo-geminal bridge carbon, and the lower (δ 4.12) to H_{ax},
"axial". Since the chemical shift of a proton α to hydroxyl has been
reported not to be remarkably affected by the change in stereo-
chemistry of the group,[3] assignments of stereochemistry of the present
carbinols are safely made as shown in Fig. 1. Deshielding of the H_o
protons of III (by 0,41 ppm lower field than those of V) is, thus,
mainly attributed to anisotropic effect of the "equatorial" oxygen
atom in a close proximity.

- 69 -

The low field absorption of the "axial" proton in the present system is consistent with those reported for the 3,4-homotropylidenes,[4] dihydropleiadenes[5] or dihydroanthracenes.[6]

A marked difference between observed ν_{O-H} of these two isomeric alcohols is also in accord with the present stereochemistry. The ν_{O-H} of II, III and dibenzosuberol (VIII) (dilute solutions in carbon tetrachloride) are shown in Fig. 3. The "axial" hydroxyl group is expected to interact with a phenyl group (Fig. 4), known as the π-hydrogen bonding,[7] shifting the ν_{O-H} of III to a relatively low frequency, 3608 cm^{-1}. On the other hand, the ν_{O-H} of V appears at relatively high frequency, 3619 cm^{-1}, again consistent with the stereochemistry, where the "equatorial" hydroxyl group does not seem to interact with the phenyl group. The above consideration is supported by IR spectra of strucurally related compounds, 9-fluorenol (3591 cm^{-1},

Fig. 3 ν_{O-H} Absorptions of III (——), V (– – – –) and VIII (—·—) in CCl$_4$. Concentration 5×10^{-4} M, cell thickness 2.5 cm.

"equatorial" OH   "axial" OH
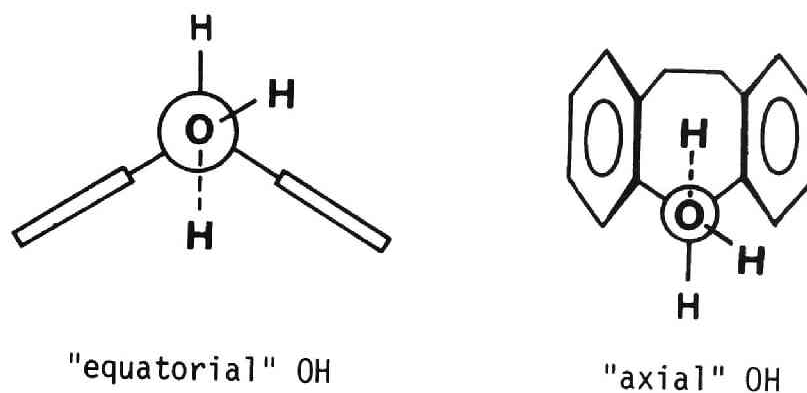
Fig. 4

only the "axial" conformation is allowed) and VIII (3620, 3609sh and
3597 cm^{-1}, more than two conformations are allowed due to its flexi-
ble structure). The stereochemistry of the alcohols (III and V),
therefore, suggests highly stereoselective attacks (*anti* to the *B*
benzene ring) of nucleophiles such as hydride or hydroxide, toward
the carbonyl carbon.

Chemical Shift of Pseudo-Geminal Bridged Tris[2.2.2]paraxylylene.

Remarkable charateristics appeared in the NMR chemical shifts
(Table 1) of the pseudo-geminal bridged tris[2.2.2]paraxylylenes are
that H_o and H_a protons absorb at considerably high field. All of
the H_a protons of the four derivatives (I, II, III and V) are ob-
served by 1.5 ppm upfield (δ from 5.51 to 5.57) than *p*-xylene. One
encounters a similar situation in the aromatic protons of 4,5:7,8-
dibenzo[2.2]paracyclophane (XI)[8] absorbing at δ 5.50, which locate
just above (*ca.* 3.0 Å) the aromatic ring. Thus, for the H_a protons
of the present compounds, considered to locate just above (3.1 Å)

the "face"[1] benzene rings (A) judging from molecular models, the observed high field shifts are attributed to a transannular shielding effect of the A rings (see II).
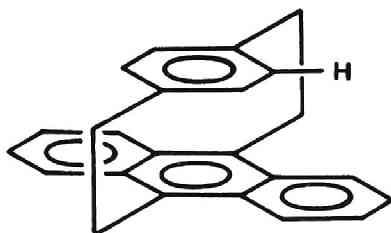
(XI)

Since the absorption of the H_o protons of II appears at δ 6.12, by 0.97 ppm higher field than the corresponding noncyclic VII, the transannular shielding of the B ring is estimated to be 0.82 ppm assuming by 0.15 ppm[*] upfield shift due to the inductive effect of the *meta* methylene bridges. This reduced transannular shielding is responsible for deviation (1.6 $\overset{o}{A}$ by the model) of location of the H_o proton from the center of the B ring.

The H_p protons of II appear only by 0.21 ppm higher field than VII. This relatively small shift is mostly attributable to the *meta* methylene bridges, and only a negligibly small transannular shielding seems to be present at this position.

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[*] Aromatic protons of 1,2,4-trimethylbenzene absorbed at by 0.15 ppm higher field than those of *p*-xylene.[9]

An interesting difference (0.06 ppm) between the chemical shifts of the H_p protons is seen for V compared with III. A similar difference (0.08 ppm) is also observed between the corresponding *p*-nitrobenzoates (δ 6.96 for IX and δ 7.04 for X). Since a distance between the H_p hydrogen and hydroxyl oxygen atoms is estimated to be 6.0-6.1 Å, at most by 0.2 ppm difference is responsible for the change in the chemical shift due to anisotropic shielding and electrostatic field effects.[10,11] The main part of the difference is, therefore, interpreted with change in electron densities of the *para* carbon atoms. Linear correlations of chemical shifts of aromatic protons with electron densities of ring carbon atoms have been well established.[12] Thus, the CNDO/2[13] calculations were carried out for two conformations, where the hydroxyl was perpendicular or coplanar to the phenyl plane, of benzyl alcohol as a model compound. The calculated electron density of the *para* carbon was lower (by 0.003 *e*, which caused by 0.04 ppm down field shift according to the equation[12b]) for the perpendicular form. This result is clearly consistent with the observed lower chemical shift in V.

5.4   EXPERIMENTAL

Measurements and Calculations.   All melting points were uncorrected. NMR spectra were recorded with a Varian HA-100 or an EM-360 spectrometer. The former was also employed for the variable-temperature and the nuclear Overhauser experiments. A sample used for the latter

experiment was degassed. Mass spectra were determined by a Hitachi RMU-6C mass spectrometer at 70 eV. Electronic spectra were measured with a Hitachi EPS-3T recording spectrophotometer, and IR spectra were taken on a Hitachi EPI-G3 grating infrared spectrophotometer. Theoretical calculations were carried out by using the FACOM 230 75 computer at the Data Processing Center of Kyoto University.

Pseudo-Geminal "Equatorial" Carbinol of Tris[2.2.2]paraxylylene (III).
(a) Zinc reduction. To a hot solution of 520 mg of pseudo-geminal ketone of tris[2.2.2]paraxylylene (I) in 70 ml of ethanol was added a mixture of 7 g of zinc powder, 7 g of sodium hydroxide and 10 ml of water. The mixture was refluxed for 2 hr and was concentrated to half volume. After cooling to room temperature, the mixture was filtered. The filtrate was extracted with ether six times. The combined ether extract was washed with saturated aqueous sodium chloride, dried over anhydrous magnesium sulfate, and the solvent was evaporated. The residual solids were recrystallized with benzene-methylene chloride (6:1) to give 370 mg (71 %) of III as colorless prisms: mp 181.0°; mass spectrum m/e (rel intensity) 340 (M^+,88), 322 (36), 311 (54), 218 (100), 205 (31), 193 (32), 133 (47), 104 (36); ir (KBr) 3470, 3000, 2930, 2840, 1495, 1440, 1155, 1045, 1040, 805, 620, 455 cm^{-1}; uv (cyclohexane) λ_{max} 279sh (ε 800), 265 (900), 272sh (930), 274 (1000), 281 nm (910).

    Anal. Calcd for $C_{25}H_{24}O$: C, 88.19; H, 7.11.
       Found   : C, 88.48; H, 7.05.

(b) Borohydride reduction. To a stirred solution of 430 mg (1.27 mmol) of I and 0.5 ml of 0.1 *M* aqueous sodium hydroxide in 10 ml of dioxane, 242 mg (6.35 mmol) of sodium borohydride was added at room temperature, and sirring was continued for 3 hr. Excess borohydride was removed by boiling the solution for 5 min, then the solution was cooled and extracted with chloroform three times. The combined chloroform extract was washed with saturated aqueous sodium chloride, dried over anhydrous sodium sulfate and the solvent was evaporated. The residual white solids were chromatographed on a silica gel column with benzene to give 397 mg (92 %) of III.

Pseudo-Geminal Methanotris[2.2.2]paraxylylene (II). A mixture of 50 mg of I, 200 mg of sodium hydroxide, 10 drops of hydrazine hydrate (abt. 80 %) and 4 ml of diethylene glycol was refluxed for 40 min. After cooling, the mixture was extracted with ether. The ether extract was washed with aqueous sodium chloride and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was chromatographed on a silica gel column with *n*-hexane-methylene chloride (1:1) and then methylene chloride. The first fraction gave 21 mg (44 %) of II, and the second fraction gave 23 mg (46 %) of III which was identified with an authentic III by NMR and IR spectra. Recrystallization of II from *n*-hexane-chloroform gave colorless plates: mp 189.5-190.5°; mass spectrum *m/e* (rel intensity) 324 (M^+, 100), 220 (26), 219 (40), 205 (61), 129 (26), 104 (21), 83 (28); ir (KBr) 3000, 2930, 2850, 1500, 1440, 1100, 810, 590, 460 cm^{-1};

uv (cyclohexane) λ_{max} 258sh (ε 650), 261sh (690), 266 (860), 274 (1060), 279 (830), 282 nm (1070).

Anal. Calcd for $C_{25}H_{24}$: C, 92.54; H, 7.46.

Found : C, 92.42; H, 7.48.

The Trifluoromethanesulfonate of III (IV). To a stirred solution of 190 mg of III in 5 ml of dry ether, was added 0.3 ml of 20 % *n*-butyl-lithium in hexane at room temperature, and stirring was continued for 10 min. Then several drops of trifluoromethanesulfonyl chloride were added, and stirring was continued for additional 10 min at room temperature. Then, the solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column with benzene. The crystals from the major fraction were recrystallized from petroleum ether to give 180 mg (68 %) of IV as colorless needles: mp 158.5-159.0° (dec); ir (KBr) 2930, 1415, 1250, 1215, 1200, 950, 890, 805, 635, 605, 580, 515, 460 cm^{-1}; nmr δ (CDCl$_3$, TMS) 2.0-3.5 (12H, m, -CH$_2$-), 5.13 (1H, s, H$_{eq}$), 5.56 (2H, m, H$_a$), 6.39 (2H, m, H$_o$), 6.93 (2H, d, J= 8.0 Hz, H$_m$), 7.01 (2H, dd, J= 8.0, 1.5 Hz, H$_p$), 7.12 (2H, m, H$_b$).

Anal. Calcd for $C_{26}H_{23}F_3O_3S$: C, 66.09; H, 4.91.

Found : C, 66.18; H, 5.19.

Pseudo-Geminal "Axial" Carbinol of Tris[2.2.2]paraxylylene (V). A solution of 52 mg of IV in 9 ml of dioxane and 6 ml of water in a sealed tube was placed in a bath kept at 110.6 $\pm$ 0.1° for 23 hr.

After cooling, the reaction mixture was diluted with water and extracted with ether-benzene (1:1). The ether-benzene extract was washed with aqueous sodium bicarbonate and then with saturated aqueous sodium chloride, and dried over anhydrous sodium sulfate. The solvent was evaporated to yield 39 mg (100 %) of colorless crystals of V, which were recrystallized from benzene to give colorless needles: mp >300°; mass spectrum m/e (rel intensity) 340 (M^+,6), 322 (45), 218 (46), 202 (19), 104 (100), 103 (27), 78 (32); ir (KBr) 3430, 3000, 2930, 2840, 1500, 1440, 1045, 1030, 810, 630, 580, 460 cm^{-1}; uv (cyclohexane) λ_{max} 244sh (ε 4940), 265sh (1240), 274 (1320), 284 nm (1110).

Anal. Calcd for $C_{25}H_{24}O$: C, 88.19; H, 7.11.

Found   : C, 88.42; H, 7.26.

The p-Nitrobenzoate of III (IX). A mixture of 210 mg of III, 130 mg of p-nitrobenzoyl chloride and 6 ml of dry pyridine was stirred for 1 hr in an ice bath. Then, water was added to the mixture, and the precipitate was filtered and washed with water. The residue was recrystallized with n-hexane-chloroform to give 290 mg (97 %) of IX as pale yellow prisms: mp 283.0–284.0°; ir (KBr) 2915, 1730, 1525, 1280, 1115, 1100, 805, 720, 460 cm^{-1}; nmr δ ($CDCl_3$, TMS) 2.3–3.6 (12H, m, $-CH_2-$), 5.63 (2H, m, H_a), 6.38 (2H, br.s, H_o), 6.96 (4H, br. s, $H_{m,p}$), 7.12 (2H, m, H_b), 7.22 (1H, s, H_{ax}), 8.35 (4H, AA'BB', NO_2- C_6H_4-CO).

Anal. Calcd for $C_{32}H_{27}NO_4$: C, 78.50; H, 5.56; O, 13.07

Found   : C, 78.27; H, 5.44; O, 13.33.

The p-Nitrobenzoate of V (X). A mixture of 68.0 mg of V, 37.5 mg of *p*-nitrobenzoyl chloride and 2 ml of dry pyridine was stirred for 7 hr in an ice bath, and then was allowed to stand over night in a refrigerator. The mixture was extracted with benzene-ether and washed with diluted hydrochloric acid. The benzene-ether extract was washed with saturated aqueous sodium chloride, dried over an- hydrous magnesium sulfate, and the solvent was evaporated. The residue was chromatographed on a silica gel column with benzene to give 101 mg of white solids. Recrystallization from benzene-petrole- um ether (1:3) gave 90 mg (92 %) of X as pale yellow needles: mp 204.5-205.5°; ir (KBr) 2920, 1720, 1710, 1530, 1350, 1275, 1100, 810, 720, 590, 460 cm^{-1}, (CCl_4) 1725 cm^{-1}; nmr δ ($CDCl_3$, TMS) 2.3-3.2 (10H, m, $-CH_2-$), 3.62-3.83 (2H, m, $-CH_2-$), 5.57 (2H, m, H_a), 6.17 (1H, s, H_{eq}), 6.34 (2H, m, H_o), 6.96 (2H, d, J= 7.8 Hz, H_m), 7.04 (2H, dd, J= 1.8, 7.8 Hz, H_p), 7.10 (2H, m, H_b), 8.10 (4H, AA'BB', $NO_2-C_6H_4-CO$).

Anal. Calcd for $C_{32}H_{27}NO_4$: C, 78.50; H, 5.56.

Found   : C, 78.15; H. 5.50.

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CHAPTER 6

Solvolyses of Pseudo-Geminal "Equatorial" and

"Axial" Systems of Tris[2.2.2]paraxylylene

6.1   SUMMARY

Solvolyses of pseudo-geminal "equatorial" and "axial" systems of
tris[2.2.2]paraxylylene (III and IV) are investigated. An extremely
large difference ($10^{14.7}$ times) in solvolysis rates between III and IV
are interpreted with the difference in directions of the incipient
carbonium ions toward the assisting "face" benzene ring. Hydrolyses
of the "equatorial" triflate (III-OTf) and the "axial" chloride
(IV-Cl) give the "axial" alcohol as a sole product, which demon-
strate the transannular π participation is greatly responsible not
only for the rate difference in the transition state but also for the
stereochemistry in the product determining step of the present
systems. A significantly slow rate (by $10^{18.1}$ times) of III compared
with a structurally related dibenzosuberyl (V) system is mainly
attributed to bond angle strain about the carbonium ion center upon
ionization of the III system.

6.2   INTRODUCTION

Although remarkable enhancement of solvolysis rate has been ob-
served by introduction of π electrons nearby the carbonium ion center,
the relative ease of ionization is quite sensitive to the direction of
the generating carbonium ion toward the assisting π electron cloud.[*,1]
On one hand, based on spectral properties of pseudo-geminal
ketone of tris[2.2.2]paraxylylene (I)[**] compared with those of

dibenzosuberone (II), very slow ionization at the pseudo-geminal

bridge position has been expected. Borohydride or alkaline zinc

reductions of I gave only the "equatorial" alcohol (III-OH) stereo-

specifically,[6] and the "axial" alcohol (IV-OH) was obtained from

hydrolysis of the "equatorial" triflate (III-OTf) again stereospecif-

ically.[6] These reactions suggested highly stereoselective attacks

(*anti* to the "face"[5] benzene ring) of nucleophiles such as hydride or

hydroxide toward the pseudo-geminal bridge carbon. Therefore, it

is not only interesting but important to investigate the solvolyses

of the "equatorial" (III) and the "axial" (IV) systems in connection

with their stereochemical environments.

In this chapter, the extremely large transannular effect on

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* The effectiveness of π-participation in the bicyclo[n.2.1] series

seems to be a sensitive function of puckering of the five ring.[2,3]

	n = 1	n = 2	n = 3
$k_{rel}^{25°}$	2.5×10^6	5×10^2	1
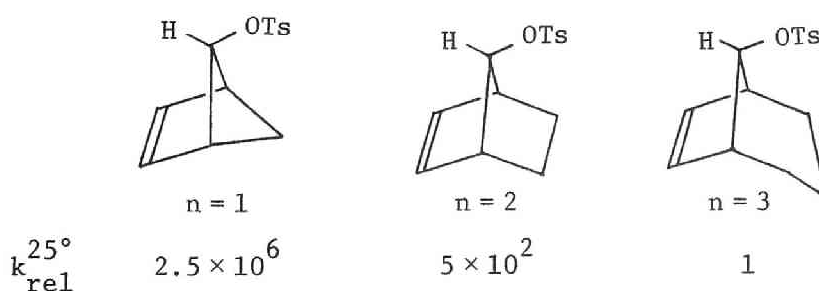
Similar results are also reported for the benzobicyclo[n.2.1] series.[4]

** The large high frequency shift (by *ca.* 50 cm^{-1}) of $\nu_{C=O}$ band in

the IR spectrum and the remarkable hypochromic effect in the elec-

tronic spectrum were observed for I compared with II.[5]

solvolysis rate and the significantly slow ionization of the IV

system compared with the structurally related compound, dibenzo-

suberyl (V) system, are described.

