THE SYNTHESIS AND CHEMISTRY OF THE CYCLOPHANENES AND THEIR METAL COMPLEXES

by

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ABSTRACT

A new synthetic route to cyclophanenes **56**, starting from an appropriate 2,6-dihalogen-substituted toluene via monothiacyclophanes as intermediate compounds, was developed. By this method, *anti*-5,8,13-16-tetramethyl[2,2](1,3)cyclophan-1-ene, **56b**, and *anti*-4,6,8,12,14,16-hexamethyl[2,2](1,3)cyclophan-1-ene, **56c**, were first synthesized as well as three new monothiacyclophanes, *anti*-9,17-dimethyl-2-thia[3,2](1,3)cyclophane, **72a**, *anti*-6,9,14,17-tetramethyl-2-thia[3,2](1,3)cyclophane, **72b**, *anti*-5,7,9,13,15,17-hexamethyl-2-thia[3,2](1,3)cyclophane, **72c**. An X-ray structural determination of the monothiacyclophane **72a** revealed an *anti*-stepped geometry of the molecule and that the aromatic rings were bent outward in a slightly distorted boat form. A reciprocal relationship between deviations of the inner carbons from their basal planes and distances between the inner carbons was found by comparison of X-ray data of four metacyclophanes.

Several tricarbonylchromium(0) and η^5-cyclopentadienyliron(I) complexes of cyclophanenes **56** were also prepared for the first time. The complexation effect and ring current reduction effects in these complexes were investigated through studies of their proton nmr spectra. An X-ray structure analysis of *anti*-8,16-dimethyl[2,2](1,3)cyclophan-1-ene-cyclopentadienyliron(I), **105a**, was determined and it was found that the bridge double bond (1.345Å) has a *cis* geometry but with very large torsional angles: 24.7° for C-C=C-C and 41.6° for H-C=C-H.

The bridge chemistry of cyclophanenes **56** and their metal complexes was investigated through some selected reactions. It was found that the cyclophanenes **56** were easily oxidized in attempted electrophilic additions to the bridge double bond. Bromination of the cyclophanene-iron complexes **105b** and **105c** did give the desired bromine adducts. However, it was found that the reactivity of the bridge double bond in cyclophanenes **56** is very low since most of the attempted reactions failed to give the desired products.

The first synthesis of the $(\eta^6,\eta^6$-*anti*-4,6,8-trimethyl[2,2](1,3)cyclophan-1,9-diene)-bis(tricarbonylchromium(0)), **133**, was achieved through the dithiacyclophane route. An X-ray structure analysis of **133** was also determined and found that the two aromatic rings were inclined at 19.8° with respect to each other.

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LIST OF ABBREVIATIONS

Ar	aromatic ring
ax.	axial
bp	boiling point
n-Bu$_2$O	*n*-Butyl ether
^{13}C NMR	carbon-13 nuclear magnetic resonance
conc.	concentrated
compl.	complexed
Cp	cyclopentadienyl
decomp.	decomposition
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
eq.	equatorial
gem	geminal
^{1}H NMR, pnmr	proton nuclear magnetic resonance
br	broad
d	doublet
dd	doublet of doublets
ext.	external
int.	internal
m	multiplet
t	triplet
s	singlet
IR	infrared spectrum

m	medium
s	stong
v	very
w	weak
LDA	lithium diisopropylamide
Me	methyl
mp	melting point
MS	mass spectrum
CI	chemical ionization
EI	electron impact
Ph	phenyl
THF	tetrahydrofuran
uncompl.	uncomplexed
UV	ultraviolet spectrum

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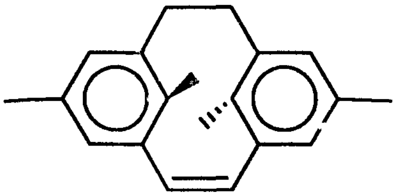
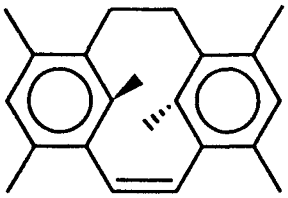
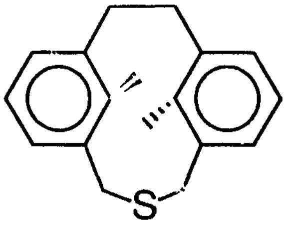


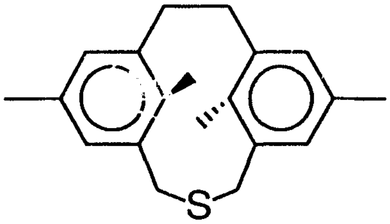
56b



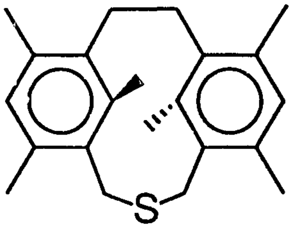
56c



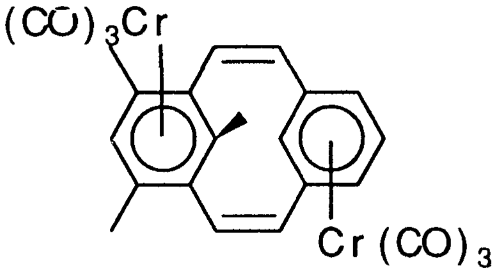
72a



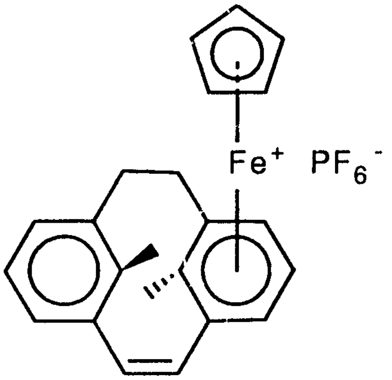
72b



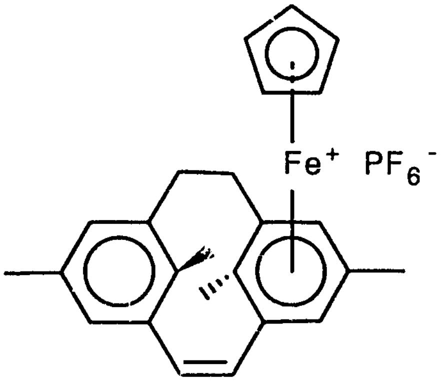
72c



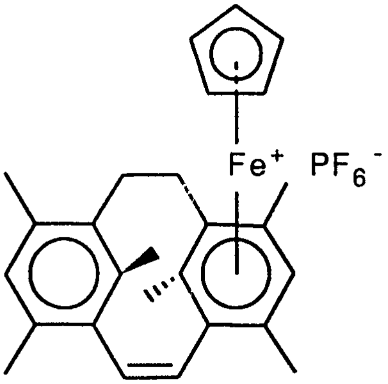
133



105a



105b



105c

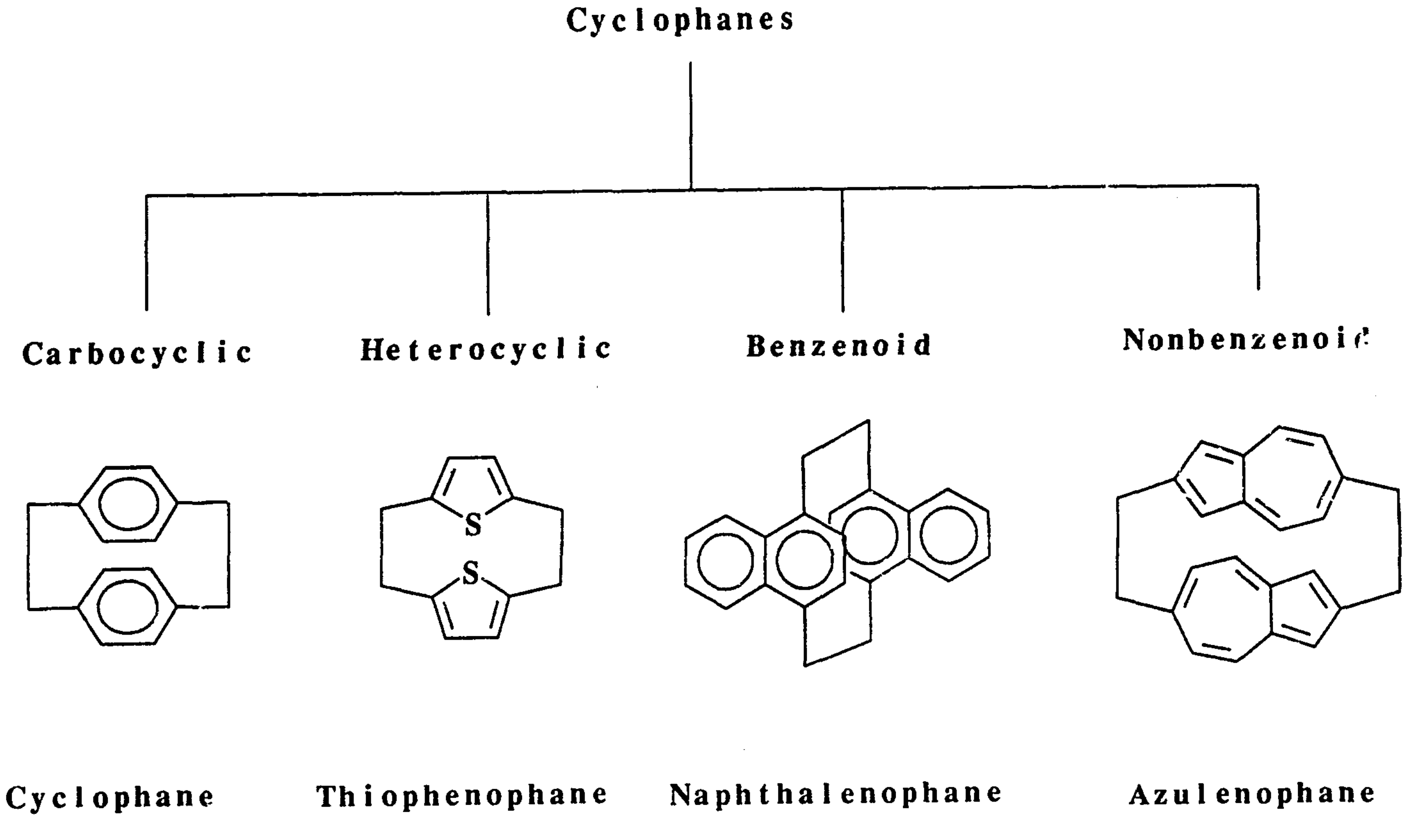
CHAPTER ONE

INTRODUCTION

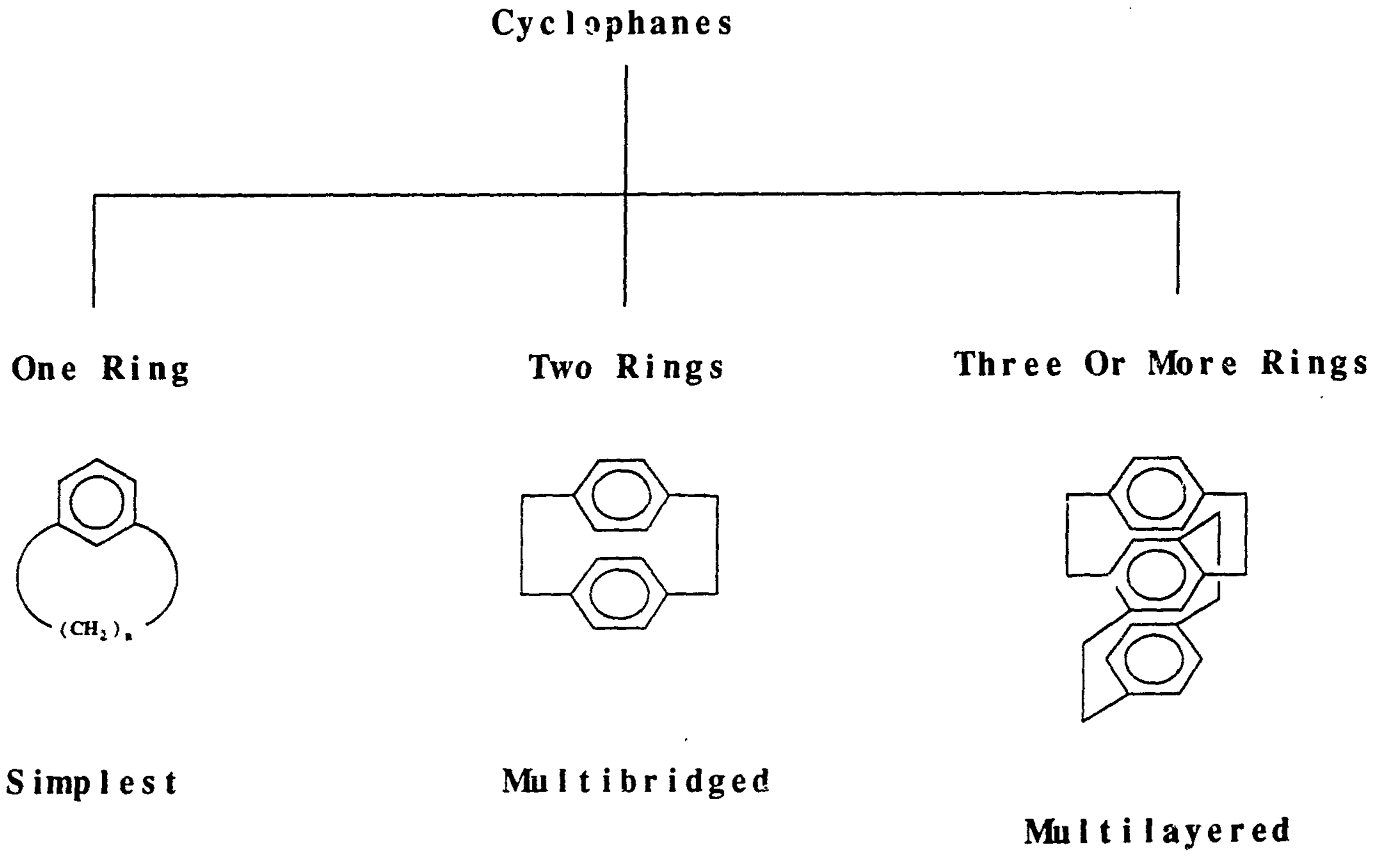
1.1 Classification and nomenclature of cyclophanes

Since the pioneering work of D. J. Cram and his students,$^{1)}$ cyclophane chemistry has evolved into a specific field in organic chemistry, and has shown growth in the last four decades.$^{2)}$ The rigid geometries, strain energies, and transannular interactions of the aromatic pi-electrons in cyclophane molecules are some of the more interesting properties which attract attention. Generally, the cyclophane compounds prepared so far can be classified in four classes (Scheme I): carbocyclic, heterocyclic, benzenoid, and nonbenzenoid. Carbocyclic cyclophanes are phanes in which only benzene ring systems are present and heterophanes contains at least one heteroaromatic ring in the molecule. Benzenoid cyclophanes must have one of the condensed benzenoid molecules such as naphthalene. Tropone and azulene are some of the molecules in nonbenzenoid cyclophanes. In each of the four classes, cyclophanes can also be further divided into three types according to the number of the aromatic rings in the molecule -- the simplest (one aromatic ring), the multibridged (two aromatic rings), and the multilayered (more than two aromatic rings).

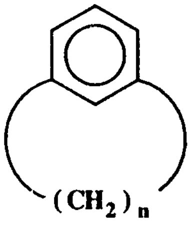
Scheme I The Classification of Cyclophanes



Scheme II Different types of cyclophanes



Generally, the word "cyclophanes" designates all classes of the bridged aromatic compounds in which more than two atoms of the aromatic ring are incorporated into a larger ring system.[3] In naming carbocyclic phanes[4] (this word is used for all bridged aromatic molecules), the word *cyclophane* is used for a specific compound and the prefix *cyclo* indicates the arenes are benzene rings.[a] Each bridging unit is indicated by a number, representing the number of the bridging atoms, placed in a bracket before the full name. In a simple case, the positions of the bridge attachment on the aromatic ring are indicated by usual names *ortho, meta, para*. For example, compound **1** is called [n]metacyclophane.



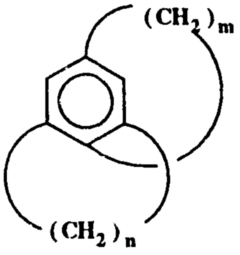
1

For the complicated molecules, the positions of the bridgeheads are indicated by numbers in parentheses following the brackets. Numbering starts at such a bridgehead atom (the anchor point) that counting in a clockwise manner will give the lowest possible number for

---

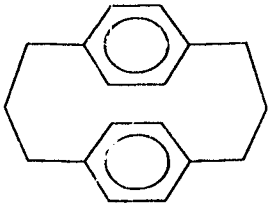
[a] *Here only the nomenclature of carbocyclic phanes has been presented*

the next bridgehead position. Thus, compound **2** is given the name of [n](1,3)[m](2,5) cyclophane.



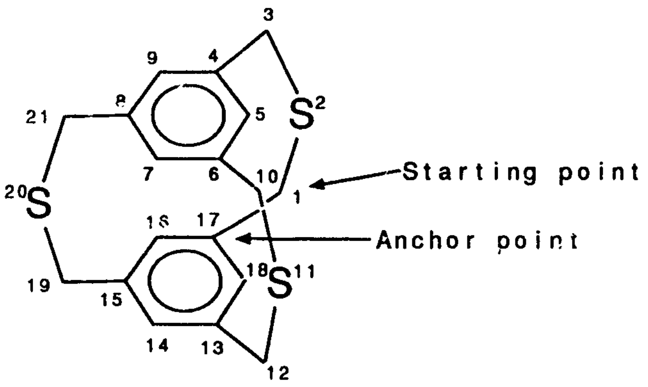
2

Cyclophanes with more than two bridges of equal lengths are simply called $[m_n]$cyclophanes. The prefix $[m_n]$ denotes that the number of bridging atoms is *m* in each of the *n* bridges. For example, compound **3** can be called $[3_2]$paracyclophane or [3.3]paracyclophane.



3

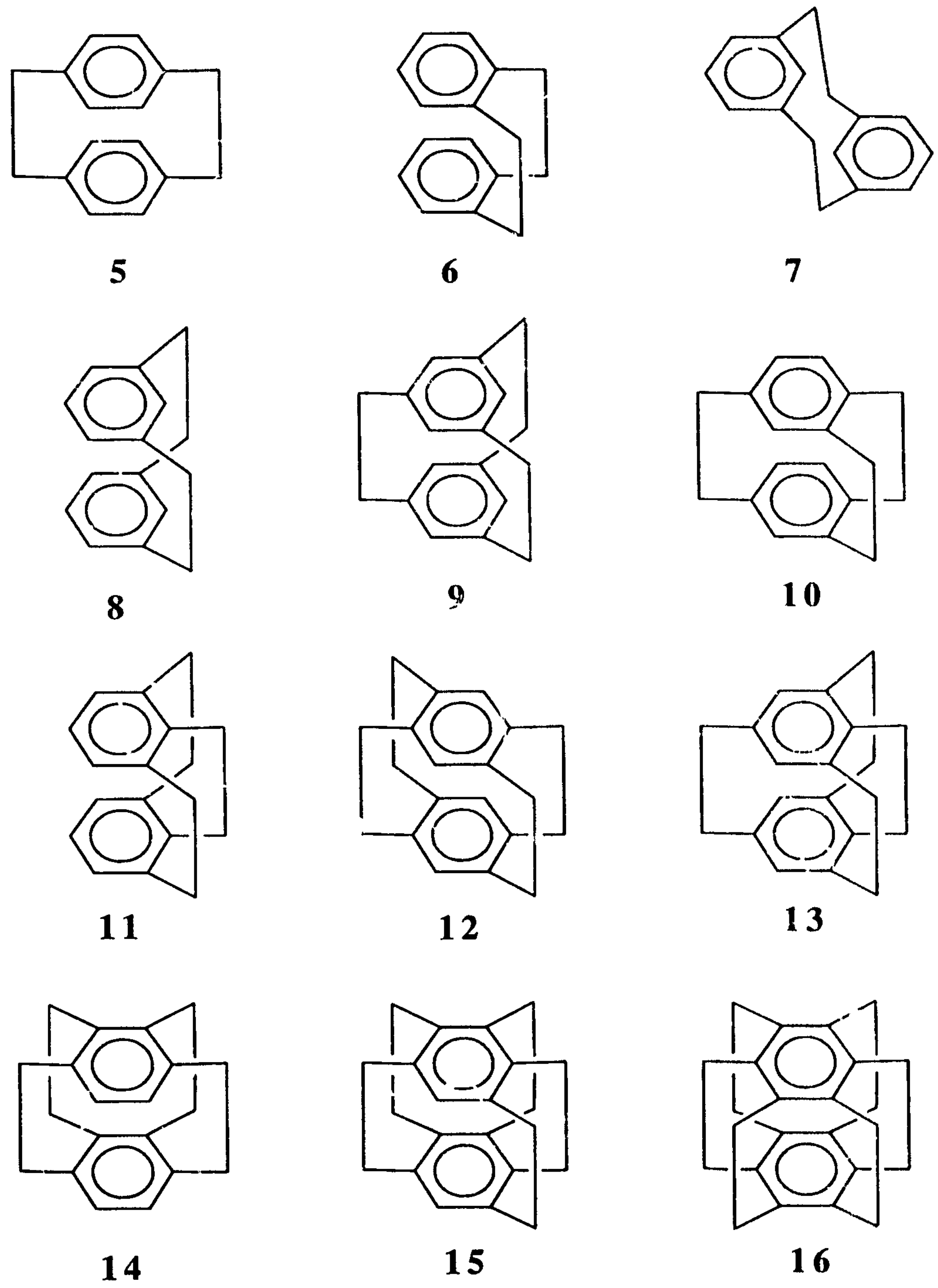
When cyclophane molecules contain heteroatoms in the bridging unit, numbers preceding the bracket are used to denote the positions of the hereroatoms in the bridges. To number the overall skeleton of the cyclophane one starts at the bridging atom attached to the anchor point of a ring and numbers along the bridge to the bridgehead of a ring and then continues to number this ring in a *clockwise* manner. From the stopping point one proceeds *clockwise* to the next bridgehead on the ring and continues numbering from the bridging atom attached to that bridgehead. Numbering in this manner would be continued until all of the bridges and benzene rings had been numbered. Thus, the compound **4** is called 2,11,20-trithia[3_3](1,3,5)cyclophane.



4

1.2 [2_n]Cyclophanes

[2_n]Cyclophanes are phanes in which two benzene rings are connected by at least two ethano bridges ($-CH_2-CH_2-$). By this definition, twelve known symmetrical [2_n]cyclophanes are shown in Figure 1. Since the pioneering work of Becker[48] and Cram,[5] all of these [2_n]cyclophanes(**5**[5], **6**[6], **7**[7], **8**[8], **9**[9], **10**[10], **11**[11], **12**[12], **13**[13], **14**[14], **15**[15],



5 6 7

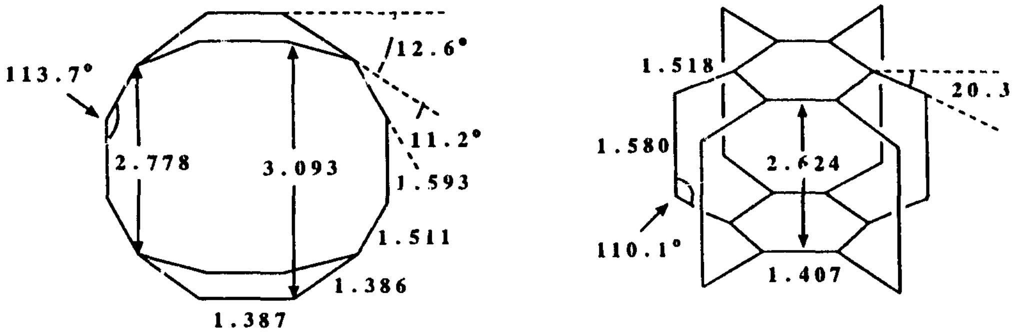
8 9 10

11 12 13

14 15 16

Figure 1. All the known [2$_n$]cyclophanes.

16[16)]) have been synthesized. Structurally, the symmetrical [2_n]cyclophanes have two basic types of geometries: 1) those in which the two benzene rings are stacked one over the other (face to face geometry), as in **5** and **9** to **16**; 2) those of rigid geometry where there is partial overlap of the benzene decks (step-like geometry), as in compound **7**. In these molecules, the benzene rings are bound within van der Waals distance by virtue of the short ethano bridges. For this reason, [2_n]cyclophanes are very strained molecules and exhibit many interesting structural properties. Indeed, the outstanding characteristic of the [2_n]cyclophanes is that unusual deformations of the benzene rings occur. The departure of the benzene rings from planarity is brought about by strong π-electron repulsion when the two aromatic rings are compressed towards each other. From X-ray structural analyses of the [2_n]cyclophanes, boat deformation of the benzene rings is observed in [2_2](1,4)cyclophane[17)] (paracyclophane) **5**, *anti*-[2_2](1,3)cyclophane[18)] (metacyclophane) **7**, [2_4](1,2,4,5)cyclophane **12**,[19)] and [2_5](1,2,3,4,5) cyclophane **15**.[20)] Figure 2 shows the bond angles and bond lengths of [2_2]paracyclophane which reveal many structural features of these molecules. In this molecule, the shortest interplanar distance between the benzene decks is 2.778Å. This distance is about 0.062Å shorter than the closest intermolecular distance between stacked aromatic nuclei in crystals.[21)] The inward bent shape of the benzene rings, the stretched σ benzyl-benzyl bond, and the abnormal bond angles all contribute to the distribution of the high energy (31 kcal/mol)[22] over the whole molecular skeleton.



5

16

Figure 2. X-ray structures of **5** and **16**

X-ray structural studies of $[2_3]$(1,2,3)cyclophane **11**,[23] $[2_4]$(1,2,3,4)cyclophane **14**,[24] and $[2_3]$(1,3,5) cyclophane **9**[25] also show to some extent, departure of the benzene rings from planarity. Only in the case of $[2_6]$(1,2,3,4,5,6)cyclophane[26] (also called superphane) **16** do the benzene rings remain planar. Although it is planar, the molecule **16** is the most strained member (estimated, 79 kcal/mol) of the $[2_n]$cyclophane series. The striking features of **16** are the short interplanar distance (2.624Å) between the benzene decks, the large deviation (20.3°) of the β angle (the angle between the benzene ring plane and the $C_{aromatic}$-C_{benzyl} bond), and the slightly elongated benzyl-benzyl σ bond (1.58Å) (see Figure 2).

Another important observation in the [2$_n$]cyclophanes, is that the benzene rings in these molecules can tolerate considerable deviations from planarity without losing their aromatic properties. In the case of **16**, although the rings are still planar, the p orbitals of the aromatic carbons are deflected from the rotation axis (perpendicular to the plane of the ring) by about 10°, giving a bowl shape to the π cloud. The evidence that these compounds retain their aromaticity is obtained from studies of their proton nuclear magnetic resonance (NMR) spectra.

The π-electrons of an aromatic ring (4n+2 electron system), such as a benzene ring, are considered to be in a doughnut shaped cloud situated above and below the plane of the ring. When a strong external magnetic field is applied perpendicular to the plane of the ring it induces a circulation of these π-electrons, as shown in Figure 3. This electron current, called the diamagnetic ring current, generates a small magnetic field which opposes the applied field inside the ring and reinforces the applied field outside the ring. As a consequence of the induced ring current, the protons situated in the plane of the ring and outside of it will resonate at a slightly low field and are therefore deshielded, whereas protons situated above the plane and inside of the ring will resonate at relatively high field and are shielded, compared to protons that are not influenced by the induced ring current.

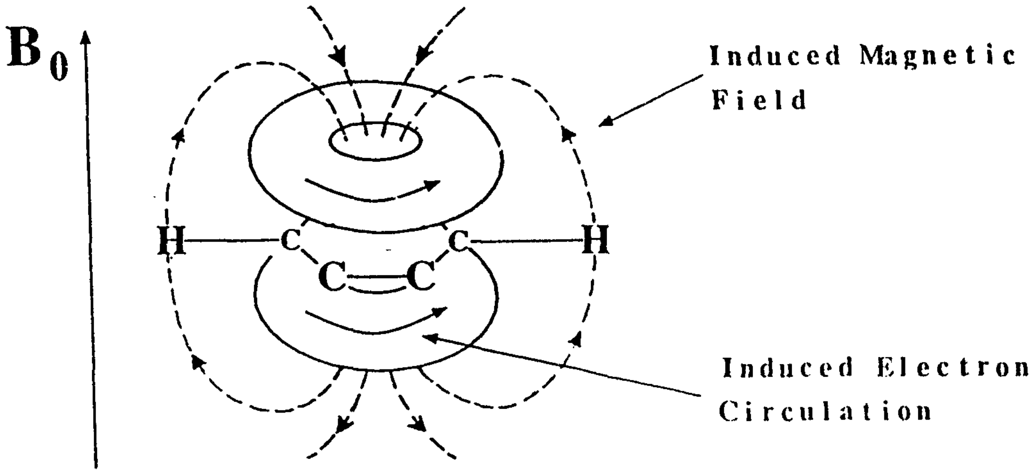
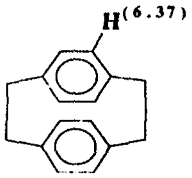
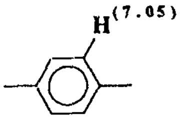
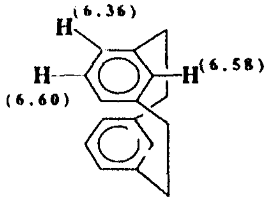
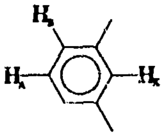
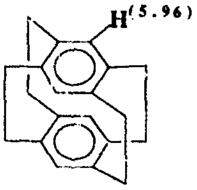
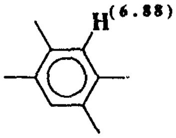


Figure 3. Ring current effects in aromatic systems

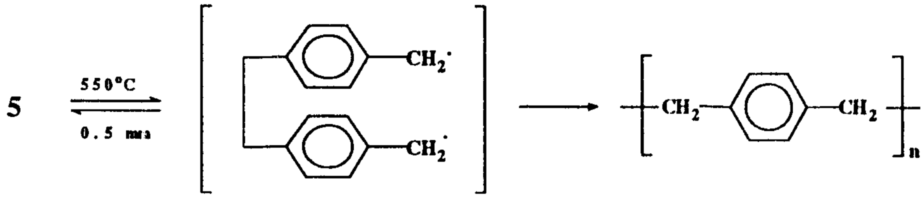
Proton nuclear magnetic resonance spectroscopy has been the most important technique in providing information regarding the structure and geometries of the [2_n]cyclophanes. The importance of this technique in making stereochemical assignments of cyclophanes lies in the anisotropic effect of the diamagnetic ring current in aromatic systems. If the two benzene rings are fixed in space close to each other, the magnetic environment of each proton in each benzene deck is generally influenced by the magnetic anisotropy of the other aromatic ring. In the stacked [2_n]cyclophanes, in which the benzene rings are directly over each other, the aromatic protons of one benzene ring are just in the shielding zone of the opposite aromatic ring and therefore the signal for each aromatic proton appears at higher field (upfield shift) than the corresponding protons in reference compounds. Table 1 shows the change in chemical shift ($\Delta\delta$) of the aromatic protons in some of $[2_n]$cyclophanes from that of reference compounds.

TABLE 1 Change in chemical shift ($\Delta\delta$) of aromatic protons in $[2_n]$cyclophanes

Compound	Reference	$\Delta\delta$
		$0.58^{27)}$
	 AB_2X Multiplet (6.92 - 7.22)	$0.56 - 0.62^{8)}$
		$0.92^{12b)}$

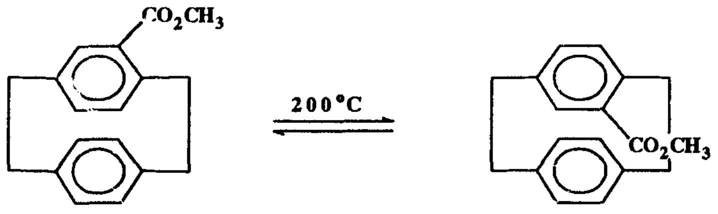
1.2.1 Structure and reactivity of [2$_2$]paracyclophane

[2$_2$]paracyclophane **5** is the most important member of the [2$_n$]cyclophanes and has been extensively studied. As we have seen before, the two benzene rings are held rigidly face to face by the two *para* attached ethano bridges. The pi-pi repulsion between the benzene decks bends them into shallow boats, and slightly lengthens the benzyl-benzyl bond. As a result, [2$_2$]paracyclophane gives rise to reactions that reflect the high strain in the molecule. One of the reactions peculiar to the system is thermal benzyl-benzyl bond cleavage. Pyrolysis of **5** in the gas phase at 550°C and 0.5 mm pressure produces a polymer **18**, *p*-xylylene.[28)]



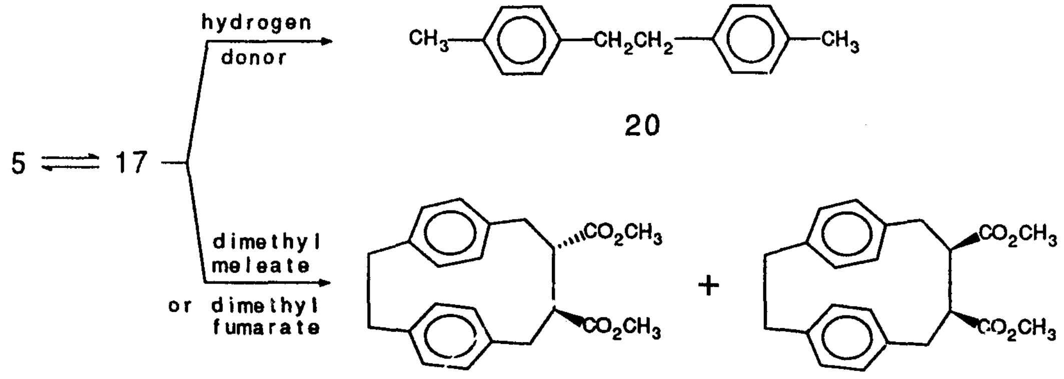
17 **18**

It is believed that a diradical intermediate **17** might be involved in the thermal cleavage reaction. Optically active ester **19** racemizes on being heated to 200°C.[29)] The recemization must occur via ring rotation that is impossible in this system without benzyl-benzyl bond cleavage.



19a **19b**

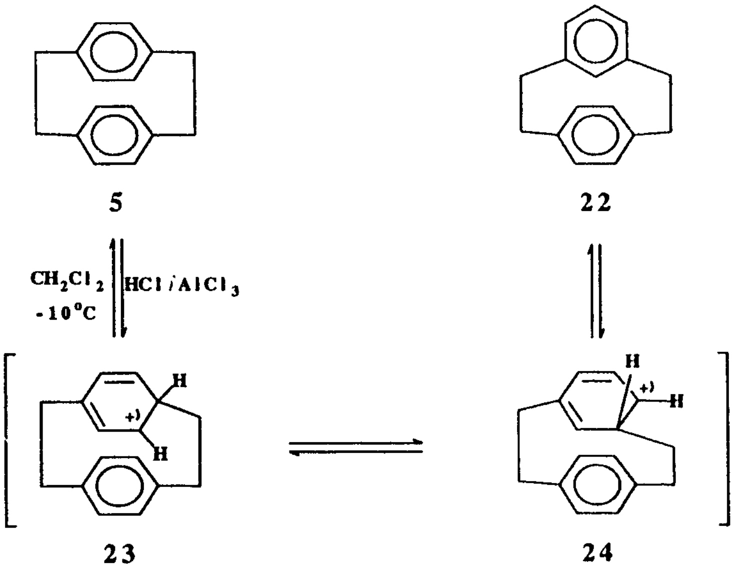
The existance of the diradical intermediate is supported by results from the trapping experiments. When **5** was heated to 200°C in the presence of hydrogen donors such as thiophenol, 1,2-bis(*p*-tolyl)ethane, **20**, was produced in good yield.[1c] The diradical intermediate can also be intercepted by dimethyl maleate or dimethyl fumarate, generating equal amounts of *cis*- and *trans*-**21**.[29] The fact that the same isomeric mixture **21** is obtained from either dimethyl maleate or dimethyl fumarate is consistent with the predicated radical mechanism.



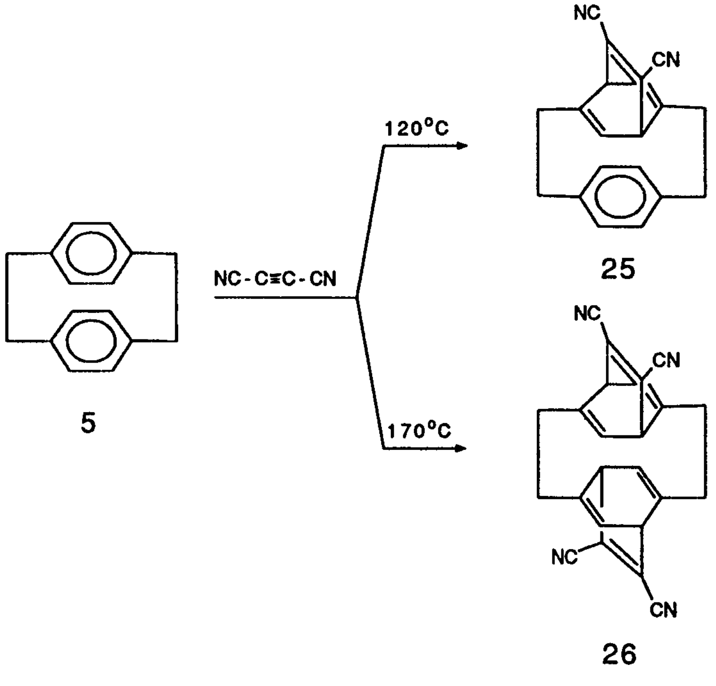
20

21a 21b

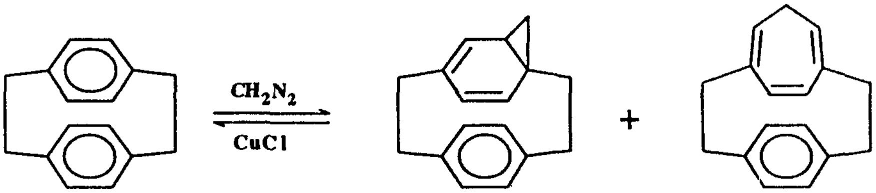
The molecule **5**, on treatment with aluminum chloride and anhydrous hydrogen chloride in dichloromethane at -10°C, rearranges to a mixture of hydrocarbons from which [2_2](1,3)(1,4)cyclophane (metaparacyclophane) **22** was obtained in 44% yield.[30] From a separate study using an optically active derivative of **5**, it was concluded that the rearrangement was intramolecular and very likely took place via the σ complexes **23** and **24**. The driving force for this reaction is the reduction of steric stain in going from **5** to **22**. The strain energy of **22** determined experimentally is 23 kcal/mol, 7 kcal/mol less than that of **5**.[31]



Because the benzene rings in **5** are severely distorted from planarity, the overlap between the p orbitals can not be as effective as in a normal benzene ring. The molecule therefore shows some 'abnormal' benzene ring reactions. For example, alkyl benzenes are used as solvents in the Diels-Alder reaction because they do not serve as dienes in these additions. However, [2_2]paracyclophane can participate in these [4+2] additions as readily as polyolefinic hydrocarbons. The first example was addition with dicyanoacetylene to form the mono- and bis-adducts **25** and **26** (note the different conditions). Considerable steric stain is relieved by formation of the Diels-Alder mono-adduct, however the addition of the second molecule of dienophile to the opposite aromatic ring becomes more difficult and requires more strenuous conditions.

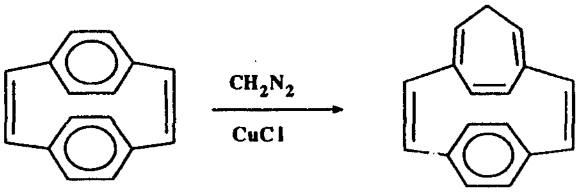


Given that [2_2]paracyclophane easily participates in Diels-Alder additions in which it behaves like a polyene, it is not difficult to understand that **5**, on treatment with diazomethane in the presence of cuprous chloride (Simmons-Smith reaction) affords a mixture of the ring cyclopropanated product **27** and the subsequent ring-enlarged cyclophane **28**, although in poor yield (~10% each).32)



5 **27** **28**

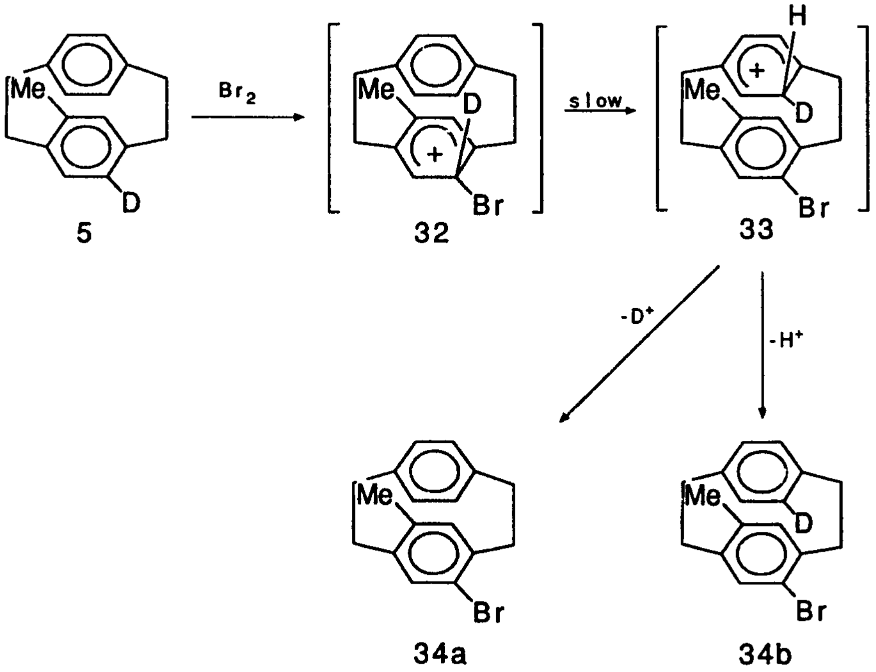
However, it is surprising that [2_2]paracyclophane-1,9-diene, **29**, is attacked by carbene preferentially on one of the benzene rings to give the ring-enlarged product **30**.1a)



29 **30**

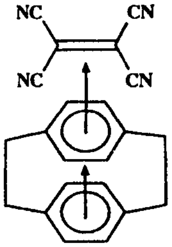
The high reactivity of the benzene rings toward electrophilic reagents such as methylene or its derivatives, arises from rehybridisation of some of the aromatic carbons in the cyclopropanated ring.33) Such a rehybridisation (from sp^2 to sp^3) increases the p character of the C-H bond and therefore reduces the electron density of the interior of the molecule. As a result, the relief of some steric strain, due to reduction of pi-pi electron repulsion between the benzene decks in the cyclopropanation process, is attributed to an enhanced reactivity of the benzene rings.

As a consequence of their proximity, transannular electronic interaction occurs between both benzene rings of **5**, for example in the electrophilic substitution of derivatives of **5**. In the catalyzed bromination of **31**,$^{34)}$ it has been found that the slow step in this reaction is loss of the proton from the σ complex **32** rather than formation of **32** as in the usual electrophilic substitution of arenes. In part this may be due to steric hindrance of approach of



Lewis bases, but it is also evident that the aromatic π-electron cloud of the opposite ring can serve as an internal base. Thus, the internal transfer of the deuterium to the *pseudo-gem* position of the adjacent opposite ring has occurred, giving a bromo derivative **34** with or without the deuterium atom from the σ-intermediate **33**.

Transannular electronic interaction between the benzene decks makes **5** a good π base. It has been found that the non-bound benzene ring releases electrons to the bound ring in the charge transfer complex **35** by measuring its equilibrium constant.[35] As expected, electron-withdrawing groups in the non-bound ring decrease the π basicity of the complexed ring by reducing the electron density of the non-complexed ring as shown in **36**.



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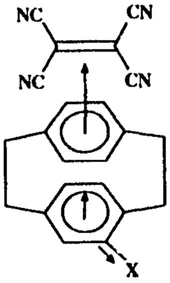
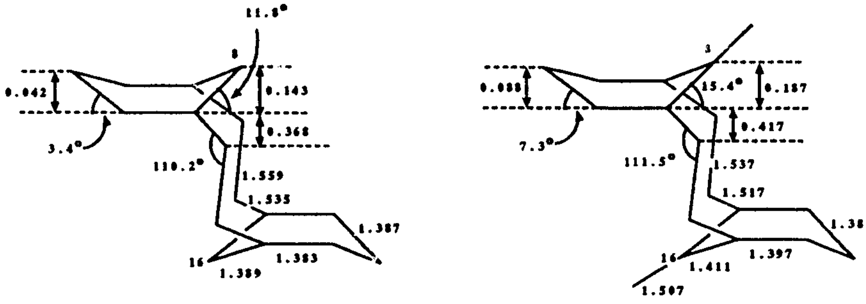


36

1.2.2 Structures and reactivities of [2$_2$]metacyclophanes

anti-[2$_2$]Metacyclophane, **7**, probably has been known for almost a century,[7a] and is one of the most studied members of the [2$_n$]cyclophane family.[36)] X-ray structural analysis revealed that the molecule has an *anti*-stepped geometry in which there is partial overlap between the benzene rings,[37)] as shown in Figure 4. One of the interesting features of the structure is the very short non-bonded distance (2.689Å) between the internal carbon atoms 8 and 16, compared to 2.778Å in **5**. As a result, the aromatic rings adopt a boat deformation with internal carbon atoms C_8 and C_{16} being out of the mean plane of the two ortho and meta aromatic C atoms, minimizing the transannular steric interaction between them. The bridge carbon atoms C_1 and C_2 are also displaced from that plane by 0.368Å.

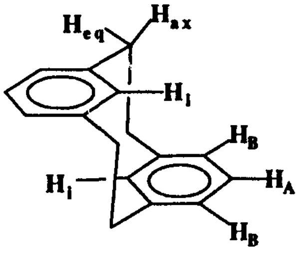


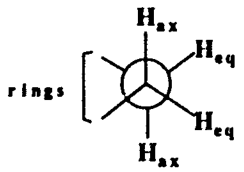
7 **37**

Figure 4. X-ray structures of **7** and **37**.

It is found that the *anti*-stepped geometry of **7** is shared by many [2$_2$]metacyclophanes -- derivatives of **7**. X-ray structural analysis of the analogue 8,16-dimethyl derivative **37** shows that the distortions in **37** are similar to, but greater than, those in **7** because of the replacement of the internal hydrogen atoms with the bulkier methyl groups.[38] The increased strain in the molecule **37** is evident from the larger deviations of bond lengths and bond angles, especially the increased distance (2.819Å) between the inner carbon atoms C_8 and C_{16} (see Figure 4).

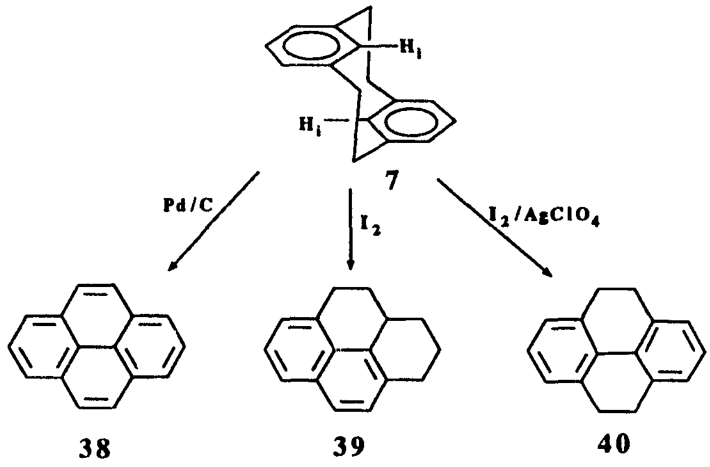
The numerous ^1H NMR studies on dissolved $[2_2]$metacyclophane **7**[39] confirm that the *anti*-stepped conformation found in the crystal is also maintained in solution. The methylene protons of the two ethano bridges are nonequivalent and appear as an AA'BB' system since they have a fixed, staggered arrangement.[39a] The most striking feature of the ^1H NMR spectrum of **7** is that the internal aromatic protons (H_i) appear at $\delta = 4.25$[39b], very strongly shielded ($\Delta\delta = 2.75$ ppm) from the signal of *m*-xylene itself. In contrast, the external aromatic protons (H_A and H_B) are only slightly deshielded, appearing at $\delta = 6.98\text{-}7.30$.[39a] This is explained by the rigid conformational geometry of **7**, where the proton H_i is extended in the shielding zone of the opposite deck and the H_A and H_B are far away from that center.





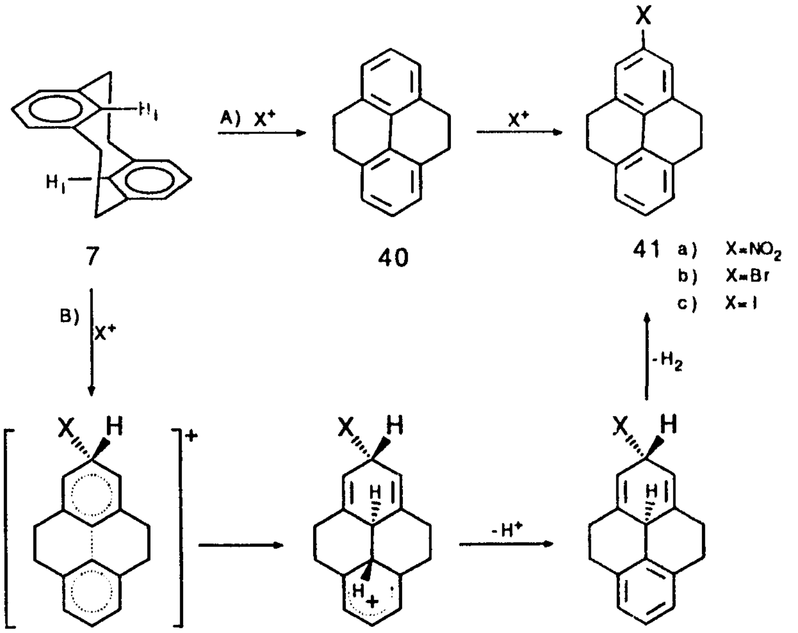
The pnmr spectrum of **37** is similar,[40)] with the internal methyl protons Me_i appearing at $\delta = 0.56$, showing again a strong upfield shift of 1.6 ppm from those of 1,2,3-trimethylbenzene ($\delta 2.15$). The difference between the upfield shifts of the internal protons H_i of **7** and Me_i of **37** probably reflects the different conformational geometries of **7** and **37**. The C_8-C_{16} distance in **37** is 2.82Å compared to 2.69Å for **7** and the methyl protons are further from the center of the opposite ring, and hence less shielded.[41)]

Transannular ring closure reactions are common in [2_2]metacyclophanes. Bond formation between the inner carbons, C_8 and C_{16}, occurs easily under a variety of conditions, leading to derivatives having a pyrene skeleton, such as **38**. For example, dehydrogenation of **7** with palladium/charcoal at about 300°C produces pyrene, **38**, in 60% yield.[42)] When **7** and iodine are warmed up in a non-



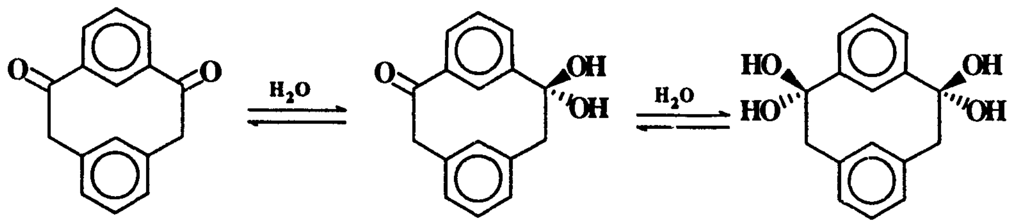
polar solvent, ring closure occurs to give ,2,3,3a,4,5-hexahydropyrene, **39**, in quantitative yield.[43)] In the attempted iodination of **7** with silver perchlorate, only 4,5,9,10-tetrahydropyrene, **40**, was obtained.[44)]

The involvement of the transannular ring closure process in electrophilic substitution of **7** is suggested from the fact that such reactions do not lead to derivatives of **7** but to derivatives of the tetrahydropyrene **40**. From studies by Allinger,[39f)] on the nitration and the bromination of **7**, the 2-substituted 4,5,9,10-tetrahydropyrene derivatives **41** are presumedly produced via the tetrahydropyrene **40** as intermediate. There is also the possibility that the reaction proceeds as a concerted transannular aromatic



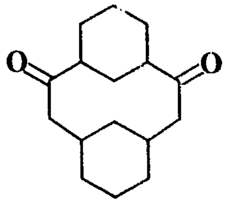
substitution via path B. This pathway has been suggested by Sato for the iodination of $[2_2]$metacyclophane **7** with iodine and nitric acid, which leads to 2-iodo-4,5,9,10-tetrahydropyrene, **41c**.[45)]

The tendency of the $[2_2]$metacyclophanes to undergo transannular ring closure probably results from the great relief of steric strain in these molecules by allowing σ-bond formation between C_8 and C_{16}. Obviously, the chemistry of the $[2_2]$metacyclophanes is mainly governed by the steric strain as the result of the rigid geometries of these molecules. One good example to demonstrate this phenomenon is the hydration of $[2_2]$metacyclophane-1,10-dione, **42**. Normally, the addition of water to carbonyl compounds, especially ketone molecules, does not happen except for ketones with electronegative substitutents in the α positions. However, compound **42** exhibits a pronounced tendency towards adduct formation with nucleophiles. In dioxane solution, containing 20% water, an equilibrium is attained between **42** (9%) and the mono- and the dihydrates



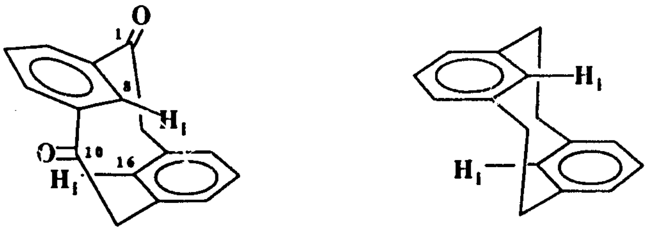
42 **42a** **42b**

42a (55%) and **42b** (36%).[46)] In contrast, the aliphatic compound **43** does not form a hydrate under the same condition with catalytic amounts of acid or base even after ten days.



43

The introduction of oxo-functions into the bridge of **7** to give **42** entails an increase of the bond angles at the C_1 and C_{10} positions. Thus, one benzene ring in **42** is forced to turn inwards and the resultant conformational change is that the two benzene rings are no longer situated in parallel planes, as shown in Figure 5. This enhances the transannular steric compression between C_8 and C_{16} in **42** when compared to **7**. A rehybridization of the sp^2 carbons in C_1 and C_{10} of **42** via adduct formation with water will inversely induce a more parallel orientation of the two benzene rings resulting in a relief of the steric strain.



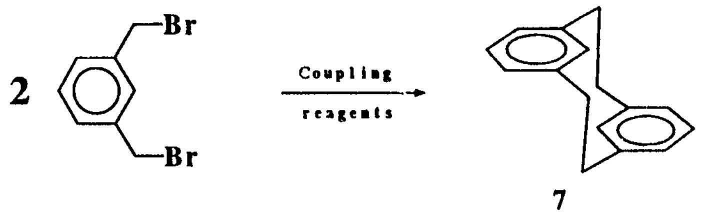
42 **7**

Figure 5. Comparison of the geometries of **42** and **7**

1.3 Synthetic methods available for [2$_n$]cyclophanes

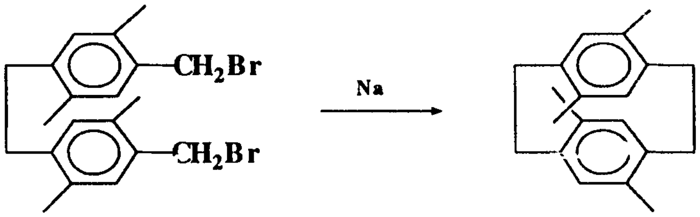
During the period from Cram's initial studies on [2$_2$]paracyclophane **7** in 1951, to the exciting synthesis of superphane **16** in 1979, many synthetic methods were developed for the challenging synthesis of the sterically strained [2$_n$]cyclophane molecules.47) Among these various techniques, some have been found to be quite general and provide basic methods for making all types of cyclophanes. The Wurtz coupling reaction is the oldest successful method employed for the formation of [2$_2$]cyclophanes. It was first used by Pellegrin for the synthesis of *anti*-[2$_2$]metacyclophane **7** in 1899,7a) whose structure was confirmed by Baker et al. in 1950.48) Since then, a variety of derivatives of [2$_2$]paracyclophane, **5**, and [2$_2$]orthocyclophane, **6**, and especially *anti*[2$_2$]metacyclophane, **7**, have been prepared by this coupling reaction.40, 39c, 49) Although the Wurtz coupling can be conveniently employed provided that the required dihalides are readily available, the yields in the coupling reactions are generally quite low (~20%).

The original coupling using metallic sodium has been improved by Müller and Röscheisen50) by addition of tetraphenylethylene (TPE), such that the sodium is dissolved in tetrahydrofuran and the reaction is then



7

Coupling reagents	yield
Na	11.7[48]
PhLi	39[39b]
Na/THF/TPE	35[51]

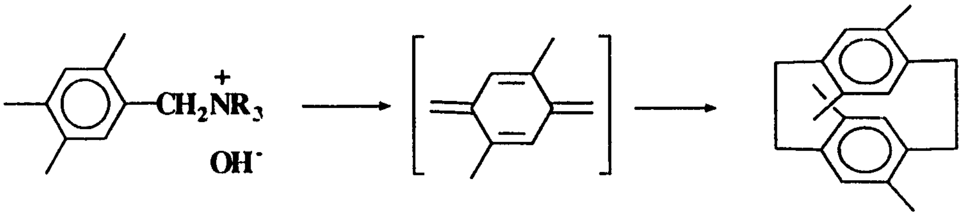


44

homogeneous. This improves the yields.

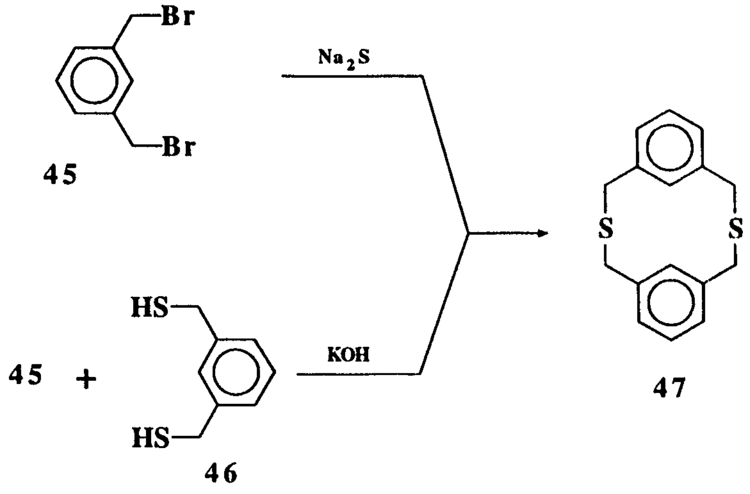
Organometallic compounds such as phenyllithium or butyllithium may be used in place of sodium to bring about inter or intra-molecular coupling of benzylic halides. The inter-molecular cyclization of 1,3-bis-(bromomethyl)benzene with phenyllithium gave *anti*-$[2_2]$metacyclophane **7** in 39% yield, compared to the yield of 12% using metallic sodium,[39b] although it is about the same using tetraphenylethylene.

For the synthesis of $[2_2]$paracyclophanes, the Hofmann elimination of benzylammonium hydroxide which contains a methyl group at the para position has been used successfully, although yields in this 1,6-elimination reaction are usually low. The major product in the elimination is a polymer of *p*-xylylene, which is the proposed intermediate. By careful attention to solvent, concentration, and polymerization inhibitor, the yield of the desired product can be improved, as shown for **44** from 2,4,5-trimethylbenzylammonium hydroxide **43**.[52)]



43 **44**

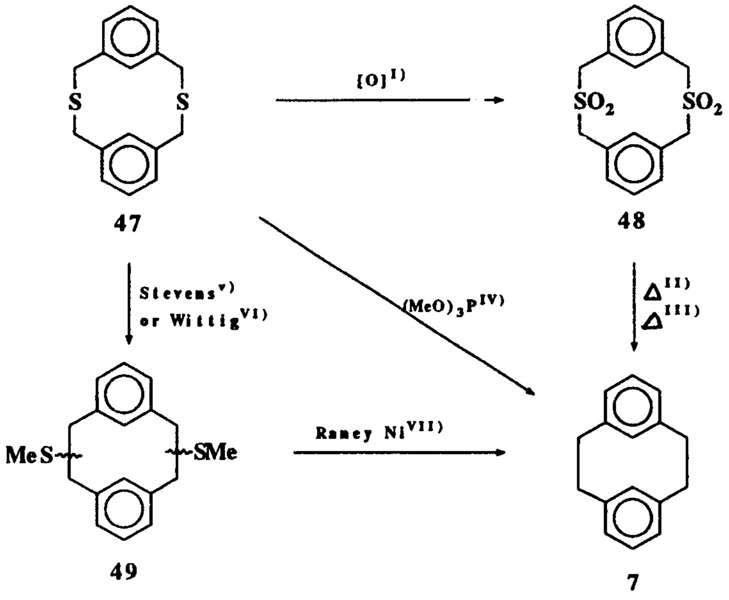
Nowadays the most important method for preparing cyclophanes is the thiacyclophane-sulfur extrusion procedure, which was introduced in 1969.[7a)] Since then, the easy preparation of dithiacyclophanes in high yields, and the variety of methods for extruding sulfur, have made this route the method of choice for making all kinds of cyclophanes. Basically, there are two ways to prepare a thiacyclophane from a dihalide: (1) the coupling of the dihalides with sodium sulphide; (2) the cross coupling of the dihalide with a dimercaptan under high dilution conditions. The yields in the direct coupling are usually much lower than those of the optimized cross coupling technique.53)



The conversion of the thiacyclophanes to cyclophanes can be easily achieved by extruding the sulfur atom from the bridges in several ways. These include photolysis of the thiacyclophanes in the presence of $(MeO)_3P$, pyrolysis and photolysis of sulfones, and reduction of the sulfides produced on ring contraction with Raney nickel (Scheme III).

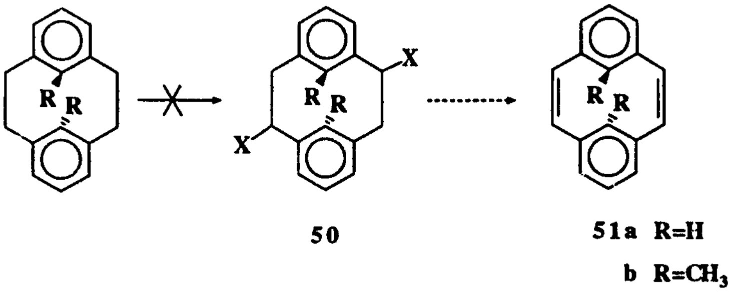
Another synthetic application of the thiacyclophane-sulfur extrusion route is the introduction of unsaturation in the ethano bridges to give the cyclophanedienes **51**.54) In contrast to the alkyl-substituted benzenes, the bridge of [2_2]metacyclophane **7** can not be functionalised to form bridge substituted cyclophanes **50**,58) which would be the precusors to the diene **51**. However, ring contraction with a Stevens or Wittig rearrangement of thiacyclophanes leaves a

Scheme III:

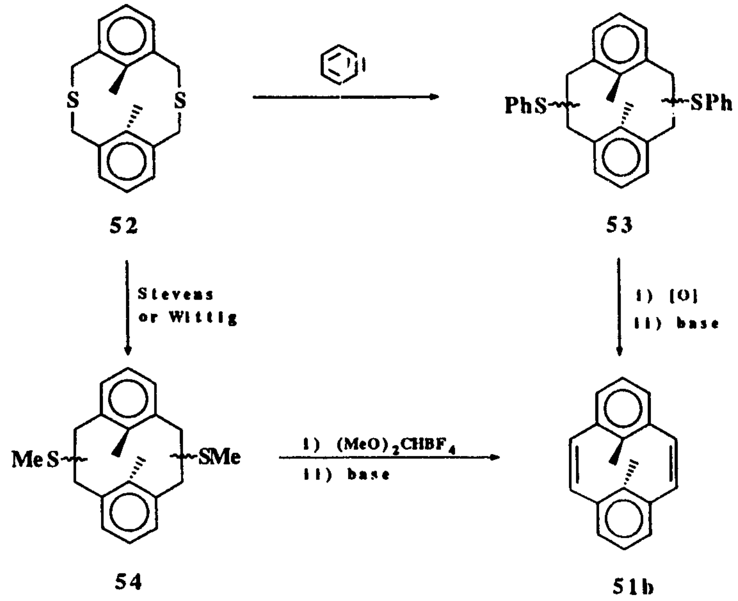


Paths: I[55]; II[7a]; III[56]; IV[57]; V[58]; VI[59]; VII[57]

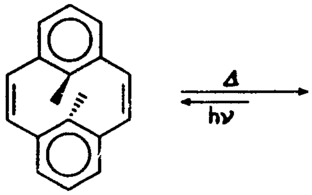
substituent on each bridge, which can then be subjected to Hofmann elimination to produce the cyclophanediene **51**.[60] This general route to cyclophanedienes is summarized in Scheme IV using 9,18-dimethyl-2,11-dithia[3$_2$]cyclophane, **52**, as an example.



Scheme IV:

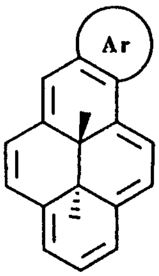
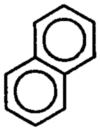


The diene **51b**, which can be isolated below 0°C, but undergoes spontaneous valence isomerization in the dark at room temperature or above to form the more stable *trans*-10b,10c-dimethyl-10b,10c-dihydropyrene **55**.[61] The compound **55** is a planar molecule with a closed electronic shell of 14 π-electrons and hence is classified as a 14π aromatic system.[49c] A striking structural feature of **55** is the central placement of the methyl substituents within the 14 π-electron cloud. As a consequence, the methyl protons are strongly shielded (δ -4.25) by the diamagnetic ring current and the chemical shift of these protons is highly sensitive to a change in the ring current. Thus, the chemical shift of the internal methyl substituents of **55** serves as an excellent probe to monitor any ring current change which is brought about when another aromatic system is fused to this 14π system. Table 2 shows the change in chemical shift (Δδ) of the internal methyl protons in some fused dimethyldihydropyrenes.

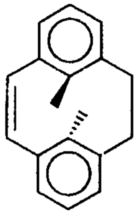


51b **55**

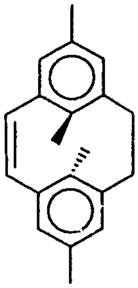
Table 2. The change in chemical shift of the internal methyl protons in fused dimethyldihydopyrenes

	Ar	ppm	Δδ
	**H**	-4.25	--
		-1.60	-2.35[62]
		-0.44	-3.81[63]
		-2.60	-1.65[64]

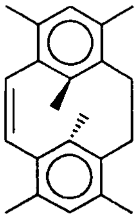
The diene **51b**, apart from being the valence isomer of the theoretically interesting dihydropyrene **55**, is a structurally and chemically interesting molecule itself. Unfortunately, the chemistry of the bridge double bond is hard to study due to this facile isomerization of **51b** to **55**. We thought it would be desirable to block this process in order to study the bridge double bond of **51b**. Complexation of **51b** with transition metals that require 6π electrons holds **51b** in its diene form. An alternative to the study of the diene is to employ the cyclophanenes which do not spontaneously isomerize, as models for the diene, so that the chemistry of the bridge might be studied. Thus the synthesis of the cyclophanenes **56**, and the study of their bridge chemistry, as well as the synthesis and chemistry of several metal complexes of **56** were the objective of this project.