6.3   RESULTS

As shown in Scheme 1, the trifluoromethansulfonate of pseudo-

geminal "equatorial" alcohol of tris[2.2.2]paraxylylene (III-OTf)

was prepared from III-OH,[6] which was obtained stereospecifically by

reduction of I with sodium borohydride in aqueous dioxane.   IV-OH[6]
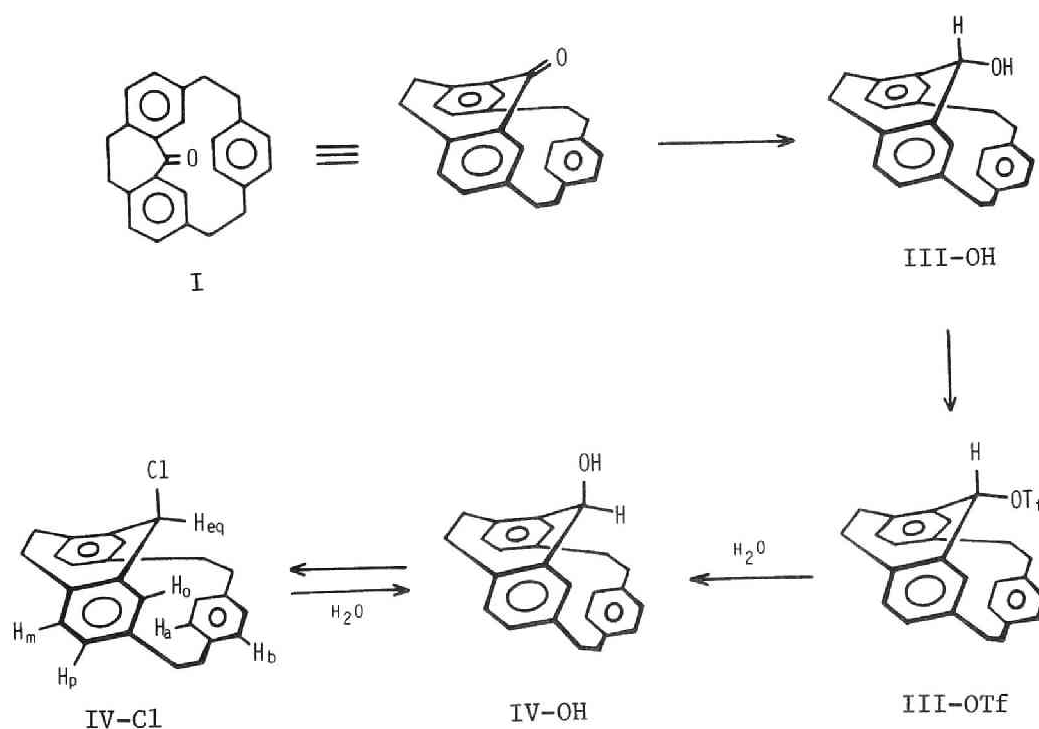
Scheme 1

was converted to the corresponding pseudo-geminal "axial" chloride (IV-Cl) on treatment with thionyl chloride in dry pyridine in quantitative yield. The stereochemistry of IV-Cl was confirmed with its NMR spectrum, *i.e.*, the chemical shift of the proton α to chlorine was observed at δ 5.12, similar to the α proton of IV-OH (δ 5.01).[6]
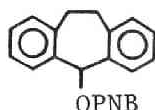
OPNB

V-OPNB

Dibenzosuberyl *p*-nitrobenzoate (V-OPNB) was prepared in 67 % yield from dibenzosuberol (V-OH) in the usual method.

On hydrolysis in 60 % (v/v) aqueous dioxane, all of the derivatives, III-OTf, IV-Cl and V-OPNB, displayed good first-order kinetics up to 60-85 % reaction (Fig. 1), where the reactions were follwed conductometrically.

Table 1 summerizes the results of the kinetic investigations on these compounds.

From hydrolysis of IV-Cl under the present condition, IV-OH was obtained quantitatively and stereospecifically[*] (Scheme 1), which was identified with an authentic IV-OH by NMR and IR spectra.

From hydrolysis of V-OPNB, V-OH was obtained as a sole product

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* Under the present condition, interconversion between III-OH and IV-OH was not occured.[6]
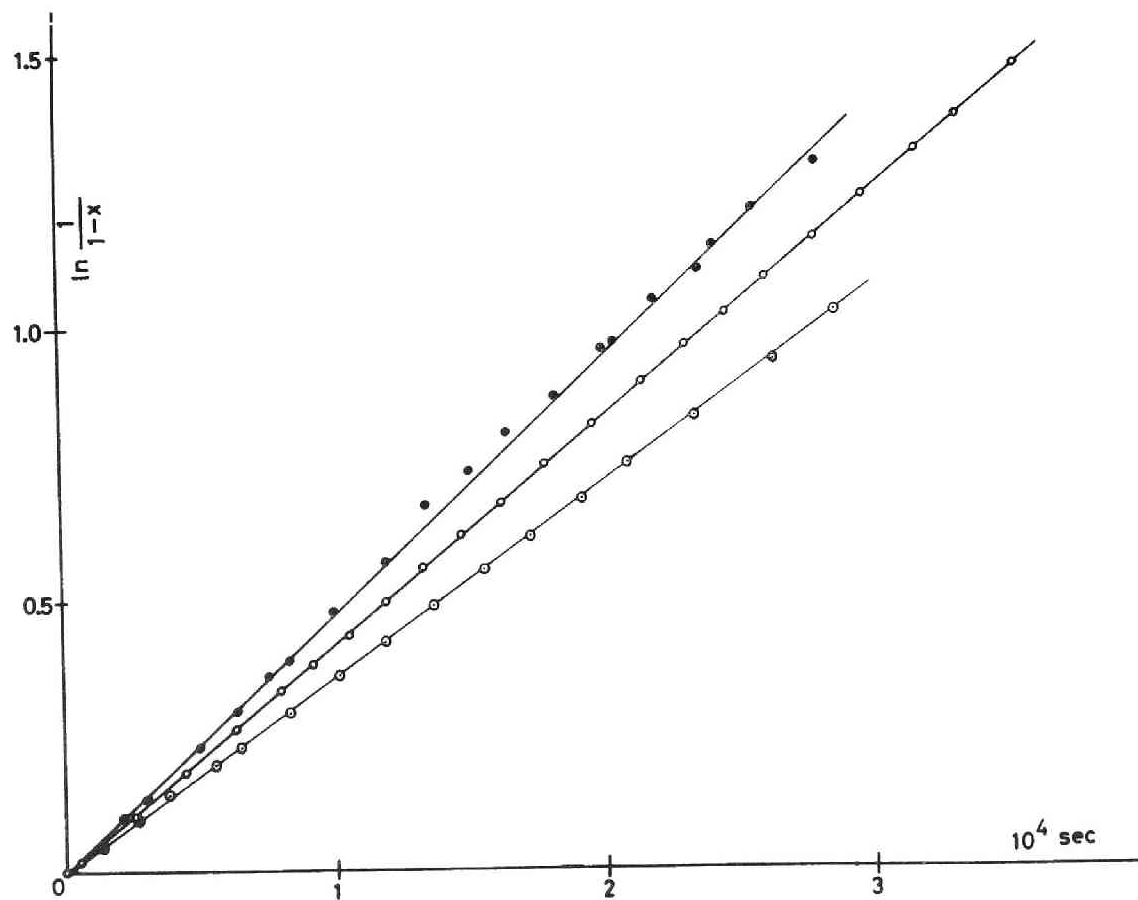
Fig. 2 First-order rate plots for the solvolyses of III-OTf,

IV-Cl and V-OPNB in 60 % (v/v) aqueous dioxane: o , III-OTf

at 98.9°; ⊙ , IV-Cl at 25.0°; ● , V-OPNB at 25.0°.

Table 1. Kinetic Data for Solvolysis in 60 % (v/v) Aqueous Dioxane.[a]

Compd	Temp, °C[b]	k_1, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k_{rel}
III-OTf	110.6	$(1.39 \pm 0.07) \times 10^{-4}$			
	98.9	$(4.24 \pm 0.07) \times 10^{-5}$	28.0	-3.6	
	25.0	2.72×10^{-9} [c]			$10^{-18.1}$
IV-Cl	40.0	$(2.45 \pm 0.00) \times 10^{-4}$			
	25.0	$(3.58 \pm 0.00) \times 10^{-5}$	23.2	-1.2	
IV-OTf	25.0	1.3×10^{6} [d]			$10^{-3.4}$
V-OPNB	35.0	$(1.62 \pm 0.00) \times 10^{-4}$			
	25.0	$(4.50 \pm 0.11) \times 10^{-5}$	22.8	-2.0	
V-OTf	25.0	3.4×10^{9} [d]			1

a. Determined conductometrically.   b. All temperatures $\pm 0.1°$ or better.
c. Extrapolated from high temperatures.   d. Estimated with the appropriate
corrections for reactivities of leaving groups.

in 99.5 % yield, which was identified with NMR and IR spectra.

6.4   DISCUSSION

As shown in Table 1, the relative rates of III-OTf, IV-OTf and V-OTf are estimated to be $10^{-18.1}$, $10^{-3.4}$ and 1 using correction for triflate-tosylate reactivity difference[7] of $10^{4.8}$, for tosylate-p-nitrobenzoate[8] of $10^{9.1}$ and for tosylate-chloride[9] of $10^{5.7}$.

Since IV-OH is the sole product from both III-OTf and IV-Cl, and the both solvolytic reactions obey the first—order kinetics, the reaction must proceed *via* the same intermediate (VI), where the 2p
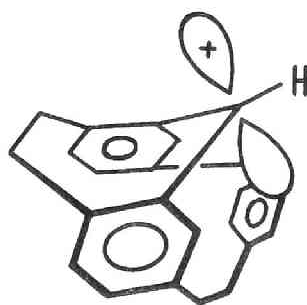
VI

orbital of the carbonium ion can transannularly interact* with the

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* ^{1}H and ^{13}C NMR spectra of 7-norbonenyl cation was measured and indicated presence of the π-participation in this system,[10,11] though the conditions were different from those of the solvolysis.

"face"[5] benzene ring,* and therefore water can attack the carbonium ion from the opposite side to this ring, or in the manner of double inversion. This explanation is also applicable to the similar attack of hydride in the reduction of I.[6]

This extremely large difference ($10^{4.7}$ times) between the rates of III-OTf and IV-OTf, thus, greatly depends whether the carbonium ion is generated in the direction where the π electrons of the "face" benzene ring can favorably interact with it (for III) or not (for IV).** One may consider that the difference in the direction of the incipient carbonium ion relative to the benzene rings substituted directly with the pseudo-geminal bridging carbon affects the ionization rate,[14] but only a small reduction (at most 10^{-3}) of the rate due to loss of conjugation between the carbonium ion and the π system has been reported *e.g.*, for α-alkylbenzyl systems.[12],***

The difference in the solvolysis rates attributed to the difference in the directions of the incipient carbonium ions toward assisting π electron clouds has been well recognized for *anti-* or *syn*-7-norbonenyl and related systems,[1] however, skeletal rearrange-

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* Based on Dreiding model, the distance between the carbonium ion center and the "face" ring is evaluated to be more than 3.5 Å.

** Interconversion between the "equatorial" and the "axial" conformations is very difficult, because the NMR spectrum of pseudo-geminal methanotris[2.2.2]paraxylylene in hexachlorobutadiene shows no substantial temperature dependence up to 180°.[6]

ments often undergo for the *syn*-systems under the solvolytic conditions.[1d,1h] It is, therfore, interesting to note that no skeletal rearrangements are observed for III-OTf and IV-Cl under the present conditions.[****]

Although several studies using cyclophane systems have been made in order to elucidate the transannular effects on reactivity and/or reaction path in solvolysis[16] or electrophilic substitution,[17,18] relatively small rate change and poor selectivity, in general, have been reported. The present systems (III and IV) are, therefore, the first and the most remarkable examples for the transannular effect on solvolytic reactivity and stereospecificity of the reaction path.

[***] The conformational environments of the seven membered rings in 2,3:5,6-dibenzo-*cis*-4-acetoxybicyclo[5.1.0]octa-2,5-diene (VII) and the corresponding *trans*-4-acetoxy isomer (VIII) are very similar to those of the present systems. Contrary to the present results, however, the *cis* ("equatorial") isomer reacts 240 times faster than the *trans* ("axial") isomer.[13]
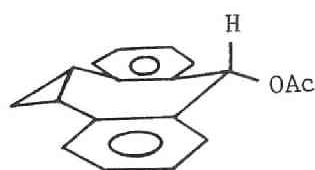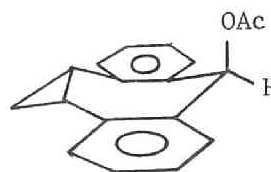
VII   VIII

[****] On treatment of V-OH with conc. hydrochloric acid gave dibenzo-4-suberene.[15]

The significantly large depletion ($10^{-18.1}$) of the rate constant of III-OTf compared with V-OTf (Table 1) is attributable to an energetically unfavorable change in angle strain about the carbonium ion center upon ionization.[19],* Steric hindrance in ionization[20] by the "face" ring or the ethano bridge in the seven membered ring is considered to be minor based on molecular model (CPK). Loss of conjugation due to lack of coplanarity is also minor as described above.

When the rate constant of the III system is compared with those of the secondary systems under the present condition, 9-fluorenyl triflate[21] is estimated to be $10^{11.7}$ times reactive than III-OTf, and *exo*-bicyclo[3.1.0]hex-6-yl triflate (IX-OTf),[7d] reported as the least reactive secondary alicyclic system, is merely 44 times less

IX-OTf

reactive than III-OTf. Therfore, III is the least reactive benzhydryl system ever reported.

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* The $J(^{13}C-H)$ value for the "axial" hydrogen in pseudo-geminal methanotris[2.2.2]paraxylylene was observed to be *ca*. 137 Hz, though that for the "equatorial" hydrogen could not be determined.

6.5   EXPERIMENTAL

Melting points were uncorrected. NMR spectra were recorded
with a Varian HR-220, HA-100 or EM-360 spectrometer. IR spectra
were taken on a Hitachi EPI-G3 grating infrared spectrophotometer.
Mass spectrum was determined with a Hitachi RMU-6C mass spectro-
meter.

Pseudo-Geminal "Axial" Chloride of Tris[2.2.2]paraxylylene (IV-Cl).

To a stirred solution of 102 mg of pseudo-geminal "axial" alcohol
(IV-OH) and 3 drops of dry pyridine in 10 ml of dry benzene was added
1 ml of thionyl chloride at room temperature. The stirring was con-
tinued for 2 hr and then the solution was warmed to 50° for 15 min.
After cooling, a mixture of benzene-ether and cold aqueous sodium
bicarbonate was added into the solution, and the organic layer was
separated. The benzene-ether extract was washed with saturated
aqueous sodium chloride, dried over anhydrous sodium sulfate, and the
solvent was evaporated to give 110 mg (100 %) of IV-Cl as white
solids. Recrystallization from petroleum ether-methylene chloride
(1:1) gave colorless needles: mp 204.0–206.0°; mass spectrum m/e (rel
intensity) 358 (M^+,21), 324 (59), 323 (100), 321 (21), 219 (46), 218
(37), 205 (58), 204 (26), 203 (26), 202 (29), 105 (16), 104 (15), 91
(14); ir (KBr) 2900, 2830, 1500, 1440, 810, 740, 610 cm^{-1}; nmr δ
($CDCl_3$, TMS) 2.24–3.17 (10H, m, $-CH_2-$), 3.78–3.99 (2H, m, $-CH_2-$),
5.13 (1H, s, H_{eq}), 5.51 (2H, m, H_a), 6.14 (2H, d, J = 1.7 Hz, H_o),

6.94 (2H, d, J = 8.0 Hz, H_m), 7.00 (2H, dd, J = 1.7, 8.0 Hz, H_p), 7.07 (2H, m, H_b).

    Anal. Calcd for $C_{25}H_{23}Cl$: C, 83.66; H, 6.46.

        Found   : C, 83.45; H, 6.34.

Dibenzosuberyl p-Nitrobenzoate (V-OPNB).   To a stirred solution of 400 mg of dibenzosuberol (V-OH) in 4 ml of dry pyridine was added 400 mg of *p*-nitrobenzoyl chloride at 0°, and stirring was continued for 2 hr.   Then 10 ml of cold water was added into the solution, and the solution was stirred for additional 15 min.   The whole was poured into 200 ml of water, and precipitates were separated by filtration, washed with water, and dried under reduced pressure. The residual solids were recrystallized from *n*-hexane-methylene chloride to give 460 mg (67 %) of V-OPNB as pale yellow prisms: mp 169.0-170.0°; ir (KBr) 1720, 1525, 1350, 1340, 1265, 1095, 720 cm^{-1}; nmr δ ($CDCl_3$, TMS) 2.9-3.8 (4H, m, $-CH_2-$), 7.1-7.6 (9H, m, Ph and H_α), 8.20 (4H, s, NO_2PhCOO).

    Anal. Calcd for $C_{22}H_{17}NO_4$: C, 73.53; H, 4.77; O, 17.81.

        Found   : C, 73.56; H, 4.67; O, 17.80.

Kinetic Procedures.

    Solvolyses of III-OTf, IV-Cl and V-OPNB were carried out in 60 % aqueous dioxane[*] at the temperatures indicated in Table 1.   The

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* Dioxane was dried by refluxing over sodium metal and distilled before use (bp 102°)

reactions were followed conductometrically with a Yanagimoto Model MY-8 conductivity outfit. The conductivity cells used had bright platinum electrodes. Typically *ca.* 10^{-3} *M* solutions were used. Each reaction was run at least in duplicate. The data were fitted to the first-order rate equation by means of the least square method.

Product Analysis of IV-Cl. The chloride (IV-Cl, 44.0 mg) dissolved in a mixture of 30 ml of dioxane and 20 ml of water was heated at 40° for 16 hr. The solution was poured into a mixture of ether-benzene and aqueous sodium bicarbonate, and the organic layer was separated. The ether-benzene extract was washed with saturated aqueous sodium chloride and dried over anhydrous sodium sulfate. The solvent was evaporated under the reduced pressure to give 41.5 mg (99.5 %) of IV-OH with NMR and IR spectra identical with an authentic material.

Product Analysis of V-OPNB. The *p*-nitrobenzoate (V-OPNB, 34.3 mg) was heated in a mixture of 15 ml of dioxane and 10 ml of water at 45° for 4 hr, and the work-up in the manner described above gave 20.1 mg (99.5 %) of V-OH with NMR and IR spectra identical with an authentic V-OH.

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CHAPTER 7

Preparations, Reactions and Properties of

2,11-Dithiatris[3.3.2]paracyclophanes

7.1   SUMMARY

Several 2,11-dithiatris[3.3.2]paracyclophanes (Ia-e and II) are
prepared by coupling reactions of 4,4'-bis(chloromethyl)bibenzyl and
the corresponding dithiols (IIIa-e and IV), and a new facile synthesis
of tris[2.2.2]paraxylylene (VIII) from Ia is investigated together with
the synthesis of tris[2.2.2]paraxylylene-1,9-diene (X). Both the high
field shift of aromatic protons (H_x) of Ia-e or II compared with IIIa-e
or IV and the temperature dependence of the H_x signal of Ia-e or II in
the NMR spectra are ascribed to the difference in statistical conforma-
tions of the three benzene rings in Ia-e or II, which are largely
affected by the steric effect of the substituents.

7.2   INTRODUCTION

In order to improve yield and to overcome difficulties in prep-
arations of cyclophanes,[1] several routes *via* thiacyclophanes have
often been explored as the useful preparations, especially for [2.2]-
type compounds.[2] The author has attempted to prepare 2,11-dithia-
tris[3.3.2]paracyclophanes (Ia-e and II) as new macrocyclic compounds
and also as starting materials to the syntheses of larger systems
such as tris[2.2.2]paraxylylene (VIII) and its 1,9-diene (X).

NMR and electronic spectral studies[3-5] on VIII and related com-
pounds have indicated that benzene rings in VIII are statistically
facing each other, and the high field signal (δ 6.62 in carbon tetra-
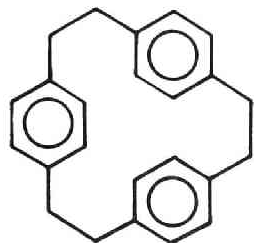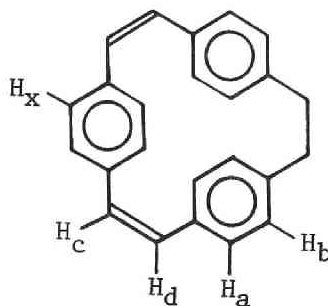
VIII	X

chloride)[3a] of aromatic protons of VIII has resulted from transannular
shielding effect of the "face"[6] benzene rings in VIII. Molecular
model (CPK) of VIII shows that the internal rotation of the benzene
rings is difficult, while that of Ia suggests that the benzene rings
in Ia can rotate easily. These considerations prompt the author to
investigate NMR characteristics of Ia-e, II and X relating to their
structures in comparison with the results for $[2^n]$paraxylylenes.[3,5]

   In this chapter are described the results of the preparations
and of the transformations, and are discussed spectral properties of
these cyclophanes.