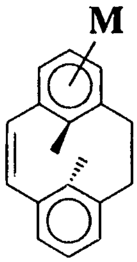
56a



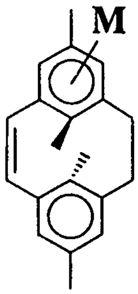
56b



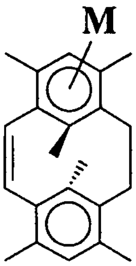
56c



57a



57b



57c

Chapter Two

Results and Discussion

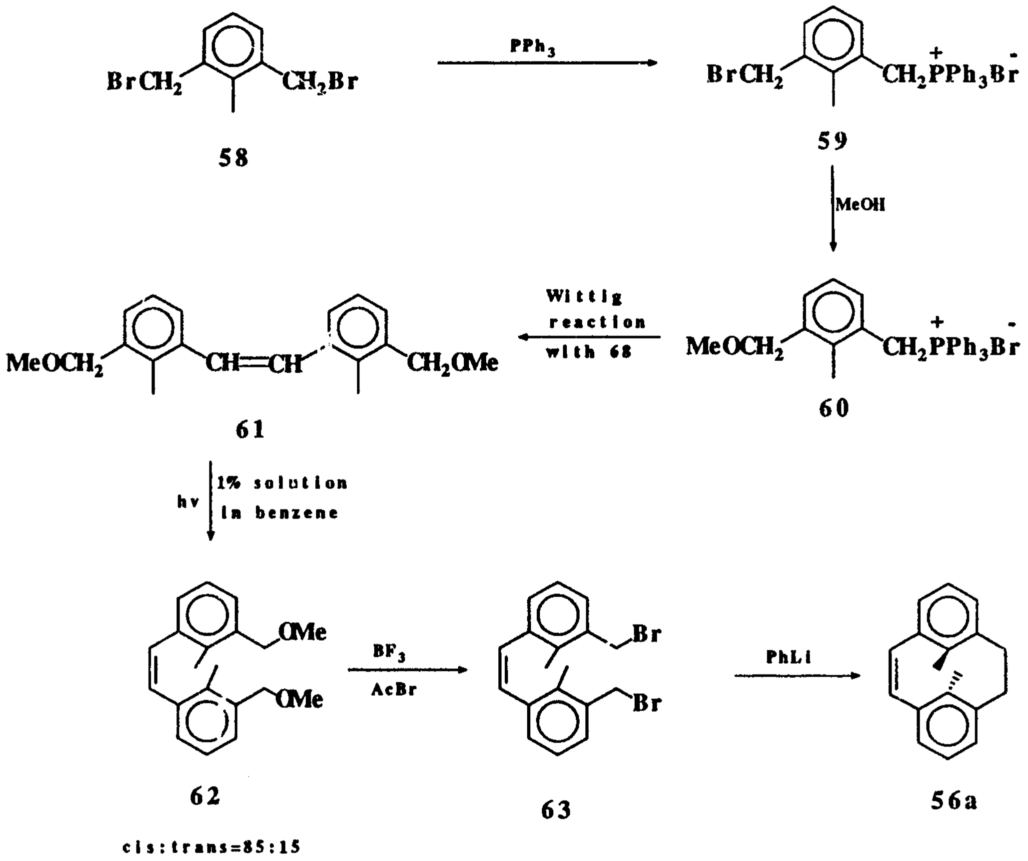
2.1 $[2_2]$Metacyclophanenes

2.1.1 Synthetic methods available for the cyclophanenes 56

The first synthetic route to **56a** was reported by Boekelheide in 1970,[65)] when alternative routes to dihydropyrenes were being investigated. Boekelheide prepared three cyclophanenes, **56a**, **56d**, and **56e** using the method shown in Scheme V, for **56a** as an example. This synthesis started with 2-chloro-6-nitrotoluene, which was converted in six steps to the key intermediate, 2,6-bis(bromomethyl)-toluene, **58**[66)] (see Scheme VI). This dibromide was then converted to the mono-triphenylphosphonium bromide **60** and to the mono-aldehyde **68** via the method shown in Scheme VII. The combination of **60** and **68** in a Wittig reaction, Scheme V, gave **61** as a mixture of the *cis* and *trans* isomers. Since the *cis* isomer is needed for cyclization in a later stage, the *trans* isomer of **61** was isomerized photochemically to the desired *cis*-**61**. Finally, coupling of the dibromide **63**, by a Wurtz reaction using phenyllithium, gave the cyclophanene **56a**. Similarly, cyclophanenes **56d** and **56e** were also synthesized in this way.

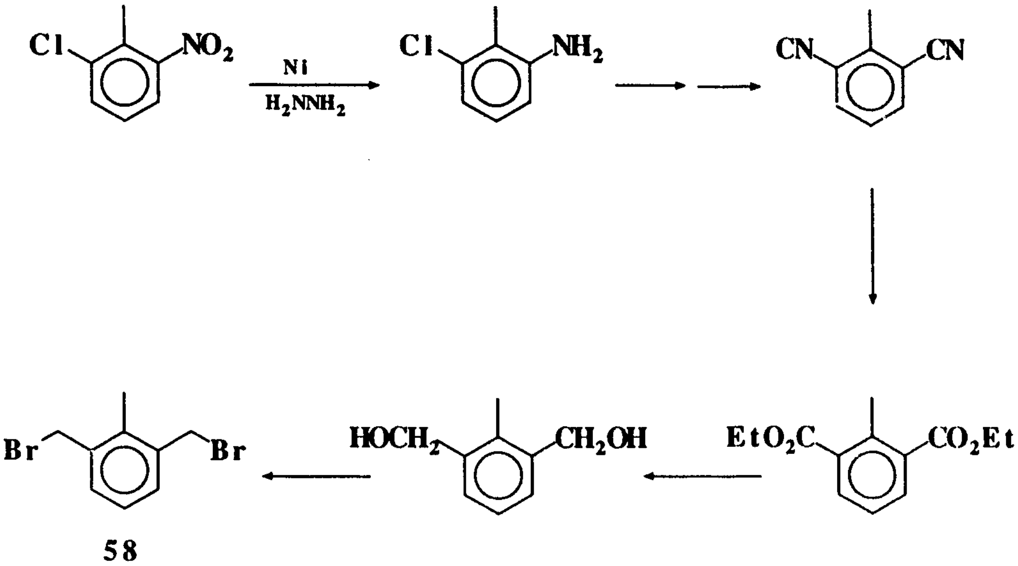
Although the above synthetic route was successful in the synthesis of three different cyclophanenes, it is

Scheme V:

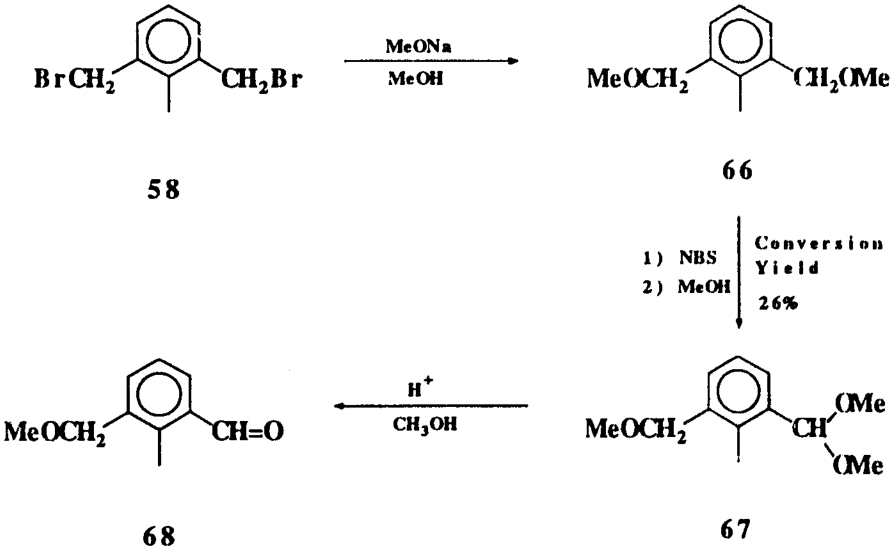


limited to preparation of the cyclophanene in small quantity. In the preparation of the mono-aldehyde **68**, Scheme VII, a low conversion yield of the acetal **67** to the ether **68** was obtained if formation of the undesired diacetal was avoided. Photoisomerization of *trans*-**61** to *cis*-**61** was achieved by irradiation in a 1% solution of **61** in benzene. Conversion of the *trans* isomer to the *cis* isomer on the

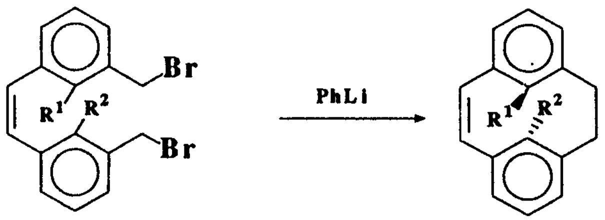
Scheme VI:



Scheme VII:



hundred-gram scale would thus be very tedious due to the dilute conditions necessary for this photoisomerization process. Moreover, the yields of the Wurtz coupling reactions of **63** in the final steps of this route were also generally low, (see below), especially for **56a** (10%), where the bulkier internal methyl groups probably introduce a large steric compression during the cyclization process. Due to these limitations, we decided to explore alternative preparations of the cyclophanenes.



63 **56**

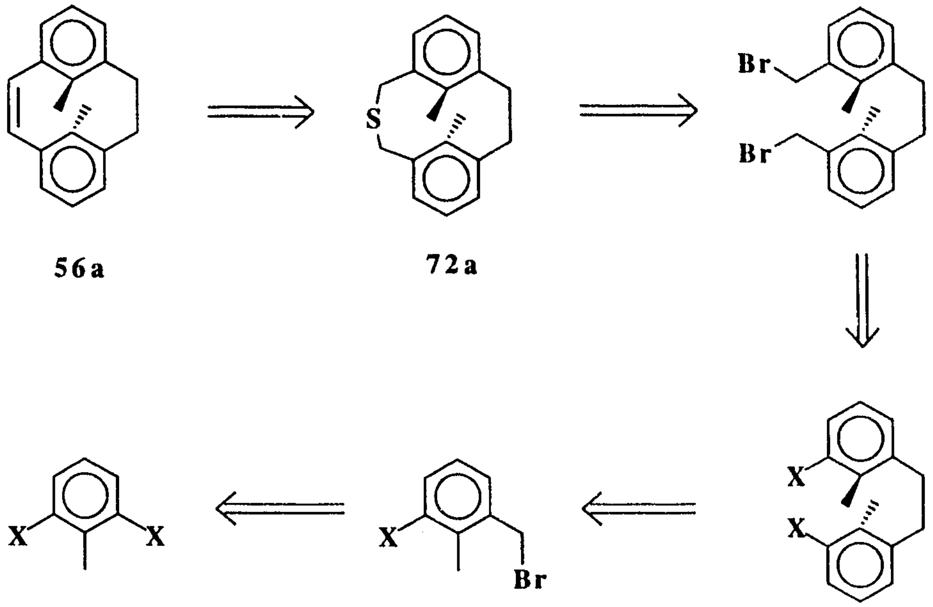
Yields

45%	56d	$R_1=R_2=H$
18%	56e	$R_1=CH_3$, $R_2=H$
10%	56a	$R_1=R_2=CH_3$

2.1.2 Investigation of a new synthetic route to 56

The target cyclophanenes have two different bridges -- a saturated ethano ($-CH_2-CH_2-$) bridge and an unsaturated etheno ($-CH=CH-$) bridge. These two bridges have to be constructed separately, because of the different synthetic

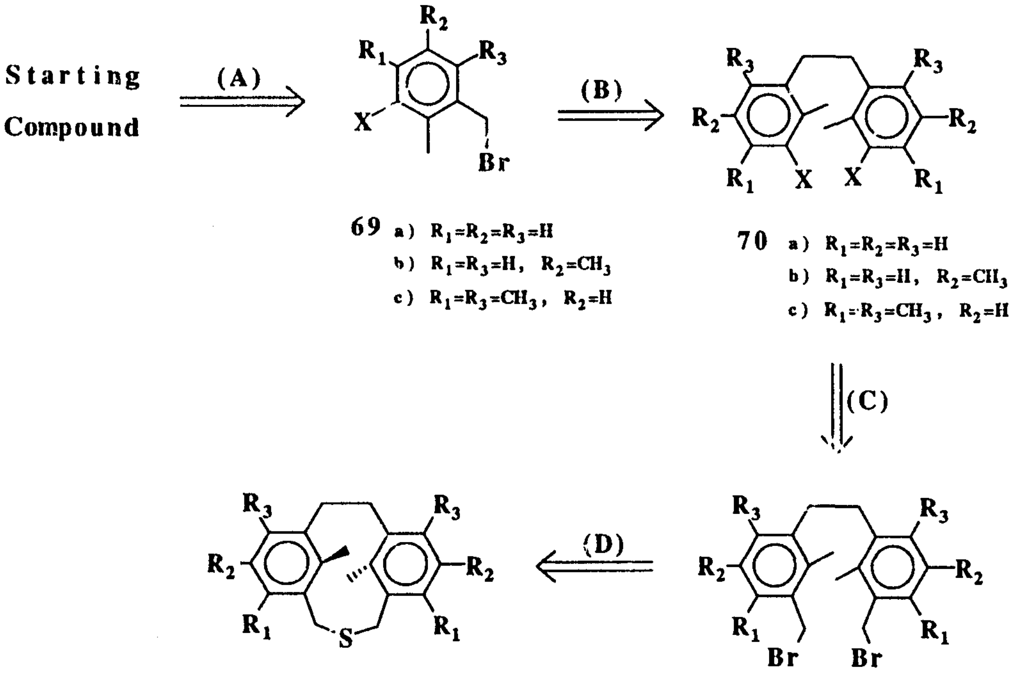
Scheme VIII:



routes used to obtain them. In Boekelheide's route, the etheno bridge was constructed first, using a Wittig reaction, and leads to a mixture of the two geometric isomers of **61**. However, only the *cis* isomer has the right geometry of the double bond for cyclization to **56**. The alternative route employs building the saturated ethano bridge first, and avoids this isomer problem, since there is free rotation about the bridge single bond. This was the route we investigated. A retrosynthetic analysis is presented in Scheme VIII using **56a** as an example. Since the dithiacyclophane route has been extensively used by our group in the synthesis of $[2_2]$metacyclophanedienes, which the valence isomers of the dimethyldihydropyrenes, it was expected that the monothiacyclophane **72a** would be a suitable precursor to **56a**, using a similar route to that in Scheme IV. Continued retrosynthetic analysis of **72a** would lead to one conclusion that an appropriate starting compound for **72a** is a 2,6-dihalogen-substituted toluene. This is now discussed in more detail.

2.1.3 Synthesis of the [2,3](1,3)monothiacyclophanes 72

Scheme IX:



69 a) $R_1=R_2=R_3=H$
b) $R_1=R_3=H$, $R_2=CH_3$
c) $R_1=R_3=CH_3$, $R_2=H$

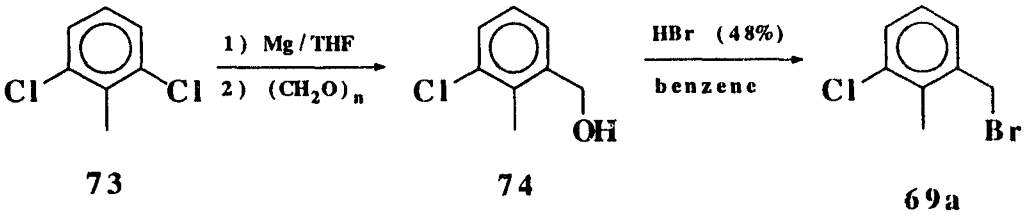
70 a) $R_1=R_2=R_3=H$
b) $R_1=R_3=H$, $R_2=CH_3$
c) $R_1=R_3=CH_3$, $R_2=H$

72 a) $R_1=R_2=R_3=H$
b) $R_1=R_3=H$, $R_2=CH_3$
c) $R_1=R_3=CH_3$, $R_2=H$

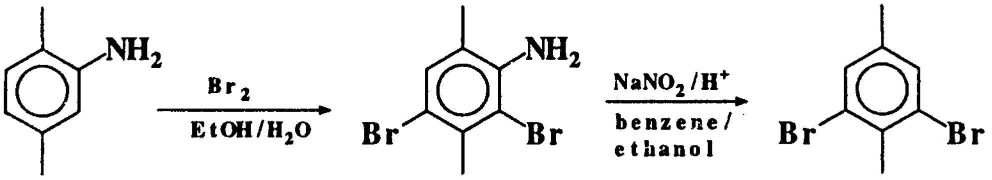
71 a) $R_1=R_2=R_3=H$
b) $R_1=R_3=H$, $R_2=CH_3$
c) $R_1=R_3=CH_3$, $R_2=H$

In this section, the syntheses of the three monothiacyclophanes, **72a**, **72b**, and **72c**, will be described together. In order to compare the differences and simplify the discussion, the total synthesis of **72** will be divided into four stages (see Scheme IX): (A) preparation of the benzyl bromide **69**; (B) coupling of **69** to give the dimer **70**; (C) conversion of the bromide **70** to the benzyl dibromide **71**; and finally, (D) cyclization of the dibromide **71** to the monothiacyclophanes **72**.

(A) Preparation of the benzyl bromides 69



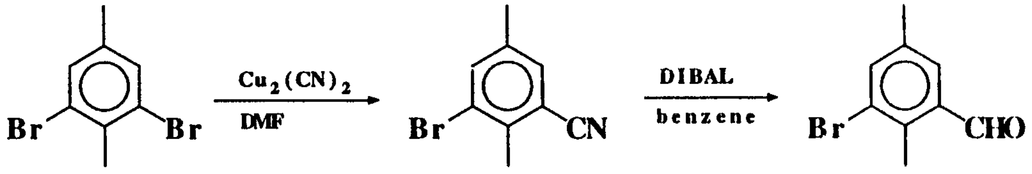
The compound **69a** (X=Cl) is easily prepared from commercially available 2,6-dichlorotoluene 73. First, a Grignard reaction of **73** with one equivalent of magnesium in dry THF and subsequent addition of paraformaldehyde to the resultant Grignard reagent gave the alcohol **74** in 70-80% yield. This was then converted to the desired bromide **69a** by refluxing in a mixture of aqueous HBr (48%) and benzene. It was found best to use the benzene solution of **69a**, so obtained after drying by azeotropic distillation, directly in the subsequent coupling reaction.



75 **76** **77**

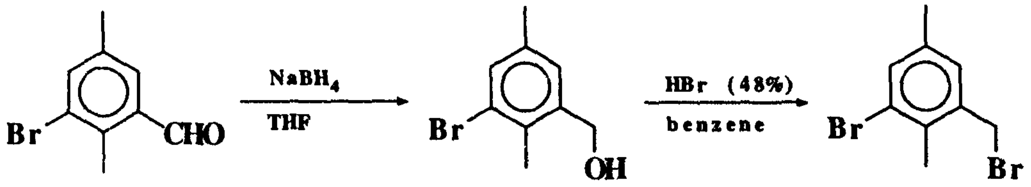
The preparation of **69b** (X=Br) proved to be the most difficult of the three bromides. Although its required precursor **77** is not commercially available, it could be readily prepared from 2,5-dimethylaniline, **75**, using the method reported.$^{67)}$ The xylidine **75** was brominated in aqueous alcohol to give the bromoaniline **76** in high yield (94%). Its ^{1}H nmr (90 MHz) spectrum showed a singlet at δ 7.22 and two singlets at δ 2.51 and 2.15. This indicated that only the dibromide **76** was obtained. Solid **76** was used directly in the subsequent deamination to give the dibromide **77** in 75% yield after vacuum distillation (133-136°C/ 13 mmHg), mp 58-59°C (lit. 61°C).

An attempt to form a mono-Grignard reagent from the dibromide **77** failed. Unlike the dichloride **73**, the dibromide **77** gives a mixture of mono- and di-Grignard with one equivalent of magnesium. The formation of the mono-lithiated reagent by lithium exchange with *n*-butyllithium at low temperature was also tried on **77** without success. The low selectivity of **77** in these reactions is probably due to the higher reactivity of the bromide compared to the dichloride **73**. Formation of a Grignard reagent should increase electron density in the aromatic ring which thus becomes less reactive towards formation of the second Grignard reagent in the same ring, as is the case with the dichloride **73**. However, the bromide is too reactive towards magnesium, and formation of the di-Grignard is unavoidable under the mildest condition (diethyl ether as a solvent at room temperature).



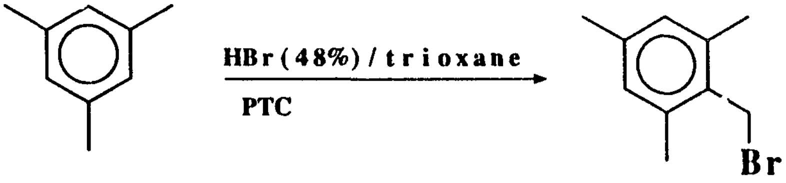
77 **78** **79**

Conversion of the dibromide **77** to the benzylic alcohol **80** was achieved, however, through the cyanide route. Reaction of aryl bromides with cuprous cyanide proceeds rapidly and efficiently in refluxing dimethylformamide (DMF).$^{68)}$ However, reaction of **77** with cuprous cyanide in DMF at reflux gave a mixture of mono- and dinitrile. The required mononitrile **78** could be easily separated from the dinitrile by column chromatography. A high conversion yield of **77** to **78** was obtained by using half an equivalent of cuprous cyanide to minimize the formation of the dinitrile. The unreacted dibromide **77** in the reaction was completely recovered by column chromatography. In a typical experiment using 0.5 equivalent of cuprous cyanide, the reaction gave 40-44% of the mononitrile **78**, mp 74-75°C, 3-5% of the 2,6-dinitrile, mp 171-172°C, and 48-53% of unreacted **77**; with one equivalent: 50-52% of **78**, 22-24% of the dinitrile, and 16-17% of the unreacted dibromide. The ir spectrum of **78** showed the CN stretch at 2132 cm^{-1} and the ^{1}H nmr spectrum gave two singlets at δ 7.57 and 7.35 from the two different aromatic protons. The ^{13}C nmr spectrum of **78** showed seven different unsaturated carbons, and its ms gave a molecular ion at *m/e* 209, and 211, correct for one bromine atom per molecule. Reduction of **78** with diisobutylaluminium hydride (DIBAL) in benzene gave a 97% yield of the monoaldehyde **79** as a liquid, bp 116-117°C/2.5 mmHg. In the ^{1}H nmr spectrum of **79**, the aldehyde proton appeared at δ 10.2 and its mass spectrum gave the MH$^+$ peak at *m/e* 213 with the correct isotope pattern. It was found that **79** was readily oxidized to the carboxylic acid when it was exposed to air.



79 **80** **69b**

Further reduction of monoaldehyde **79** with sodium borohydride in THF gave the alcohol **80** in almost quantitative yield, mp 89-90°C. Its ^{1}H nmr spectrum unusually showed the OH proton at δ 1.54 (J = 5.8 Hz) as a triplet due to the coupling with the methylene protons, which appeared as a doublet at δ 4.67. Its ir spectrum showed a characteristic OH stretch at 3240 cm^{-1} and the mass spectrum gave the MH$^+$ peak at *m/e* 215. Finally, the alcohol **80**, on refluxing with aqueous HBr (48%) and benzene, gave a 97% yield of the desired benzyl bromide **69b**, mp 51-52°C. Its ^{1}H nmr spectrum showed the methylene protons at δ 4.47. The mass spectrum showed the parent peak at *m/e* 277 with 1:2:1 isotope pattern, correct for two bromine atoms.

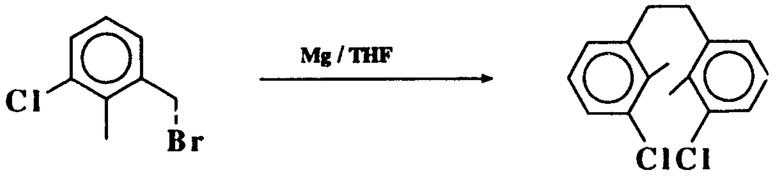


81 **69c**

The preparation of **69c** (X=H) was achieved in a single step by direct bromomethylation of mesitylene using trioxane (1 equivalent) and aqueous HBr (48%)at 80-90°C in the presence of myristyltrimethylammonium bromide as a phase transfer catalyst.$^{69)}$ An 85% yield of **69c**, mp 49-50°C (lit. 49.5-50.5°C),$^{70)}$ was obtained. In its ^{1}H nmr spectrum, the aromatic protons appeared as a singlet at δ 6.84 and the methylene protons also as a singlet at δ 4.55. The mass spectrum showed a weak molecular ion at *m/e* 212 with a 1:1

isotope pattern.

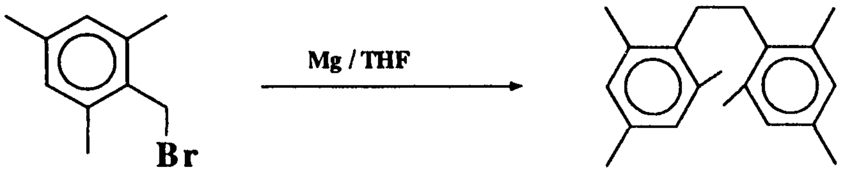
(B) Coupling of the benzyl bromides 69 to give the dimers 70



69a **70a**

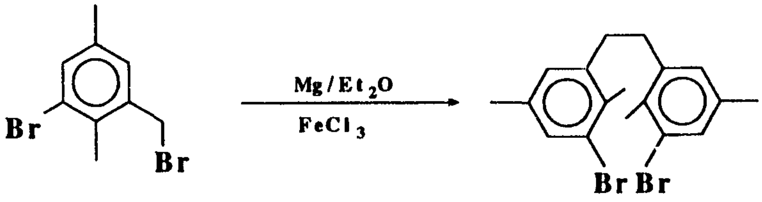
Reaction of a benzyl bromide with magnesium metal does not stop at the Grignard reagent, but forms a dimer as the newly formed Grignard reacts with a second molecule of the benzyl bromide.(71) This self-coupling reaction is employed here for the preparation of the dimers **70** -- derivatives of diphenylethane. When two equivalents of the bromide **69a** (obtained as a benzene solution) were treated with one equivalent of magnesium in THF at about room temperature,(a) the dimer **70a** was obtained in 88% yield as a white powder, mp 108-109°C. Its ^{1}H nmr spectrum showed the methylene protons at δ 2.87 as a singlet. Its mass spectrum gave a very weak molecular ion at *m/e* 278 and a base peak at *m/e* 139, corresponding to the fragment of half mass.

(a) *Once the reaction was initiated by warming the mixture, it was found better to maintain the reaction close to room temperature to prevent formation of an arylmagnesium chloride, as the formation of benzylmagnesium bromide catalyzed formation of the undesired arylmagnesium chloride.*



69c **70c**

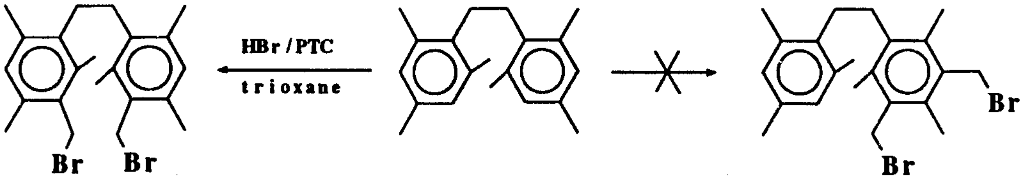
Similarly, an almost quantitative yield of the dimer **70c** (X=H), mp 113-114°C, was obtained by the reaction of the benzyl bromide **69c** with magnesium in refluxing THF. The methylene protons of **70c** appeared as a singlet at δ 2.77 in its ^{1}H nmr spectrum. The mass spectrum showed a weak molecular ion at *m/e* 266 and a base peak of half mass at *m/e* 133.



69b **70b**

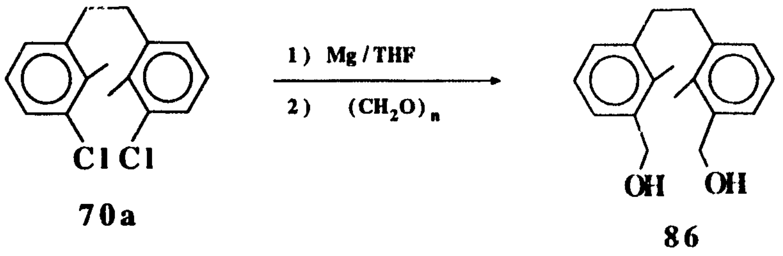
The Grignard coupling of **69b** (X=Br), however, failed under the same reaction conditions used for **69a** and **69c**. It was found that the formation of the benzylmagnesium bromide catalyzes the Grignard reaction of the arylbromide even when diethyl ether is used as a solvent at room temperature. It was known that a transition metal halide such as ferric chloride can speed up the Grignard coupling reaction.40) Thus, the solution of the benzyl bromide **69b** with magnesium metal (0.5 equivalent) in diethyl ether was warmed to initiate the reaction, and then a catalytic amount of anhydrous ferric chloride was quickly added, whereupon a 93% yield of the dimer **70b** (X=Br) as a white solid, mp 169-170°C could be obtained. In the ^{1}H nmr spectrum of **70b**, the aromatic protons appeared as two singlets at δ 7.26 and 6.85 and the methylene bridge protons appeared as a singlet at δ 2.79. The mass spectrum showed a very weak molecular ion at *m/e* 395. A satisfactory elemental analysis **70b** was also obtained.

(C) Conversion of 70 to the benzyl dibromide 71



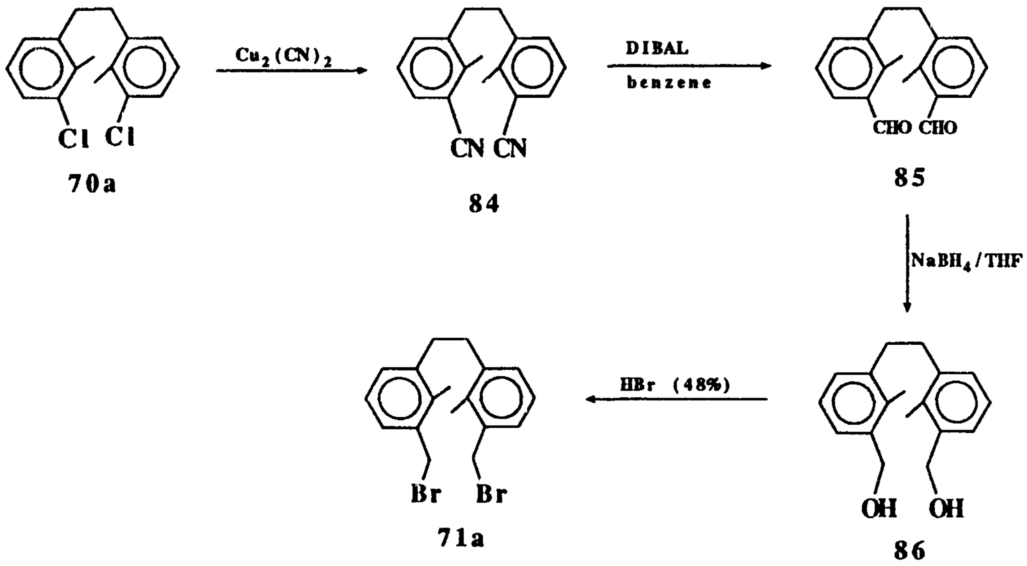
71c **70c** **83**

Conversion of **70c** to the dibromide **71c** was achieved by direct bromomethylation of **70c** using the same conditions as for the preparation of **69c**. Since compound **70c** is symmetrical, bromomethylation at either of the *meta* positions to the ethano bridge will result in the formation of **71c**. Indeed, reaction of **70c** with two equivalents of trioxane gave the desired dibromide **71c**, mp 244-246°C, in 85% yield. The aromatic protons, the methylene protons ($-CH_2Br$), and the bridge protons all appeared as singlets at δ6.85, 4.57, and 3.47, respectively, in the ^1H nmr spectrum. The mass spectrum gave a weak MH^+ peak at *m/e* 451 with a base peak at *m/e* 371 (1:1 isotope pattern), corresponding to loss of one bromine atom. Both the ^1H nmr spectrum, which showed three types of methyl protons with a 1:1:1 ratio, and the ^{13}C nmr spectrum, which showed six different aromatic carbon peaks, indicated that bis-bromomethylation on the same benzene ring to give **83** rather than **71c** did not occur here. The first bromomethyl substituent introduced evidently decreases the reactivity of that ring towards further bromomethylation in this case.



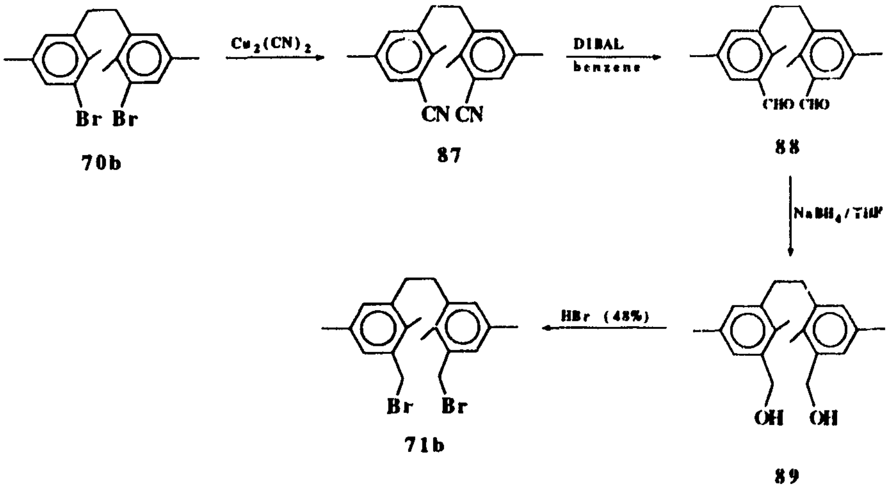
Conversion of the dichloride **70a** to the dibromide **71a** was first tried through the di-Grignard reaction. It was found that the di-Grignard was generated by reaction of **70a** with two equivalents of magnesium in refluxing THF, which after addition of paraformaldehyde, gave a mixture which contained the diol **86**. Although **86** could be obtained from the mixture in low yield (30-40%), the separation was very difficult due to the low solubility of each component. Also, formation of the di-Grignard reagent was found to be incomplete even after the mixture was refluxed for two days.

Scheme X:



An alternative route to **71a** via the dinitrile proved to be better even though more steps were involved (see Scheme X). The dichloride **70a** was transformed into the dinitrile **84** by refluxing with cuprous cyanide in N-methyl-2-pyrrolidinone. The reaction mixture was effectively decomposed by addition of aqueous ethylene diamine. After column chromatography, the dinitrile **84** was obtained as a white solid in 84% yield, mp 204-205°C. Its ir spectrum showed a strong CN stretching band at 2224 cm^{-1} and the mass spectrum (CI) gave a very strong MH$^+$ peak at *m/e* 261. Treatment of **84** with DIBAL in benzene gave an 84% yield of the aldehyde **85** as a yellowish powder, mp 116-117°C. The structure of **85** was evident from the aldehyde protons at δ 10.29 in its ^{1}H nmr, a strong absorption of the carbonyls at 1688 cm^{-1} in the ir spectrum. The mass spectrum showed a MH$^+$ peak at *m/e* 267 (CI). The subsequent reduction of **85** with $NaBH_4$ in THF, yielded the diol **86** in almost quantitative yield, mp 156-158°C (lit. 158-160°C).40) On refluxing with aqueous HBr (48%), the alcohol **86** was finally converted to the desired bromide **71a** in 93% yield, mp 140-142°C (lit. 142-143°C).40) The methylene protons of the CH_2Br group appeared as a singlet at δ 4.54 in the ^{1}H nmr spectrum.