7.3   RESULTS AND DISCUSSION

Preparation of Dithiacyclophanes.   The dithiacyclophanes (Ia-e and
II) were prepared by coupling reactions between 4,4'-bis(chloro-
methyl)bibenzyl (VI) and sodium salts of the corresponding dithiols
(IIIa-e and IV) in benzene-ethanol under the high dilution conditions

Ia X = H
Ib X = F
Ic X = Cl
Id X = Me
Ie X = OMe

II

IIIa X = H
IIIb X = F
IIIc X = Cl
IIId X = Me
IIIe X = OMe

IV
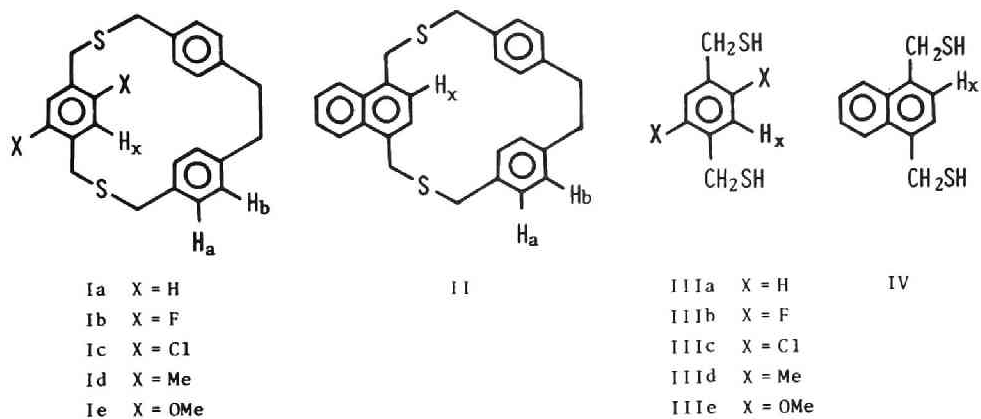
at room temperature.   The yields and the melting points of Ia-e and II thus obtained are listed in Table 1. When the coupling reaction for the preparation of Ia was carried out with relatively fast drop-

Table 1.   Yields and Melting Points

of Dithiacyclophanes.

Compd	Yield	Mp
Ia	55 %	162.0–162.5°
Ib	18	131.1–131.9
Ic	37	113.0–113.5
Id	23	143.2–143.5
Ie	15	163.0–163.5
II	46	192.0–193.0

ping of the both solutions, 2,11,28,37-tetrathiahexakis[3.3.2.3.3.2]-
paracyclophane (V), mp 223.7–225.8°, was obtained in 16 % yield to-
gether with 31 % of Ia.
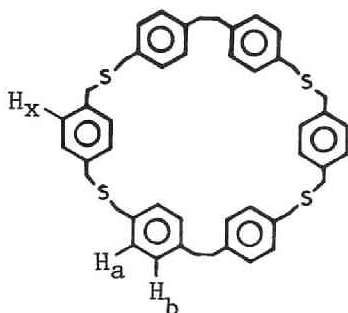
V

Transformations of Ia to VIII and X.   Ia was converted to the bis-
thioether (VII) by the Wittig rearrangement[2d] using *n*-butyllithium
in boiling tetrahydrofuran.   Reduction of VII with the Raney nickel
in dioxane-ethanol gave VIII in 26 % yield based on Ia.   Either the
Wittig rearrangement of Ia at low temperatures or the Stevens rear-
rangement[7] of the sulfonium salt (XI), which was prepared on treat-
ment of Ia with dimethoxycarbonium fluoroborate,[8] gave at best poor
yield of VIII after the reduction.

In spite of the three-step procedure, the present route is supe-
rior to the usual modified Wurtz coupling of *p*-xylylene chloride[3] in
terms of facilities of reaction conditions and isolations.

The modified Ramberg-Bäcklund rearrangement[9] of the disulfone
(IX), obtained by oxidation of Ia with *m*-chloroperbenzoic acid, gave
tris[2.2.2]paraxylylene-1,9-diene (X), mp 114.0–115.0°, in 32 % yield
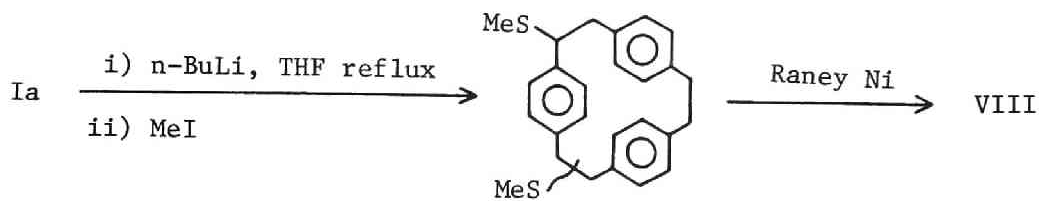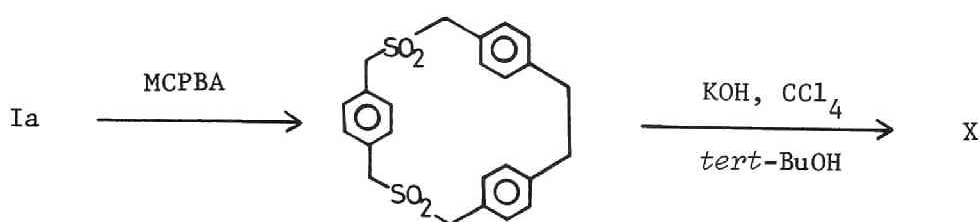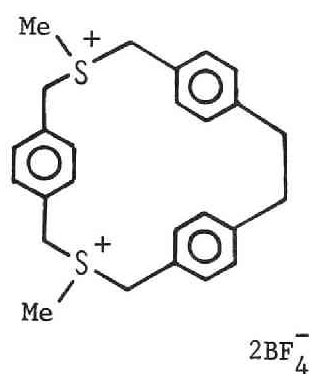
based on Ia. More strained sulfone such as 2,11-dithia-2,2,11,11-tetraoxo[2.2](2,6)pyridinophane has been reported not to give the corresponding diene under the similar condition,[10] whereas the Stevens rearrangement of 2,11-dimethyl-2,11-dithia[2.2](2,6)pyridino-phane difluoroborate undergoes easily to give the diene, though the

yield is low.[11] Thus, the Ramberg-Bäcklund rearrangement as well as the Stevens rearrangement in these cyclophanes is very sensitive to the structure or the size of the systems, *i.e.*, the latter proceeds for strained cyclophane systems, while the former for less straind systems.[12]
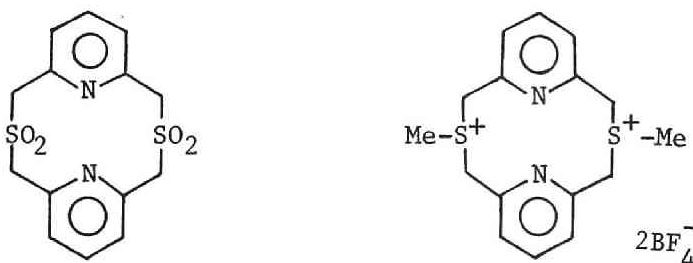
NMR Chemical Shift of Dithiacyclophanes. The NMR spectral data of Ia-e, II, IIIa-e, IV, V and X recorded in deuteriochloroform at 31.5° on a 100 MHz instrument are summerized in Table 2. The most remarkable characteristic is that the chemical shifts of the H_x protons in Ia and II are observed in very high field as for macrocyclophanes,[*] whereas those of the H_a and H_b protons in Ia and II locate in normal aromatic region.

Since both the A ring and B rings in Ia can rotate based on the

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* The aromatic protons of VIII and tetrakis[2.2.2.2]paraxylylene absorb at δ 6.62[3a] and 6.65[3b], respectively, in carbon tetrachloride at room temperature.

Table 2. NMR Data of 2,11-Dithiatris[3.3.2]paracyclophanes and Related Compounds in $CDCl_3$ at 31.5° (δ from internal TMS).[a]

Compd.	H_x	$H_{a,b}$	ArCH$_2$S		ArCH$_2$CH$_2$Ar	Other H
Ia	6.30(s)	7.02(s)	3.61(s),	3.72(s)	3.08(s)	
Ib	6.67(t)[b]	6.87(AA'BB')	3.61(s),	3.75(s)	2.92(s)	
Ic	7.31(s)	6.82(AA'BB')	3.45(s),	3.54(s)	2.87(s)	
Id	6.87(s)	6.71(AA'BB')	3.64(s),	3.73(s)	2.83(s)	2.09(s, Me)
Ie	6.54(s)	6.83(AA'BB')	3.71(AB),[c]	3.82(s)	2.83-3.24(m)	3.46(s, OMe)
II	6.12(s)	6.97(s)	3.80(s),	4.06(s)	3.05(s)	7.47, 7.84(m's, Naph.)
IIIa	7.25(s)		3.71(d)[d]			1.73(t, SH)[d]
IIIb	7.03(t)[e]		3.69(d)[f]			1.85(t, SH)[f]
IIIc	7.37(s)		3.75(d)[g]			1.94(t, SH)[g]
IIId	7.02(s)		3.58(d)[h]			1.63(t, SH)[h], 2.33(s, Me)
IIIe	6.79(s)		3.70(d)[i]			1.90(t, SH)[i] 3.82(s, OMe)
IV	7.36(s)		4.17(d)[j]			1.86(t, SH)[j], 7.58, 8.10(m's, Naph.)
V	7.06(s)	6.99(AA'BB')	3.51(s),	3.53(s)	2.88(s)	
X	6.59(s)	6.77(AA'BB')			3.00(s)	6.79(AB, $H_{c,d}$)[k]

a. Recorded on a 100 MHz instrument. Abbreviations are: s, singlet; d, doublet; t, triplet; m, multiplet. b. J(H-F)= 8.3 Hz. c. J_{AB}= 15.0 Hz, $\Delta\nu_{AB}$= 8.0 Hz. d. J= 7.5 Hz. e. J(H-F)= 8.1 Hz. f. J= 8.0 Hz. g. J= 8.0 Hz. h. J= 7.5 Hz. i. J= 7.8 Hz. j. J= 7.5 Hz. k. J_{AB}= 10.7 Hz, $\Delta\nu_{AB}$= 9.5 Hz.
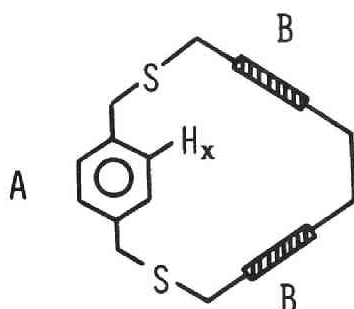
Fig. 1

molecular model (CPK), the observed chemical shift represents an average value at various rotational conformations. The upfield shift of the H_x protons in Ia, by 0.95 ppm compared with the H_x protons in IIIa, is, therefore, attributed to the transannular shielding effect of the B rings in the conformation shown in Fig. 1, where the A ring prefers a "lateral"[6] conformation and the B rings "face"[6] conformations. This interpretation is supported with the larger upfield shift of the H_x in II than in Ia, because the benzo substituent of the A ring in II is too large to rotate and therefore the H_x protons are forced to locate close to the B rings.

The high field shifts of the H_x signals of Ib-e are small but still appreciable. The magnitudes of the shifts compared with the parent dithiols (IIIb-e) are in the decreasing order Ib (0.36 ppm), Ie (0.25 ppm), Id (0.15 ppm) and Ic (0.06 ppm), which is just in accord with the increasing steric effect* of the substituents. That is, although the complete "lateral" conformation is not allowed for Ib-e due to steric repulsion between the substituents and the B rings,

the A ring can incline more largely from the "face" conformation with decreasing of the steric effect of the substituents. Thus, the H_x protons are shielded much effectively by the transannular shielding of the B rings when the substituents are small.

The temperature dependence of the chemical shifts of the H_x protons of Ia-e and II measured in carbon disulfide at low temperatures and deuterated dimethylsulfoxide at high temperatures are shown in Fig. 2. The high field shifts with lowering of the temperature (from 150° to -105° for Ia,c-e and II, and from 150° to -100° for Ib) amount to 0.95, 0.13, 0.05, 0.10, 0.39 and 1.20 ppm** for Ia-e and II, respectively. Remarkable large shifts are seen again for Ia and II. Taking account of small down field shifts of the H_a and H_b protons in Ia and II (-0.18 and -0.30 ppm, respectively), and that the splitting of the H_x signal of Ia is at most 2 Hz at -105°, these results indicate that at low temperatures the internal rotation of the B rings become slow on the NMR time scale and the population of the "face" conformation of the B rings increases, while the internal rotation of the A ring does not become slow.

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* The sum of the van der Waals radius[13] of the substituent, X, and the C-X bond length[14] is one of the valuable estimations for the steric effect.[15]

** These values are obtained from simple additions of the shifts in the high and the low temperatures, $i.e.$, for Ia, 0.95 (ppm) = 0.35 (150°-31.5°) + 0.65 (31.5°-(-105°)).
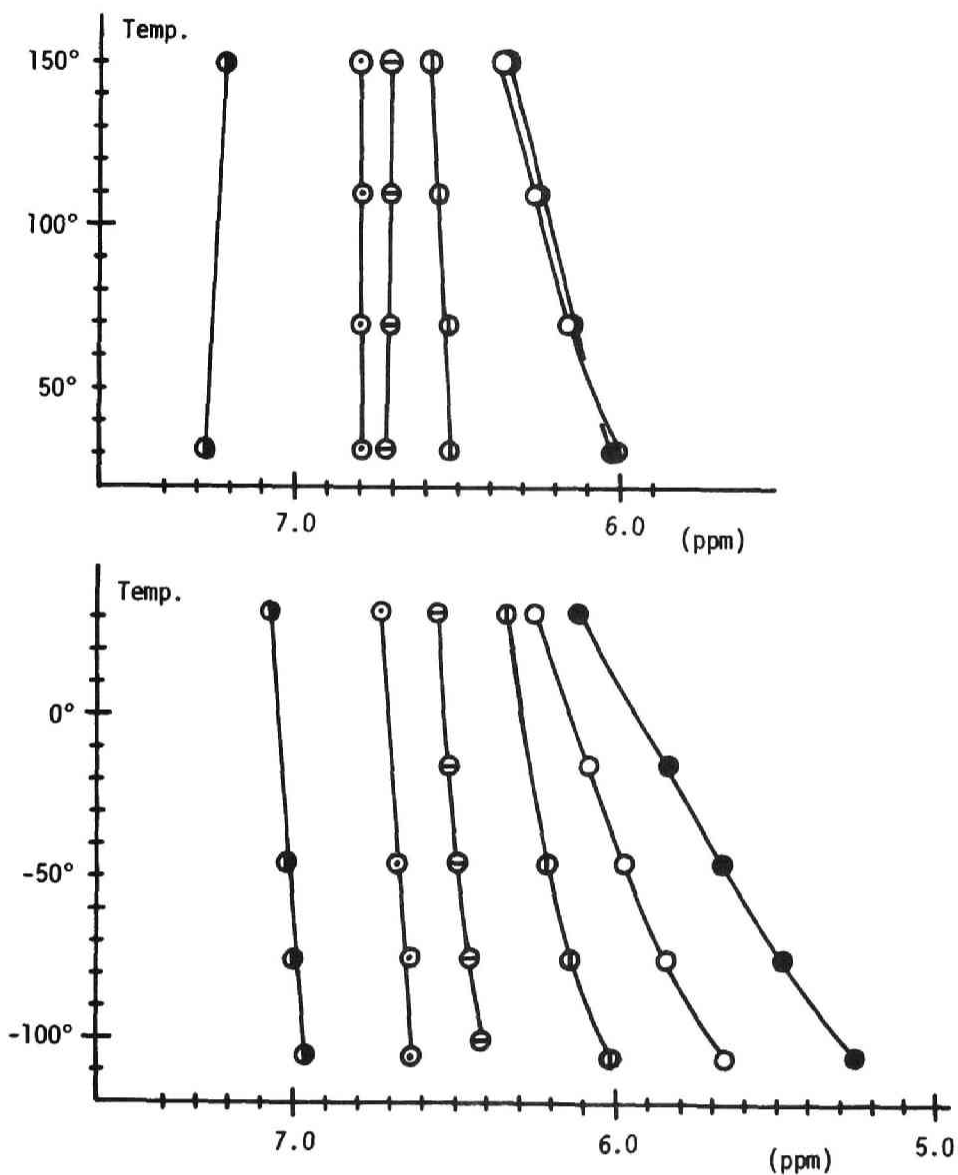
Fig. 2 Temperature dependence of the chemical shifts of the H_x protons: O , Ia; ⊖ , Ib; ◑ , Ic; ⊙ , Id; ⊕ , Ie; ● , II. The upper; in DMSO-d_6, δ from internal hexamethyldisiloxane. The lower; in CS_2, δ from internal TMS.

Another interesting result in this variable-temperature experiment is the relatively large upfield shift of the H_x protons in Ie at the low temperatures, which suggests that the A ring of Ie prefers the inclined conformation at the low temperatures in order to avoid repulsion between π electron clouds of the "face" B rings and the A ring, where π electron density of the A ring increases by the substitution of the two methoxyl groups.

Structure of X.   The assignments of the chemical shifts of the aromatic and vinylic protons in X, shown in Table 2, are confirmed with the 220 MHz spectrum of X. The H_x protons are observed in higher field than the H_a and H_b protons, and is comparable to the aromatic protons of VIII (δ 6.62). This observation of the high field shift is very interesting, because similar aromatic protons of cyclophanes containing olefin bridges have been reported to show their signals in lower field than those of parent cyclophanes involving ethylene bridges.[*,**,16]

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* The aromatic protons of tris[2.2.2]para-xylylene-1,9,17-triene absorb at δ 6.74 in carbon tetrachloride.[17]

** The coalescence temperature for the *para*-brideged aromatic protons of [2.2]metaparacyclophane-1,9-diene (-96° at 100 MHz) is much lower than that for [2.2]metaparacyclophane (157°). This remarkable change is ascribed to the difference in the lengths of the bridges.[2c,18]

Since a large hypochromic effect of the longer wavelength absorption (279sh nm, ε 5480 in cyclohexane) of *cis*-stilbenoid[*] is observed in the electronic spectrum of X, the A and B rings are considered to prefer statistically "face" conformations. The A ring, however, can take more inclined conformation than the B rings because of the larger distance of the olefin bridge compared with the ethylene bridge. Thus, the H_X protons are transannularly shielded by the B rings effectively as described in the previous section.

7.4   EXPERIMENTAL

All melting points were uncorrected. NMR spectra were recorded with a Varian HR-220 or HA-100 spectrometer. Mass spectra were determined by a Hitachi RMU-6C or RMS-4 mass spectrometer. Electronic and IR spectra were taken on Hitachi EPS-3T recording and Hitachi EPI-G3 grating infrared spectrophotometers, respectively.

2,11-Dithiatris[3.3.2]paracyclophane (Ia). A solution of 5.6 g of 4,4'-bis(chloromethyl)bibenzyl (VI) in 200 ml of benzene was added from one dropping funnel while simultaneously and at the same rate a solution of 3.4 g of 1,4-bis(mercaptomethyl)benzene (IIIa) in 200 ml of 60 % aqueous ethanol containing 1.6 g of sodium hydroxide was

[*] The molar extinction coefficient of the longer wavelength absorption (280 nm) of *cis*-stilbene is 10450 in ethanol.[19]

being added from a second dropping funnel to a vigorously stirred mixture of 1000 ml of ethanol and 600 ml of benzene. Addition was complete in 5 hr and the mixture was stirred for additional 5 hr before being concentrated. Chloroform and water were added to the residue. The chloroform extract was washed with water, dried over anhydrous sodium sulfate, and the solvent was evaporated. The residual white solids were chromatographed on a silica gel column with benzene. The crystals from the main fraction of the eluates were recrystallized from benzene to give 4.1 g (55 %) of Ia as colorless prisms: mp 162.0–162.5°; mass spectrum m/e (rel intensity) 376 (M^+, 14), 135 (24), 105 (58), 104 (100), 103 (25), 91 (82), 78 (37), 77 (21), 45 (21); ir (KBr) 2980, 1505, 1415, 1230, 1195, 1095, 845, 835, 810, 765, 715, 685, 565, 550, 510 cm^{-1}.

Anal. Calcd for $C_{24}H_{24}S_2$: C, 76.55; H, 6.42.
Found : C, 76.26; H, 6.54.

2,11,28,37-Tetrathiahexakis[3.3.2.3.3.2]paracyclophane (V). A solution of 31.1 g of VI in 550 ml of benzene and a solution of 19.0 g of IIIa in 550 ml of 60 % aqueous ethanol containing 4.4 g of sodium hydroxide were simultaneously added dropwise for 5 hr. After work-up as described for the preparation of Ia, the residual materials were chromatographed on a silica gel column with benzene. The first fraction gave 12.8 g (31 %) of Ia and the second 5.9 g (16 %) of V. Recrystallization of V from chloroform gave colorless needles: mp 223.7–225.8°; ir (KBr) 2830, 1515, 835, 720 cm^{-1}.