Scheme XI:

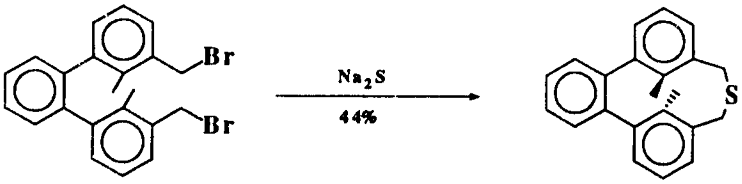


The dibromide **71b** was also prepared via this dinitrile route as shown in Scheme XI. Usually a bromide is more reactive than a chloride in a cyanation reaction as seen from the lower temperature used in the preparation of the mononitrile **79**. However, treatment of **70b** with cuprous cyanide in refluxing DMF did not give the dinitrile **87** but instead unreacted **70b** was recovered. The low reactivity of **70b** may be due to the lack of electron-withdrawing substituents, which are known activating groups in this reaction. With the use of N-methyl-2-pyrrolidinone (bp 202°C) as the solvent, **70b** was successfully converted to the dinitrile **87** in 96% yield, mp 206-207°C. Its ir spectrum showed the characteristic CN stretch at 2223 cm^{-1} and the mass spectrum gave a strong molecular ion at *m/e* 289 (CI). Reaction of **87** with DIBAL in benzene, gave an 82% yield of the aldehyde **88**, mp 142-144°C. In the ^{1}H nmr spectrum, the aldehyde protons appeared as a singlet at δ 10.28 and the *ortho* aromatic protons, deshielded slightly by the carbonyl groups, appeared at δ 7.49. The ir spectrum showed a strong carbonyl absorption band at 1670 cm^{-1} and the mass spectrum (CI) gave a base MH$^+$ peak at *m/e* 295. The aldehyde **88** was further reduced with NaBH$_4$ to the diol **89** in almost quantitative yield, mp 174-175°C. Its ^{1}H nmr spectrum also showed coupling (J=5.7 Hz) between the O$\underline{H}$ protons (δ 1.48) and the adjacent methylene protons (δ 4.68). The ir spectrum showed the characteristic OH stretch centred at 3330 cm^{-1}. The mass spectrum did not give a molecular ion peak, but a base peak at *m/e* 282 corresponding to loss of one H_2O molecule was observed.

The desired dibromide **71b** was obtained in 95% yield by refluxing **89** in aqueous HBr (48%), mp 178-179°C. In its ^1H nmr spectrum, the methylene protons (CH_2Br) appeared as a singlet at δ 4.51. The mass spectrum showed no molecular ion peak but a base peak at *m/e* 343 was observed with 1:1 isotope pattern, corresponding to loss of one bromine atom.

(D) Cyclization of 71 to give the monothiacyclophanes 72

Thiacyclophanes such as the thiacyclophane **47** were first made by the coupling of dihalides with sodium sulphide.[57, 60)] In this method, the coupling reaction was carried out using a two funnel technique, i.e., a solution of the halide in benzene in one funnel and a solution of sodium sulphide in aqueous ethanol in the second funnel were added dropwise simultaneously, and at the same rate, to a large quantity of ethanol. A good yield was obtained by maintaining very low concentrations of the halide and sodium sulphide in the reaction mixture at all times. The slow addition of both solutions and the large amount of solvent used in the flask meet the high dilution conditions that are required to avoid the formation of undesired polymers. This sodium sulphide coupling, under high dilution conditions, has also been used successfully for the preparation of the monothiacyclophane **91**.[72)]

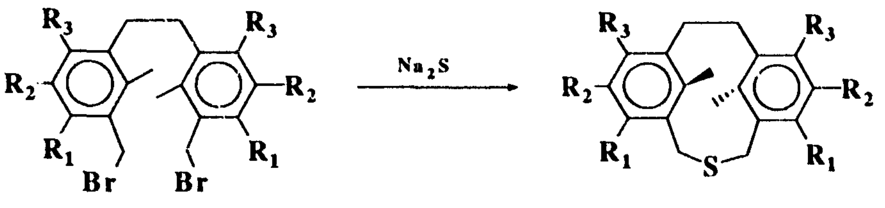


90 **91**

However, a problem arose when this coupling method was tried for preparations of monothiacyclophanes **72**. It was found that the solubility of the bromides **71**, especially the bromide **71c**, was very low in benzene as well as in most other solvents. Thus, we modified the technique by using solid **71** directly instead of a solution. Since the dibromide **71** is very insoluble, it was thought that the dilution condition necessary would be effectively obtained by using a suspension of the bromide **71**, in that the concentration of the dissolved bromide **71** would be low as required for the coupling, but would remain constant due to the saturation process.

$$\text{Solid 71 (suspended)} \rightleftharpoons \text{Dissolved 71 (in solution)} \xrightarrow{Na_2S} \text{Thiacyclophane}$$

After several trials, an appropriate solvent system was found for the coupling of each of the bromides **71**. High yields of the monothiacyclophanes **72** were obtained by slow



71 a) $R_1=R_2=R_3=H$
b) $R_1=R_3=H,\ R_2=CH_3$
c) $R_1=R_3=CH_3,\ R_2=H$

72 a) $R_1=R_2=R_3=H$
b) $R_1=R_3=H,\ R_2=CH_3$
c) $R_1=R_3=CH_3,\ R_2=H$

addition of a solution of sodium sulphide in aqueous ethanol to the suspension of the corresponding bromide **71** in a mixture of several solvents at room temperature (see Table 3).

Table 3. The solvent system used in the coupling of the bromide **71** with sodium sulphide

Bromides **71**	solvents used water:ethanol:benzene	yields of **72**(%)
71a	23 : 77 : 0	66
71b	16 : 70 : 14	83
71c	12 : 63 : 25	72

After column chromatography, each of the monothiacyclophanes **72** was obtained as white crystals which were found to be only the *anti*-isomers in each case. This was clearly indicated by their ^1H nmr spectra in which the internal methyl groups appear at about δ 0.8 due to the shielding effect of the opposite deck. The properties and some of the spectroscopic data of the monothiacyclophanes **72** are summarized in Table 4.

Table 4. The properties and spectroscopic data of the monothiacyclophanes **72**

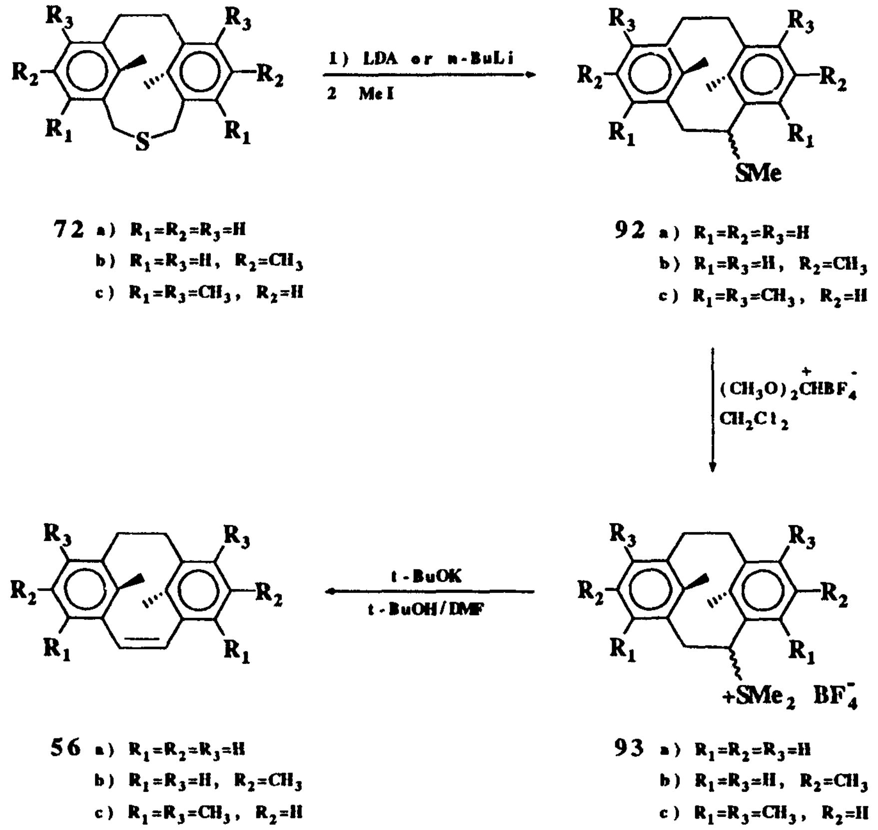
	72a	**72b**	**72c**
mp (°C)	171-173	175-176	208-210
MS (*m/e*)	268 (M^+)	297 (MH^+)	325 (MH^+)
^1H nmr (δ)			
int. Me	0.85	0.84	0.81
CH_2SCH_2	3.85 (A)	3.80 (A)	3.82 (A)
	3.73 (B)	3.70 (B)	3.70 (B)
J (Hz)	13.9	13.9	13.5
CH_2-CH_2	2.94 (AA')	2.85 (AA')	3.02 (AA')
	2.64 (XX')	2.60 (XX')	2.51 (XX')
J (Hz)	12.6; 12.4	12.5; 12.5	13.3; 12.8
	4.5; 2.6	4.4; 2.7	4.2; 3.0

2.1.4 Syntheses of the [2_2]metacyclophanenes 56

With the desired precursors to the cyclophanenes **56** now at hand, the conversion of **72** to **56** was then achieved by employing the Wittig rearrangement-Hofmann elimination sequence, which has been used previously in preparations of cyclophane-dienes such as **51b** (see Scheme IV). Wittig rearrangement of **72** using freshly prepared LDA, or *n*-butyllithium in the case of **72a**, as the base in THF, proceeded well at room temperature and gave, in each case, a quantitative yield of the ring contracted product **92** (see Scheme XII).

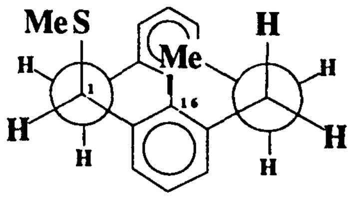
As we expected, the sulphide **92** was found to be a mixture of two stereoisomers which differ from each other only in the orientation of the $-SCH_3$ group on C-1. One isomer of **92** has a pseudo-equatorial $-SCH_3$, while the other has a pseudo-axial $-SCH_3$ on the bridge carbon-1. For characterization, the two isomers of **92a** were separated by column chromatography on silica gel using petroleum ether as the eluent. Eluted first was the equatorial isomer, **eq-92a**, and next was the axial isomer, **ax-92a**. The assignment of **eq-92a** and **ax-92a** as the isomer with an equatorial and an axial $-SCH_3$ was made on the basis of their ^{1}H nmr spectra. The internal methyl protons of **ax-92a** appear separated from each other by 0.35 ppm. The internal methyl on C-16 is spatially closer to the axial $-SCH_3$ group and hence is sterically

Scheme XII:

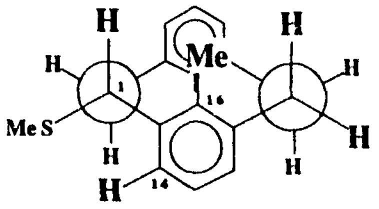


deshielded by this -SCH_3 group. In the ^1H nmr spectrum of **eq-92a**, no large separation of the two internal methyl protons ($\Delta\delta$=0.02) was observed, but instead a deshielding was seen for the proton H-14. In this case the equatorial -SCH_3 group is spatially closer to H-14 but away from the internal methyl on C-16.

The stereoisomers **eq-92b** and **ax-92b** were also separated using column chromatography on silica gel with petroleum ether and dichloromethane (10:1) as eluent. The structures



ax-92a



eq-92a

of **eq-92b** and **ax-92b** were confirmed by their mass and ^{1}H nmr spectra (see Table 5).

The separation of **eq-92c** from **ax-92c** by column chromatography was tried without success. A pure sample of **eq-92c** was obtained as the by-product in the Hofmann elimination of the sulfonium salt **93c**. Table 5 shows some of the properties and ^{1}H nmr features of these equatorial and axial-isomers of the sulphide **92**.

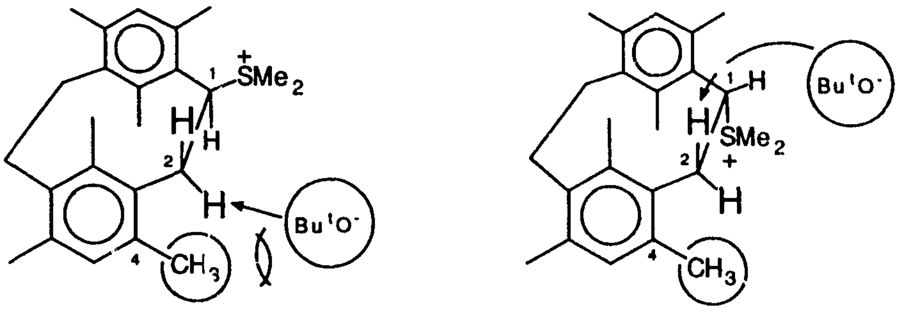
Table 5. The properties and ^{1}H nmr features of **92**

Compd	mp(°C)	MS(*m/e*)	^{1}H nmr (δ)		
			int. Me	-SMe	H-14
eq-92a	95- 96	283(MH$^+$)	0.59, 0.57	2.12	7.70
ax-92a	156-157		0.88, 0.53	2.18	7.26
eq-92b	114-115	311(MH$^+$)	0.60, 0.58	2.13	7.47
ax-92b	176-177		0.89, 0.54	2.20	7.05

eq-92c	142-143	338(M^+)	0.57, 0.56	2.25
ax-92c	---		0.79, 0.41	2.21

For preparations of the cyclophanenes **56**, the mixture of the two isomers of each sulphide **92** was methylated using dimethoxy-carbonium fluoroborate (Borch reagent)[73] in dry dichloromethane to give the sulfonium fluoroborate 93 in high yield. Treatment of the sulfonium salt **93a** or **93b** with potassium t-butoxide in a mixture of t-butanol:DMF (1:1) at room temperature gave the corresponding cyclophanene **56a** or **56b** in high yield. The yield of **56c** from salt **93c** was only moderate under the same conditions. Considering that an E1cb elimination requires an *anti* or *syn* relationship between the β-proton and the leaving group, the base t-BuO$^-$ will prefer to attack the equatorial and the axial proton H-2 in **eq-93c** and **ax-93c** respectively. The approach of the bulkier t-BuO$^-$ to the equatorial H-2 in **eq-93c** is hindered by the external methyl group on C-4, whereas access to axial H-2 in **ax-93c** is not blocked by that methyl group. Therefore, elimination of the SMe$_2$ from the salt **ax-93c**, which is the minor product (28%), should be easier and faster than that from the salt **eq-93c** under the same conditions. This explanation accounts for the fact that 26% of the sulphide **eq-92c** was recovered after the elimination but no **ax-92c**. The sulphide **eq-92c** might be formed from transferring one methyl carbocation of

eq-93c to the solvent and this transferring process proceeded at a competitive rate, compared with the slow elimination of SMe_2 which leads to the desired product.



eq-93c ax-93c

Figure 6. Steric hindrance in the elimination of SMe_2 from **eq-93c**

The cyclophanene **56a** prepared by this method has exactly the same properties as those previously reported by Boekelheide.[65)] In its ^1H nmr (360 MHz) spectrum, the olefinic protons H-1 and H-2 appeared as a singlet at δ 6.59 (lit. 6.60 in CCl_4)[65b)] and the internal methyl protons also as a singlet at δ 0.76 (0.79). The structures of **56b** and **56c** were also confirmed by their mass spectra, with correct molecular ion peaks, and their ^1H nmr spectra in which the olefinic protons and the internal methyl protons appeared in the same region as the corresponding protons in **56a**. For comparison, some properties and spectroscopic data of cyclophanenes **56** are summarized in Table 6.

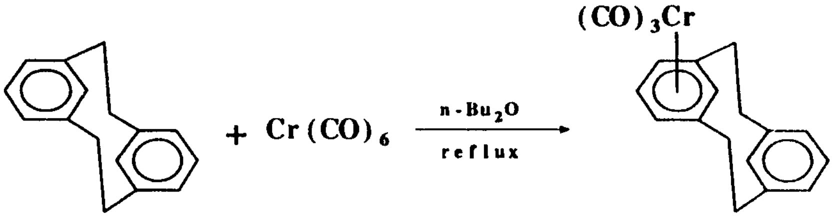
Table 6. The properties and spectroscopic data of **56**

Compound	**56a**	**56b**	**56c**
mp(°C)	148-150	151-152	>220(decomp)
	(lit. 151-152)[65b]		
MS(*m/e*)	235(MH^+)	263(MH^+)	291(MH^+)
UV ($\lambda_{max}(\varepsilon)$)	212(36,000)	203(42,000)	205(43,000)
	225(24,000)	214(37,000)	217(44,000)
	307(2000)	260(28,000)	260(29,000)
		301(1900)	309(2400)
^{1}H NMR (δ)			
H-1/2	6.59	6.54	6.64
int. Me	0.76	0.73	0.63
CH_2-CH_2	2.89(AA′)	2.81(AA′)	3.06(AA′)
	2.50(XX′)	2.48(XX′)	2.17(XX′)
J(Hz)	12.2; 12.1	12.2; 12.1	13.1; 12.0
	3.9; 2.8	3.9; 2.8	4.0; 3.0

2.2 Cyclophanene Metal Complexes

2.2.1 Cyclophane metal complexes

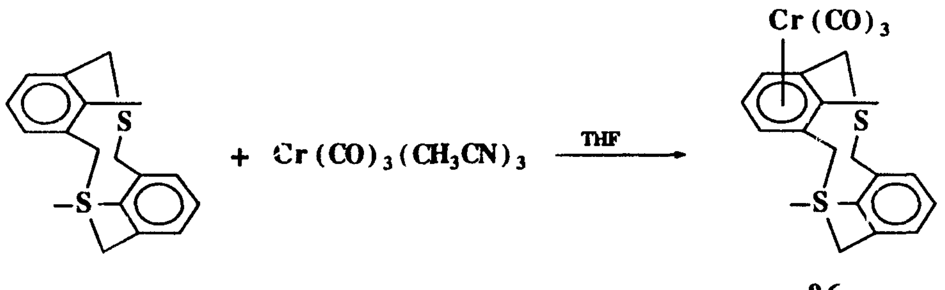
In the last decade, arene-metal complexes of cyclophanes have attracted much attention because of the interest in their crystal structures[74] and their NMR spectra with regard to the anisotropic effect of the metals.75) The most widely used transition metals in such complexes are chromium, iron, and ruthenium. The Cr(CO)$_3$ complexes of the cyclophanes are prepared mostly by the reaction of a cyclophane and Cr(CO)$_6$ in a high-boiling-point solvent such as dibutyl ether.76) Although the yields of complexes are low in many cases, this method is still widely used because of its simplicity.



7 **94**

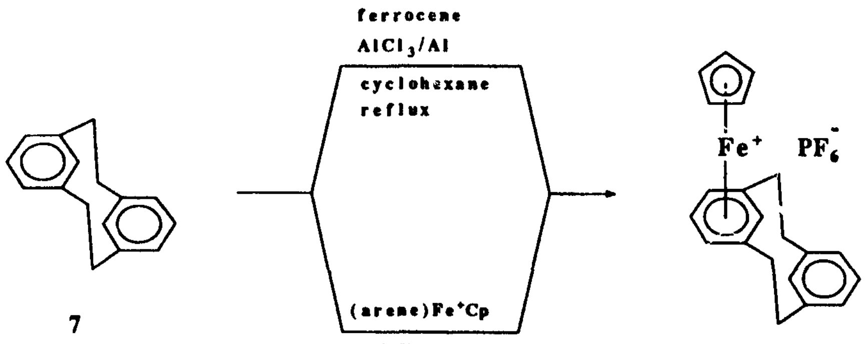
The thermal replacement of a more labile ligand L from a complex of the type [Cr(CO)$_3$L$_3$] (L=pyridine,77) acetonitrile,78) ammonia79)) is another method of choice to make the Cr(CO)$_3$ complexes. This method is superior to that using chromium hexacarbonyl in situations where the complex decomposes at the relatively high temperatures (>100°C) involved. One good example using this mild method is the preparation of the dithiacyclophane-Cr(CO)$_3$ complex **96**, which could not be obtained by simply refluxing **95** and Cr(CO)$_6$ in n-butyl ether.80)

More recently, charged iron and ruthenium complexes of



95 **96**

cyclophanes have been actively studied, partly because of their interesting electronic properties. η^5-Cyclopentadienyliron complexes of cyclophanes are synthesized by arene-metal exchanges with ferrocene derivatives, effected either photochemically[81] or thermally in the presence of Lewis acid catalysts[82] (the Nesmeyanov procedure.[83]). The synthesis of the CpFe$^+$ complex of **7** is shown as an example.



7 **97**

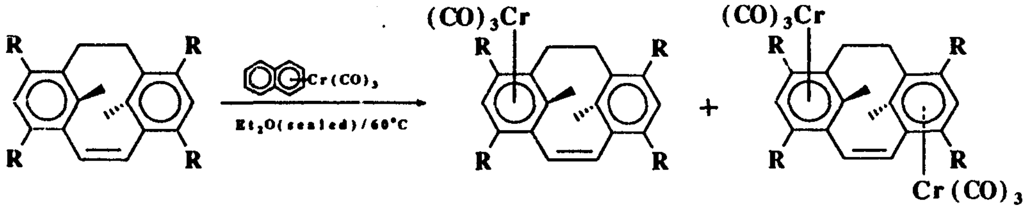
Under photochemical conditions, the ferrocene derivatives used are the η^6-*p*-xylene-η^5-cyclopentadienyliron, **103**, or the η^6-*p*-chlorotoluene-η^5-

cyclopentadienyliron, **104**, cations. The latter was found better in some cases because of the electron-withdrawing chloro substituent.[84)]

All the $CpFe^+$ complexes made by either of the methods were obtained as hexafluorophosphate salts, which are soluble only in solvents such as dichloromethane, acetone, and acetonitrile.

2.2.2 Syntheses of cyclophanene chromiumtricarbonyl complexes

As we have seen above, the thermal replacement of a mobile ligand from a complex of the type $[Cr(CO)_3L_3]$ is a very mild reaction. Recently, use of tricarbonylchromium-naphthalene as the $Cr(CO)_3$ source in the thermal replacement reaction has been reported.[85)] It has been found that naphthalene exchange using the naphthalene-$Cr(CO)_3$ complex, **98**, outperforms other precursors such as $Cr(CO)_3L_3$ (L=ammonia, acetonitrile) in preparations of some arene-tricarbonylchromium complexes. So for us, the naphthalene-chromium complex appears to be a suitable reagent for preparations of the $Cr(CO)_3$-cyclophanene complexes under mild conditions. The naphthalene-$Cr(CO)_3$ complex **98** was prepared by the literature method.[86)] We found that addition of 5% THF to the reaction mixture of $Cr(CO)_6$ and naphthalene in $n\text{-}Bu_2O$ sped up the reaction. After column chromatography under nitrogen, pure **98** was obtained in low yield as red crystals, which are quite stable under nitrogen at room temperature.



56 a) R=H
c) $R=CH_3$

99 a) R=H
c) $R=CH_3$

100 a) R=H
c) $R=CH_3$

The arene-exchange reaction of **98** with cyclophanenes **56** was carried out in ether at 60°C under presure in a sealed tube. The mixture of **98** and **56c** (molar ration 3:1), for example, in deaerated diethyl ether and THF (20%) was heated with an oil bath to 60°C for 20 h. The nearly insoluble bis-chromium complex **100c** precipitated from the reaction mixture and was collected by filtration. Recrystallization from dichloromethane and hexane gave pure **100c** as an orange solid.[a)]

The filtrate containing the mono-chromium complex **99c** was evaporated and then the residue was chromatographed under nitrogen to give **99c** as a red solid. Similarly, the mono- and bis-chromium complexes **99a** and **100a** were also synthesized by the same procedure (see Table 7).

[a)] *The complex **100c** was first dissolved in minimum amount of dichloromethane and then hexane was added to this resultant solution to cause **100c** to precipitate.*

Table 7. Properties of the mono- and bis-chromium complexes **99** and **100**

Compound	mp (°C)	MS (*m/e*)	yield (%)
99a	178-179	371 (MH$^+$)	38
100a	>245 (decomp.)	507 (MH$^+$)	57
99c	196-198	427 (MH$^+$)	16
100c	267-268	563 (MH$^+$)	66

The structure of **100a** was assigned on the basis of its ^{1}H nmr spectrum, in which all aromatic protons appeared at δ 5.45-5.28, indicating that both benzene rings were complexed by the Cr(CO)$_3$ moiety. The upfield shift (in the range of $\Delta\delta$ 1.6-1.8) probably results from a combination of effects including quenching of the ring current, withdrawal of electron density from the ring by the Cr(CO)$_3$ moiety, the magnetic anisotropy of the chromium-ligand bond, and partial rehybridization of the ring carbon atoms.[76d)] The olefinic protons (H-1 and H-2) and the internal methyl protons appeared at δ 6.65 and 1.11, respectively, both as singlets, consistent with a symmetrical structure. Notably both types of protons are slightly less shielded compared to the chemical shift values of δ 6.59 and 0.76 for the corresponding protons in the parent cyclophanene **56a**. This downfield shift might arise from a net result of the two main opposing effects: (a) an upfield shift caused by the $Cr(CO)_3$ complexed to the ring attached to these protons and (b) a downfield shift caused by the reduced ring current in the opposite $Cr(CO)_3$ coordinated ring (hence reduced shielding). The large shift (Δ=0.35 ppm) for the internal methyl protons and small value (Δ=0.06 ppm) for the olefinic protons clearly reflects the fact that the internal methyls extend over the shielding zone of the opposite ring while the olefinic protons may be just at the edge of this shielding zone. The weak MH^+ peak in its mass spectrum and strong absorptions of CO in its ir spectrum also confirmed the structure of **100a**.

The ^1H nmr spectrum of **100c** showed similar features to that of **100a** (see Table 8). The olefinic protons appeared as a singlet at δ 6.69, showing a very small downfield shift (Δ=0.05 ppm) compared to the value of δ 6.64 in the parent **56c**. The internal methyl protons appeared at δ 1.11 and were less shielded by 0.48 ppm compared to δ 0.63 in **56c**. The aromatic protons H-5 and H-13 appeared as a singlet at δ 5.06, an upfield shift of 1.62 ppm compared to the chemical shift of δ 6.68 in **56c**. The mass spectrum of **100c** gave a weak MH^+ peak at *m/e* 427.

The structures of the mono-chromium complexes **99a** and **99c** were indicated by the base MH^+ peak at *m/e* 371 and 427 in their mass spectra respectively. The ^1H nmr spectra of

Table 8. Some features of ^1H nmr spectra of **99** and **100**

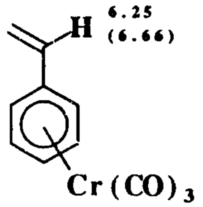
Compd	H-1/H-2	H-4,5,6/H-12,13,14	CH_3-C_8/CH_3-C_{16}
99a	6.88/6.55	5.44-5.22/7.03-6.96	0.51/1.33
100a	6.65	5.45-5.28	1.20
56a	6.59	7.01-6.84	0.76
99c	6.95/6.36	5.10a)/6.72b)	0.49/1.11
100c	6.69	5.06 b)	1.11
56c	6.64	6.68a, b)	0.63

a) The chemical shift value of H-5.

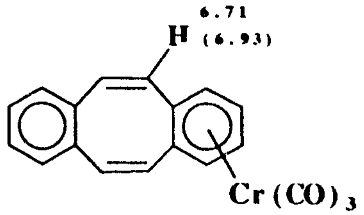
b) The chemical shift value of H-13

99a and **99c** unambiguously confirmed their structures (see Table 8). In the ^1H nmr spectrum of **99a**, the uncoordinated ring protons (H-12,13,14) appeared at δ 7.03-6.96 which is the normal chemical shift range for these aromatic protons, while the coordinated ring protons (H-4,5,6) appeared at δ 5.44-5.22 which is the typical chemical shift for $Cr(CO)_3$ coordinated arene protons. The non-equivalent olefinic protons H-1 and H-2 appeared as two sets of doublets at δ 6.88 and 6.35 due to the coupling between them. The assignment of these doublets to the proton H-1 (the downfield doublet) and H-2 (the upfield doublet) was based as follows on their chemical shifts: upon complexation of a

$Cr(CO)_3$ moiety to an aromatic ring, the chemical shift of the proton adjacent to the benzene ring is shielded to higher field as seen in the molecules **101**[87] and **102**[88].



101



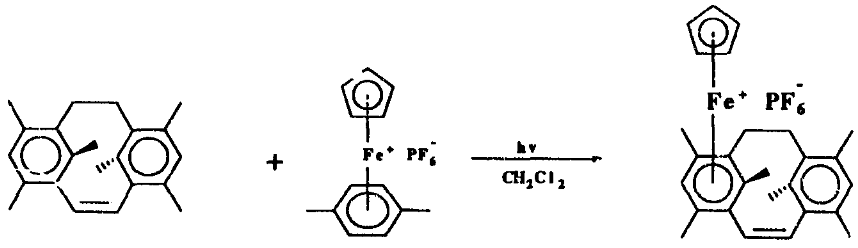
102

The two internal methyl protons are also different and appeared as two singlets, a singlet at δ 1.31 and a singlet at δ 0.51, which were assigned to the methyl on C-16 and C-8 respectively. The large reduction of shielding (Δ=0.55 ppm) of the methyl protons on C-16 in **99a** indicates the reduction in ring current in the opposite complexed ring (and hence less shielding), whereas the upfield shift of the methyl on C-8 is caused by complexation of the $Cr(CO)_3$ moiety on this ring. The ^1H nmr spectrum of **99c** showed very similar features of the mono-chromium complexes as seen in the case of **99a**. The olefinic protons apppeared as two sets of doublets at δ 6.95 and 6.36, the uncoordinated aromatic proton H-13 at δ 6.72, while the coordinated ring proton H-5 at δ 5.10, and the two different internal metyls as two singlets at δ 1.11 and 0.49.

All the mono- and bis-chromium complexes **99a**, **99c**, **100a**, and **100c**, gave strong characteristic absorptions of a carbonyl group around 1850 and 1950 cm^{-1} in their ir spectra.

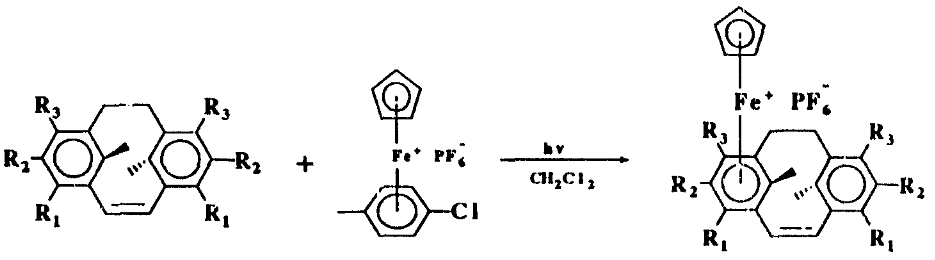
2.2.3 Syntheses of cyclophanene iron complexes 105

Since several CpFe$^+$ complexes of metacyclophanes have been successfully synthesized by Swan and Boekelheide,[81a)] we decided to use η^6-*p*-xylene-η^5-cyclopentadienyliron hexafluorophosphate, **103**, as the CpFe$^+$ source in preparations of the cyclophanene-iron complexes **105**. Irradiation of **103** (2 equivalents) and **56c** in dry dichloromethane using an incandescent flood lamp led to the formation of the iron complex **105c** in 82% yield.



56c **103** **105c**

However, reaction of **103** and **56a** under the same conditions afforded a low yield of the iron complex **105a**. This indicated that the exchange of *p*-xylene in **103** for the cycylophanene **56a** was not favoured; the electron density of the benzene rings in **56a** is not as rich as those in **56c**, relative to a xylene molecule. We thought that the presence of an electron withdrawing substituent on the arene in the iron source complex of the type CpFe$^+$(arene) would make this arene less basic and more easily replaced in the arene exchange reaction. Thus we then employed the η^6-chlorotoluene-η^5-cyclopentadienyliron hexafluorophosphate, **104**, which was prepared by the standard procedure,$^{89)}$ in preparations of the complex **105**. Reaction of **56c** with two equivalents of **104** gave **105c** in 82% yield, which was the same yield as when **103** was used as the CpFe$^+$ source. However, a good yield (78%) of the iron complex **105a** was obtained by irradiation of **104** (2 equivalents) and **56a** under the same conditions, which was only poor with **103**.



56 a) $R_1=R_2=R_3=H$
b) $R_1=R_3=H$, $R_2=CH_3$
c) $R_1=R_3=CH_3$, $R_2=H$

104

yield
78%
47%
82%

105 a) $R_1=R_2=R_3=H$
b) $R_1=R_3=H$, $R_2=CH_3$
c) $R_1=R_3=CH_3$, $R_2=H$

The iron complex **105b** was also prepared using both **104** and **103** as the CpFe$^+$ sources, but the yield of **105b** was lower in both cases (47% and 43% respectively). Considering that the arene replacement reaction is assisted by using nucleophilic solvents, such acetonitrile,[90] we then tried this as the solvent. However, reaction of **104** and **56b** in acetonitrile or in dichloromethane with a catalytic amount of acetonitrile (5%), failed to give any of **105b**. No further attempts have been made to improve the yield of **105b**.

The structures of **105** were assigned on the basis of their ^{1}H nmr spectra. In the ^{1}H nmr spectrum of **105a**, the coordinated ring protons were markedly shifted upfield: δ 6.66 (H-5), 5.96 (H-4), 5.69 (H-6), whereas the uncoordinated ring protons H-12, H-13, and H-14 were slightly shifted downfield: δ 7.15-7.04, compared to the chemical shift value of δ 7.01-6.84 in the parent cyclophanene **56a**. The assignment of these protons was made on the basis of their coupling patterns. The proton H-5 was the downfield triplet due to large couplings with H-4 and H-6, which were the two upfield doublets. The downfield one of these two doublets was assigned to H-4 after considering the deshielding effect of the adjacent double bond.

Notably, the differences in chemical shifts of these protons on the coordinated ring in **105a** are very large: 0.7 ppm between H-5 and H-4, 0.97 ppm between H-5 and H-6, and 0.27 ppm between H-4 and H-6. This reflects the change in geometry of the molecule and the change in bond orders of the aromatic carbons upon complexation, as well as for a direct influence of the magnetic anisotrotpy of the iron ion on neighboring protons.

The non-equivalent olefinic protons H-1 and H-2 appeared as two sets of doublets, one was slightly shifted upfield (δ 6.53) and the other markedly shifted downfield (δ 7.13), compared to the chemical shift value of δ 6.59 in the parent **56a**. The downfield doublet was assigned to the proton H-1, based on the reduction in ring current (hence less shielding) of the opposite ring on complexation by the CpFe' moiety. For a similar reason, the downfield singlet at δ 0.92 and the upfield singlet at δ 0.67 were assigned to the internal methyls on C-16 and C-8 respectively. The four protons on the ethano bridge in **105a** were resolved on complexation and were assigned on the basis of the coupling constant analysis (the details of this analysis will be discussed in Chapter Three): δ 3.11 (H-10(eq.)), 3.00 (H-9(eq.)), 2.58 (H-10(ax.)), 2.42 (H-9(ax.)).