Anal. Calcd for $C_{48}H_{48}S_4$: C, 76.55; H, 6.42; S, 17.03.

Found : C, 76.32; H, 6.61; S, 16.99.

2,5-Difluoro-1,4-bis(mercaptomethyl)benzene (IIIb). To a hot solution of 1.42 g of thiourea in 20 ml of ethanol was added 2.8 g of 2,5-difluoro-1,4-bis(bromomethyl)benzene[20] with stirring. After addition was complete, the mixture was boiled under reflux for 15 min. Then ethanol was distilled off under reduced pressure, and the residue was cooled. A solution of 14.1 g of potassium hydroxide in 40 ml of water was added onto the residue and the mixture was boiled under reflux for 35 min with stirring. After cooling, a mixture of 9 ml of sulfuric acid and 15 ml of cold water was added dropwise into the mixture, and the whole was extracted with ether–*n*–hexane three times. The combined ether–*n*–hexane extraxt was washed with saturated aqueous sodium chloride three times, and dried over anhydrous sodium sulfate. The solvent was evaporated to give 1.6 g (83 %) of IIIb as white solids. A small sample was recrystallized from *n*-hexane-benzene (3:1) to give colorless needles: mp 53.8-54.1°; mass spectrum *m/e* (rel intensity) 206 (M^+,31), 173 (81), 149 (14), 141 (16), 140 (100), 127 (26), 45 (50); ir (KBr) 2530, 1500, 1410, 1250, 1200, 1160, 1135, 890, 845, 725, 690 cm^{-1}.

Anal. Calcd for $C_8H_8F_2S_2$: C, 46.58; H, 3.91; F, 18.42.

Found : C, 46.90; H, 4.13; F, 18.30.

5,8-Difluoro-2,11-dithiatris[3.3.2]paracyclophane (Ib). The cou-

pling of IIIb (1.4 g) and VI (1.9 g) was carried out in the same manner described previously for the preparation of Ia. The crude products were chromatographed on a silica gel column with benzene. Evaporation of the solvent of the main fraction gave 515 mg (18 %) of Ib as whith solids: mp 131.1-131.9°; mass spectrum m/e (rel intensity) 412 (M^+, 12), 136 (76), 135 (97), 105 (19), 104 (100), 91 (26), 78 (76), 45 (12); ir (KBr) 2910, 1510, 1495, 1420, 1405, 1240, 1205, 1160, 885, 710, 580 cm^{-1}.

Anal. Calcd for $C_{24}H_{24}F_2S_2$: C, 69.87; H, 5.38; F, 9.21.
Found : C, 69.73; H, 5.60; F, 9.35.

2,5-Dichloro-1,4-bis(mercaptomethyl)benzene (IIIc). As well as described for the preparation of IIIb, IIIc was prepared in 78 % yield (1.89 g) from 2,5-dichloro-1,4-bis(bromomethyl)benzene (3.3 g, mp 122.5-123.5°, lit.[20] mp 112-114°). Recrystallization of IIIc from benzene gave colorless needles: mp 85.0-85.5°; mass spectrum m/e (rel intensity) 240 (M+2, 22), 238 (M^+, 31), 207 (70), 205 (100), 174 (41), 172 (68), 102 (49), 101 (33), 75 (23); ir (KBr) 2540, 1465, 1370, 1075, 890, 700, 600, 535, 450 cm^{-1}.

Anal. Calcd for $C_8H_8Cl_2S_2$: C, 40.17; H, 3.37; S, 26.81.
Found : C, 40.41; H, 3.39; S, 26.59.

5,8-Dichloro-2,11-dithiatris[3.3.2]paracyclophane (Ic). The coupling of IIIc (1.5 g) and VI (1.75 g) was performed in the same manner described for the preparation of Ia. The product separated

through a silica gel column with benzene was recrystallized from

benzene-n-hexane (1:1) to give 1.1 g (37 %) of Ic as colorless col-

umns: mp 113.0-113.5°; mass spectrum m/e (rel intensity) 446 (M+2, 7),

444 (M$^+$, 9), 207 (5), 137 (5), 136 (7), 135 (10), 105 (27), 104 (100),

103 (6), 91 (27), 78 (10). 45 (8); ir (KBr) 2910, 2870, 1510, 1465,

1420, 1400, 1360, 1070, 920, 910, 835, 820, 730, 585 cm^{-1}.

Anal. Calcd for $C_{24}H_{24}Cl_2S_2$: C, 64.71; H, 4.98; S, 14.40.

Found   : C, 64.97; H, 4.72; S, 14.41.

5,8-Dimethyl-2.11-dithiatris[3.3.2]paracyclophane (Id). The coupling

reaction of 1.0 g of 2,5-dimethyl-1,4-bis(mercaptomethyl)benzene

(IIId, mp 80.4-81.3°, lit.[21] mp 74.5-77.5°) and 1.4 g of VI was car-

ried out as described for the preparation of Ia. The product sepa-

rated through a silica gel column eluted with benzene was recrystal-

lized from benzene-n-hexane (2:1) to give 470 mg (23 %) of Id as

colorless columns: mp 143.2-143.5°; mass spectrum m/e (rel intensity)

404 (M$^+$, 42), 165 (24), 163 (24). 135 (25), 134 (24), 133 (58), 132

(100), 119 (26), 117 (27). 105 (50), 104 (76), 91 (76); ir (KBr)

2910, 1510, 1500, 1410, 825, 585 cm^{-1}.

Anal. Calcd for $C_{26}H_{28}S_2$: C, 77.17; H, 6.98.

Found   : C, 77.40; H, 7.14.

5,8-Dimethoxy-2,11-dithiatris[3.3.2]paracyclophane (Ie). In the

same manner as described for the preparation of Ia, 1.8 g of 2,5-

dimethoxy-1,4-bis(mercaptomethyl)benzene (IIIe, mp 113.5°, lit.[22]

mp 111-113°) was coupled with 2.1 g of VI. After separation through

a silica gel column eluted with benzene, the product was recrystal-

lized from benzene to give 500 mg (15 %) of Ie as colorless prisms:

mp 163.0-163.5°; mass spectrum m/e (rel intensity) 436 (M^+, 43), 197

(21), 166 (21), 165 (100), 164 (59), 135 (33), 105 (21), 104 (36), 91

(43); ir (KBr) 2920, 1500, 1460, 1445, 1415, 1390, 1235, 1210, 1035,

580 cm^{-1}.

Anal. Calcd for $C_{26}H_{28}S_2O_2$: C, 71.52; H, 6.46; S, 14.69.

Found : C, 71.57; H, 6.64; S, 14.57.

1,4-Bis(mercaptomethyl)naphthalene (IV). This compound was prepared

from 1,4-bis(bromomethyl)naphthalene (960 mg) as described for the

preparation of IIIb. Recrystallization of the product from benzene-

n-hexane (1:2) yielded 624 mg (93 %) of IV as pale yellow needles:

mp 86.0-87.0°; mass spectrum m/e (rel intensity) 220 (M^+, 6), 187

(29), 155 (30), 154 (100), 153 (82), 76 (20), 34 (49); ir (KBr) 2550,

1590, 1440, 1230, 1155, 840, 760, 580 cm^{-1}.

Anal. Calcd for $C_{12}H_{12}S_2$: C, 65.41; H, 5.49.

Found : C, 65.38; H, 5.61.

5,6-Benzo-2,11-dithiatris[3.3.2]paracyclophane (II). The coupling

reaction of 505 mg of IV and 643 mg of VI was performed as described

for the preparation of Ia. The product separated through a silica

gel column eluted with benzene was recrystallized from benzene to

give 450 mg (46 %) of II as colorless needles: mp 192.0-193.0°; mass

spectrum m/e (rel intensity) 427 (M+1, 21), 426 (M$^+$, 53), 187 (34),

185 (62), 184 (32), 155 (74), 154 (97), 136 (30), 135 (27), 105 (33),

104 (100), 91 (74), 78 (60); ir (KBr) 2930, 1510, 1440, 1430, 1425,

1230, 860, 840, 825, 770 cm^{-1}.

Anal. Calcd for $C_{28}H_{26}S_2$: C, 78.82; H, 6.14.

Found : C, 78.58; H, 6.02.

Wittig Rearrangement of Ia and Raney Nickel Desulfurization to give

Tris[2.2.2]paraxylylene (VIII). Into a stirred solution of 376 mg

of Ia in 10 ml of dry tetrahydrofuran was added 0.9 ml (1.25 equiv)

of n-butyllithium in hexane under reflux. After refluxing for 10

min, the mixture was cooled and 0.4 ml of methyl iodide was added

into the mixture. Then the solvent was evaporated under reduced

pressure, and the residue was chromatographed on a silica gel column.

Elution with benzene gave 353 mg of colorless paste. Into a solution

of this colorless paste in 20 ml of dioxane, 20 ml of ethanol con-

taining *ca.* 10 g of W-7 Raney nickel was added and the mixture was

boiled under reflux for 4 hr. After removal of the catalyst and the

solvent, the residue was chromatographed on a silica gel (TLC 20 × 20

× 0.2 cm) with n-hexane-benzene (8:2) to give 81 mg (26 % based on

Ia) of colorless needles, identical in all respects with an authentic

sample of VIII.

2,11-Dithia-2,2,11,11-tetraoxotris[3.3.2]paracyclophane (IX). A

solution of 1.64 g (1.25 equiv) of 70 % m-chloroperbenzoic acid in

20 ml of chloroform was stirred in an ice bath. Into this solution another solution of 1.00 g of Ia in 50 ml of chloroform was added dropwise with stirring. The mixture was stirred for 1 hr at room temperature. Then a small amount of sodium bisulfite was added to the mixture, and the mixture was extracted with chloroform. The chloroform extract was dried over anhydrous sodium sulfate, and evaporation of the solvent gave 1.14 g (97 %) of IX as white solids. A sample was recrystallized from ethylene chloride to give colorless needles: mp >300°; mass spectrum m/e (rel intensity) 440 (M^+, 0.0005), 312 (3), 207 (4), 193 (8), 105 (11), 104 (100), 103 (14), 78 (19), 77 (6); ir (KBr) 2920, 1510, 1420, 1310, 1260, 1110, 1020, 840, 810, 740 cm^{-1}.

Tris[2.2.2]paraxylylene-1,9-diene (X). A mixture of 1 g of freshly powdered potassium hydroxide, 5 ml of *tert*-butanol, 5 ml of carbon tetrachloride and 220 mg of IX was efficiently stirred at 80°. After 1 hr, a few drops of water was added to the mixture, and the stirring was continued for additional 2 hr. Then the whole was extracted with ether. The ether extract was washed with saturated aqueous sodium chloride, dried over anhydrous sodium sulfate, and the solvent was evaporated. The residual yellow oils were chromatographed on a silica gel column with *n*-hexane to give 51 mg (33 %) of X. Recrystallization from ethanol gave slightly pale yellow needles: mp 114.0-114.5°; mass spectrum m/e (rel intensity) 309 (M+1, 25), 308 (M^+, 100), 307 (29), 293 (21), 279 (31), 203 (20), 191 (37), 154 (37),

115 (21); ir (KBr) 3000, 1500, 900, 810, 730, 660, 560 cm^{-1}; uv

(cyclohexane) λ_{max} 233 (ϵ 21100), 279sh nm (5840).

Anal. Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54.

Found   : C, 93.36; H, 6.76.

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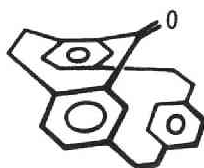
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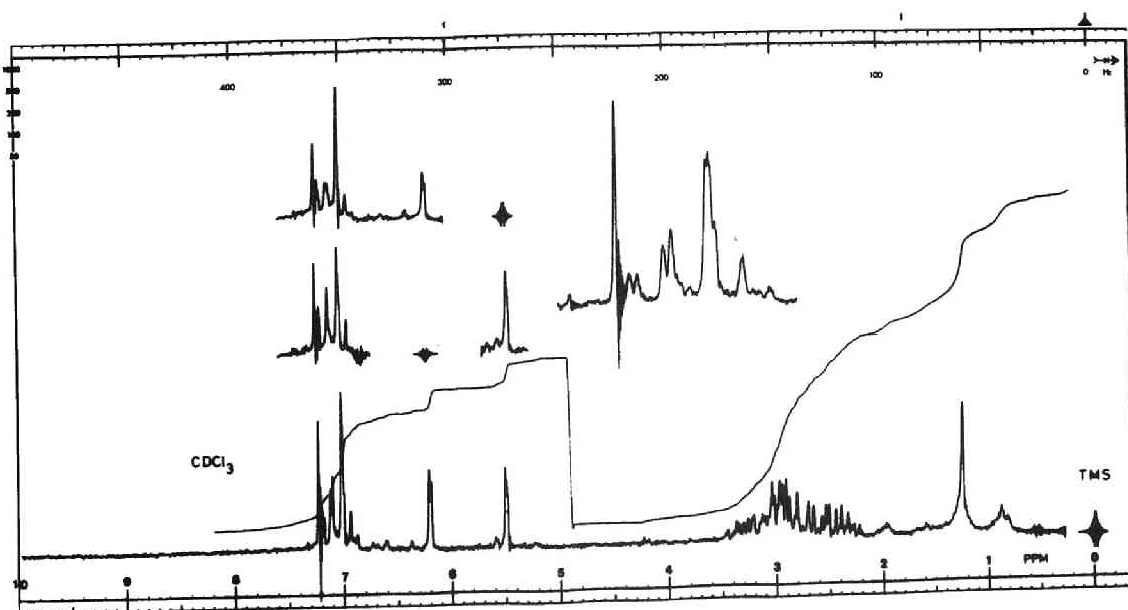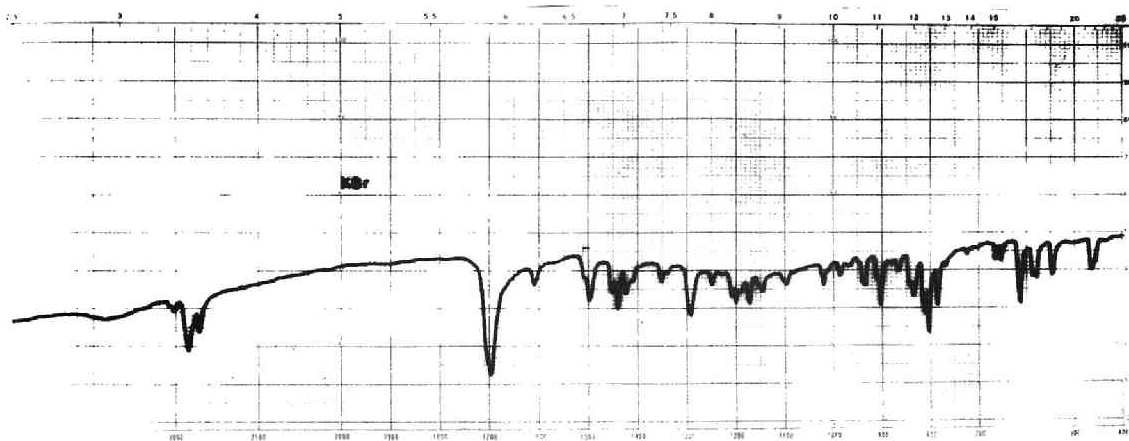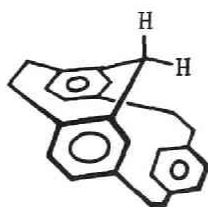
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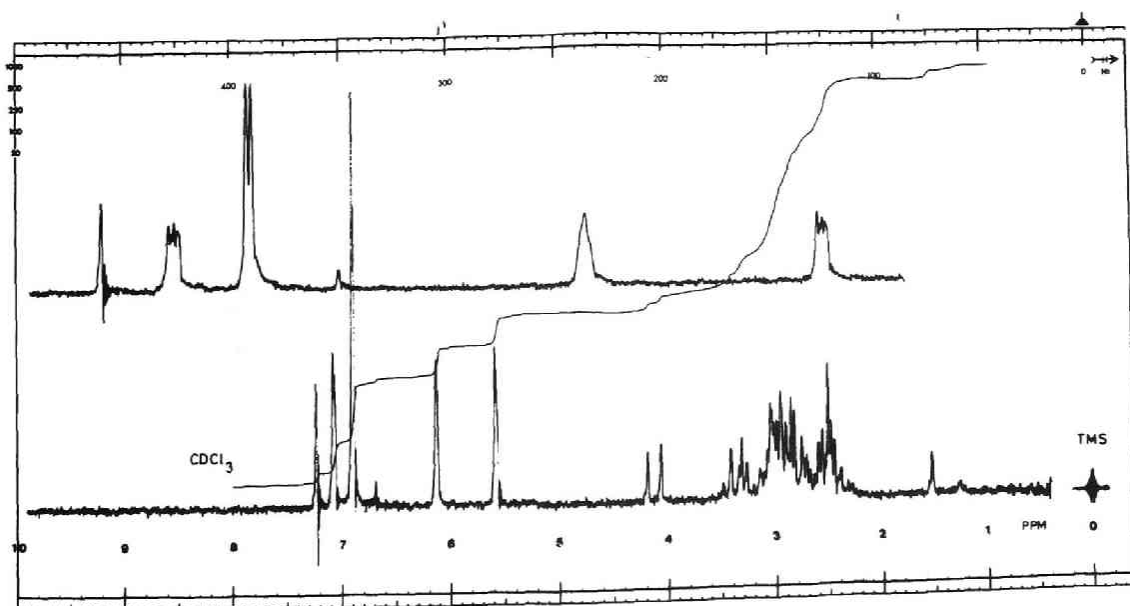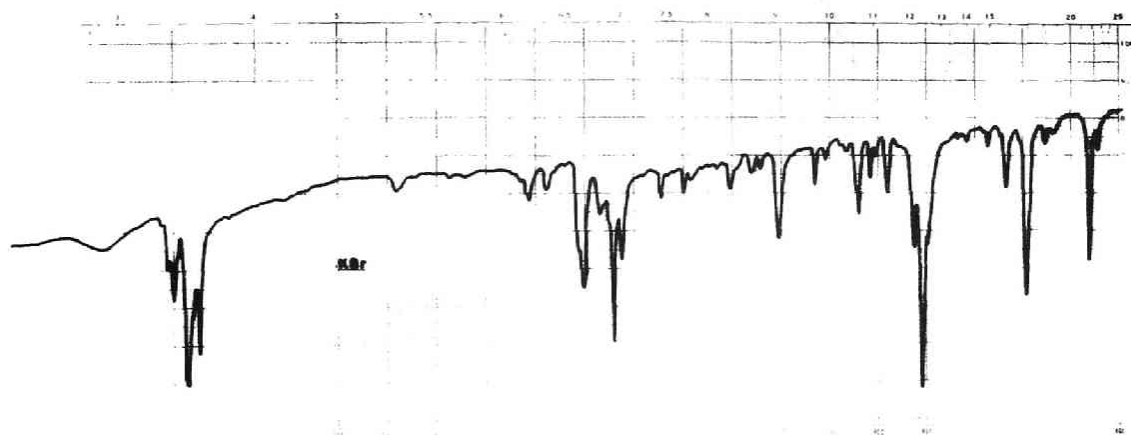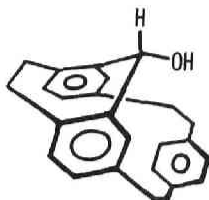
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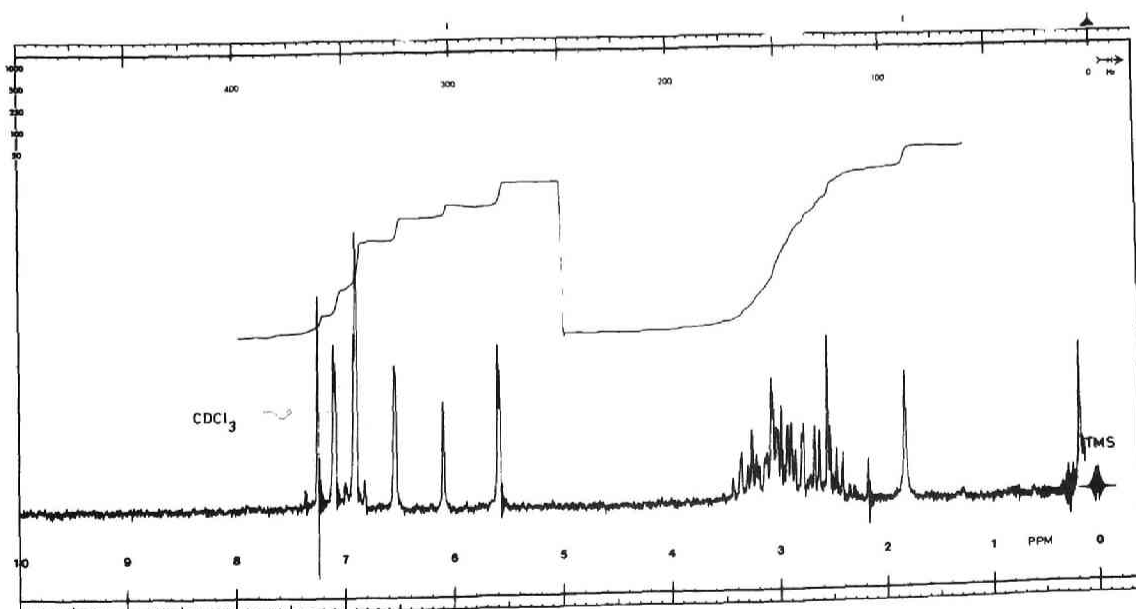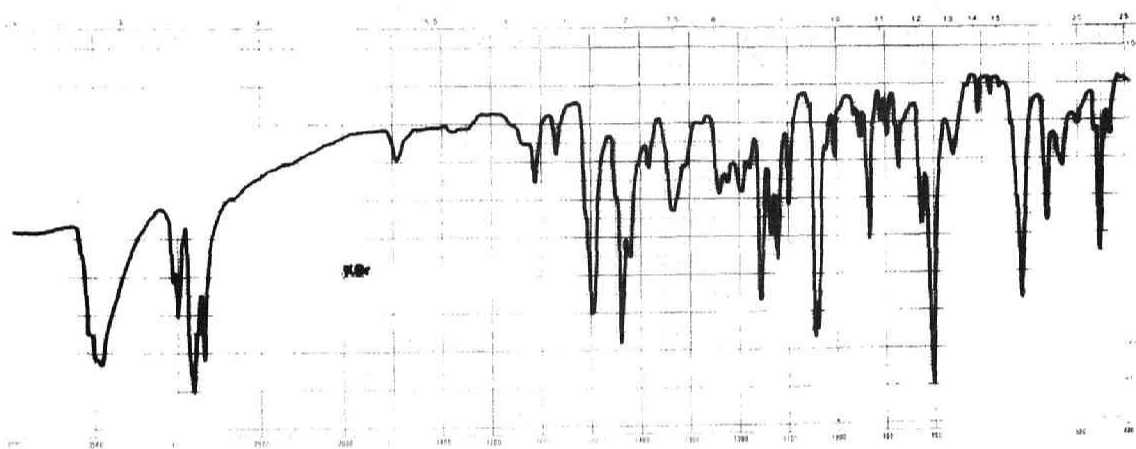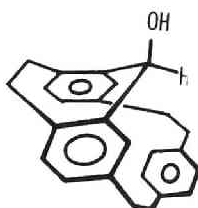
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p-Nitrobenzoate of

Pseudo-Geminal "Equatorial" Carbinol of Tris[2.2.2]paraxylylene

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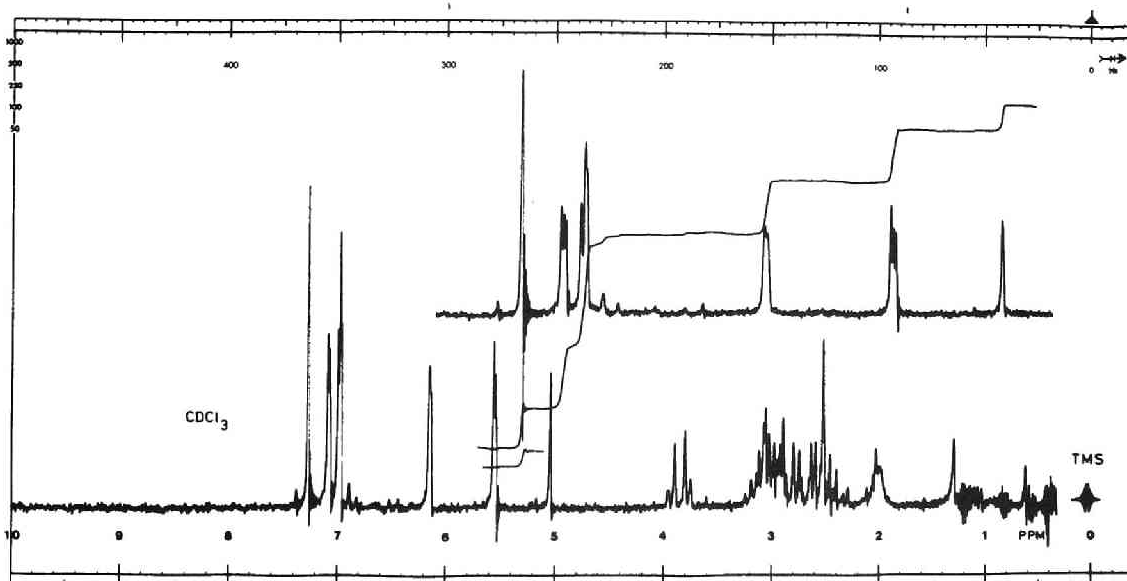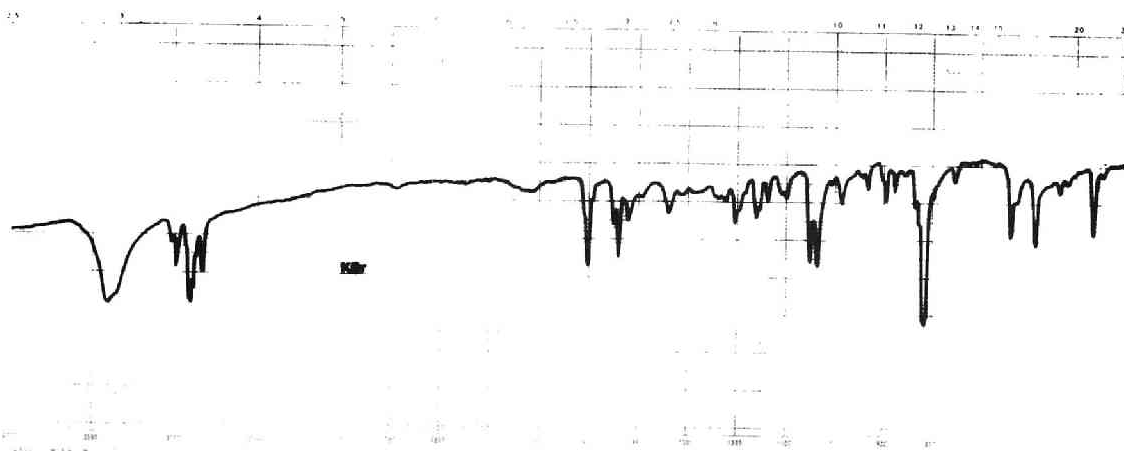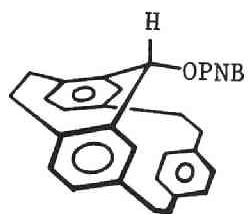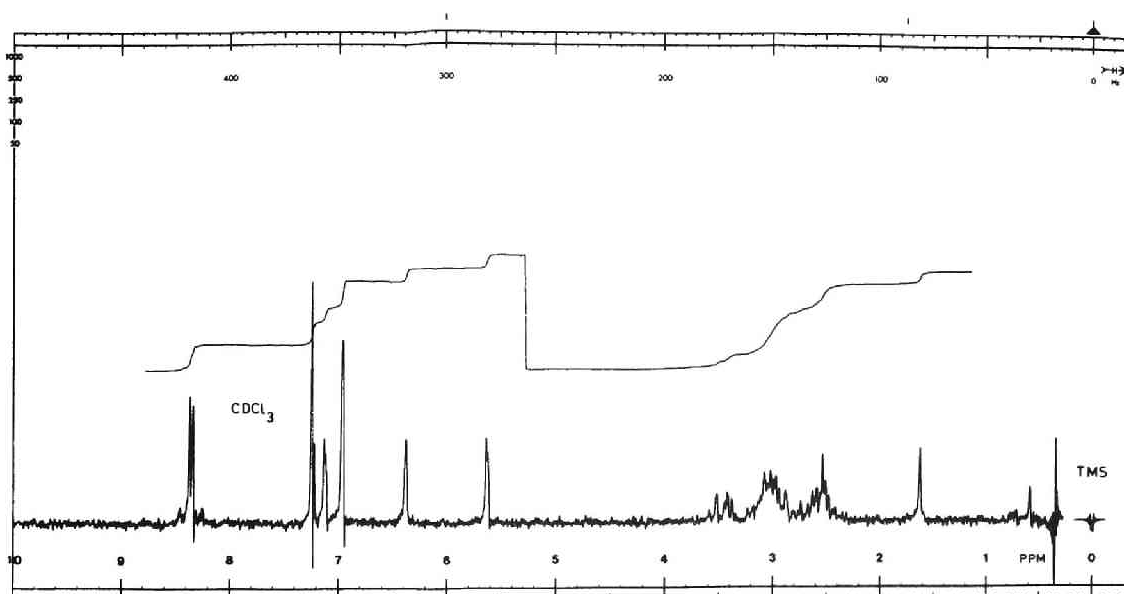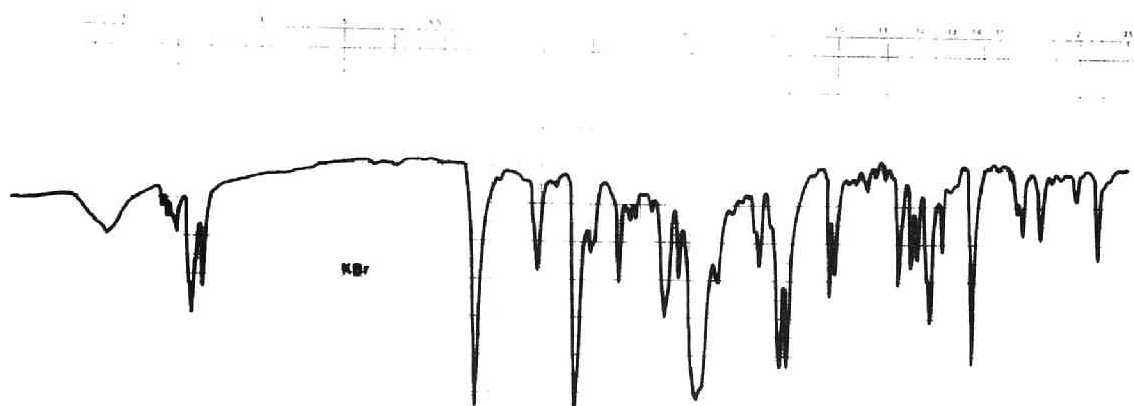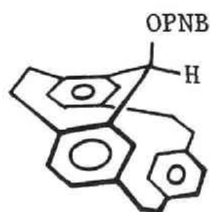
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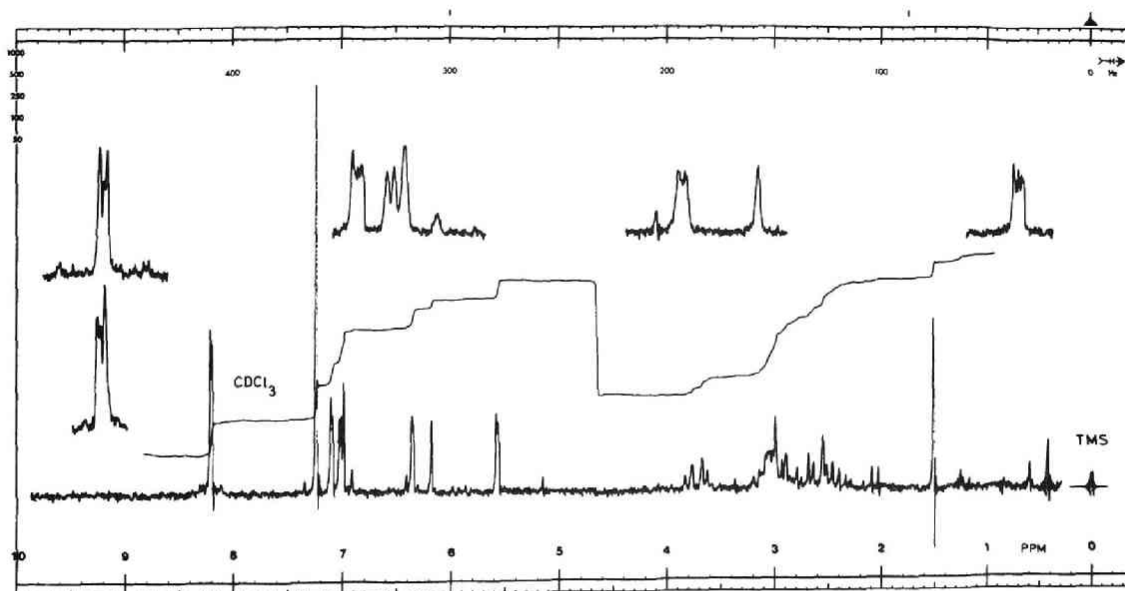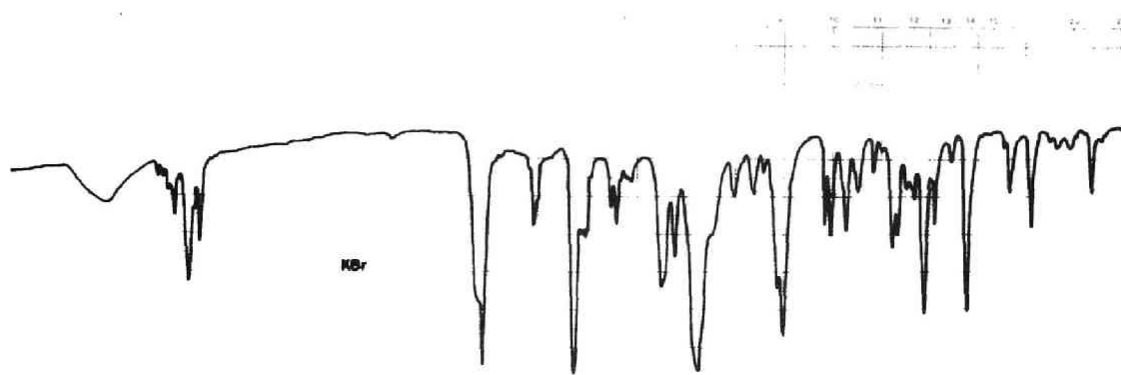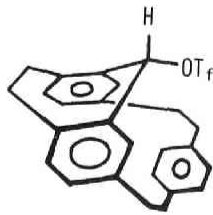
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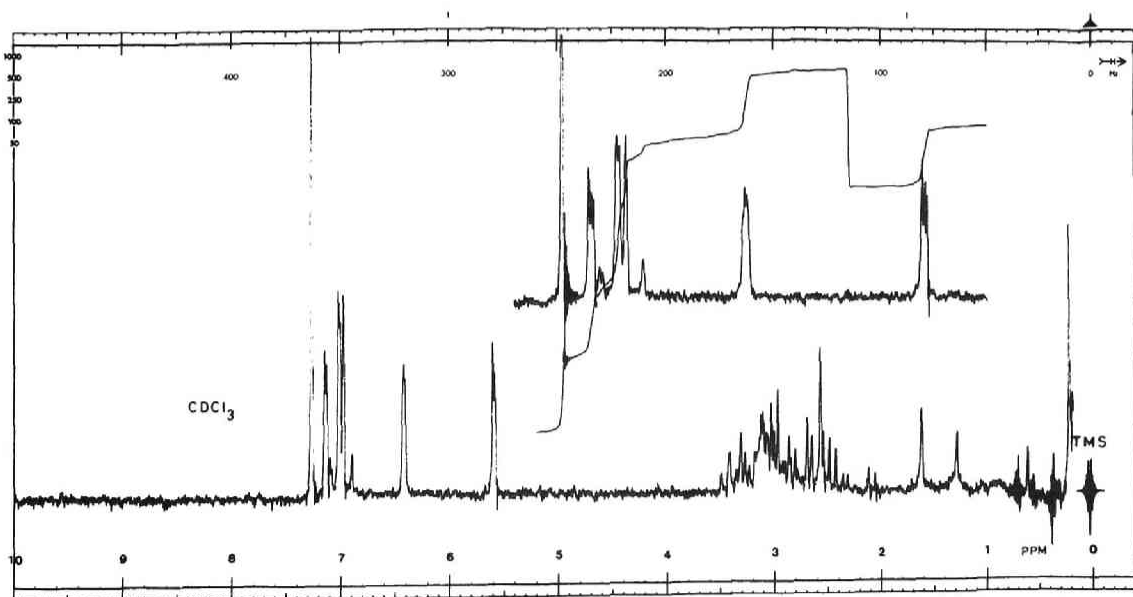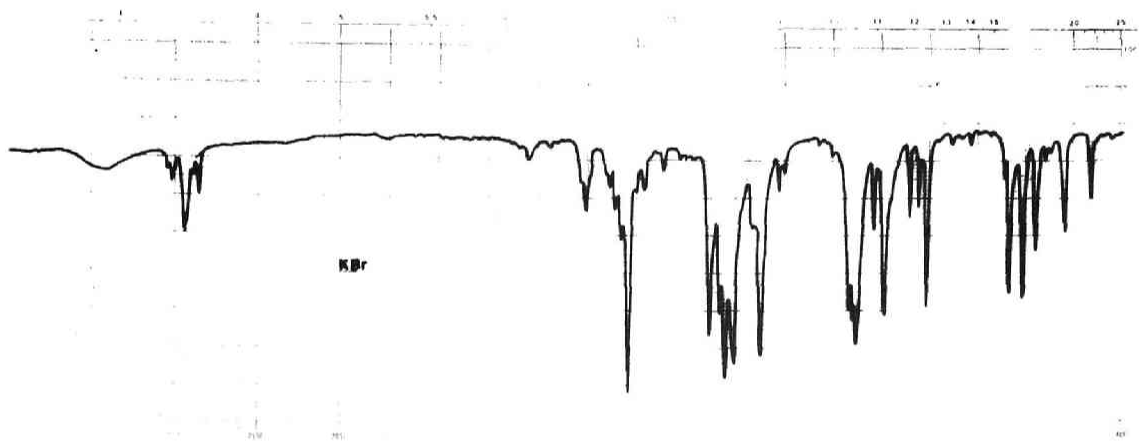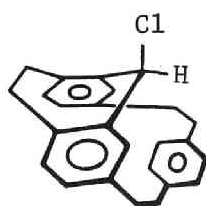
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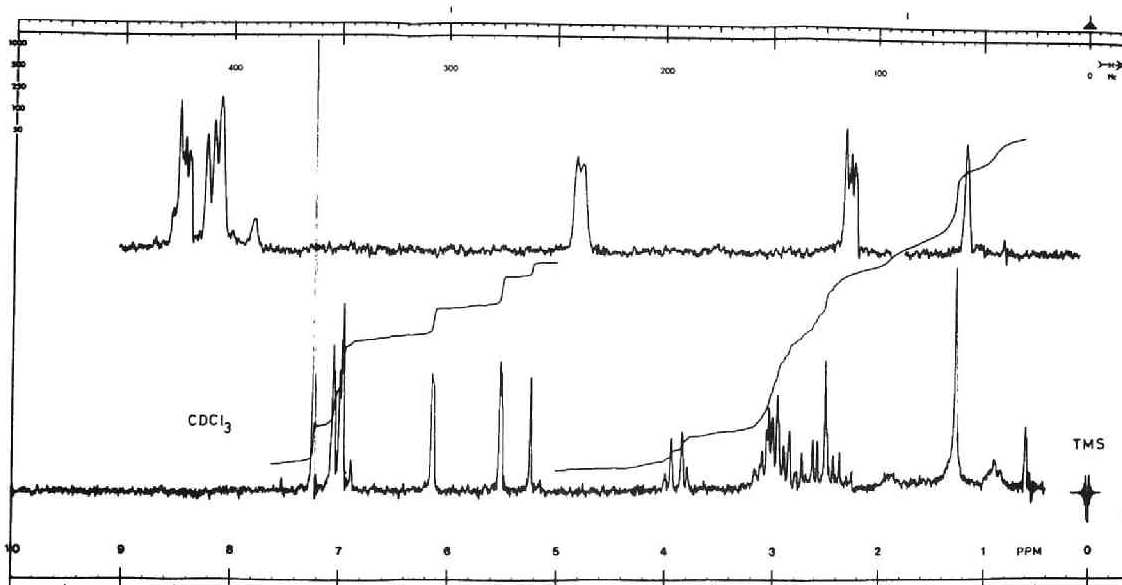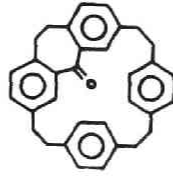