In the ^{1}H nmr spectrum of **105b**, the coordinated ring protons were shifted upfield: δ 5.89 (H-4) and 5.61 (H-6), and the uncomplexed ring protons were shifted downfield: δ 6.95 (H-14) and 6.84 (H-12), compared to δ 6.77 and 6.66 for the corresponding protons in **56b**. A large difference (Δ=0.28 ppm) between H-4 and H-6 on the complexed ring but normal value (Δ=0.11 ppm) between H-14 and H-12 on the uncomplexed ring were seen, compared to the difference (Δ=0.10 ppm) between these two protons in **56b**. The two olefinic protons appeared as two doublets at δ 7.08 and 6.49 and the two internal methyls as two singlets at δ 0.90 and 0.62. The ethano bridge protons were also separated and appeared at δ 3.05 (H-10(eq.)), 2.95 (H-9(eq.)), 2.54 (H-10(ax.)), and 2.42 (H-9(ax.)). It is interesting to note that all these chemical shift values are quite close to the chemical shifts of the corresponding protons in **105a** (Δδ <= 0.05 ppm). This suggests a similarity in geometry between these two molecules, **105a** and **105b** in solution.

Table 9. ^{1}H nmr data of the iron complexes **105a-105c**.

	105a	**105b**	**105c**
H-1/2	7.13/6.53	7.08/6.49	7.24/6.64
	(6.59)	(6.54)	(6.64)
H-5/4/6	6.66/5.96/5.69	--/5.89/5.61	6.45/--/--
	(7.01-6.[illegible]	(--/6.77/6.66)	(6.68/--/--)
H-13/14/15	7.15-7.04	--/6.95/6.84	6.84/--/--
eq_H-10/9	3.11/3.00	3.05/2.95	3.22/3.14
	(2.89)	(2.81)	(3.06)
ax_H-10/9	2.58/2.42	2.54/2.42	2.19/2.17
	(2.50)	(2.48)	(2.17)
Me-C16/C8	0.92/0.67	0.90/0.62	0.83/0.48
	(0.76)	(0.73)	(0.53)

In the ^{1}H nmr spectrum of the iron complex **105c**, the coordinated ring proton H-5 appeared at δ 6.45 and the proton H-13 at δ 6.83, while these two protons in **56c** appear at δ 6.68. Two doublets at δ 7.24 and 6.64 were assigned to the two olefinic protons H-1 and H-2 respectively. The internal methyl on C-16 in the complexed ring was less shielded (δ 0.83) and the internal methyl on C-8 in the complexed ring was further shielded (δ 0.48), compared to the value of δ 0.63 in **56c**.

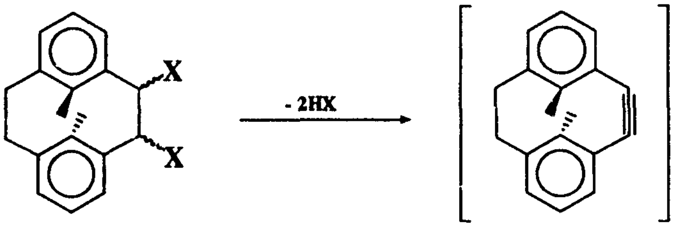
In all three iron complexes, the protons on the cyclopentadienyl moiety showed a singlet: δ 4.77 in **105a**, 4.66 in **105b**, and 4.62 in **105c**. Parts of the ^{1}H nmr data for the three iron complexes **105a**, **105b**, and **105c** are summarized in Table 9 (the chemical shift values of the corresponding protons in the parent **56a-56c** are given in parentheses).

2.3 Bridge Chemistry of [2_2]Metacyclophanenes and Their Metal Complexes

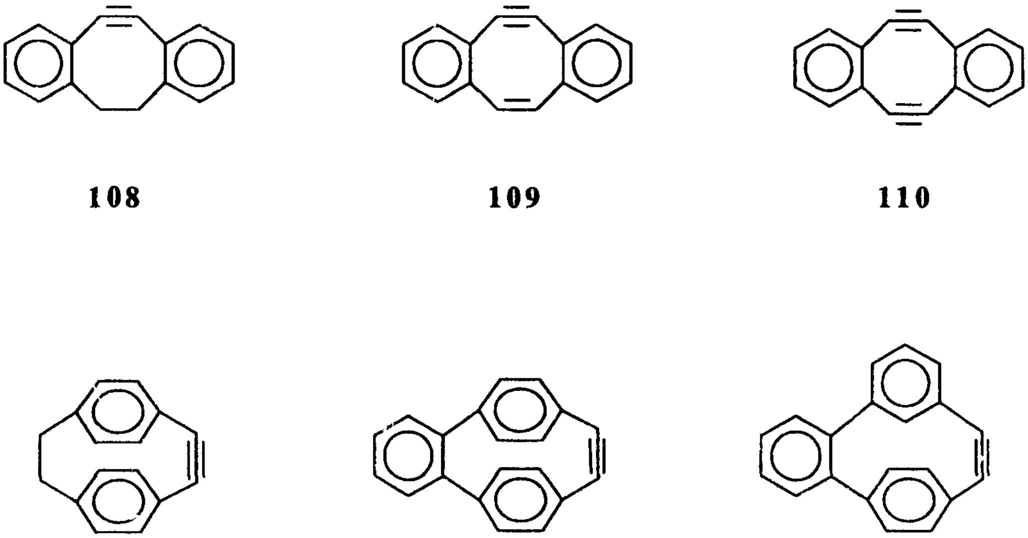
2.3.1 Synthetic utility of difunctionalized bridges

One of the important potential synthetic utilities of the bridge-difunctionalized metacyclophanenes of the type **106** is to be the precursors to [2_2]metacyclophanynes **107** which are not yet known.

Angle strained cycloalkynes have been known for some time.[91] Cyclophanes with acetylenic bridges such as



106 **107**



108 **109** **110**

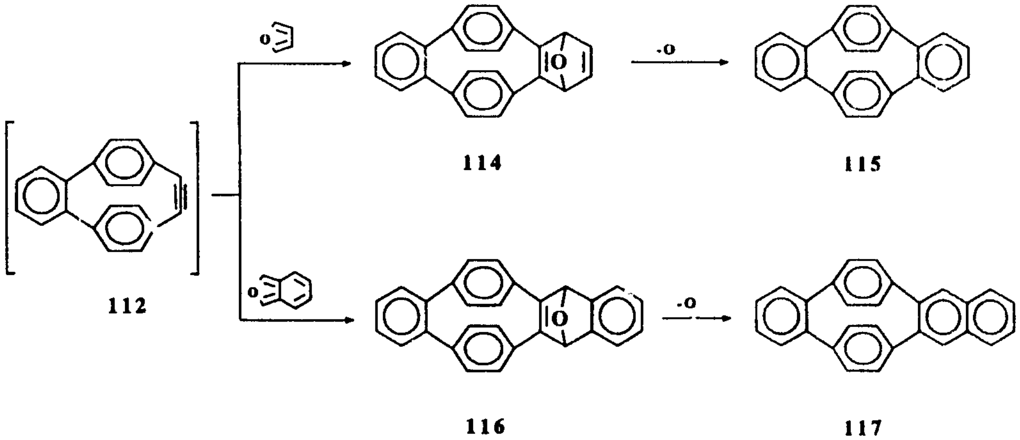
111 **112** **113**

Figure 7. Examples of the known cyclophanynes.

$[2_2]$orthocyclophanyne **108**[92], **109**[93], and **110**[94] have been prepared. Surprisingly, these molecules are quite stable, and can be isolated as crystalline compounds. In the $[2_2]$paracyclophane series, the $[2_2]$paracyclophanyne **111**[95] has also been generated as an intermediate, which trimerizes to give a benzene derivative. More recently, the dibenzo-$[2_2]$paracyclophanyne **112**[96] and dibenzo$[2_2]$ metaparacyclophanyne **113**[97] have been generated and trapped with some furan derivatives.

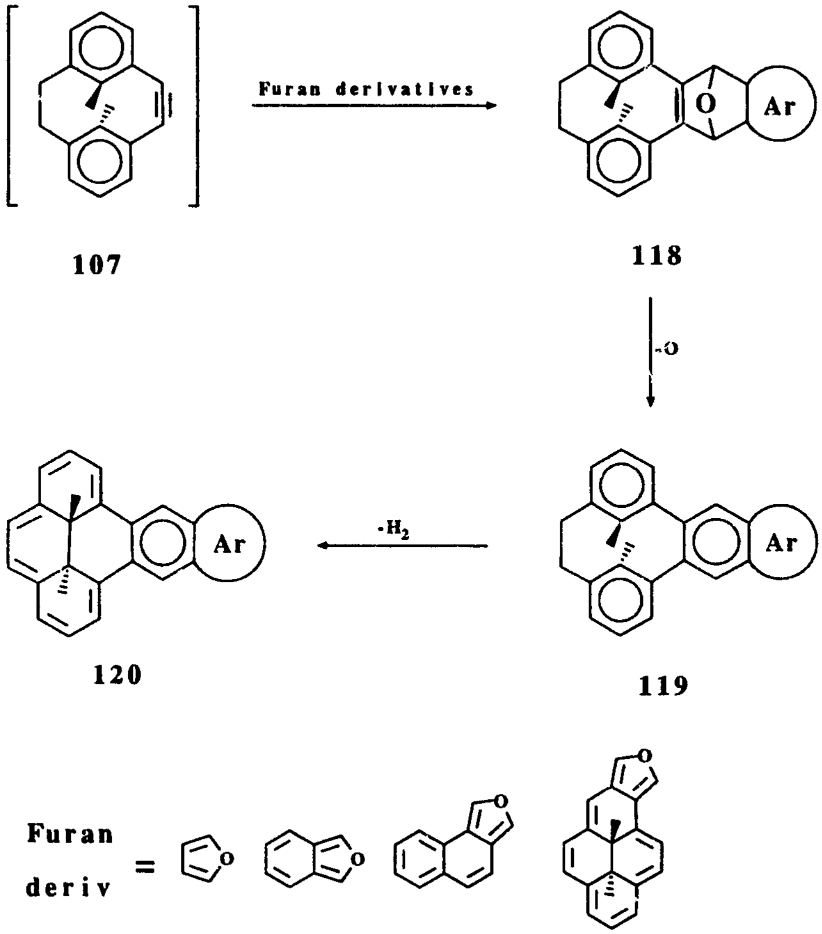
As the acetylenic bonds in these molecules are considerably strained, these compounds show enhanced reactivities. This is indicated by the fact that the Diels-Alder reaction of these cyclophanynes with dienes such as furan proceed at room temperature.[97] Subsequent deoxygenation of the adducts leads to the corresponding arenes and this sequence provides a general method to fuse an arene system to these cyclophanynes at the triple bond positions.[96] This synthetic method is shown in Scheme XIII using **112** as an example.

Scheme XIII:

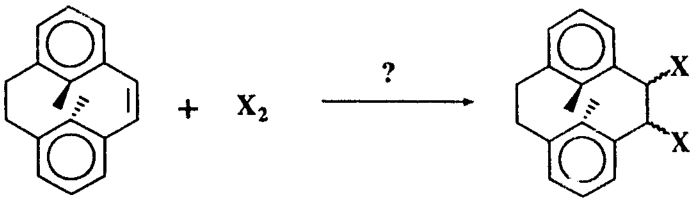


Similarly, the [2_2]metacyclophanyne **107**, if it could be generated, should also be very reactive due to the strain of the acetylenic bond. Trapping it with furan derivatives and then deoxygenation of the adduct would provide a very useful synthetic route to [e]-ring annulated dihydropyrenes **120**, which are a class of structurally and theoretically interesting molecules. The proposed synthetic route to **120** is shown in Scheme XIV.

Scheme XIV:

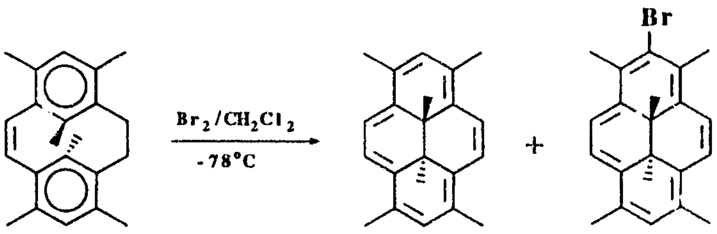


Since the bridge of [2_2]metacyclophane **7** can not be functionalized to give the bridge-difunctionalized metacyclophane **106**, we hoped that electrophilic addition to the bridge double bond in the cyclophanenes **56** would lead to formation of the desired **106**



56a **106**

2.3.2 Attempted electrophilic additions to the bridge double bond of the cyclophanenes 56



56c **121** **122**

minor

The most common and well studied electrophilic addition to a double bond is perhaps the halogenation of alkenes. Bromine is the reagent of choice in most cases. Upon addition of a solution of bromine in dichloromethane, the solution of **56c** in dichloromethane at -78°C turned to dark green immediately, indicating formation of a dihydropyrene.

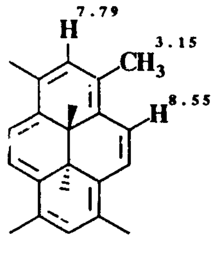
In fact the product was dihydropyrene **121** and a minor amount of the bromopyrene **122**. This clearly indicated that bromine oxidized **56c** prior to addition to its bridge double bond. The dihydropyrene **121** was easily recognized from the upfield singlet at δ -4.02 in the ^{1}H nmr spectrum of the bromination product.

Use of another mild bromination reagent -- pyridinium hydrobromide perbromide ($PyH^+Br_3^-$),[98] in the bromination of **56c** also led to the pyrene **121**. We found that oxidation of **56c** to **121** was brought about by any reagent which provides a Br^+ species, even NBS. The mechanism of the oxidation might be initiated by addition of Br^+ to one of the benzene rings, followed by rapid transannular ring closure, similar to the case of electrophilic substitution of [2_2]metacyclophane **7** (see page 23). Subsequent aromatization of the intermediate by loss of one molecule of hydrogen would lead to formation of **121**. The minor bromopyrene **122** was probably formed by attack of bromine on the oxidation product **121**. This has been proved by using more than one equivalent of bromine reagent in this bromination reaction. For example, when two equivalents of NBS were used, the major product was the monobromopyrene **122**, together with **121** and the dibromopyrene **123**. If three of four equivalents of NBS were used, the major products were the dibromopyrene **123** and the tribromopyrenes (**124** and **125**) respectively. In each case, this oxidation-aromatization and subsequent bromination always resulted in a mixture of several bromopyrenes, showing no selection at all. As a different ratio of these bromopyrenes was obtained each time, and fortunately most of the proton signals of these compounds did not overlap, the assignment of the signals to each bromopyrene was achieved by examining the relative intensities of signals and excluding the signals that had already been assigned. The chemical shift values of the protons in the pyrene **121** and in its bromo derivatives **122** to **126** are give in Figure 8.

An attempt at electrophilic addition to the double bond in **56a** using similar conditions met the same fate, in that **56a** was also rapidly oxidized by these reagents.

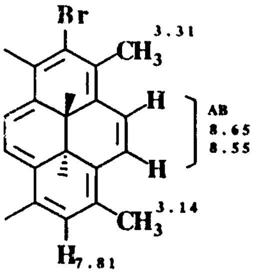
Phenylselenenyl halide (PhSeX) is known to undergo electrophilic addition to olefins.99) Oxidation of the PhSeX (X=Cl, Br) adducts and subsequent selenoxide elimination provides a method of introducing a halogen atom to olefins at vinylic or allylic positions. Unfortunately, the reaction of PhSeCl with the cyclophanene **56c** did not give the addition product **128** but a mixture of the pyrene **121**, the chloropyrene **127**, and diphenyl diselenide (PhSeSePh).

The structure of **127** was confirmed by two singlets at δ -3.94 and -3.93 (internal methyls), two singlets at δ 3.14 and 3.25 (external methyls), and two doublets at δ 8.61 and 8.56 (AB system, H-4,5,9,10) in the ^{1}H nmr spectrum of the first fraction product from column chromatography, which



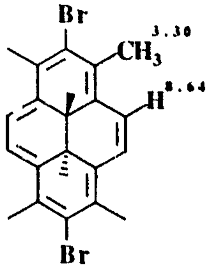
Me' = -4.02

121



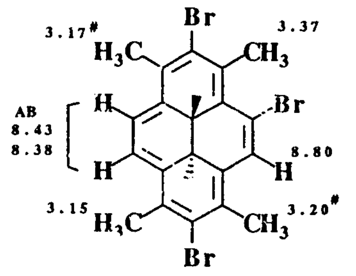
Me' = -3.91

122



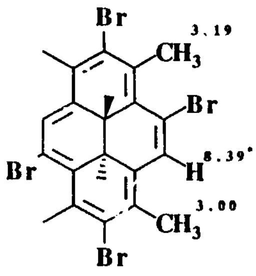
Me' = -3.84

123



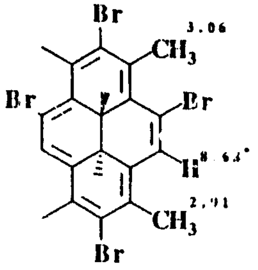
Me' = -3.31
-3.27

124



Me' = -2.51

125



Me' = -2.28
-2.25

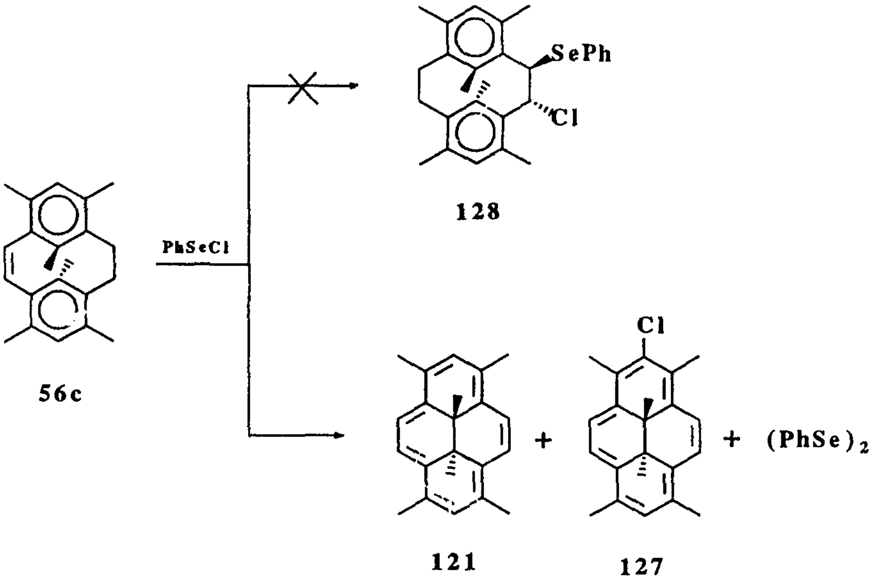
126

Note: *) Uncertained values
#) Values might be exchanged

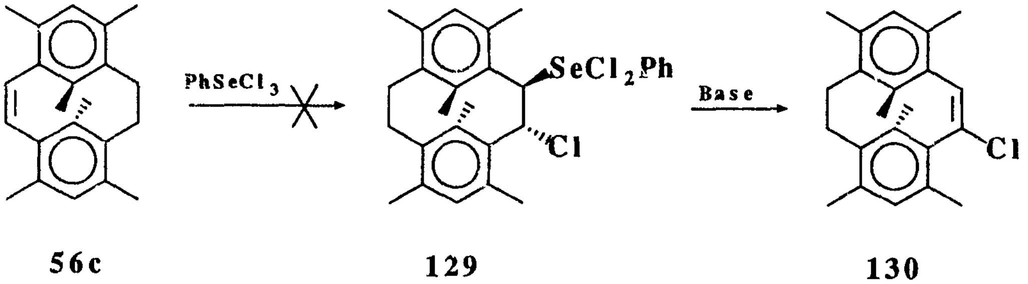
Figure 8. The ^1H nmr data of **121** and its bromo derivatives.

only contained **121** and **127**.

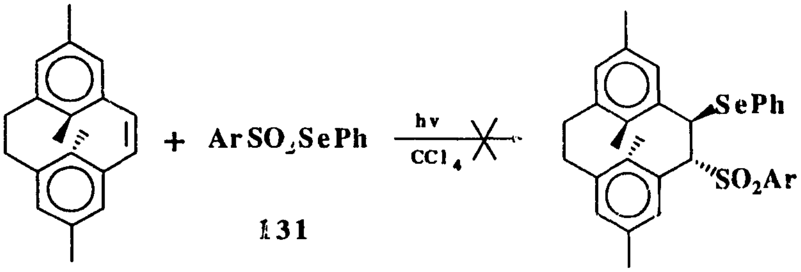
Phenylselenium trichloride, $PhSeCl_3$, has been reported to react with a number of olefins to give (β-chloroalkyl) phenylselenium dichlorides.[100] When the (β-chloroalkyl) phenylselenium dichlorides are treated in dichloromethane with aqueous sodium bicarbonate, the selenium dichloride moiety is readily hydrolysed to a selenoxide, which



undergoes a selenoxide elimination reaction to produce an allylic or a vinylic chloride. However, reaction of $PhSeCl_3$ with the cyclophanene **56c** failed to give any expected vinylic chloride **130**.



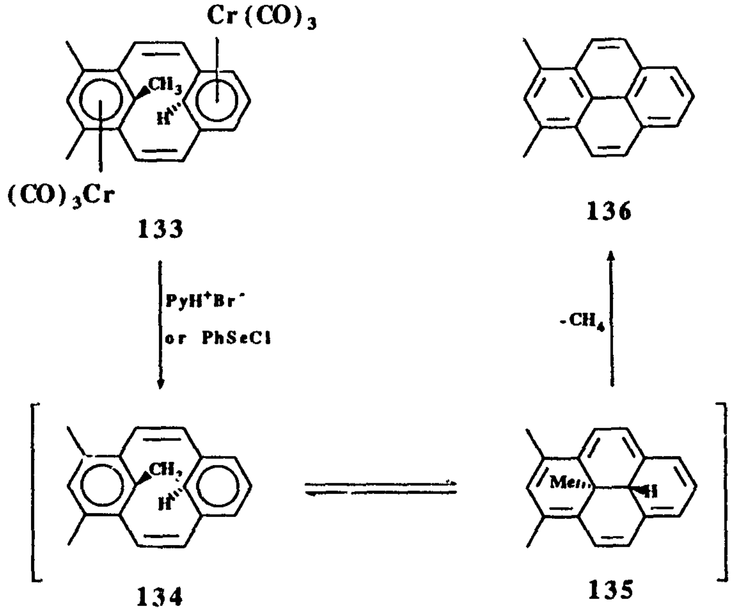
At this point, we were convinced that the cyclophanenes **56** easily undergo a transannular ring closure reaction and subsequent aromatization in the presence of oxidizing agents. We then searched for non-oxidizing reagents which can add to the double bond and give synthetically useful products. The areneselenosulfonate, $ArSO_2SePh$[101], seems to be a suitable reagent, which adds photochemically to olefins via a free-radical mechanism to produce β-seleno sulfones.[102] Then oxidation-elimination of β-seleno sulfones provides a synthetic route to vinyl sulfones, a class of compounds of proven value in synthesis.[103] However, irradiation of $ArSO_2SePh$ and **56b** in degassed carbon tetrachloride failed to give the vinylic sulfone **132**. Only the unreacted **56b** was recovered from the reaction.



56b **132**

2.3.3 Electrophilic additions to the bridge double bond in 105

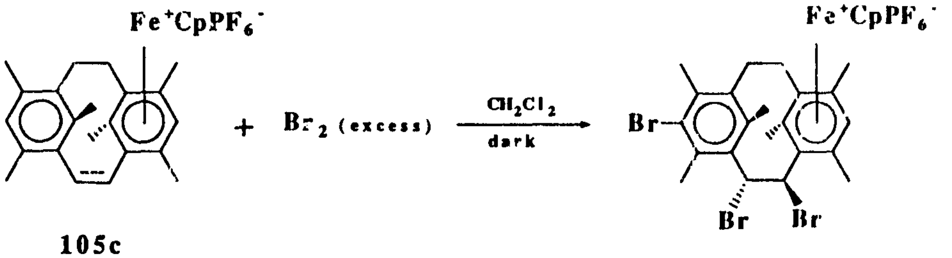
Since the cyclophanenes **56a-56c** were readily oxidized by reagents used in the bromination reaction, we thought that complexation of transition metals on one of the two benzene rings in **56** would block the facile transannular ring closure reaction when **56** was treated with bromination reagents. The photoconversion of the diene could indeed be stopped by preparation of the cyclophanediene bischromium complex **133**. This was sufficiently stable that crystals of **133** could be exposed to air for several days without obvious signs of decomposition (The synthesis of **133** will be discussed in Section 4 of this chapter).



However, the complex **133** did not survive under bromination conditions. Attempted electrophilic addition to the double bonds in **133** with various reagents such as $PyH^+Br_3^-$, $PhSeCl_3$, and PhSeCl, led to decomposition of the complex. This was indicated by a rapid colour change (red to black) of the solution of the complex upon the addition of these reagents. The only product isolated from these reactions was the pyrene **136**, which was formed from the unstable decomplexed cyclophanediene **134**. It was known that a dihydropyrene with one internal methyl and one internal proton is not stable enough to be isolated due to a fast loss of a molecule of methane.[65b)]

The structure of **136** was confirmed by its ^{1}H nmr spectrum, in which the methyl protons appeared as a singlet at δ 2.93, the aromatic protons gave two doublets at δ8.19 and 8.02 (J=9.2 Hz), a doublet and a triplet at δ 8.13 and 7.95 (J=7.6 Hz) respectively, and a singlet at δ 7.73.

In contrast to (arene)$Cr(CO)_3$ complexes, $CpFe^+$(arene) complexes are remarkably stable towards the action of strong oxidants such as concentrated H_2SO_4, HNO_3, peroxides, bichromate, and permanganate.[104)] For example, boiling an aqueous $KMnO_4$ solution of an $Cp'Fe^+$(arene) salt results in oxidation of the alkyl side chains on either the arene or Cp ligands without decompostion of the complex itself. With the $CpFe^+$(cyclophanene) complexes at hand, we thus tried the reaction of bromine with the iron complex **105c**.



105c

138

Reaction of **105c** with excess bromine (about 10 equivalents) in dry dichloromethane in the dark for two days gave dark red crystals. These were found to be the bromine adduct **138**. The structure of **138** was confirmed without doubt by comparison of the proton and carbon nmr spectra of **138** with these of **105c** (see Figure 9). In the ^{13}C nmr spectrum of **138**, the number of sp^2 carbon peaks in the range of 120-150 ppm was six, compared with eight peaks in **105c**. For **138**, two new peaks appeared at δ 54.2 and 51.1, indicating the addition of bromine to the bridge double bond. In the ^1H nmr spectrum of **138**, the two doublets (δ 7.24 and 6.64) of the olefinic protons and a singlet (δ 6.84) belonging to the uncoordinated ring proton in **105c** disappeared and two broad singlets showed up at δ 6.45 and 6.24, which were assigned to the bromine-substituted ethano protons H-1 and H-2 in **138** respectively. Notably, all the signals due to the ethano protons, the external methyl protons, and especially the internal protons were largely shifted downfield. This might be caused by deshielding effects of the two bridge bromine atoms in the pseudoaxial positions, as indicated by a very small coupling constant (J<1 Hz) between H-1 and H-2 in **138**.

The presence of a bromine atom on the uncomplexed ring was confirmed not only by the disappearance of that aromatic proton in the ^1H nmr spectrum of **138**, but also was supported by the ^1H nmr spectrum of the decomplexed product **139**. In the attempted dehydrobromination of **138** using various

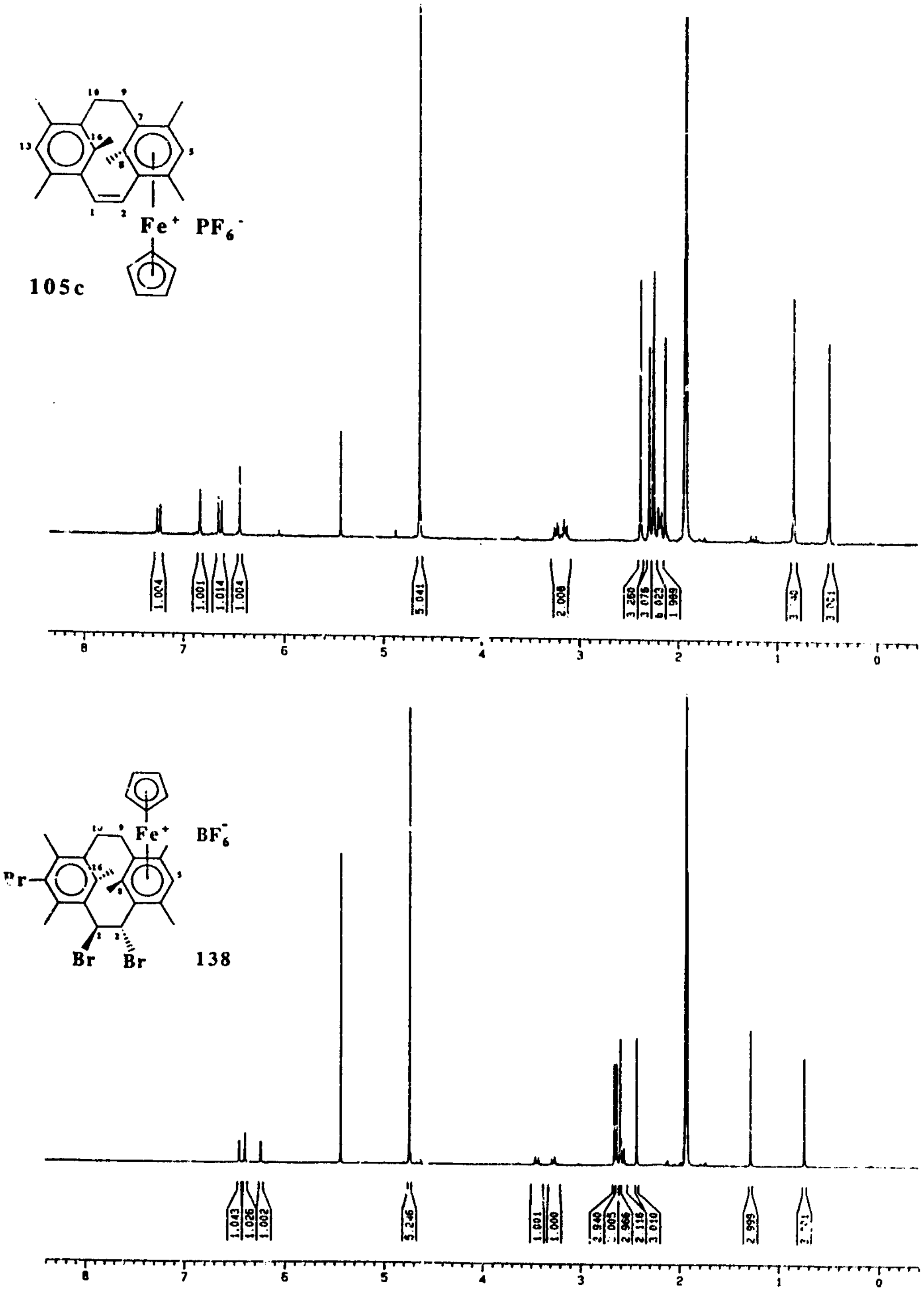
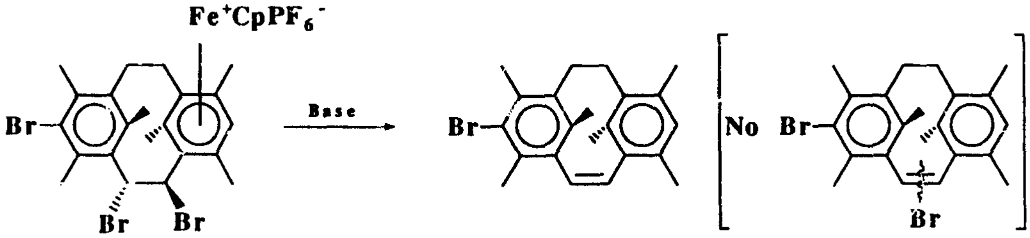


Figure 9. Comparison of ^{1}H nmr spectra of **105c** and **138**.

conditions such as $NaOCH_3$ in refluxing methanol, t-BuOK in a mixture of t-BuOH and THF, DBU both as the base and solvent, and irradiation with UV light in acetonitrile, the only product isolated in each case was the bromocyclophanene **139** rather the expected vinylic bromide **140**. This clearly indicated that the bromine adduct **138** easily undergoes debromination to regenerate a bridge double bond. It was not known whether the debromination occurred before or after decomplexation of **138**.



138 **139** **140**

The structure of **139** was confirmed by its ^1H nmr spectrum, which showed an AB system at δ 6.67 for the olefinic protons (J=11.4 Hz), a singlet at δ 6.59 for the aromatic proton H-13, two singlets at δ 0.83 and 0.63 for the internal methyls, and four singlets at δ 2.48, 2.40, 2.27, and 2.21 for the external methyls. The mass spectrum of **139** gave a molecular ion peak at *m/z* 368.