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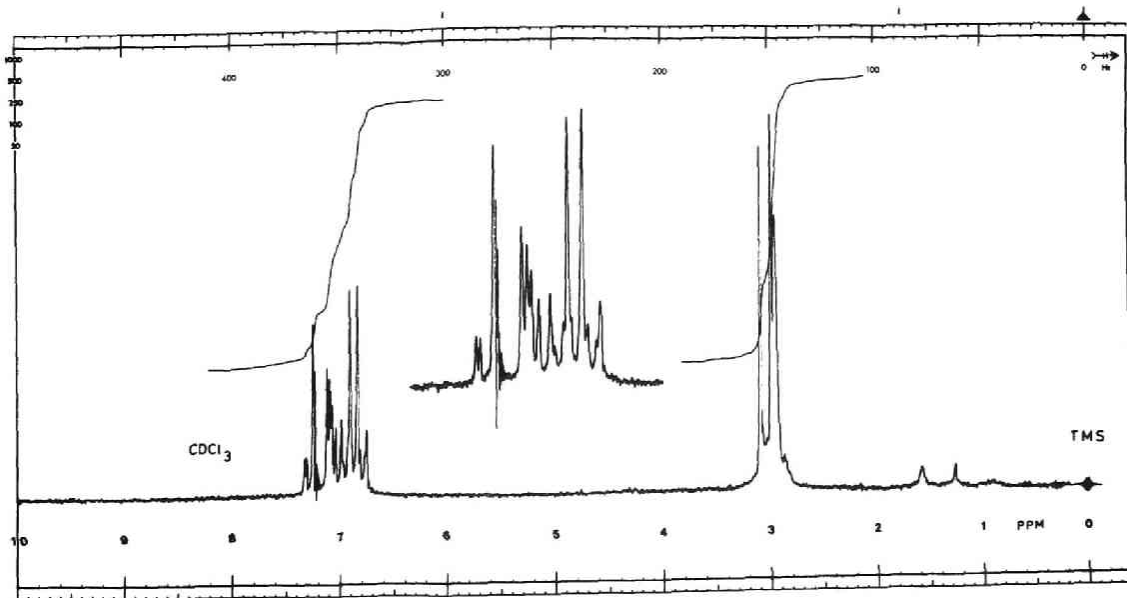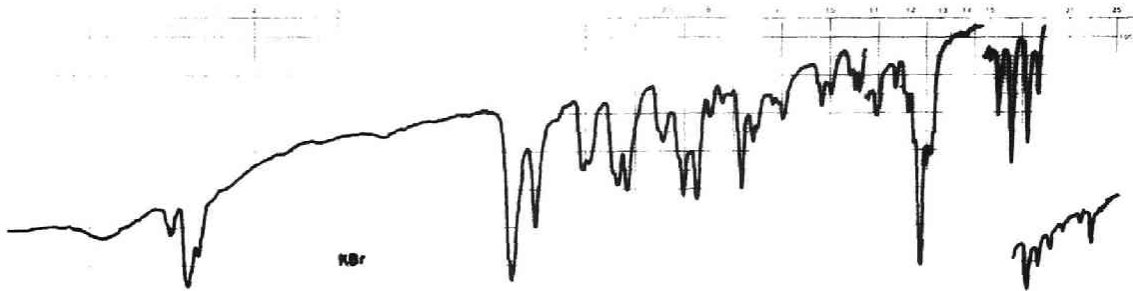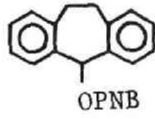
Dibenzosuberyl *p*-Nitrobenzoate
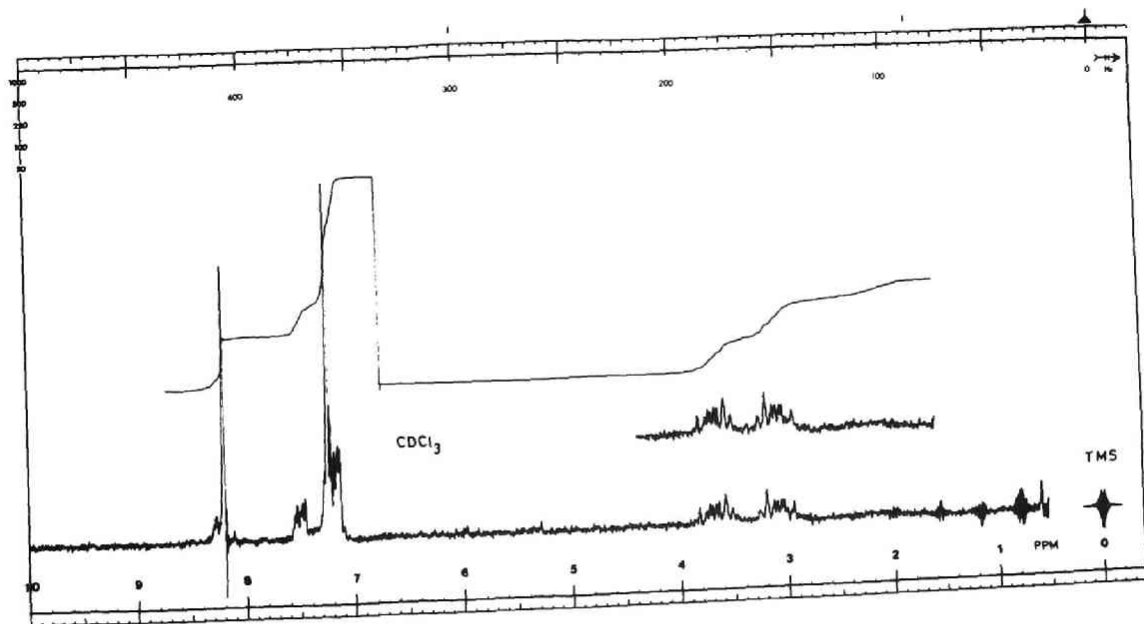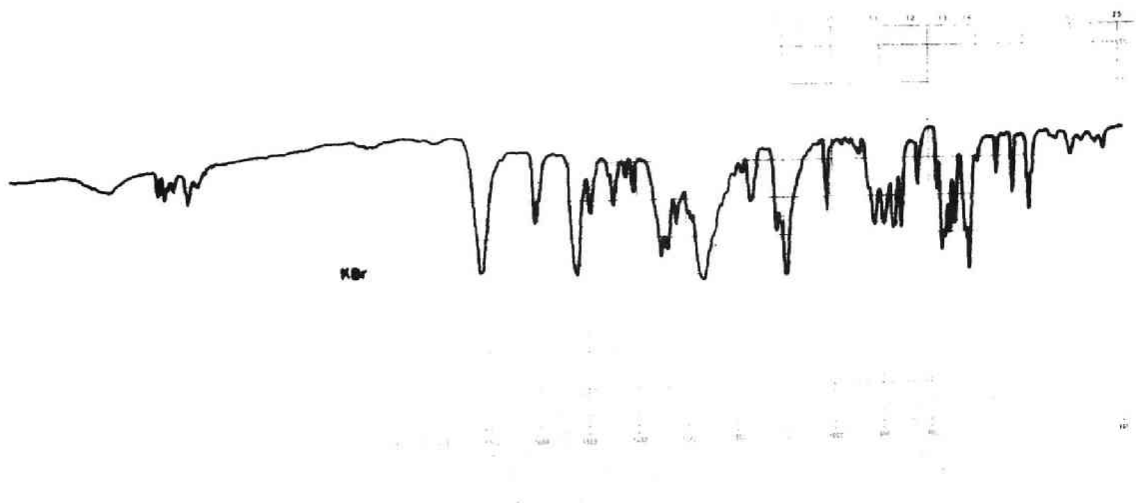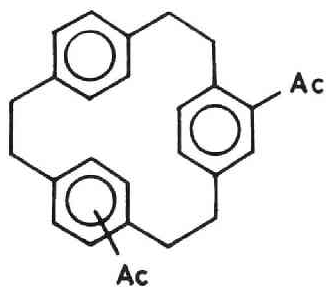
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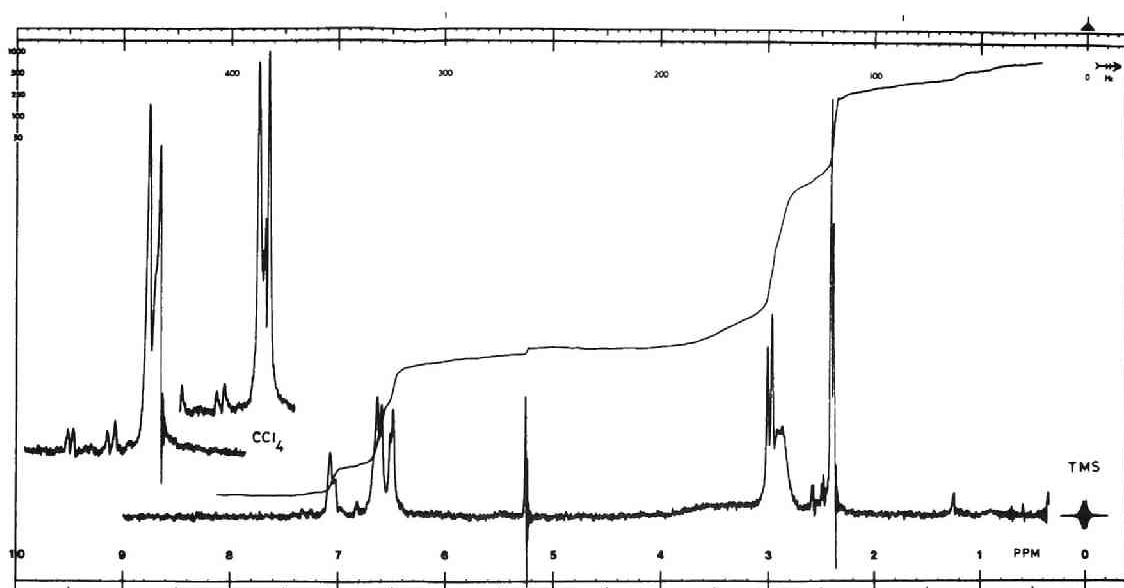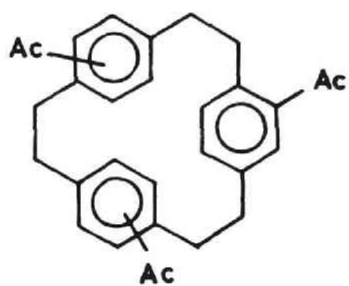
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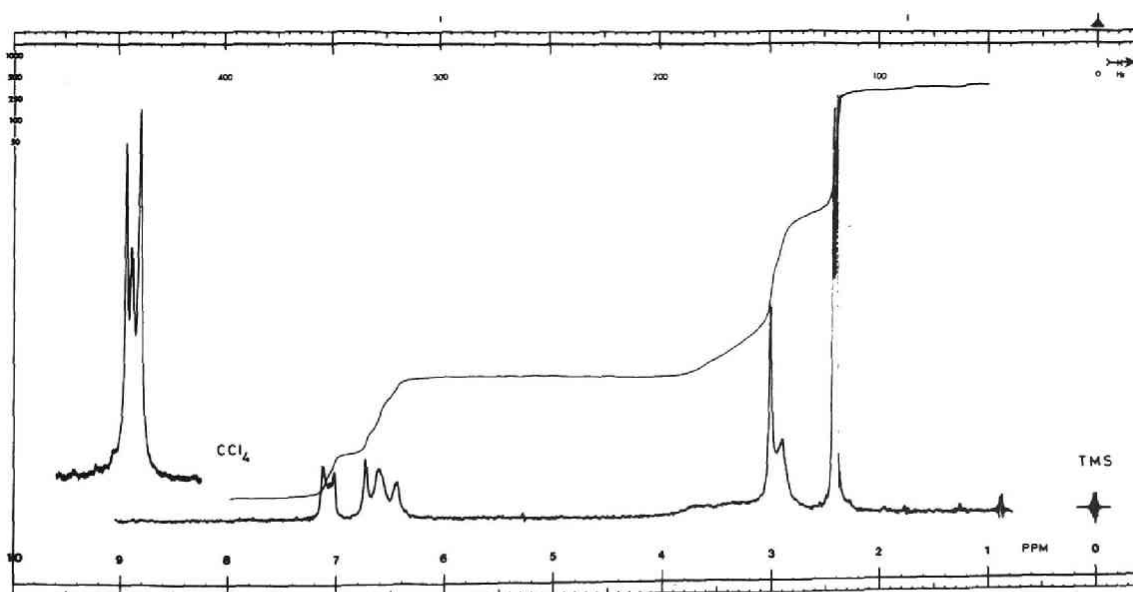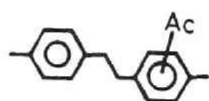
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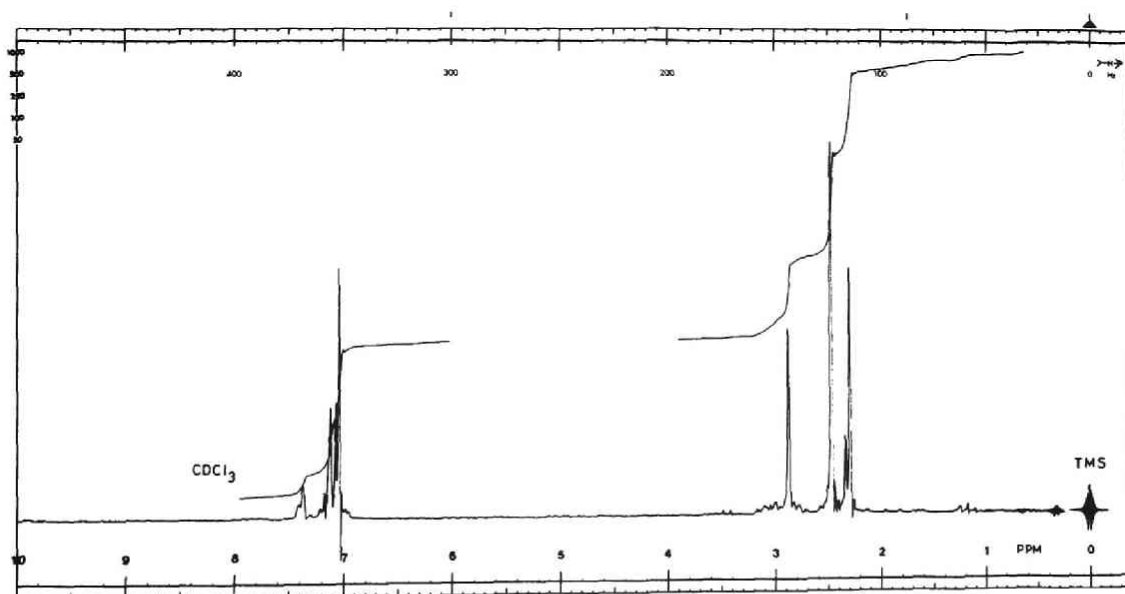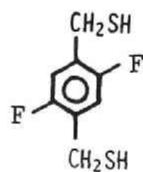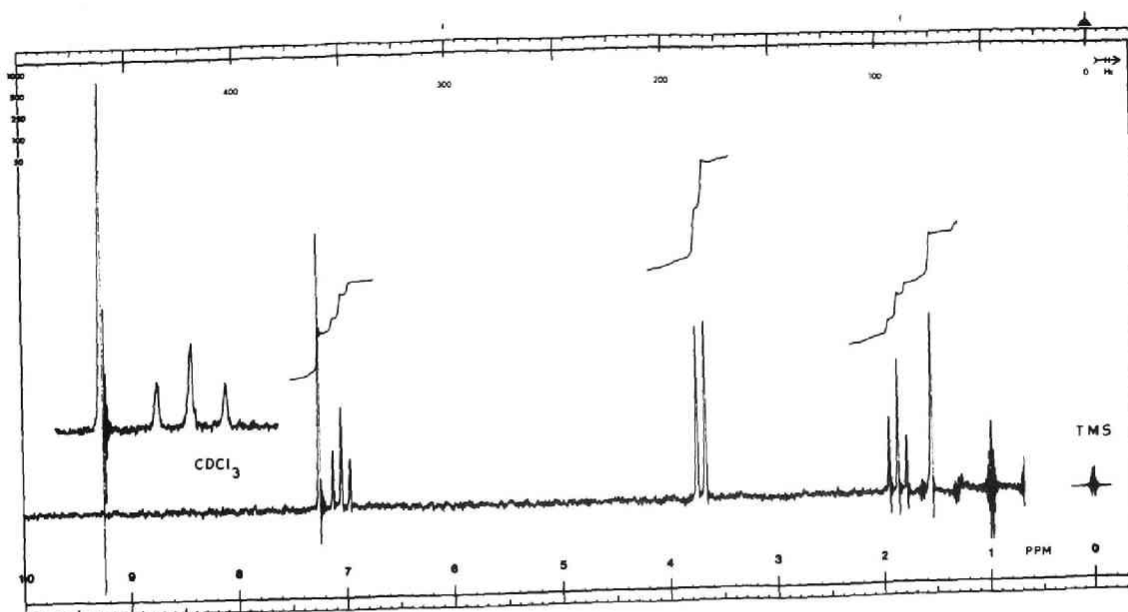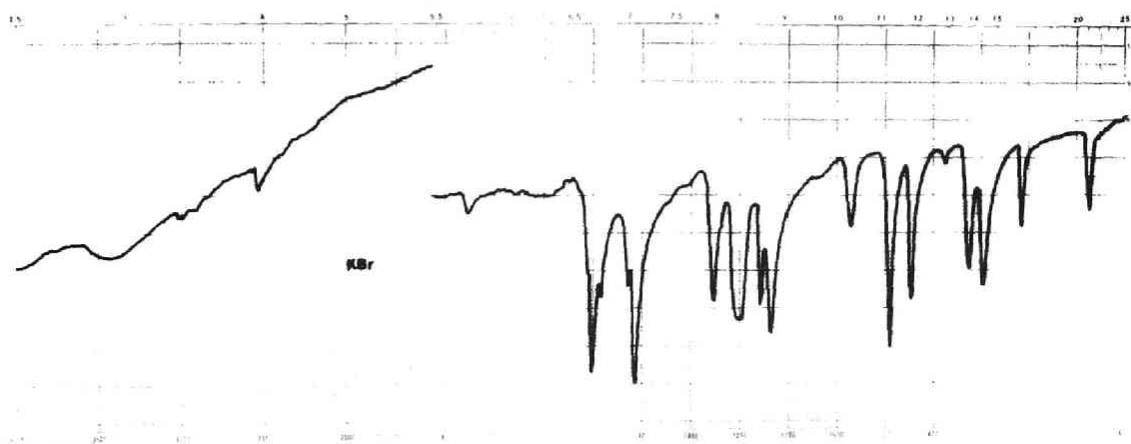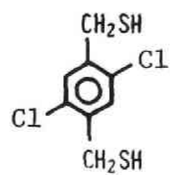
CH₂SH
F
F
CH₂SH

2,5-Difluoro-1,4-bis(mercaptomethyl)benzene

KBr

CDCl₃

TMS

2,5-Dichloro-1,4-bis(mercaptomethyl)benzene

CH$_2$SH

CH$_2$SH

1,4-Bis(mercaptomethyl)naphthalene

KBr

CDCl$_3$

TMS

PPM
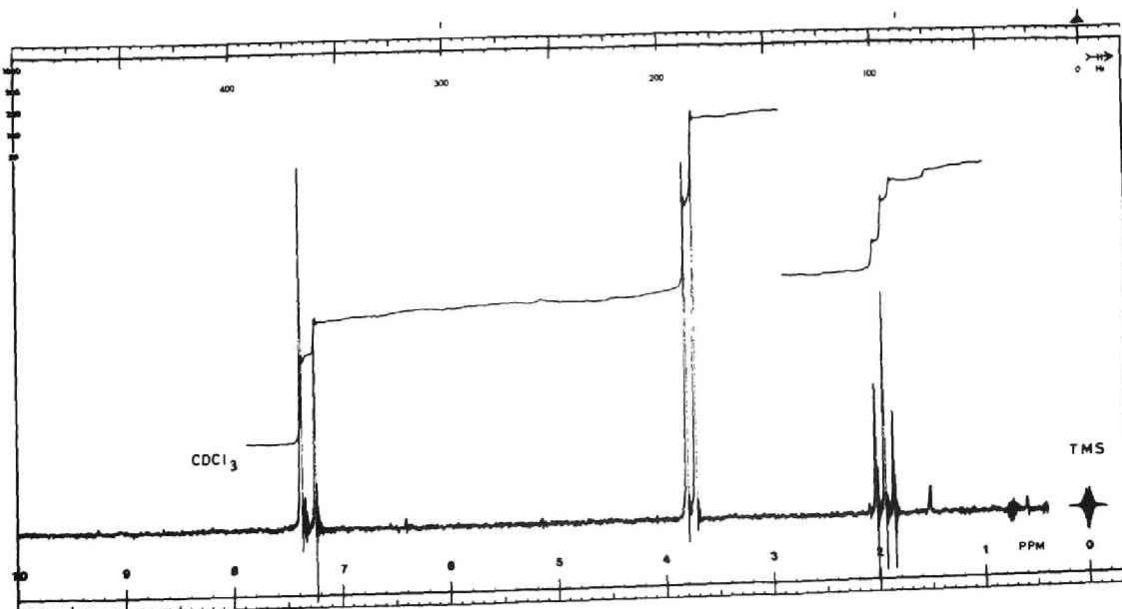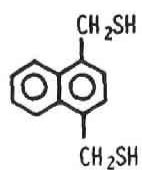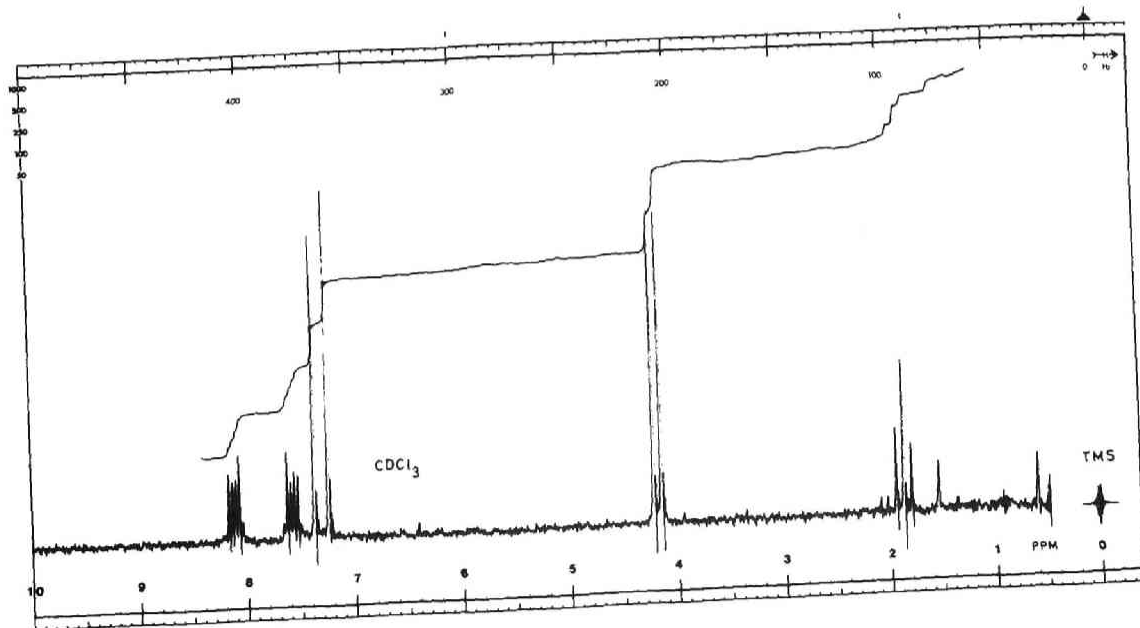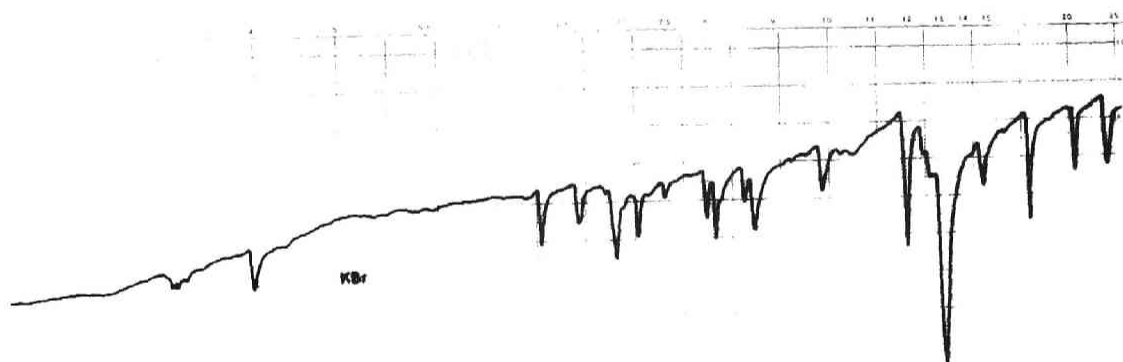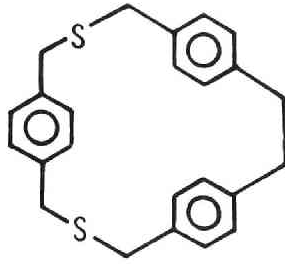
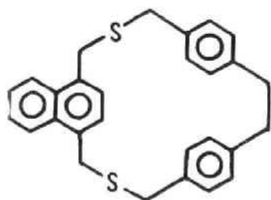2,11-Dithiatris[3.3.2]paracyclophane