The reaction of **105b** with excess bromine proceeded well as indicated by monitoring the reaction using proton nmr. After 10 min, the spectrum showed that the addition of

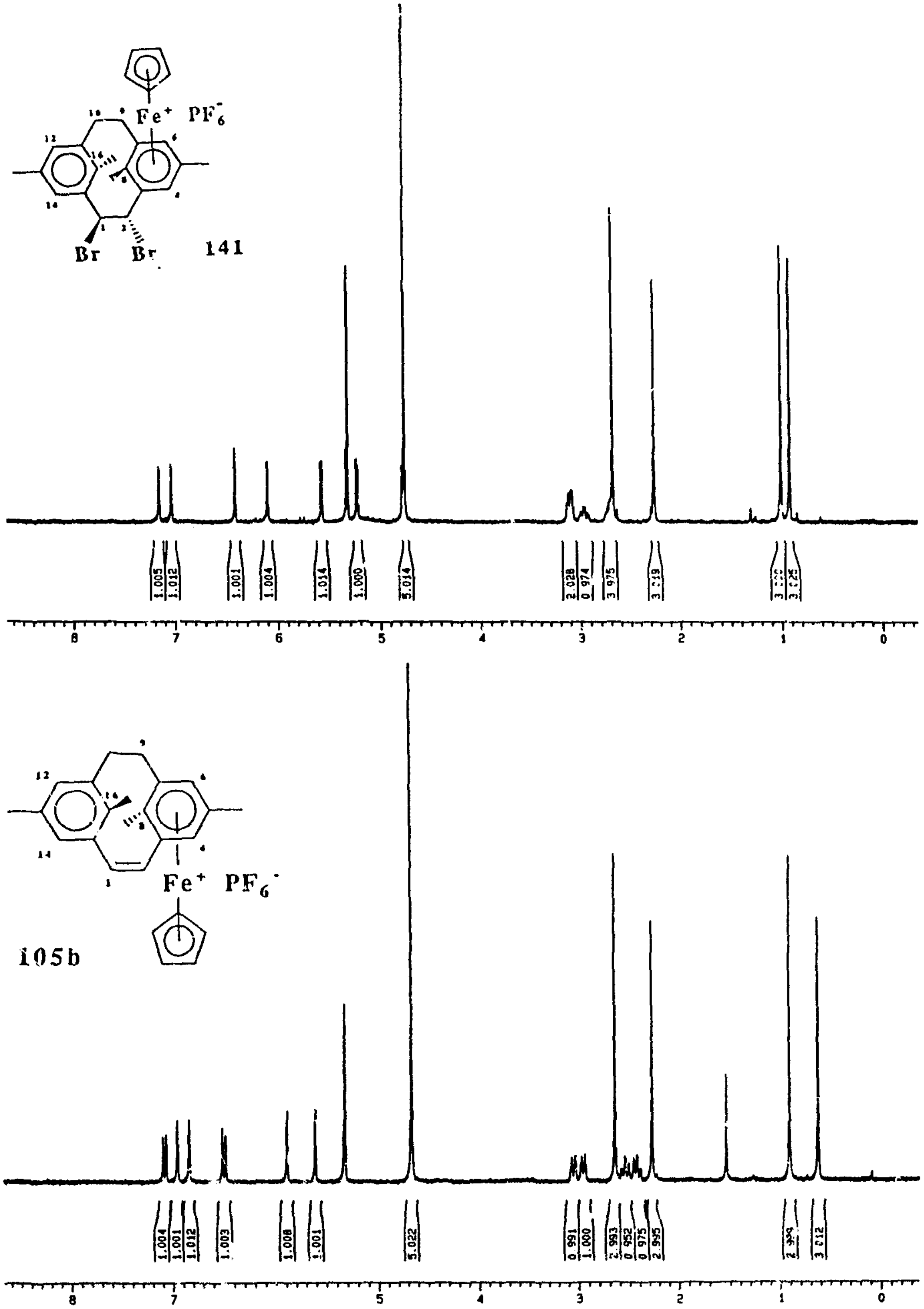
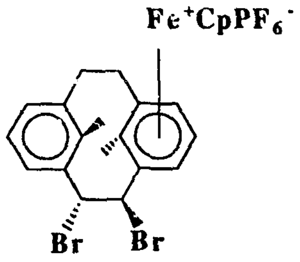


Figure 10. Comparison of ^1H nmr spectra of **105b** and **141**.

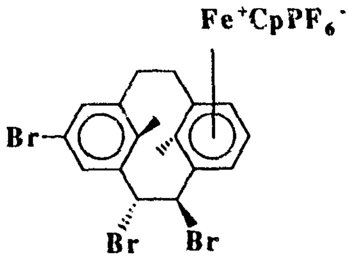
bromine to the bridge double bond was complete and gave the bromine adduct **141** as the only product. In this spectrum (see Figure 10), the bromine-substituted ethano bridge proton H-1 and H-2 appeared as two sets of doublets at δ 5.57 and 5.23 (J=5.0 Hz) respectively. Large changes in chemical shift values were observed for the aromatic protons, especially the coordinated ring protons, and for the pseudoaxial protons on C-9 and C-10, and for one of the internal methyl protons.

The reaction of **105a** with bromine gave two major bromine adducts which were indicated by two sets of signals for each carbon in the ^{13}C nmr of the adducts. In this spectrum, six pairs of the complexed ring carbons, one pair of the Cp carbons, and two pairs of internal methyl carbons of the two adducts appeared quite close to each other. whereas some of the signals from the uncoordinated ring carbons of the two adducts were quite far apart from each other. This indicated that the major structural differences lay in the uncoordinated ring. It was also found that the rate of electrophilic substitution on the uncoordinated ring was about the same as the rate of bromine addition to the double bond. From these two pieces of evidence, we concluded that the two adducts are the dibromide **142** and the tribromide **143**, which precipitate from the mixture once they are formed.

Although the bromine addition to the bridge double bond

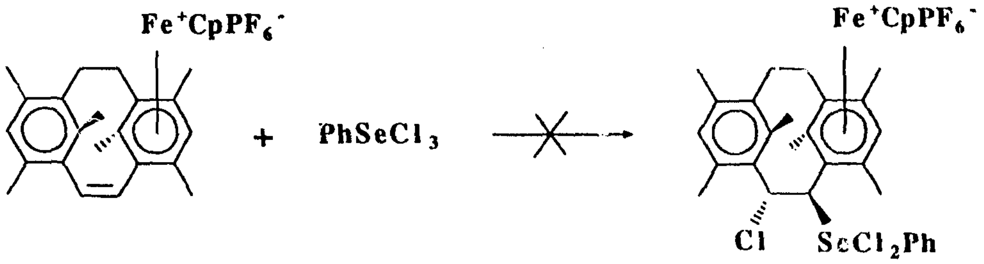


142



143

was finally achieved using the CpFe$^+$ complexes **105**, attempted electrophilic addition of $PhSeCl_3$ to the double bond in **105c** failed to give any the expected product **144**.

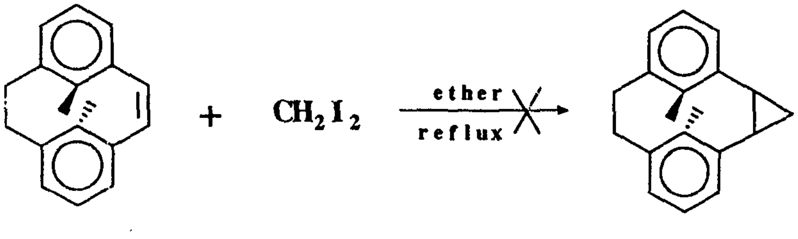


105c

144

2.3.4 Attempted cyclopropanations of cyclophanenes

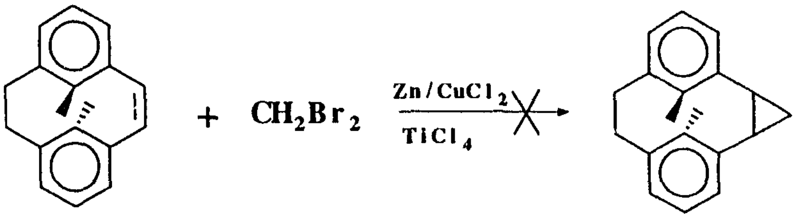
As part of an exploration of the bridge chemistry of the cyclophanenes, we also studied the possibility of cyclopropanation of the cyclophanenes **56**. Among various methods available for generation of cyclopropanes, the Simmons-Smith procedure[105] -- the reaction of an organozinc reagent prepared from methylene iodide and zinc-copper couple with substituted unsaturated compounds is generally quite effective106) and has been employed widely in preparation of cyclopropane derivatives.107) Various modifications of this method have been introduced with some success.108) Thus, we decided to try the Simmons-Smith procedure first. Unfortunately, the reaction of diiodomethane and the cyclophanene **56a** in refluxing diethyl ether in the presence of zinc-copper prepared by LeGoff's method,108a) did not yield the expected cyclopropanated product but returned the unreacted **56a**.



56a **145**

More recently, a convenient procedure for cyclopropanation of alkenes using titanium(IV) chloride as a catalyst has been reported.109) The $TiCl_4$-promoted cyclopropanations are generally carried out in refluxing ether with use of 1 to 2 to 3 molar ratios of alkene to CH_2I_2 to zinc dust in the presence of titanium (IV) chloride (2 mol % of CH_2I_2 used). With this method, the reaction times are much shorter (2-4 h) than those using the Simmons-

Smith procedure (20-40 h), but the yields of cyclopropane products obtained are as good or better than those found by using diiodomethane and a zinc-copper couple. In the model reactions using this method, cyclohexene and *trans*-stilbene were successfully converted into the corresponding cyclopropanes, as indicated by the ^1H nmr spectra of the products. However, cyclopropanation of the cyclophanenes **56a** and **56c** under the same conditions failed to give any cyclopropanated product.



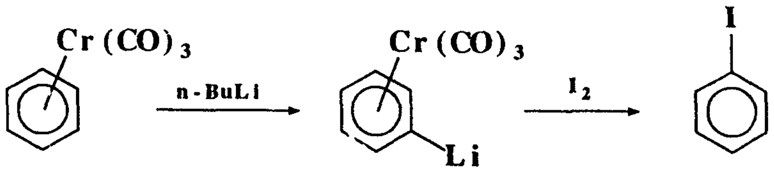
56a **145**

It was known that dichlorocarbene can be generated from solid sodium trichloroacetate (Cl_3CCO_2Na) in the presence of a phase transfer catalyst.110) Reaction of sodium trichloroacetate with alkenes (molar ratio = 2:1) in chloroform with benzyltriethylammonium chloride as the phase transfer catalyst (2 mol % of alkene used) usually gives 65-88% yields of dichlorocyclopropane derivatives.111) However, the dichlorocarbene generated by this method did not react with the cyclophanene **56a** and simply unreacted **56a** was recovered. However, the dichlorocarbene did react with the cyclophanene **56c**, and gave a mixture of a yellow semi-solid which could not be separated by column chromatography. The ^1H nmr spectrum of this mixture did not give any useful information that could indicate the addition of $:CCl_2$ to the bridge double bond. It seemed that $:CCl_2$ might have added to the benzene rings, similar to the case of $[2_2]$paracyclophane-diene, **29**, which was preferentially attacked by carbene on the benzene rings.

2.3.5 Electrophilic and nucleophilic substitutions of the metal cyclophanene complexes

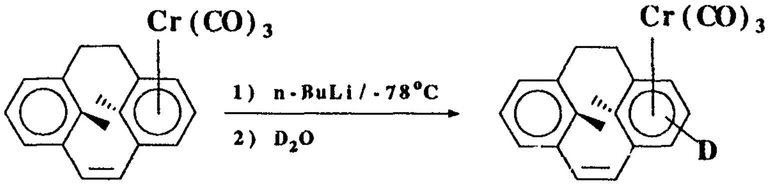
Coordination of a chromium tricarbonyl unit to an aromatic ring via π-bonding perturbs the reactivity of the arene ligand in several distinct ways,112) including enhanced acidity of the coordinated ring protons,113) and increased reactivity of the ring toward attack by nucleophiles.114) It has been found that the reaction of *n*-butyllithium with η^6-(benzene)chromium tricarbonyl, **146**, gave predominantly ring-proton abstraction species **147**, which was trapped by electrophiles such as iodine to yield iodobenzene.113)

Thus, proton abstraction from the aromatic ring using the chromium cyclophanene complex **99a** was studied. The reaction of **99a** and n-butyllithium in THF at -78°C and then subsequent quenching of the resultant mixture with D_2O gave



146 **147**

a mixture of deuterium-substituted complexes **148** in 87% yield.



99a **148**

The ^{1}H nmr spectrum of **148** was almost exactly the same as that of **99a** since all the proton signals of **148** appeared at the same chemical shifts as the corresponding protons in **99a**. The only difference between these two spectra is in the coupling pattern of the coordinated ring protons appearing in the region of δ 5.43-5.20. Morever, the number of these coordinated protons in the ^{1}H nmr spectrum of **148** just equaled two, indicating the presence of one deuterium atom on this coordinated ring. The most convincing structural evidence was obtained from the ^{2}H nmr spectrum of **148**, which showed two major broad peaks at the exact same chemical

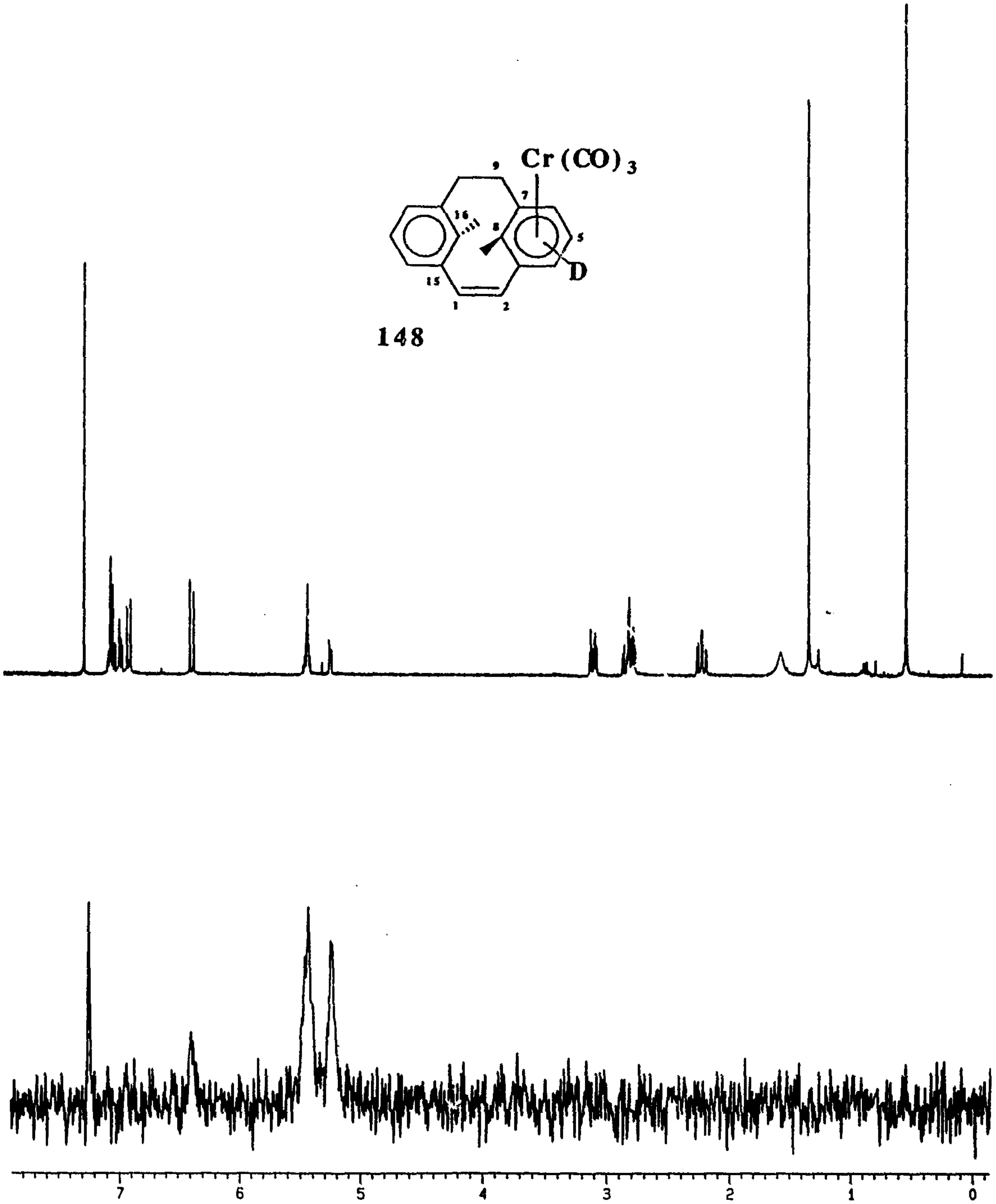
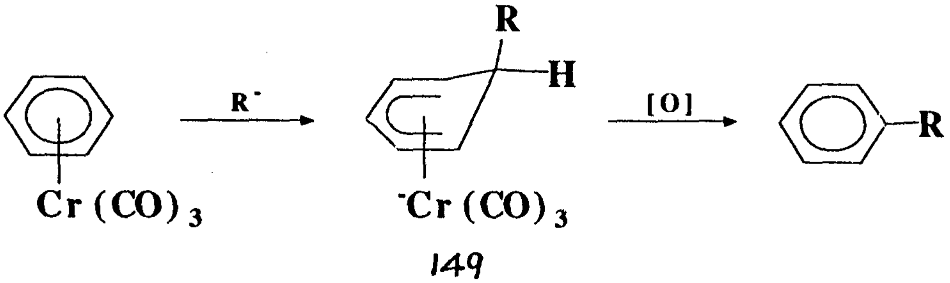


Figure 11. The ${}^1H$ and ${}^2H$ nmr spectra of **148**.

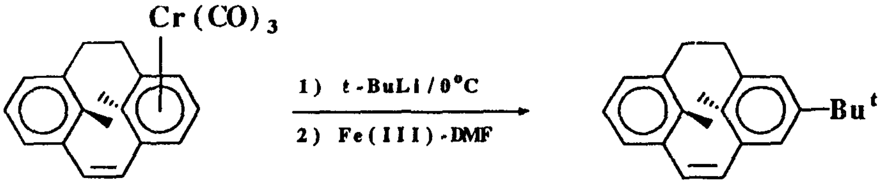
shifts as the coordinated ring protons of **99a** (see Figure 11). The presence of two peaks in the ^2H nmr spectrum of **148** indicated that the proton abstraction showed no selectivity as regard to any of the three coordinated ring protons and that the deuterium atom was randomly distributed among these three positions. The very weak peak at δ = 6.37 corresponds to a deuterium atom attached to the olefinic carbon adjacent to the complexed ring. It is known that the electron-withdrawing power of the $Cr(CO)_3$ moiety strongly increases the acidity of benzylic hydrogens.[115)] We were suprised to observe that the etheno proton but not the ethano proton was attacked by n-butyllithium under these reaction conditions.



149

It is known that tertiary cabanions add to (η^6-arene) $Cr(CO)_3$ and produce η^5-cyclopentadienyl anionic complexes, **149**, which can be oxidized by a variety of oxidizing agents to give the nucleophilic aromatic substitution products.[114b)] We found that the reaction of **99a** with t-butyllithium indeed gave the t-butyl-substituted cyclophanene **150** when the Fe(III)-DMF complex was used as the oxidant.

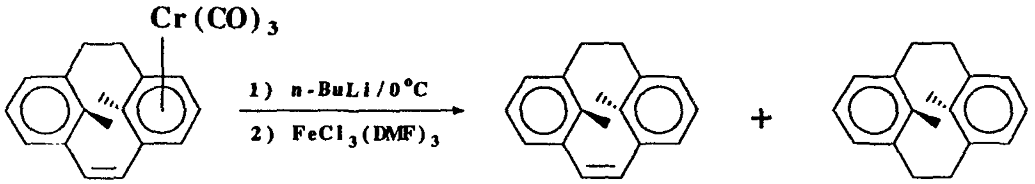
The structure of **150** was confirmed by its ^1H nmr



99a **150**

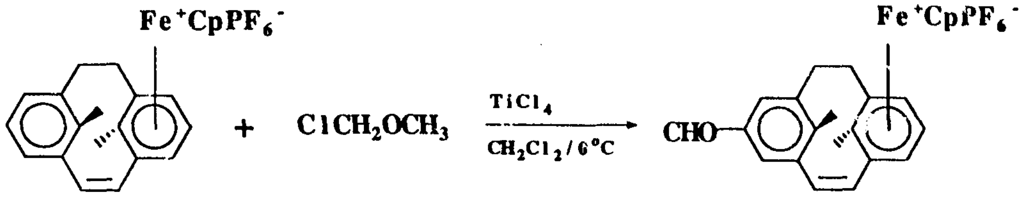
spectrum, in which the two internal methyls appeared at δ 0.76 and 0.61 and the t-butyl group as a singlet at δ 1.36.

For comparison, the reaction of n-BuLi with **99a** at 0°C was also tried and this reaction gave two compounds, the cyclophanene **56a** and [2_2]metacyclophane **37** in a ratio of six to five.



99a **56a** **37**

The presence of **37** was indicated by the ^{1}H nmr spectrum of the mixture. Signals from **37** were separated from those due to **56a**. For **37**, the internal methyl protons appeared as a singlet at δ 0.56, the ethano protons as an ABA'B' system centred at δ 2.74 and 2.93, and the aromatic protons as an AX_2 system with a doublet at δ 7.10 and a triplet at δ 6.84, all these peaks being consistant with the values reported.[40]



105a **152**

In the iron complexes **105**, one of the two benzene rings is uncomplexed and therefore electrophilic substitution on this benzene ring should be possible. We found that the formylation of **105a** using titanium(IV) tetrachloride and $ClCH_2OCH_3$ in dichloromethane did occur to give **152**, but the yield was very poor.

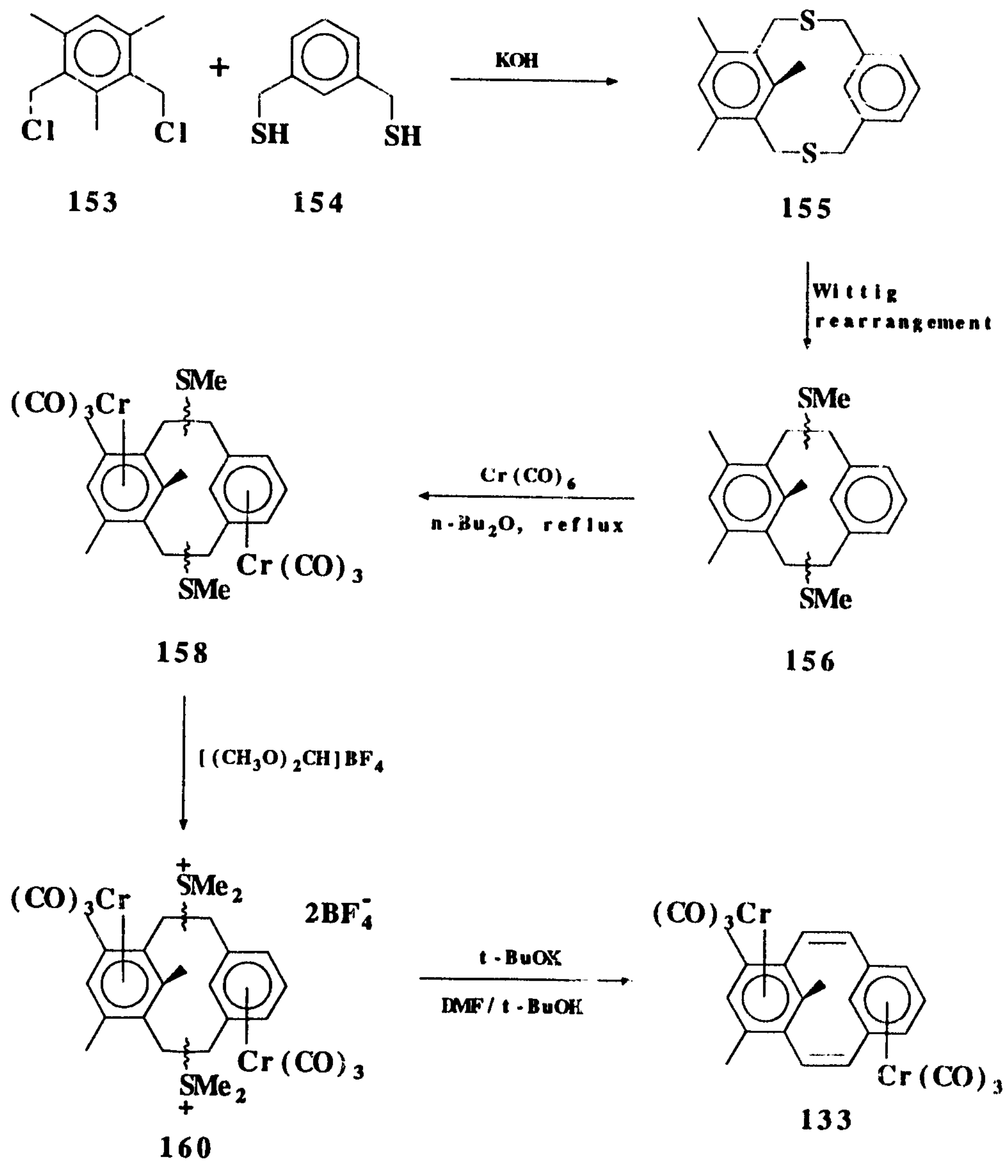
The structure of **152** was assigned on the basis of the ^1H nmr spectrum. In this spectrum, the aldehyde proton appeared as a singlet at δ 9.88, the uncoordinated aromatic protons H-12 and H-14 were deshielded by the adjacent CHO group, appearing as two singlets at δ 7.68 and 7.59; the olefinic protons H-1 and H-2 were coupled to each other to give two sets of doublets at δ 7.17 and 6.69, and the two internal methyls were different as two singlets at δ 0.87 and 0.75.

2.4.1 Synthesis of the [2_2]Metacyclophanediene tricarbonyl chromium complex 133

As part of our early work to prepare a suitable substrate for the study of the bridge chemistry of the dienes, we successfully synthesized a new diene-chromium complex **133** via the route shown in Scheme XV.

The synthesis of **133** started with the coupling of 1,3-bis(chloromethyl)mesitylene **153**, prepared by chloromethylation of commercially available mesitylene. The coupling reaction of **153** and **154** gave 75% of the dithiacyclophane **155**, which was found to be only the *anti*-isomer. In the ^{1}H nmr spectrum of **155**, the internal methyl and the internal proton, H-18, appeared at δ 1.89 and 5.66 respectively, whilst the external methyls and the external protons, H-14,15,16, appeared at δ 2.32 and 7.06-6.96. As well the bridge methylene protons were non-equivalent, and showed two sets of doublet of doublets at δ 3.89 (J = 13.1 Hz) and 3.48 (J = 15.2 Hz). This evidence clearly indicates that the compound **155** has a rigid *anti*-stepped geometry in solution at room temperature. However, it was notable that the internal methyl (δ 1.89) of **155** was not strongly shielded compared to the internal methyl (δ 1.30) of *anti*-9,18-dimethyl-2,11-dithia[3.3]metacyclophane, **52**. This suggested that there is a difference in geometry between

Scheme XV:

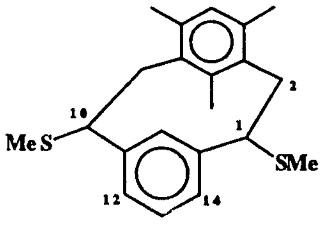


Cl
Cl
+
SH
SH
153
154
KOH
S
S
155
Wittig rearrangement
SMe
SMe
156
Cr(CO)6
n-Bu2O, reflux
(CO)3Cr
SMe
Cr(CO)3
SMe
158
[(CH3O)2CH]BF4
(CO)3Cr
SMe2
2BF4-
Cr(CO)3
SMe2
160
t-BuOK
DMF / t-BuOH
(CO)3Cr
Cr(CO)3
133

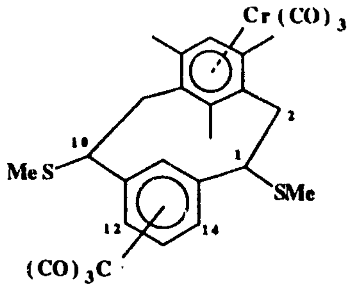
these two molecules (this will be further discussed in the next section). The mass spectrum of **155** gave a strong molecular ion peak at *m/e* 315(CI), expected for $C_{19}H_{22}S_2$.

Conversion of **155** to the sulphide **156** was achieved by using the Wittig rearrangement: treatment of **155** with *n*-butyllithium at room temperature, followed by the addition of methyl iodide, gave a mixture of ring contracted isomers **156**, in almost quantitative yield. One major isomer, **157**, with both SMe groups pseudo-equatorial on C-1 and C-10, could be separated from the other isomers of **156** by column chromatography. The structure of **157** was assigned on the basis of its ^1H nmr spectrum. The strongly shielded internal methyl (δ 0.40) and the internal hydrogen (δ 3.92) clearly indicate the *anti*-stepped geometry. The assignment of two pseudo-equatorial SMe groups on C-1 and C-10 was made based on the further deshielding of the ring protons H-12 and H14 (δ 7.68), compared to the corresponding protons (δ 7.06-6.96) in **155**. The mass spectrum of **157** showed a base molecular ion peak at *m/e* 342 (EI), consistent with $C_{21}H_{26}S_2$.

The bischromium complexes **158** were prepared in 93% yield by refluxing a mixture of the sulphide **156** and four equivalents of $Cr(CO)_6$ in dibutyl ether under nitrogen. Formation of these complexes was confirmed by the ^1H nmr spectrum, in which all the aromatic protons were shifted upfield (δ 6.16-5.39) in contrast to δ 7.69-6.87 for the corresponding protons in **156**. A downfield shift of the



157



159

internal methyl (δ 1.05-1.07) was also observed. The structure of **158** was also supported by the molecular ion peak at *m/e* 614 in its mass spectrum (EI). A single isomer of **158**, i.e., **159**, was prepared similarly from the pure isomer **157**.

By comparison with **157**, the ^{1}H nmr spectrum of **159** revealed some notable features. First, a larger separation ($\Delta\delta$ = 0.63) in chemical shift between the ring protons H-13 and H-12/14 was seen in the complex **159**, compared to the value of $\Delta\delta$ = 0.4 in the uncomplexed compound. This might reflect a change in geometry of the molecule and a change in bond orders of the aromatic carbons upon complexation; Secondly, the internal proton H-16 was further shifted upfield while the internal methyl was shifted downfield, subjected to an opposite net shielding effect. The change in chemical shifts of these internal groups is the net result of two main opposing effects: (a) shielding caused by the complexing $Cr(CO)_3$ (complexation effect); (b) reduced shielding from the opposite ring due to ring current disruption by the $Cr(CO)_3$ upon complexation (ring current reduction effect). For the internal proton, the complexation effect, which falls in the range 1.6-1.8 ppm for the complexed ring protons, overtakes the ring current reduction effect, indicated by the further upfield shift of $\Delta\delta$ 0.58. In contrast, the complexation effect for the internal methyl is quite small (about 0.1 ppm, estimated from the difference in chemical shifts between the external methyls in the complexed and those in the parent compound), and therefore the ring current reduction effect for the internal methyl dominates, causing a further downfield shift of $\Delta\delta$ 0.65.

The reaction of the bischromium complexes **158** with dimethoxy carbonium fluoroborate in dry methylene dichloride at room temperature gave 94% of the bis-sulfonium salts **160**. The final elimination of SMe_2 from the salts **160** was first attempted using t-BuOK as a base in THF and t-BuOH. The elimination was very slow and gave only a very low yield of **133**. Extensive decomposition occurred during the long reaction time (about 20 h). Using a DMSO and t-BuOH solvent system, the elimination was very fast (about 5 min) and gave a 50% yield of the complex **133** as red crystals, mp:>300°C (decomp). The highest yield (80%) was obtained using DMF and t-BuOH (1:1) as the solvent. The structure of **133** was confirmed by a base MH^+ peak at *m/e* 519 in its mass spectrum (CI). In its ^1H nmr spectrum, the ring protons H-12,13,14 appeared as an AB_2 system at δ 5.51-5.39 and the proton H-15 as a singlet at δ 5.33. The olefinic protons showed two sets of doublets (J = 11.1 Hz) at δ 6.63 and 6.28. Notably, due to deshielding by the bridge double bonds, large downfield shifts of both the internal proton H-16 (δ 5.18) and the internal methyl (δ 1.58) were observed, compared to the chemical shifts (δ 3.34 and 1.05) of the corresponding protons in **159**. The ^{13}C nmr spectrum showed singlets at 233.6 and 232.7 (carbonyl), two singlets at 131.4 and 131.0 (C=C), and six upfield singlets in the range 112-84 ppm. Its ir spectrum showed strong carbonyl absorptions at 1908, 1943 and 1980 cm^{-1}.

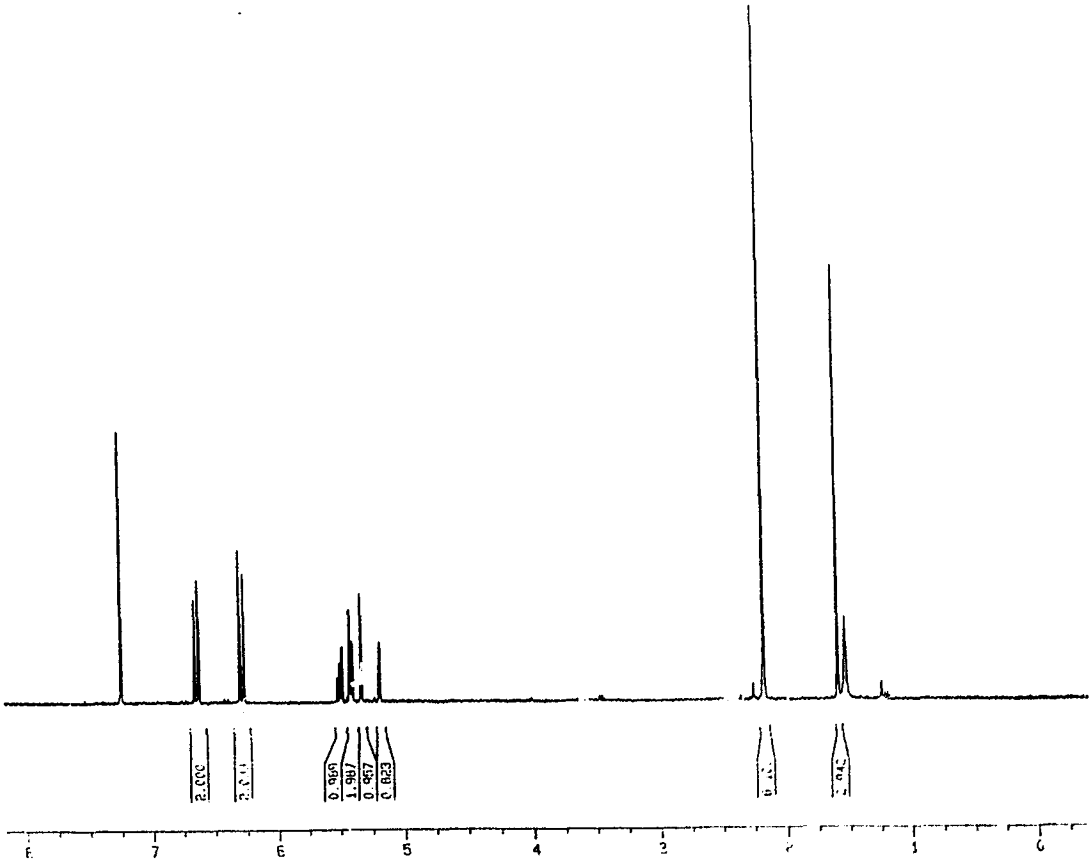


Figure 12. The ^{1}H nmr spectrum of **133**.

2.4.2 X-ray structure analyses of 155 and 133

X-ray structure analyses of the dithiacyclophane **155** and the bischromium complex **133** were determined by K. Beveridge at the University of Victoria. As mentioned in Section 2.4.1, differences in nmr spectra suggested a change in geometry between the monomethyl phane **155** and the dimethyl phane **52**. This was also supported by the X-ray structure analyses of these two molecules.