5,8-Difluoro-2,11-dithiatris[3.3.2]paracyclophane

KBr

CDCl₃

TMS
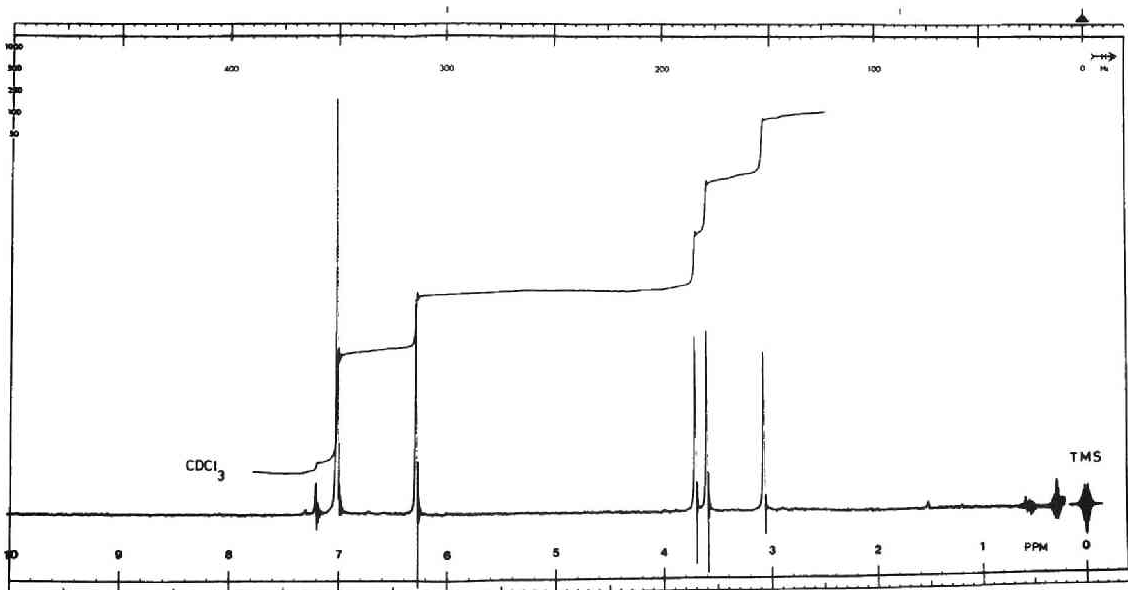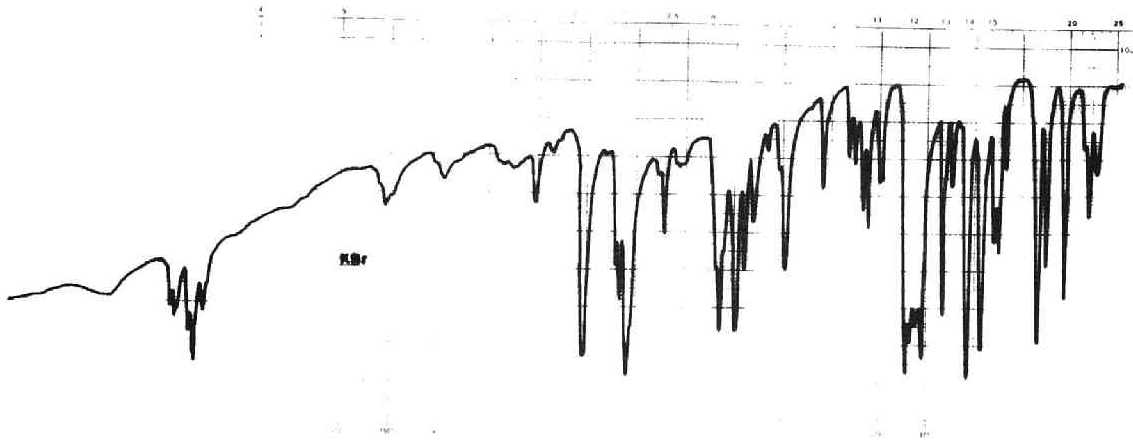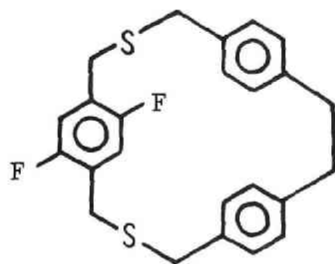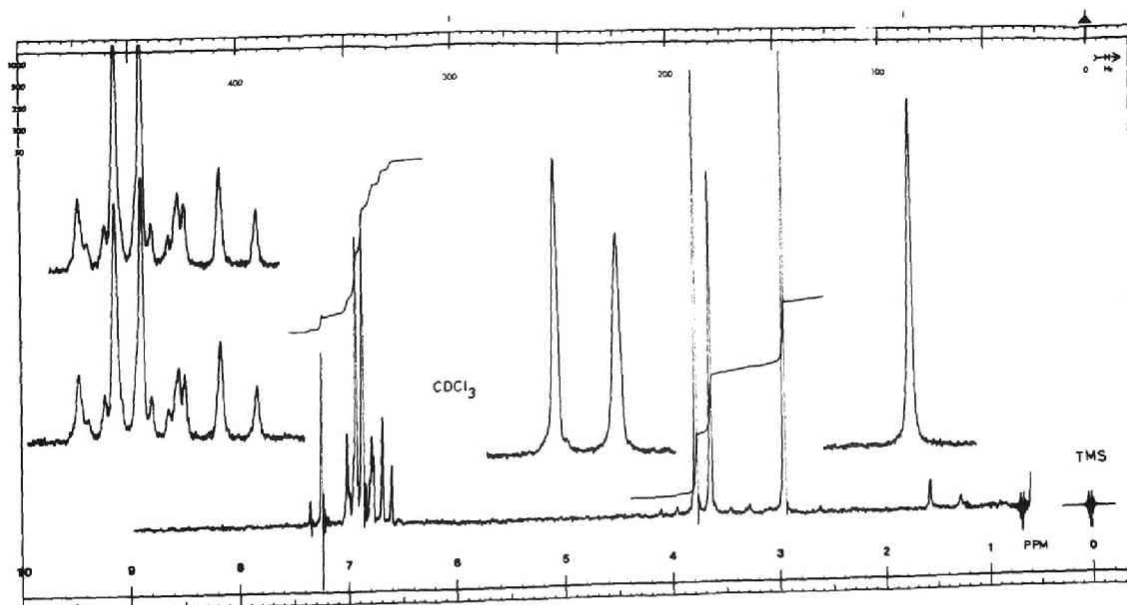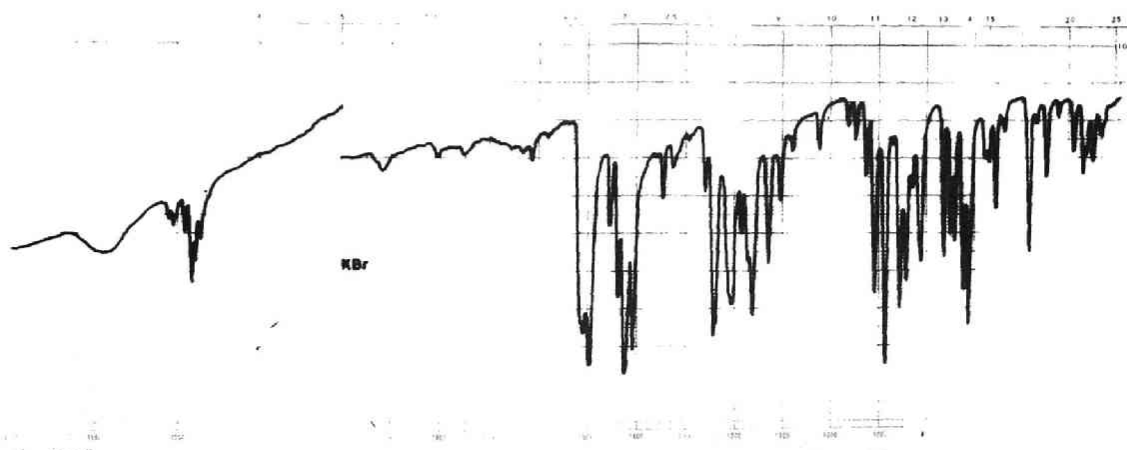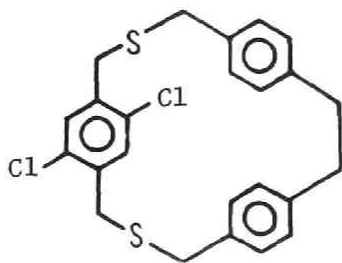
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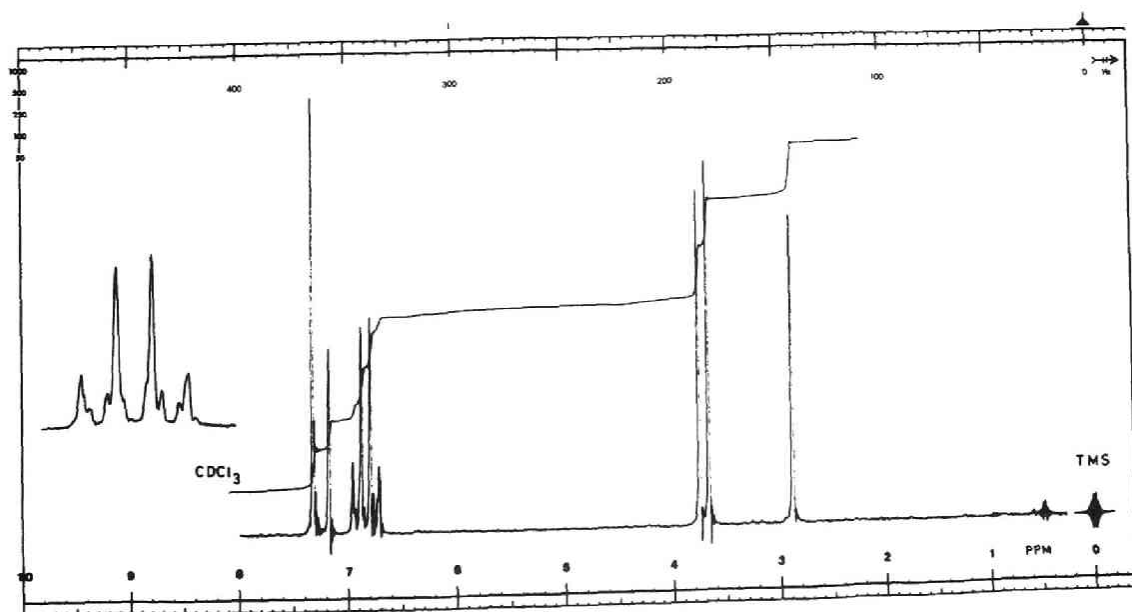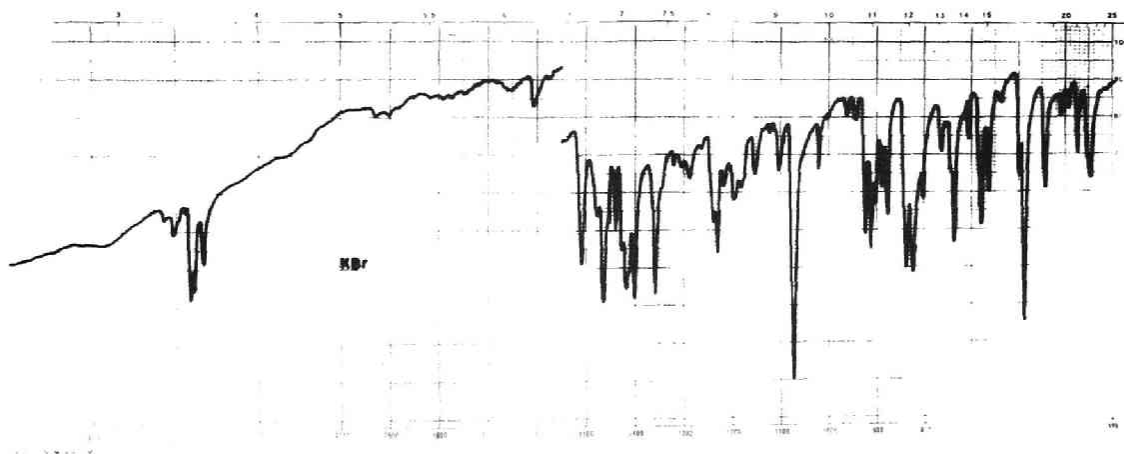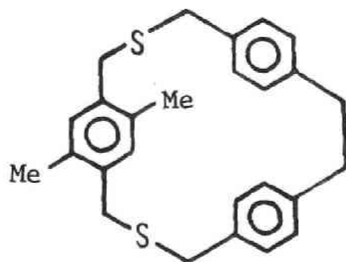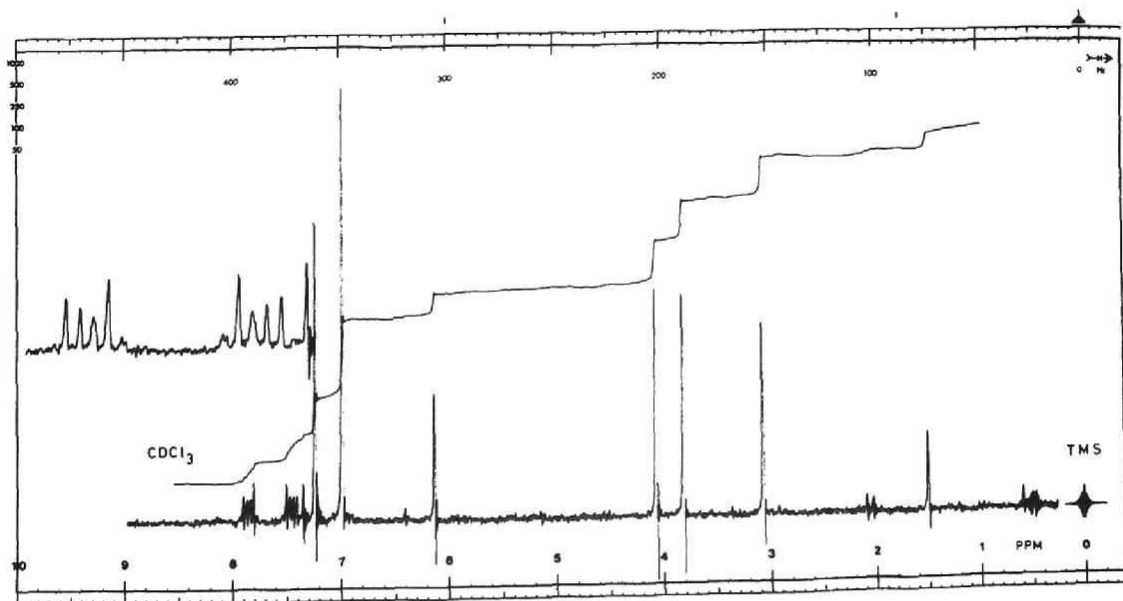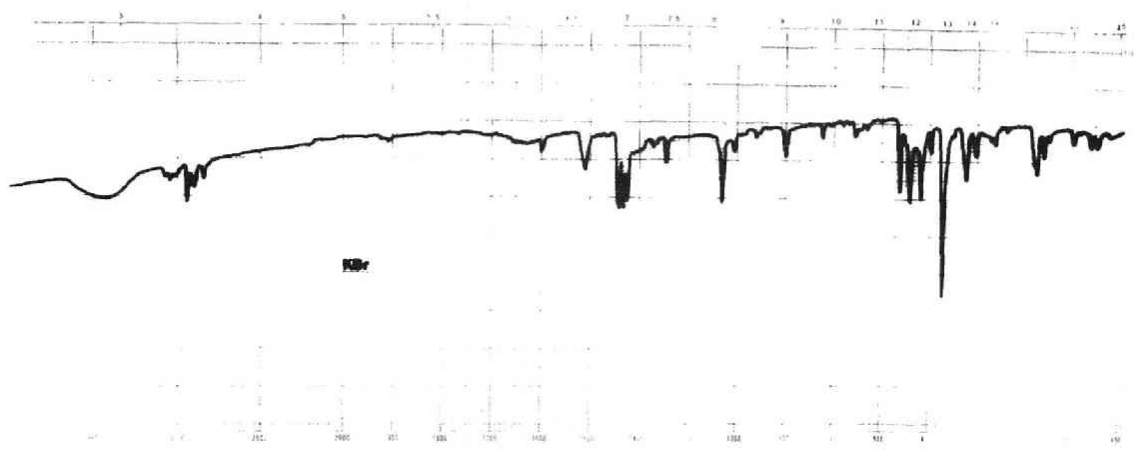
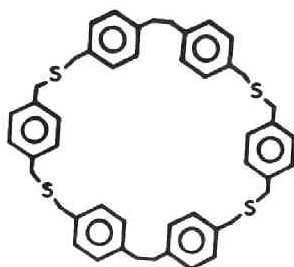5,8-Dimethyl-2,11-dithiatris[3.3.2]paracyclophane
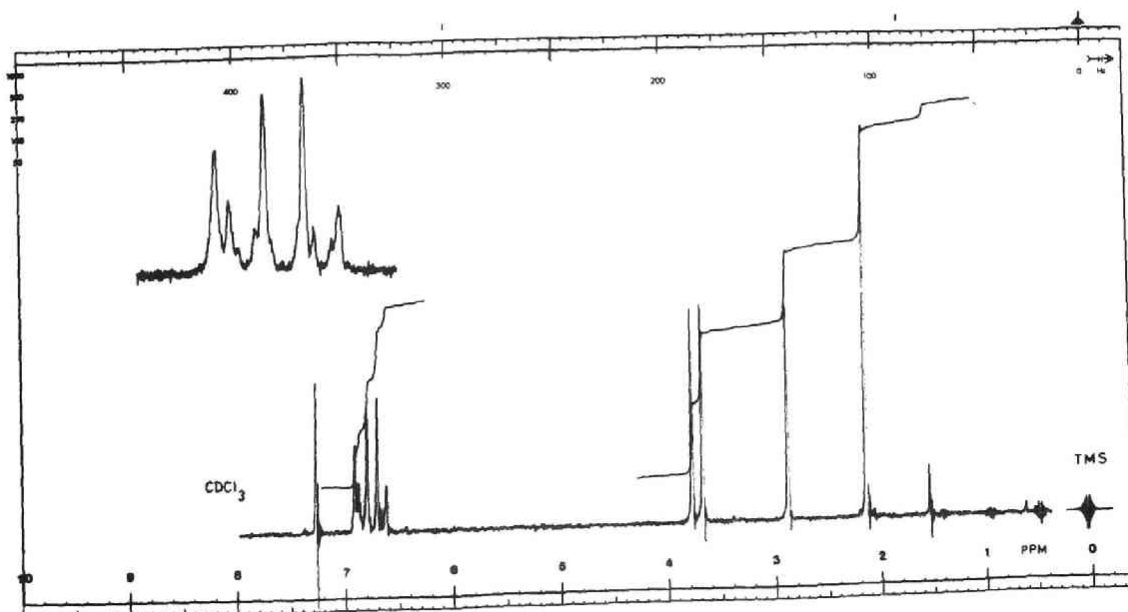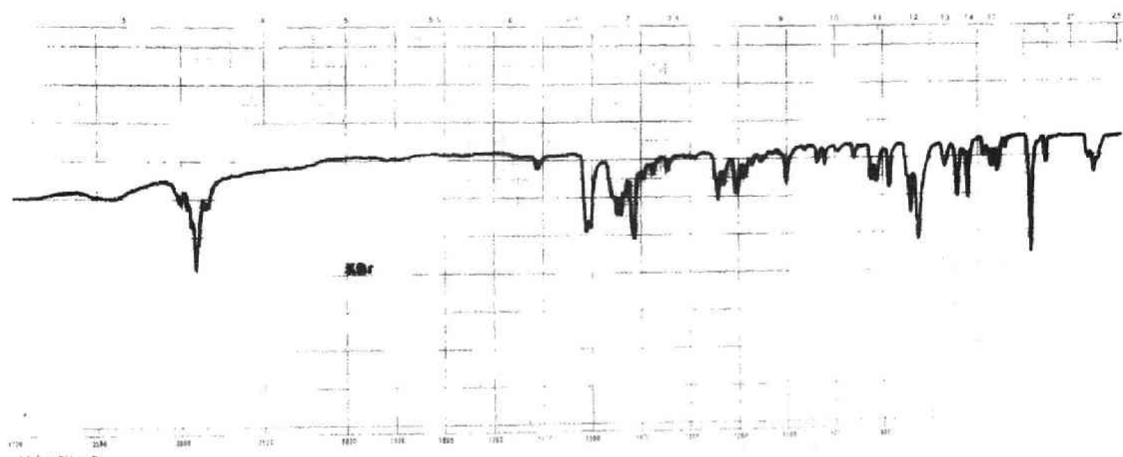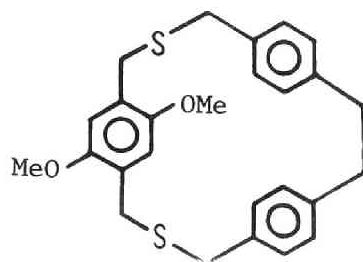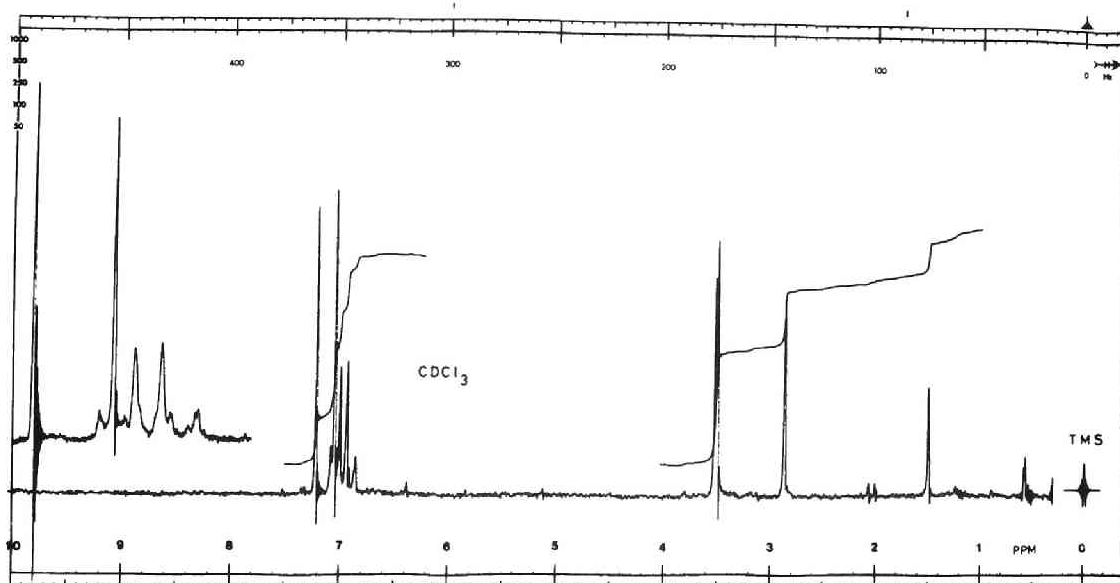
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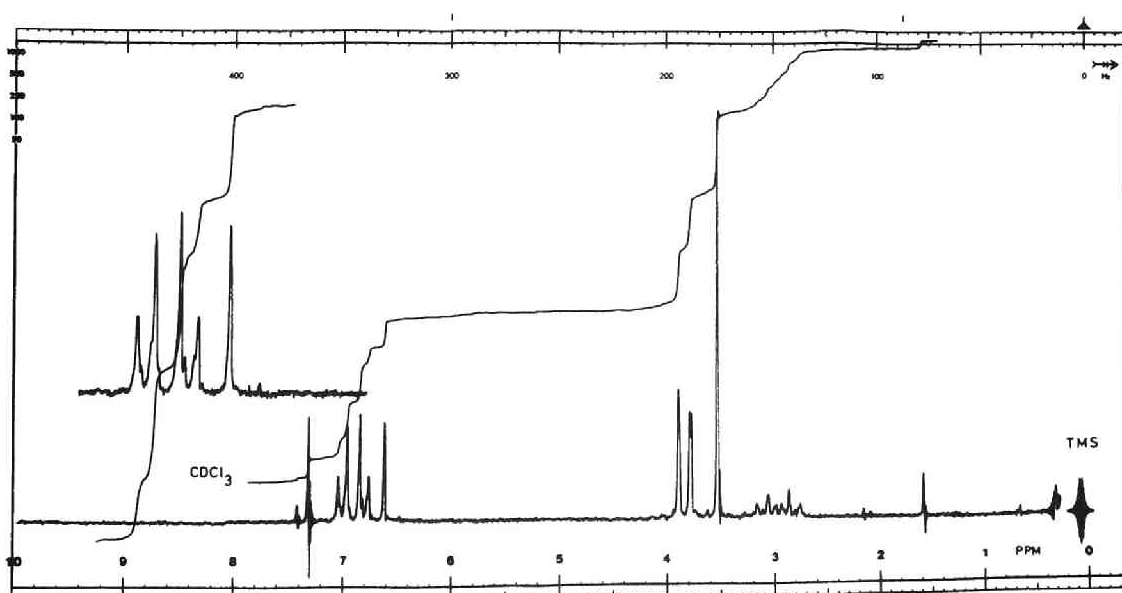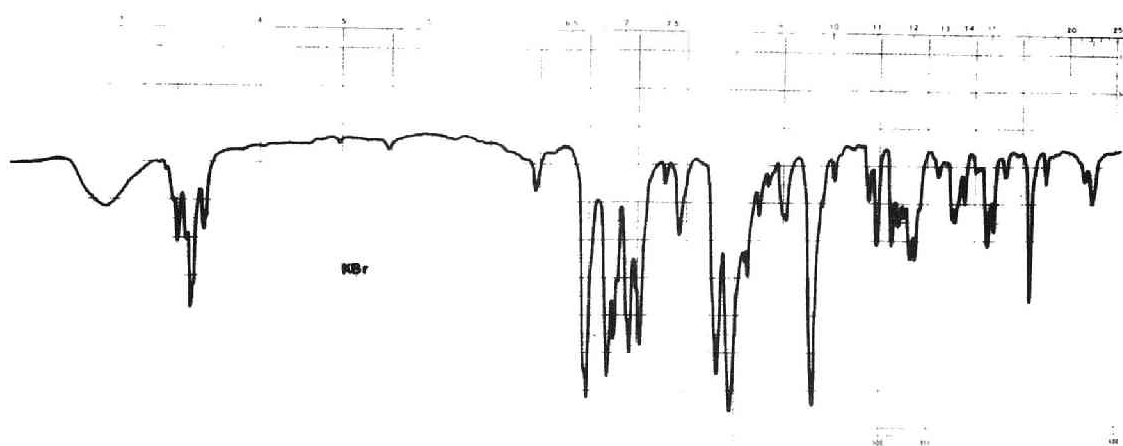
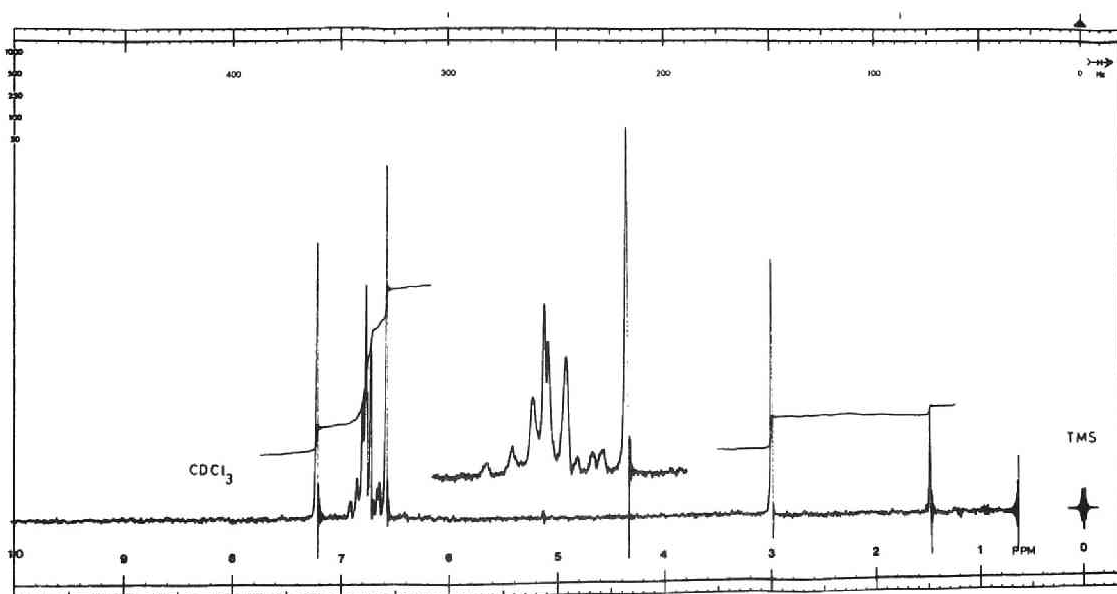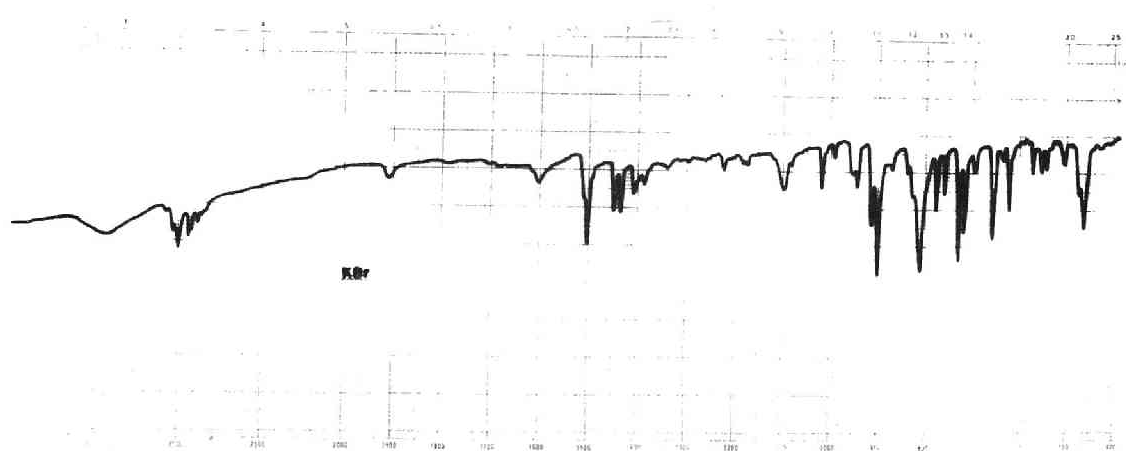5,6-Benzo-2,11-dithiatris[3.3.2]paracyclophane

2,11,28,37-Tetrathiahexakis[3.3.2.3.3.2]paracyclophane

Tris[2.2.2]paraxylylene-1,9-diene

PUBLICATION LIST

1. Electronic Structures and Charge-Transfer Spectra of
    Tris[2.2.2]paraxylylene and Related Compounds.

    F. Imashiro, Z. Yoshida and I. Tabushi, *Tetrahedron*, <u>29</u>,
    3521 (1973).

2. Transannular Effect on Friedel-Crafts Acetylation of
    Tris[2.2.2]paraxylylenes.

    I. Tabushi, Z. Yoshida and F. Imashiro, to be published.

3. Preparations and Properties of Pseudo-Geminal Ketones of
    Tris[2.2.2]- and Tetrakis[2.2.2.2]paraxylylene.

    I. Tabushi, Z. Yoshida and F. Imashiro, *Tetrahedron*, <u>31</u>,
    1833 (1975).

4. Preparations and Properties of Some Derivatives of
    Pseudo-Geminal Ketone of Tris[2.2.2]paraxylylene.

    I. Tabushi, Z. Yoshida and F. Imashiro, *Bull. Chem. Soc.
    Japan*, in press.

5. Solvolyses of Pseudo-Geminal "Equatorial" and "Axial"
    Systems of Tris[2.2.2]paraxylylene.

    I. Tabushi, Z. Yoshida and F. Imashiro, to be published.

6. 2,11-Dithiatris[3.3.2]paracyclophanes. Effects of Internal
    Rotation of Benzene Rings in Macrocyclophanes on NMR Spectra.

    F. Imashiro, M. Oda, T. Iida, Z. Yoshida and I. Tabushi,
    submitted to *Tetrahedron Letters*.

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   and Macrocyclic Compounds Containing Aromatic Rings.
   I. Tabushi, F. Imashiro, H. Yamada, Y. Kuroda and Z. Yoshida,
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   (1970).

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   I. Tabushi, Z. Yoshida and F. Imashiro, The General Discussion
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   I. Tabushi, Z. Yoshida and F. Imashiro, The 26th Annual
   Meeting of the Chemical Society of Japan, Hiratsuka (1972).

4. Preparations and Properties of Pseudo-Geminal Ketone of
   Tris[2.2.2]paraxylylene.
   I. Tabushi, Z. Yoshida and F. Imashiro, The 5th Symposium on
   Structural Organic Chemistry, Nagoya (1972).

5. Preparations and Structures of Some Derivatives of
   Pseudo-Geminal Ketone of Tris[2.2.2]paraxylylene.
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   Structural Organic Chemistry, Fukuoka (1973).

6. Transannular Effect on Friedel-Crafts Acetylation of
   Tris[2.2.2]paraxylylenes.

   I. Tabushi, Z. Yoshida and F. Imashiro, The 31st Annual
   Meeting of the Chemical Society of Japan, Tokyo (1974).

7. Structure and Reactivity of Pseudo-Geminal Carbinols of
   Tris[2.2.2]paraxylylene.

   I. Tabushi, Z. Yoshida and F. Imashiro, The 7th Symposium on
   Structural Organic Chemistry, Tokyo (1974).

8. Reactivities of Pseudo-Geminal Carbinol System of
   Tris[2.2.2]paraxylylene.

   I. Tabushi, Z. Yoshida and F. Imashiro, The 32nd Annual
   Meeting of the Chemical Society of Japan, Tokyo (1975).

9. Preparations and Properties of 2,11-Dithiatris[3.3.2]-
   paracyclophanes.

   Z. Yoshida, F. Imashiro, M. Oda, T. Iida and I. Tabushi,
   The 8th Structural Organic Chemistry, Kyoto (1975).