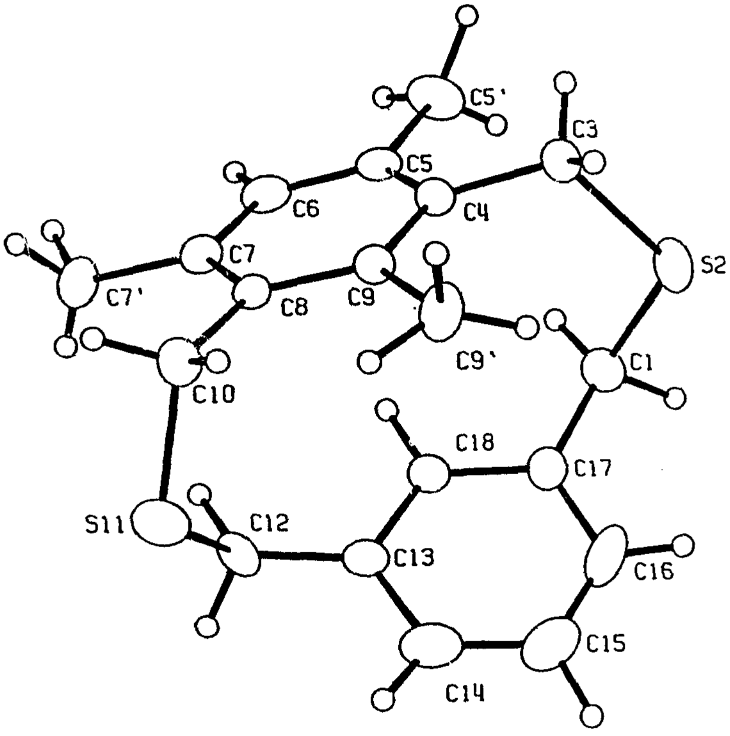
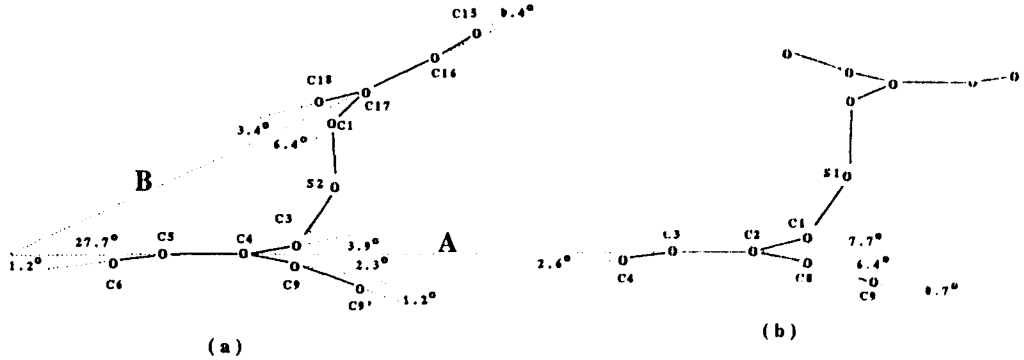


Figure 13. An ORTEP drawing of **155**.

As seen in Figure 13, the monomethyl molecule **155** has an *anti*-stepped configuration with both rings being slightly bent outwards in distorted boats, as is found for the dimethyl compound **52**[116)]. However, the two aromatic rings in **155** are not parallel, as they are in **52**, but are inclined at 27.7° with respect to one another (see Figure 14). Thus the internal methyl C9'of compound **155** is much further away from the shielding zone of the opposite deck, and hence is less shielded (δ 1.05 vs. 0.40).

Another feature of the molecule **155**, is that the deviation of C9 from the least-squares plane C4-C5-C7-C8 is about one third of that of the corresponding carbon C8 in



(a)

(b)

Figure 14. Molecular projections of **155**(a) and **52**(b).

52, indicating less steric compression on the internal carbon in **155**. Finally the closest distance between the two aromatic rings in **155** is 2.998Å, much less than that (3.242Å) in **52**. Figure 14 shows the molecular projection of the molecules **155** and **52**.

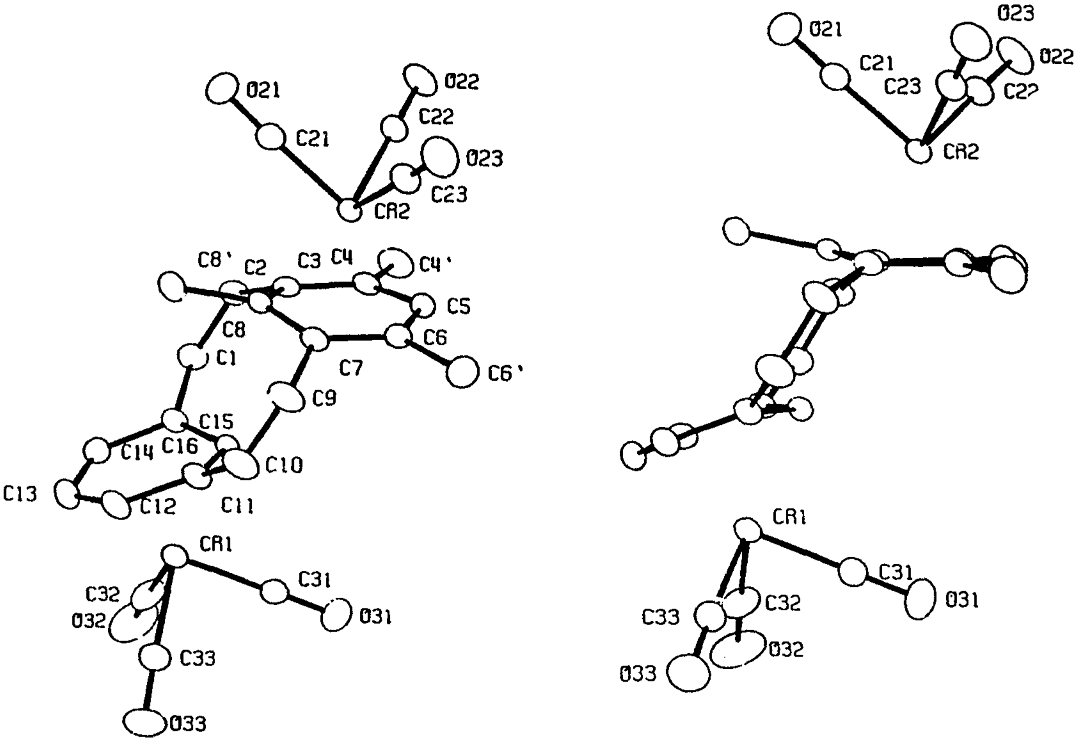


Figure 15. An ORTEP drawing of **133**.

The X-ray structure of the bischromium complex **133** (Figure 15) revealed some similar features as observed in the molecule of **155**. The angle between the plane A (the least-squares plane of C3-C4-C6-C7) and the plane B (the least-squares plane of C11-C12-C14-C15) is 19.8° (see Figure

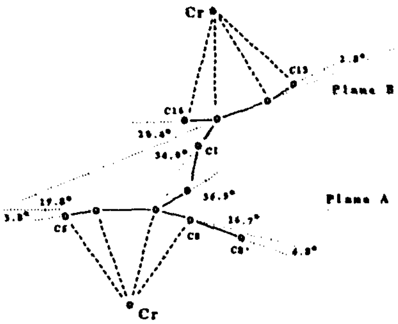


Figure 16. A molecular projection of **133** along the axis passing through the mid-points of C1-C2 and C9-C10.

16), less than that (27.7°) in **155** (see Figure 14(a)). It is notable that the deviations of C8 and C16 from their basal planes are about four to five times those in **155**, indicating much stronger steric interaction of the two aromatic rings in **133**. This is obviously a consequence of the shorter bridges (two carbons) in **133**, compared to the those in **155** consisting of three atoms. For the same reason, the closest non-bonded distance between the inner carbons C8 and C16 is 2.612Å (2.998Å for **155**), even shorter than the corresponding distance (2.819Å in *anti*-8,16-dimethyl[2.2]-metacyclophane **37**[38)]. The increase of the sp^2 bond angles C2-C1-C15 and C3-C2-C1 to 125.1° and 123.2°, (from 120°) helps increase the distance between the two aromatic rings, and hence also help the molecule to minimize the steric strain. Another significant feature of the molecule is the torsional angle along the bridge double bonds -- 16.9° for C3-C2-C1-C15, instead of the expected 0°.

CHAPTER THREE

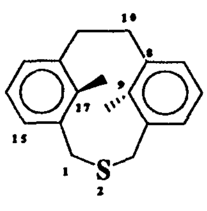
STEREOCHEMICAL FEATURES OF METACYCLOPHANES, METACYCLOPHANENES AND THEIR METAL COMPLEXES

3.1 The geometry and nmr features of the cyclophanes 72

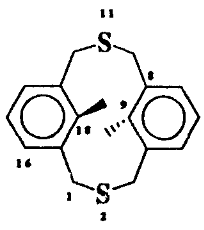
3.1.1 The X-ray structure of the cyclophane 72a

The X-ray structure analysis of **72a** was carried out by K. Beveridge of this department and an ORTEP drawing of the molecular structure is shown in Figure 17. The molecule **72a** has an *anti*-stepped geometry in the solid state, and its ^{1}H nmr spectrum suggests this geometry is also retained in solution. As with other *anti*-[2_2] and [3_2]metacyclophanes, the aromatic rings are bent outward in a slightly distorted boat.

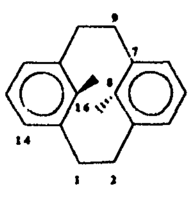
Deviations of the inner carbons (C9 and C17 in **72a**, C9 and C18 in **52**, C8 and C16 in **37**) from their basal planes



72a



52



37

(the least-squared planes of the four aromatic ring carbons excluding the inner and outer aromatic carbons) are observed to be much larger than these of the outer carbons in these molecules. Obviously the largest steric compression must occur between the two inner carbons which are very close to one another in space, and this deviation indirectly reflects the steric compression between them. We found that the deviations of these inner carbons from their corresponding basal planes were inversely proportional to the distance between the two inner carbons (see Table 10).

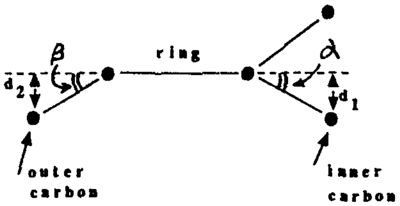


Table 10. Comparison of deviations in **72a**, **37**, and **52**

Compound	Distances(Å)		Angles(°)		Distance(Å)
	d_1	d_2	α	β	between inner C
37	0.187	0.088	15.4	7.3	2.819
72a	0.126	0.041	10.2*	3.3*	3.014
52	0.079	0.029	6.4	2.6	3.242

*) The average deviation of both inner and outer carbons.

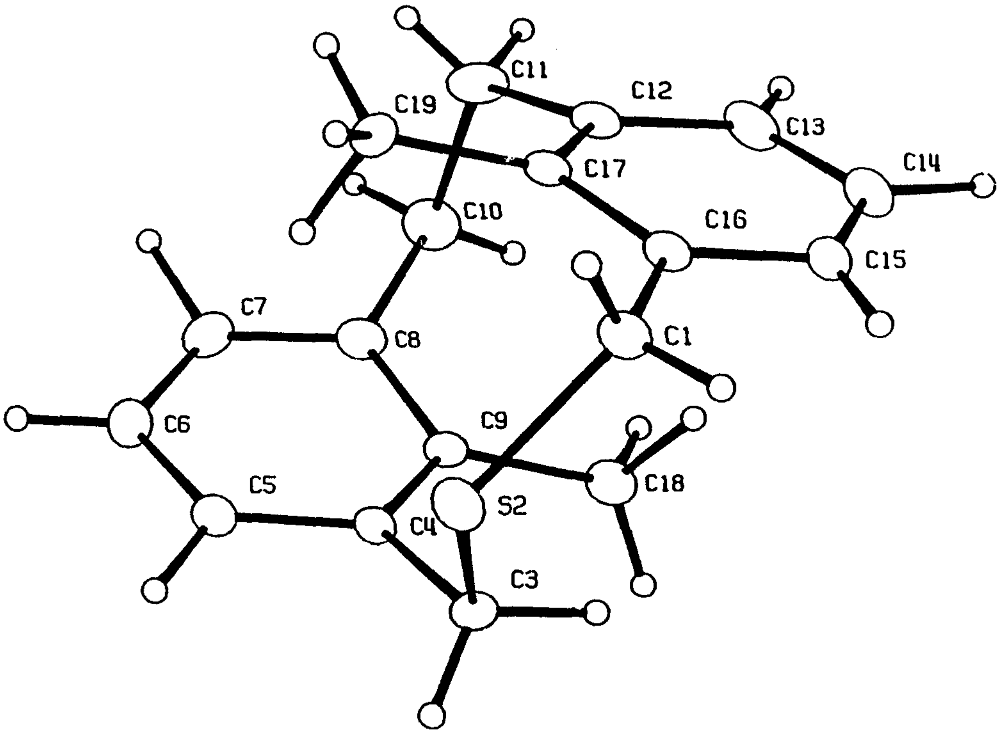
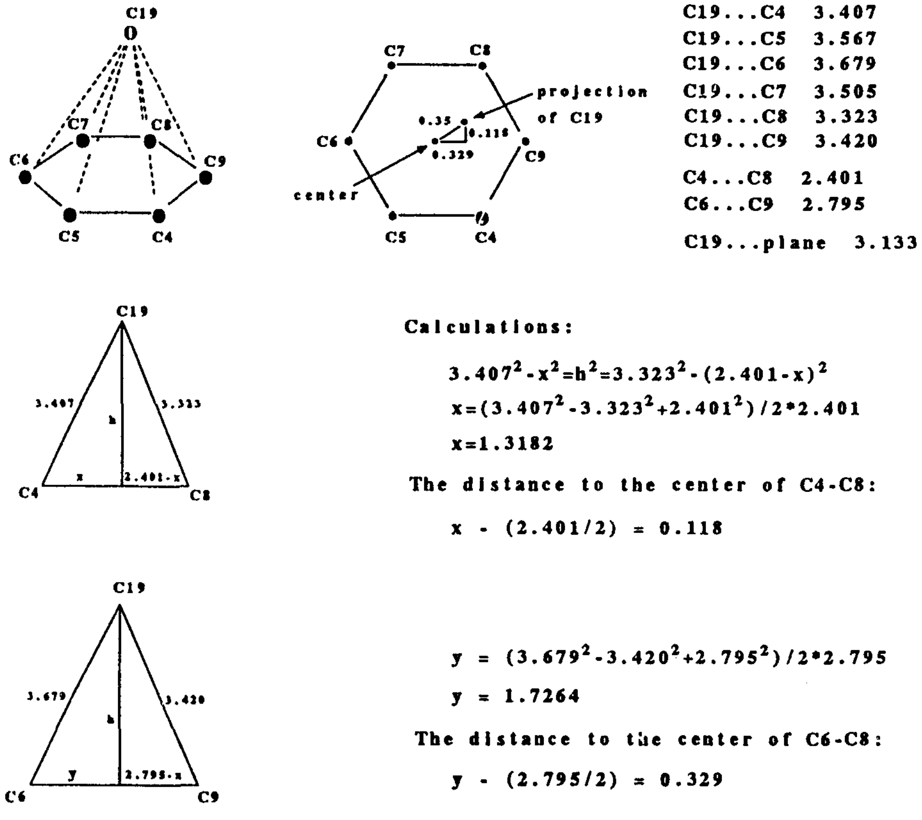


Figure 17. An ORTEP drawing of **72a**.

Among these three molecules, the shortest distance between the two inner carbons is 2.819 Å in **37** which has the two shortest bridges, and the largest distance is 3.242 Å in **52** which has the two longest bridges. Thus, the largest deviation of the inner carbons was observed in **37**, and the smallest deviation was found in **52**. Since **72a** has a short bridge as found in **37**, and a long bridge as one of these in **52**, deviations of the inner carbons in **72a** are about the average for the three molecules. As there are two bridges of different length in **72a**, the shortest distance between the two aromatic rings is the distance between C8 and C12 (3.005 Å), rather than the distance between the two inner carbons (3.014 Å between C9 and C17) as in the cases for **37** and **52** which have both bridges of equal length. For the same reason, the two arenes are not parallel, as seen in **37** and **52**, but with a dihedral angle of 11.9° along the vector passing though the mid-points of C1-C3 and C10-C11.



C19...C4 3.407
C19...C5 3.567
C19...C6 3.679
C19...C7 3.505
C19...C8 3.323
C19...C9 3.420

C4...C8 2.401
C6...C9 2.795

C19...plane 3.133

Calculations:

$3.407^2 - x^2 = h^2 = 3.323^2 - (2.401 - x)^2$
$x = (3.407^2 - 3.323^2 + 2.401^2)/2*2.401$
$x = 1.3182$

The distance to the center of C4-C8:

$x - (2.401/2) = 0.118$

$y = (3.679^2 - 3.420^2 + 2.795^2)/2*2.795$
$y = 1.7264$

The distance to the center of C6-C8:

$y - (2.795/2) = 0.329$

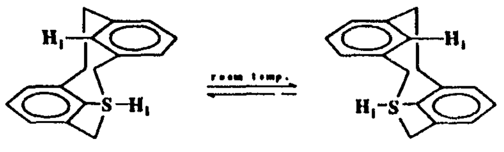
Figure 18. Calculation of the projection of the internal methyl onto the opposite aromatic ring.

Another feature of **72a** is that the internal methyl carbons are situated above the opposite aromatic ring, about

0.35 Å off the symmetric axis passing through the centre of and perpendicular to that ring. The result of these calculations (Figure 18) clearly indicates that the internal methyls in **72a** are above the opposite deck and hence are strongly shielded by the ring current of that ring.

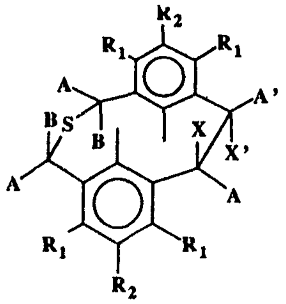
3.1.2 NMR features of the bridge protons in cyclophanes 72

The parent thiacyclophane **161** with two internal hydrogen substituents is believed to be mobile[117] in solution on the basis of its variable temperature ^{1}H nmr spectrum which only shows singlets for the bridge protons. In contrast, the rigid *anti*-stepped geometry of **72** appears to be maintained in solution since the bridge protons remain non-equivalent. The two protons on C1 (or C3) of the bridge containing the sulphur atom are chemically non-equivalent in **72**, giving an AB spin system due to coupling with one another. In all the three cases, chemical shifts of H_A and H_B and coupling constants between these two protons are very similar ($\Delta\delta \leq 0.05$ ppm in both cases). This might reflect the similarity of the sulphur-containing bridge in these three molecules **72a**, **72b**, and **72c** (see Table 11).



161 **161**

Table 11. Comparison of chemical shifts and coupling constants of the bridge protons in **72a, 72b, 72c**

		72a	**72b**	**72c**
	A(δ)	3.85	3.80	3.82
	B(δ)	3.73	3.70	3.70
	J_{AB} (Hz)	13.9	13.9	13.5
	A(δ)	2.94	2.85	3.02
	X(δ)	2.64	2.60	2.51
72a $R_1=R_2=H$	J_{AX} (Hz)	-12.6	-12.5	-13.3
72b $R_1=H$, $R_2=CH_3$	$J_{XX'}$ (Hz)	12.4	12.5	12.8
72c $R_1=CH_3$, $R_2=H$	$J_{AX'}$ (Hz)	4.5	4.4	4.2
	$J_{AA'}$ (Hz)	2.6	2.7	3.0

The four protons in the ethano bridge appear as an AA'XX' spin system with the A nuclei (the pseudo-equatorial protons in the drawing above) being upfield (δ 2.94 - 3.02) and the X nuclei (the axial protons) downfield (δ 2.51 - 2.64). The assignments of chemical shifts to the A and X nuclei are made by considering the magnitude of the four coupling constants of this AA'XX' system (see Table 11). Figure 19 shows the spectrum of the AA'XX' system for **72b** and the simulated spectrum of this part for comparison. It is noted that the values for the chemical shifts and

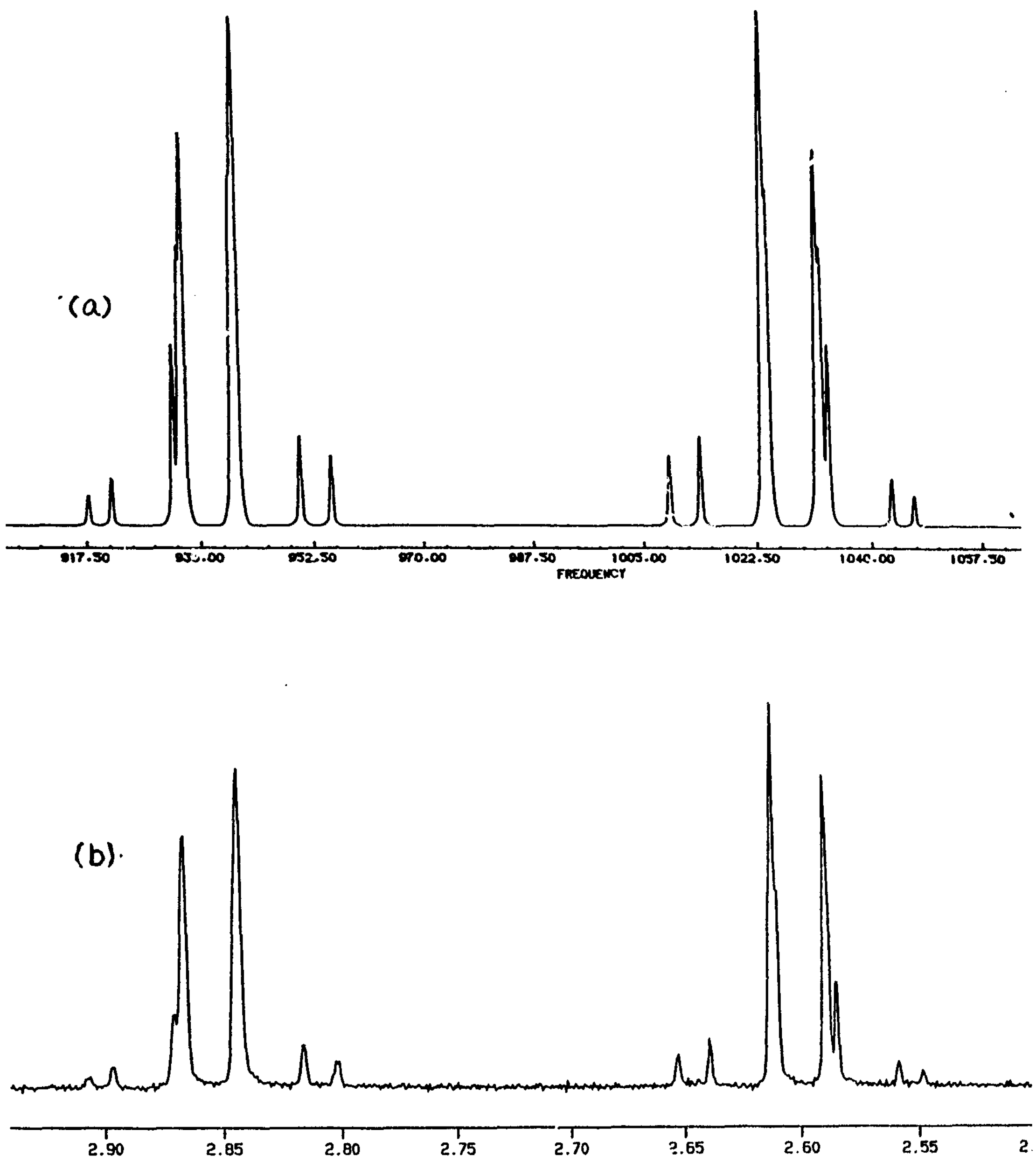


Figure 19. The ^{1}H nmr spectra of the AA′XX′ system in **72b**; (a) simulated; (b) experimental.

coupling constants of these four bridge protons in **72b** were very similar to those in **72a**, while the values for **72c** are slightly different. This might suggest that the two external methyls in **72b** have no influence on the geometry of the bridge since they are far away from the bridge protons. However, the four external methyls in **72c** are in the *ortho* positions to the bridge carbons, and hence are much closer to the bridge protons in space. As a consequence, the steric compression between the external methyls and the bridge protons might slightly change the stereochemistry of the bridge, compared to that in the reference compound **72a**.

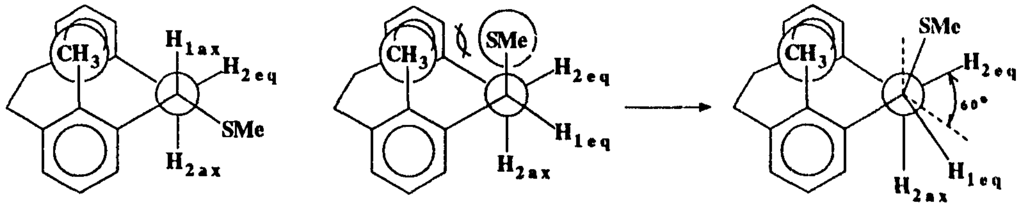
Another interesting feature of these bridge protons is that the coupling constant between the two equatorial bridge protons ($J_{AA'}$) is smaller than that between the equatorial and axial protons ($J_{AX'}$ and $J_{A'X}$). The values found for the coupling constants indirectly reflect the dihedral angles for the bridge protons. The relationship between ^3J (coupling constant of the vicinal protons in an ethane-like fragment, H-C-C-H) and the dihedral angle (θ) of H-C-C-H was first established by Karplus[118)] in the following equation:

$$^3J = A + B \times \cos\theta + C \times \cos 2\theta \qquad \text{(eqn 3.1)}$$

with A = 7, B = -1, and C = 5 Hz.[119)] It is apparent that the values of ^3J decrease as the angles increase from 0° (cis conformation) to 90°, at which the minimum is found, and then grow larger from 90° to 180° (trans conformation). Although direct calculations of dihedral angles among these bridge protons are not very reliable since the coefficients in Equation 3.1 are system dependent, it is safe to use them to compare relative values of dihedral angles. In our system, the smaller value of $J_{AA'}$ than $J_{AX'}$ and $J_{A'X}$ indicates that the dihedral angle between the equatorial protons A and A′ is larger than that between the axial (X and X′) and equatorial protons. This fact might be explained by considering the steric compression between the bulkier internal methyls and the axial bridge protons (X and X′). The repulsion might push the X nuclei further away and hence enlarge the angle between the A nuclei, but reduce the angle between the A and X nuclei. This steric compression is perhaps the only factor that can account for the small values of ^3J in **72a** (2.6 Hz) and **72b** (2.7 Hz). However, in **72c** an additional steric compression between the external methyls and the equatorial bridge protons (A and A′) counterbalances that between the internal methyls and the axial protons. Thus a slightly larger value of $J_{AA'}$ and a somewhat smaller value of $J_{AX'}$ were observed experimentally for the molecule **72c**. This suggests a smaller dihedral angle between the A nuclei, and a larger angle between the A and X nuclei. The largest value of $J_{XX'}$ (trans relationship) also indicates that the angle between the two X nuclei in **72c** is closer to 180° than that in **72a** or **72b**.

3.2 NMR features of the bridge protons in the 1-methylthio-[2.2]metacyclophanes 92

The stereochemistry of the bridge methylthio group in **92**, and similar compounds, can be assigned unambiguously by comparing chemical shifts of the internal methyl protons and the adjacent (to the bridge methylthio group) external ring proton (see Table 12). Moreover, the ^{1}H nmr spectra of these methylthio bridge compounds reveal some interesting features of the bridge protons. Firstly, it was found that the coupling constants of the equatorial H-1 proton with the two H-2 protons are both small in **ax-92** (entry 2 and 4), but are large and small in **eq-92** (entry 1,3,5-9). On the other hand, both coupling constants of the H-2ax protons are large in **eq-92**, but are large and small in **ax-92**. This can be understood by examining the dihedral angles between the H-1 and H-2 protons. From Newman projections for **eq-92** and **ax-92** (see Figure 20), we can see the difference in relationship of the H-1 proton to the two adjacent H-2 protons. In the pseudo-equatorial isomer **eq-92**, the proton H-1ax is trans to H-2ax and gauche to H-2eq. Hence a large coupling for the trans (~180°) one and a small coupling for the gauche (~60°) one are predicted by the Karplus equation. While for the other equatorial isomer **ax-92**, the H-1 proton is gauche to both the H-2 protons and as a consequence, two small couplings for H-1 are predicted.



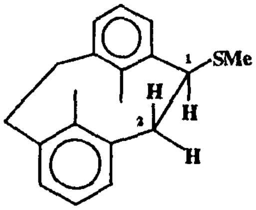
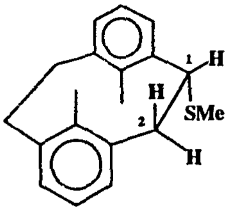
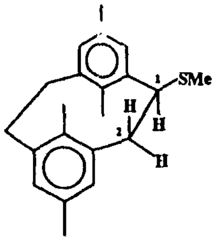
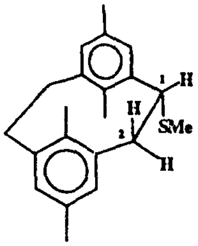
eq-92

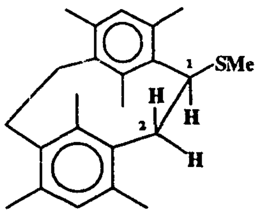
ax-92

Figure 20. Newman projections of **ax-92** and **eq-92**.

Secondly, it is noted that the two gauche coupling constants ($J_{1eq-2ax}$ and $J_{1eq-2eq}$) in **ax-92** are quite different from one another - one is about 7 Hz and the other is less than 1 Hz. Interestingly, the single gauche coupling ($J_{2eq-1ax}$) in **eq-92** is just about in between (about 4 Hz). This fact clearly indicates differences in the dihedral angles between the protons involved. These differences may be explained by considering the steric repulsion between the internal methyl and the axial SMe group in the molecule **ax-92**. Since these two bulky groups are spatially much closer in **ax-92**, a strong steric repulsion exists between them, but not in **eq-92**, in which these two groups are far apart. As a consequence, the axial SMe in **ax-92** is pushed away from the internal methyl to ease the steric repulsion between them, and this led to an increase of the dihedral angle between H-1eq and H-2eq, but a decrease of the dihedral angle between H-1eq and H-2ax. Thus, the former angle is closer to 90°, and corresponds to the smallest

Table 12. Observed chemical shifts and coupling constants of the methylthio bridge protons in [2.2]metacyclophanes

Compound	Entry No	δ (ppm)	J (Hz)
 **eq_92a**	1	1ax: 4.02 2eq: 3.16 2ax: 2.64	$J_{1ax\text{-}2ax}$: 11.3 $J_{2eq\text{-}1ax}$: 4.2 $J_{2ax\text{-}2eq}$: 12.5
 **ax_92a**	2	1eq: 4.41 2eq: 3.28 2ax: 3.04	$J_{1eq\text{-}2ax}$: <1.0 $J_{2eq\text{-}1eq}$: 6.9 $J_{2ax\text{-}2eq}$: 14.0
 **eq_92b**	3	1ax: 3.99 2eq: 3.11 2ax: 2.61	$J_{1ax\text{-}2ax}$: 11.3 $J_{2eq\text{-}1ax}$: 4.3 $J_{2ax\text{-}2eq}$: 12.4
 **ax-92b**	4	1eq: 4.34 2eq: 3.26 2ax: 2.97	$J_{1eq\text{-}2ax}$: 0.8 $J_{2eq\text{-}1eq}$: 7.1 $J_{2ax\text{-}2eq}$: 14.0



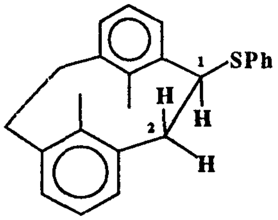
eq_92c

5

1ax: 3.68 $J_{1ax-2ax}$: 11.5

2eq: 3.25 $J_{2eq-1ax}$: 2.7

2ax: 2.85 $J_{2ax-2eq}$: 12.8



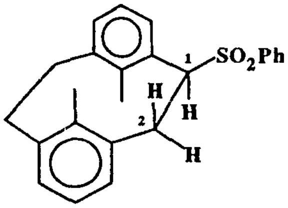
162

6

1ax: 4.48 $J_{1ax-2ax}$: 11.4

2eq: 3.33 $J_{2eq-1ax}$: 4.2

2ax: 2.79 $J_{2ax-2eq}$: 12.5



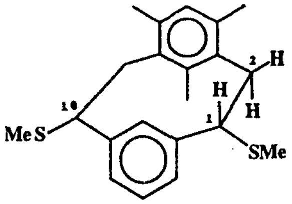
163

7

1ax: 4.20 $J_{1ax-2ax}$: 11.4

2eq: 3.64 $J_{2eq-1ax}$: 3.4

2ax: 3.20 $J_{2ax-2eq}$: 12.3



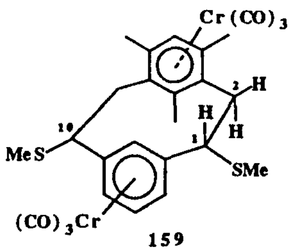
157

8

1ax: 3.36 $J_{1ax-2ax}$: 12.8

2eq: 3.24 $J_{2eq-1ax}$: 3.4

2ax: 2.37 $J_{2ax-2eq}$: 11.3



159

9

1ax: 3.30 $J_{1ax-2ax}$: 13.6

2eq: 2.97 $J_{2eq-1ax}$: 3.4

2ax: 2.35 $J_{2ax-2eq}$: 11.7

==

value of ^3J as predicted by the Karplus Equation. In the latter cases, the angle is reduced to around 30°, which gives a much larger ^3J. In **eq-92**, the dihedral angle between H-1ax and H-2eq is predicted to be around 60°, the normal angle for a gauche conformation, and hence this coupling constant is predicted to be larger than that for 90° but smaller than that for 30°.

Lastly, It was observed that the chemical shifts of the equatorial H-1 proton in **ax-92** were quite different from those of the axial H-1 proton in **eq-92**. The equatorial H-1 proton in **ax-92** appeared at relatively lower field (about 0.4 ppm) than the axial H-1 proton in **eq-92** (entry 1,2,3 and 4). This might indicate that the equatorial H-1 proton is in a stronger deshielding zone of the adjacent aromatic ring, probably due to its closeness to the plane of the six aromatic carbons, or it might also indicate that the axial H-1 proton is in a stronger shielding zone of the opposite deck than is the equatorial H-1 proton.

All of these observations are useful in making assignments of the stereochemistry of the methylthio groups, and this can be used in conjunction with criteria, based on chemical shifts of the internal groups and the adjacent (to the methylthio bridge) external proton(s), to permit unambiguous assignment of the stereochemistry for these kinds of bridges.

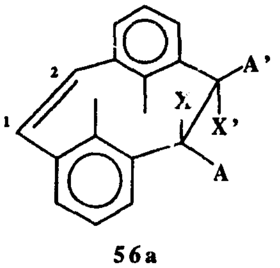
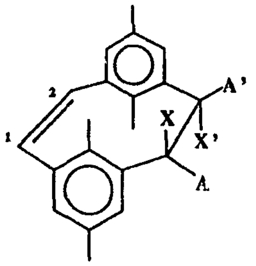
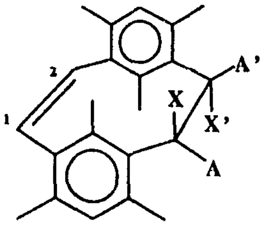
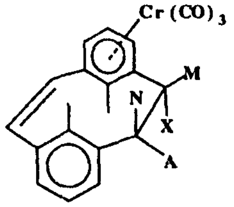
The four protons in the ethano bridge of these compounds **92** give two sets of multiplets centred at δ 2.9 and 2.7 ppm respectively. These multiplets can not be analyzed due to their complexity and lead to no useful information about the conformation of these bridges.

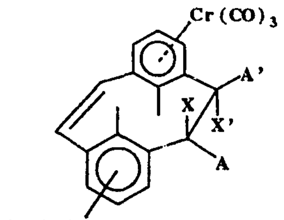
In summary, comparison of coupling constants between the methylthio bridge protons together with chemical shift data of the internal groups and the adjacent external ring protons can lead to unambiguous assignment of the stereochemistry of the methylthio group.

3.3 The geometry and nmr features of cyclophanenes 56 and their metal complexes.

Since there is a symmetric axis (C_2 rotation axis) passing through the mid-points of the C1-C2 and C9-C10 bonds for each of the molecules of **56**, the olefinic protons H-1 and H-2 are magnetically equivalent and show a singlet in the ^{1}H nmr spectra. It is notable that the chemical shifts of the olefinic protons in these compounds are very consistent, with the largest difference only being 0.1 ppm (see Table 13). However, the two pseudo-equatorial protons and the two axial protons in the ethano bridge (C9-C10) are not magnetically equivalent due to the rigid *anti*-stepped geometries of these molecules. In their ^{1}H nmr spectra, these four bridge protons show an AA'XX'multiplet which can be analyzed as a four-spin system with two chemical shifts

Table 13. ^{1}H nmr data of the olefinic and ethano bridge protons in **56** and their metal complexes.

Compound	Entry No	δ (ppm)	J (Hz)
 **56a**	1	A: 2.89 X: 2.50 H1/2: 6.59	J_{AX} :-12.2* $J_{AX'}$: 3.9* $J_{AA'}$: 2.8* $J_{XX'}$: 12.1*
 **56b**	2	A: 2.81 X: 2.48 H1/2:6.54	J_{AX} :-12.1* $J_{AX'}$: 3.9* $J_{AA'}$: 2.8* $J_{XX'}$: 12.2*
 **56c**	3	A: 3.06 X: 2.17 H-1/2:6.64	J_{AX} :-13.1* $J_{AX'}$: 3.0* $J_{AA'}$: 4.0* $J_{XX'}$: 12.0*
 **99a**	4	A: 3.07 N, M: 2.77 X: 2.19 H-1: 6.68 H-2: 6.35	J_{AN} :-13.4 J_{XN} : 3.9 J_{1-2}: 11.1



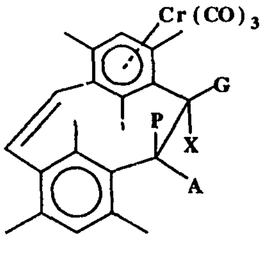
100a

5

A: 2.97 not all lines

X: 2.52 are observed

H1/2: 6.65



99c

6

A: 3.20 J_{AP} :-13.0$^{\#}$

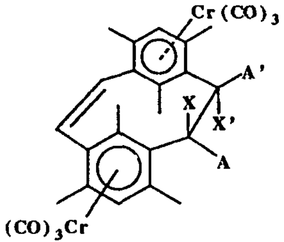
G: 2.94 J_{AG} : ~3.1$^{\#}$

P: 2.43 J_{PG} : ~3.1$^{\#}$

X: 1.92 J_{PX} : 12.7$^{\#}$

H1: 6.95 J_{1-2}: 11.1

H2: 6.36



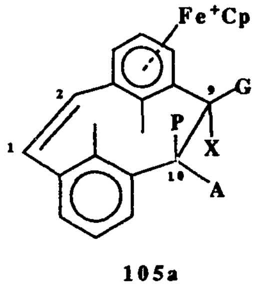
100c

7

A: 3.12 not all lines

X: 2.22 are observed

H1/2: 6.69



105a

8

A: 3.11 J_{AP} :-13.1

G: 3.00 J_{GX} : 12.3

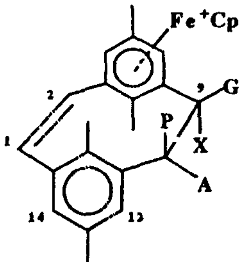
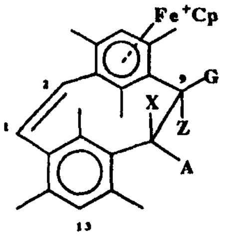
P: 2.58 J_{PG} : 3.6

X: 2.42 J_{XA} : 4.1

J_{AG} : 3.0$^{\$}$

H-1: 7.13 J_{XP} : 12.1$^{\$}$

H-2: 6.53 J_{1-2}: 11.1

 **105b**	9	A: 3.05	J_{AP} : -12.9
		G: 2.95	J_{GX} : 12.0
		P: 2.54	J_{PG} : 3.4
		X: 2.42	J_{XA} : 3.9
			J_{AG} : 3.0$^{\$}$
		H-1: 7.08	J_{XP} : 12.0$^{\$}$
		H-2: 6.53	J_{1-2}: 11.1
 **105c**	10	A: 3.25	not resolved
		G: 3.17	
		X and Y: 2.18	
		H1: 7.24	J_{1-2}: 11.3
		H2: 6.58	

*) Refined values by simulation.

#) Values are not very accurate due to lower resolution.

$) Calculated values (see discussion).

and four coupling constants.[120)] The optimum values of the chemical shifts and coupling constants were obtained by refining these values with the nmr simulation program available at the University of Victoria (see Table 13). Figure 21 shows the simulated spectrum of this four spin system, in comparison to the experimental one for the cyclophanene **56c**.

Notably, values of chemical shifts and coupling constants of the bridge protons in **56b** are almost identical to those for **56a**. However, the chemical shifts of the A and the X nuclei in **56c** are further apart and all the four coupling constants are apparently different from those in **56a**. This might suggest that the presence of external methyls ortho to the bridge introduces a steric compression between the external methyls and the equatorial protons, which bring about changes in the torsional angles between these protons.

In the bis-chromium complexes **100a** and **100c**, similar features were observed as those for the parent **56** - the olefinic protons were a singlet and the ethano bridge was an AA'XX' spin system. However, both of these two kinds of protons are slightly deshielded (about 0.05 ppm), compared to the corresponding protons in **56**. Upon complexation, the bridge protons are subject to two opposing effects: (a) an upfield shift caused by $Cr(CO)_3$ complexed to the ring where these protons are attached, and (b) a downfield shift caused by reduced ring current in the opposite $Cr(CO)_3$ coordinated ring. The observed very small downfield shift must be the net result of these two opposing effects. This explanation was further supported by the ^1H nmr data of the same bridge protons in the mono-chromium complexes. In these complexes, the protons on both sides of the bridges are not equal any more, because of the lack of symmetry in the molecules. Thus the olefinic protons become an AB two-spin system and the

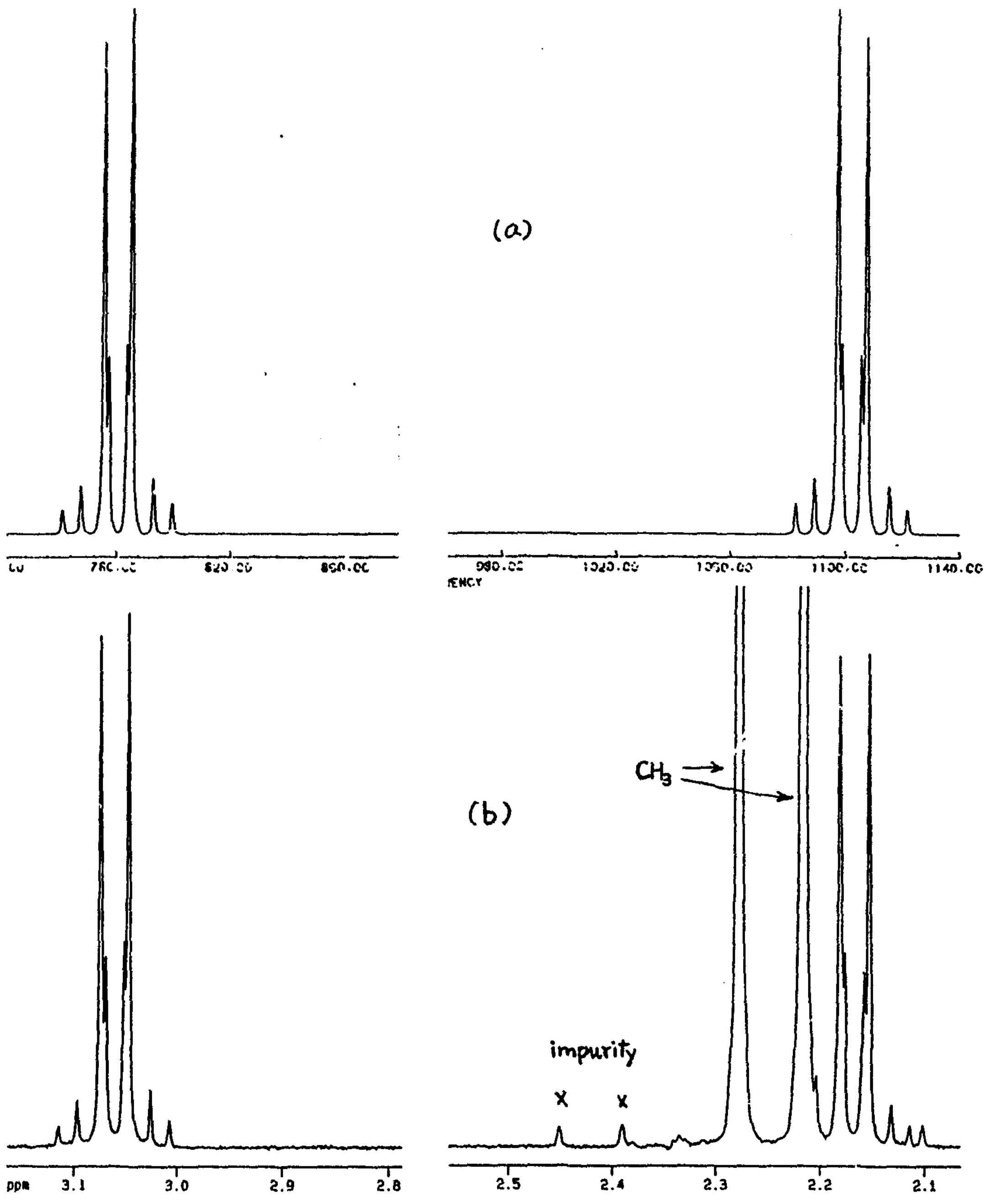


Figure 21. Comparison of the simulated(a) and experimental (b) spectra of the ethano bridge protons in **56c**

four ethano bridge protons are all chemically different. Moreover, the protons on the carbons attached to the coordinated ring are now only subject to the complexation effect (upfield shift) but not the ring current reduction effect of the opposite uncoordinated deck. In contrast, the protons on the bridge carbons attached to the uncoordinated ring are mainly subject to the ring current reduction effect of the opposite complexed ring. Thus, it becomes possible to estimate the absolute values of these two opposing effects upon the bridge protons by comparing chemical shifts of the protons in **99** to those in the parent **56**. The results obtained are summarised in Table 14.

It is interesting to note that the sums of chemical shift differences ($\Delta\delta$) for the proton H-1 (ring current reduction) and for the proton H-2 (complexation effect) in the mono-complexes **99** are almost the same as the chemical shift difference for the same protons in the bis-complexes **100**. These observations confirm that the slightly downfield shift of the olefinic protons in the bis-complexes **100** is a combination of the two opposing effects brought about upon complexation by the $Cr(CO)_3$ moiety, as we discussed above. However, there are some discrepancies when this argument is applied to the bridge protons H-9 and H-10. One possible reason for this might be that the anisotropy of the $Cr(CO)_3$ moiety still exerts a minor influence on the H-10 protons adjacent to the uncomplexed ring. With consideration of this minor complexaton effect, the chemical shift difference for

Table 14. Chemical shift differences of the bridge protons between **99** and **56**

Proton	chemical shift difference ($\Delta\delta$) **99a**	**99b**	**100a**	**100c**
H-1	+0.29	+0.31	+0.06	+0.05
H-2	-0.24(0.01)	-0.28(0.02)*		
H-10eq	+0.18(0.01)	+0.15(0.03)	+0.08	+0.06
H-10ax	+0.27(0.06)	+0.26(0.04)	+0.02	+0.05
H-9eq	-0.11	-0.12		
H-9ax	-0.31	-0.25		

Notes: $\Delta\delta = \delta_{complex} - \delta_{parent}$

*) the values in parentheses are calculated by

$$\text{value} = \Delta\delta_{bis} + \Delta\delta_c - \Delta\delta_u$$

where $\Delta\delta_c$ is chemical shift difference for the protons adjacent to the complexed ring, and $\Delta\delta_u$ for the protons adjacent to the uncomplexed ring.

the bridge protons in the bis-complexes can be treated as:

$$\Delta\delta_{bis} = \Delta\delta_c + \Delta\delta_u + x$$

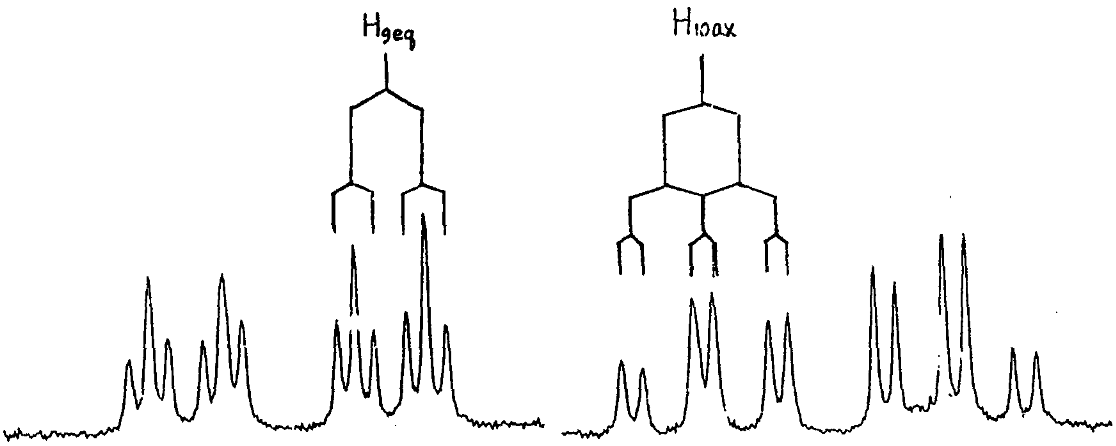
where $\Delta\delta_c$ is the chemical shift difference for the bridge protons (H-1 and H-9) adjacent to the complexed ring, and $\Delta\delta_u$ is for the bridge protons (H-2 and H-10) adjacent to the uncomplexed ring, and x is the complexation shift experienced by the H-2 and the H-10 protons. From the above equation, values of x can be calculated, using the H-10ax proton as an example, as follows

$$\begin{aligned} x &= \Delta\delta_{bis}(\text{H-10ax}) + \Delta\delta_{c}(\text{H-9ax}) - \Delta\delta_{u}(\text{H-10ax}) \\ &= 0.02 - (-0.31) - (0.27) \\ &= 0.06 \end{aligned}$$

The calculated values of x for H-2 and H-10 protons are given in parentheses in Table 14. Notably, these values (from 0.01 to 0.06 ppm) are much smaller (about one fifth) than those (from 0.11 to 0.31 ppm) experienced by the H-1 and H-9 protons which are much closer to the $Cr(CO)_3$ in space. Also, the complexation shifts for the H-10ax protons are larger than those for the H-10eq and H-2 protons, which are even further from the center of the shielding zone of the $Cr(CO)_3$ moiety.

Chemical shifts and coupling constants of the four different ethano bridge protons in the mono-complexes can be analyzed in some cases such as in **105a** and **105b** since no overlap of these proton peaks was observed in their ^1H nmr spectra. For example, the protons H-9eq and H-10eq in **105a** and **105b** appeared as doublets of triplets, while the protons H-9ax and H-10ax as triplets of doublets. In fact, these doublets of triplets or triplets of doublets are really collapsed doublets of doublets of doublets since two of the three coupling constants for each of these protons are very

No	$H10_{eq}$(Hz)	$H9_{eq}$	$H10_{ax}$	$H9_{ax}$
1	1131.324	1090.698	943.292	885.827
2	1127.821	1087.470	939.504	881.937
3	1124.164	1084.107	930.847	873.741
4	1118.125	1078.479	927.328	869.678
5	1114.702	1075.083	917.857	861.670
6	1111.096	1071.671	914.441	857.335



Equations:

$J_{eq-ax(gem)}=[(1-4)+(3-6)]/2$ $J_{ax-eq(vin)}=[(1-2)+(5-6)]/2$

Calculations:

$J_{10eq-10ax}=[(1131.324-1118.125)+(1124.164-1111.096)]/2= 13.134$

$J_{9eq-9ax}=[(1090.698-1078.479)+(1084.107-1071.671)]'2= 12.328$

$J_{10ax-9eq}=[(943.292-935.504)+(917.857-914.441)]/2= 3.602$

$J_{9ax-10eq}=[(885.827-881.937)+(861.670-857.335)]/2= 4.113$

Calulations of $J_{10eq}-{}^{9}{}_{eq}$:

$J_{10eq-9eq}+J_{10eq-10ax}+J_{10eq-9ax}=(1-6)$ then $J_{10eq-9eq}=(1131.324-1111.096)-13.134-4.113= 2.981$

or $J_{10eq}-{}^{9}{}_{eq}+J_{9eq}-{}^{9}{}_{ax}+J_{9eq-10ax}=(1-6)$ then $J_{10eq-9eq}=(1090.698-1071.671)-12.328-3.602= 3.097$

$J_{10eq-9eq}$(average)$=(2.981+3.097)/2=3.039$

Calculations of $J_{10ax-9ax}$:

$J_{10ax-9ax}+J_{10ax-10eq}+J_{10ax-9eq}=(1-6)$ then $J_{10ax-9ax}=(943.291-914.441)-13.134-3.602= 12.115$

or $J_{10ax-9ax}+J_{9ax-9eq}+J_{9ax-10eq}=(1-6)$ then $J_{10ax-9ax}=(885.827-857.350)-12.328-4.113= 12.076$

$J_{10ax-9ax}$(average)$=(12.115+12.036)/2= 12.076$

Figure 22. Calculations of coupling constants of the ethanó bridge protons in **105a**.

close (see Figure 19). Since the middle peaks of these triplets are overlapped doublets of doublets, only four of the six coupling constants can be accurately determined from the set of peaks for each proton. The other two coupling constants ($J_{10ax-9ax}$ and $J_{10eq-9eq}$) have been calculated using equations 1, and 2, and details of the calculations are given in Figure 22. The four chemical shifts and six coupling constants can be found in Table 13.

3.3.2 The X-ray structure of the cyclophanene-iron complex 105a

X-ray structure analysis of the iron cyclophanene complex **105a** was determined by K. Beveridge at the University of Victoria. An ORTEP drawing of the molecule is shown in Figure 23. This X-ray structure determination revealed some interesting features of the coordinated cyclophanene molecule **56a**. Firstly, deviations of the inner carbons C8 and C16 from their corresponding basal planes (the planes of C3-C4-C6-C7 and C11-C12-C14-C15, repectively) are 0.224Å and 0.220Å, even larger than that (0.187Å) for the inner carbons in *anti*-8,16-dimethy[2.2]metacyclophane **37**. This observation reflected that stronger steric compression exists between the two aromatic rings as a result of even shorter inter-ring distances (2.687Å between C8...C16). This inter-ring distance was the shortest

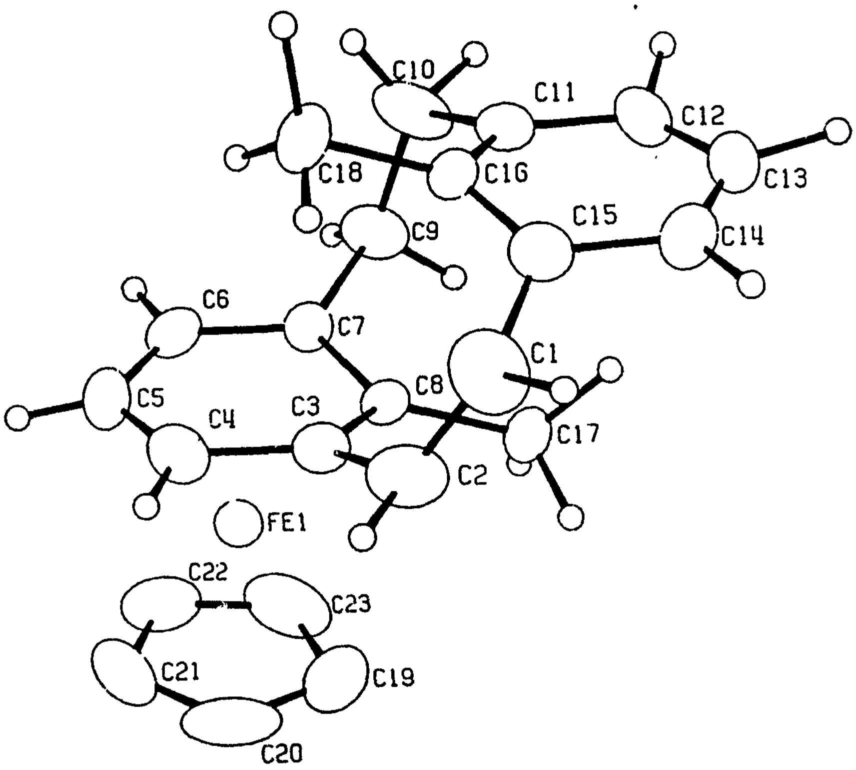


Figure 23. An ORTEP drawing of **105a**.

compared to the other three molecules **52**, **72a**, and **37** (see Table 10). The obvious reason for this is that the molecule **56a** has an etheno (C=C) bridge which is shorter than the ethano bridge as seen from the inter-ring distances between the two bridged aromatic carbons (3.152Å for C7...C11 vs. 2.997Å for C3...C15). As we discussed in Section 3.1.1, there is a reciprocal relationship between deviations of the inner carbons from their basal planes and distances between the two inner carbons, as seen from a straight line in the plot of the inner carbon deviation vs the inner carbon distance (see Figure 24).

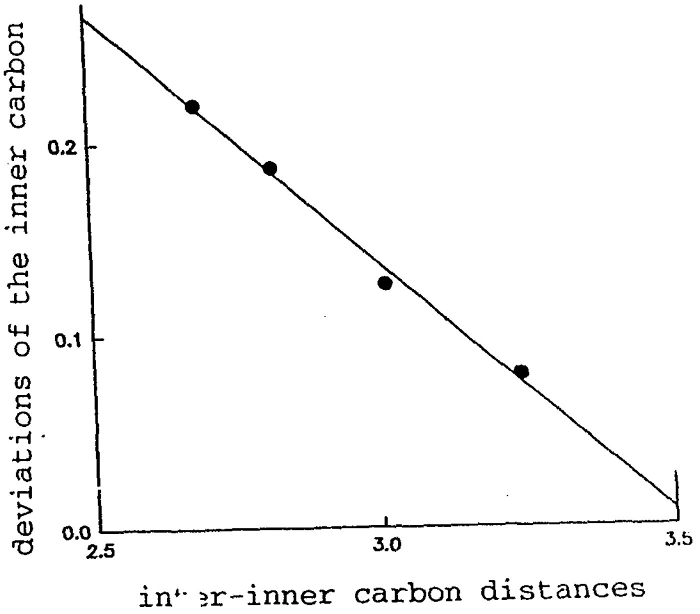
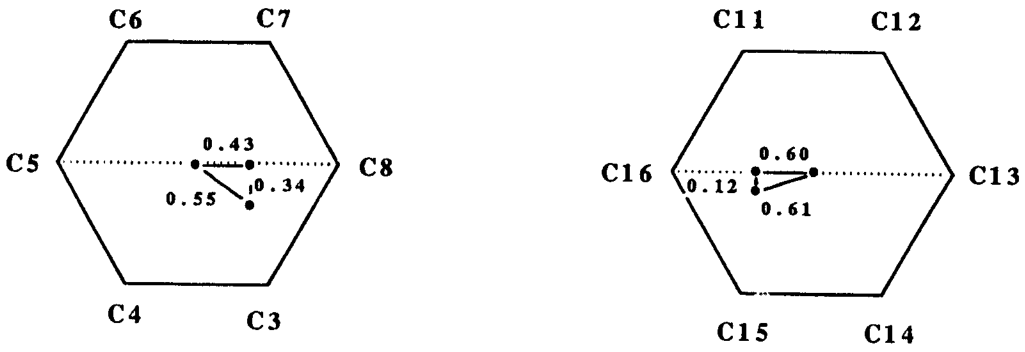


Figure 24. Correlation of the deviations of the inner carbon to the inter-inner carbon distances

Secondly, the X-ray analysis of **105a** revealed the stereochemistry of the two different bridges in the molecule **56a**. The bridge double bond (1.345Å) has a cis geometry but with larger torsional angles: 24.7° for C3-C2-C1-C15 and 41.6° for H2-C2-C1-H1. the four dihedral angles among the ethano bridge protons were found to be 173.2° for H10ax-C10-C9-C9ax, 84.3° for H10ax-C10-C9-H9eq, 54.9° for H10eq-C10-C9-H9eq, and 47.6° for H10eq-C10-C9-H9ax.

Another feature of the molecule **56a** in **105a** is that the internal methyls C17 and C18 (in the ORTEP drawing) are situated above the opposite aromatic rings. The calculated projections of C17 and C18 on the opposite rings are 0.6Å and 0.55Å off the centers of rings (see Figure 15).



C3...C7 = 2.429
C5...C8 = 2.819

C11...C15 = 2.396
C13...C16 = 2.763

Figure 25. Projections of the internal methyls onto the opposite aromatic rings in **105a**.

CHAPTER FOUR

CONCLUSIONS AND FUTURE WORK

A new synthetic route to cyclophanene **56**, starting from an appropriate 2,6-dihalogen-substituted toluene via the monothiacyclophane **72** as an intermediate compound, was developed. This new route was preferable to the previous reported method in preparations of **56** on a gram scale. By using this new synthetic method, the cyclophanenes **56b** and **56c** were first synthesized as well as the three new monothiacyclophanes **72a**, **72b**, and **72c**. An X-ray structural determination of **72a** revealed the *anti*-stepped geommetry of the molecule and showed that the internal methyls are situated 3.1Å above the opposite ring off the symmetric C_6 axis of that ring by 0.35Å.

Several tricarbonylchromium(0) and η^5-cyclopentadienyl-iron(I) complexes of cyclophanenes **56** were prepared for the first time. The complexation effect and ring current reduction effects were investigated through studies of their ^{1}H nmr spectra. The first synthesis of the bis-tricarbonyl-chromium(0) cyclophandiene complex **133** was also acheived through the dithiacyclophane route. An X-ray structure analysis of **133** was also determined which indicated that the two aromatic rings were inclined at 19.8° with respect to each other except that the aromatic rings were distorted in an outward boat form.

The bridge chemistry of cyclophanenes **56** and their metal complexes was investigated through some selected reactions. It was found that the cyclophanenes **56** were easily oxidized in attempted electrophilic additions such as bromination. But bromination of the complexes **105b** and **105c**, in which the cyclophanenes are stablized by complexation of $Fe^{+}Cp$, did give the desired bromine adducts. Neverthless, we found that the reactivity of the bridge double bond in cyclophanenes **56** is very low, since most of the attempted reactions failed to give the desired products.

Some electrophilic and nucleophilic substitutions of the metal cyclophanene complexes were also studied. The aromatic protons of the coordinated ring in the tricarbonylchromium complex **99a** could be deprotonated by n-butyllithium and be substituted by a t-butyl group in the reaction with t-butyllithium. Electrophilic substitution occurred in the uncomplexed ring as seen from formylation of the iron complex **105a**. However, this part of the work is still at a very early stage, and the potential synthetic utilities of electrophilic and nuclophilic substitutions of the metal cyclophanene complexes need to be further explored in the future.

Although the bridge-difunctionalized metacyclophanes were prepared by bromination of the iron complexes **105**, we were not able to generate the [2.2]metacyclophanyne **117**. The feasibility of generating **117** and using it as reactive intermediate in the synthesis of [e]-ring annulated dihydropyrenes needs still to be studied in the future.

CHAPTER FIVE

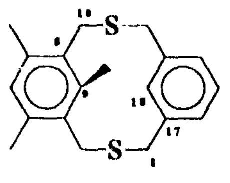
EXPERIMENTAL

6.1 Instrumentation

Melting points are uncorrected and were determined on a Reichert 7905 melting point apparatus. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer, or a Bruker IFS-25 single beam laser spectrometer. Proton nuclear magnetic resonance spectra were recorded at room temperature in $CDCl_3$ solutions (unless otherwise specified) on a Perkin-Elmer R-32 instrument (90 MHz) using tetramethylsilane as internal standard, a Bruker WM 250 (250 MHz) spectrometer or a Bruker AMX 360 (360 MHz) spectrometer using the solvent residue $CHCl_3$ peak (7.24 ppm) for calibration. Carbon-13 nuclear magnetic resonance spectra were recorded in $CDCl_3$ solutions (unless otherwise specified) on a Bruker WM 250 (62.9 MHz) spectrometer or on a Bruker AMX 360 (90.6 MHz) spectrometer using the solvent peak (77.0 ppm) for calibration. Mass spectra were recorded on a Finnigan 3300 mass spectrometer with 70eV electron impact ionization or using methane as a carrier gas for chemical ionization. Ultraviolet spectra were recorded on a Perkin-Elmer Lambda-4B spectro-meter or on a PU 8740 spectrometer using acetonitrile as solvent. Elemental analyses were performed by Canadian Microanalytical Services Ltd., Vancouver, British Columbia. X-ray diffraction studies were performed by K. Beveridge on a Picker 4-circle diffractometer automated with a PDP 11/10 computer. All evaporations were carried out under reduced pressure on a rotary evaporator.

6.2 Experimental procedures

1. 5,7,9-Trimethyl-2,11-dithia$[3_2]$(1,3)cyclophane 155



155

A solution of 1,3-bis(chloromethylmesitylene[a] **153** (15.2 g, 69.8 mmol) and the dithiol **154** (11.86 g, 69.8 mmol) in nitrogen purged 95% ethanol (800 mL) and benzene (600 mL) was added dropwise to a well stirred solution of potassium hydroxide (11.74 g, 209 mmol) in nitrogen purged 95% ethanol (1600 mL) and water (30 mL). The addition took about 30 h. After the addition, the mixture was further stirred for 1 h. The solvent was removed under reduced pressure and the resulting residue was dissolved in dichloromethane and water. The organic layer was separated, washed with water, dried and evaporated. The residue was preabsorbed onto silica gel and filtered through a column (8 x 30 cm) of silica gel using petroleum ether (30-60°C) and dichloromethane (4:1) as eluent to yield the dithia

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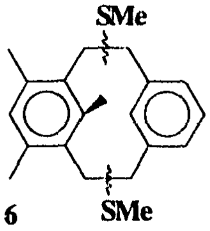
a) The dichloride was prepared by chloromethylation of mesitylene (see Tetrahedron, 1971, *27*, 2737) cyclophane **155** as colourless crystals, 16.30 g (74.4%). The sample for elemental analysis was obtained by recrystallization from hexane. **mp**:126-127°C; **^{1}H NMR (360MHz), δ**, 7.06 ~ 6.96 (m, AB_2, 3H, H-14, 15, 16), 6.72 (s, 1H, H-6), 5.67 (s, 1H, int. H-18), 4.00 (d, J_{gem} = 13.1 Hz, 2H, H-1/12(eq.)), 3.79 (d, J_{gem} = 13.1 Hz, 2H, H-1/12(ax.)), 3.62 (d, J_{gem} = 15.2 Hz, 2H, H-3/10(eq.)), 3.34 (d, J_{gem} = 15.2 Hz, 2H, H-3/10(ax.)), 2.33 (s, 6H, ext. $C\underline{H}_3$), 1.89 (s, 3H, int. $C\underline{H}_3$); **^{13}C NMR (90.6 MHz), δ**, 139.1 (C-9), 138.5, 136.1, 130.3 (C-5/7, C-4/8, 13/17), 130.2, 128.9, 128.4 (C-6, 15, 18), 126.1 (C-16), 34.7, 30.2 (C-1/12, 7/9), 20.5 (ext. $\underline{C}H_3$), 15.4 (int. $\underline{C}H_3$); **IR (KBr disc), cm^{-1}**, 584 (m), 707 (s), 729 (m), 792 (m), 798 (s), 865 (m), 920 (s), 1080 (m), 1208 (s), 1373 (s), 1409 (s), 1440 (s), 1460 (m), 1475 (m), 1485 (m), 2906 (s), 2932 (m); **MS (CI), *m/e* (%)**, 355 (M+41, 6), 343 (M+29, 33), 317 (9), 315 (M+1, 88), 183 (5), 181 (66), 177 (7), 149 (11), 147 (100).

Anal. Calcd. for $C_{19}H_{22}S_2$: C 72.56, H 7.05

Found: C 72.50, H 6.94

2. Wittig rearrangement of 5,7,9-trimethyl-2,11-dithia[3_2](1,3)cyclophane to give 156

n-Butyllithium (19.5 mmol in hexane, 13 mL) was added using a syringe to a solution of the cyclophane **155** (2.51 g, 8 mmol) in freshly distilled THF (125 mL) under nitrogen at


156

room temperature.[a] After 10 min, methyl iodide (1.3 mL, 21 mmol) was added, then aqueous HCl and dichloromethane (100 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane once (50 mL). The organic layers were washed, dried, and evaporated. The residue was preabsorbed onto silica gel and filtered through a short column (4 x 25 cm) of silica gel using petroleum ether (30-60°C) and dichloromethane (3:1) as eluent to give **156** as yellowish semi-solid, 2.70 g, (99%). **^{1}H NMR (360 MHz)**, 7.69 ~ 7.65 (m, Ar-$\underline{H}$), 7.28 (t, J = 7.6 Hz, Ar-$\underline{H}$), 7.16~7.12 (m, Ar-$\underline{H}$), 6.93 (s, Ar'-$\underline{H}$)[b], 6.90 (s, Ar'-$\underline{H}$), 6.87 (s, Ar'-$\underline{H}$), 4.66 (br s, int. Ar-$\underline{H}$), 4.34 (dd, J = 5.3 Hz, J = 2.0 Hz, -C$\underline{H}$-SMe), 3.92 (t, J_m =1.6 Hz, int. Ar-H), 3.45~3.22 (m, MeS-C$\underline{H}$-C$\underline{H}_2$), 2.97 (dd, J = 14.4 Hz, J = 2.0 Hz, -C$\underline{H}_2$-CHSMe), 2.50~2.07 (m, -C$\underline{H}_2$-C$\underline{H}_2$-), 2.36 (s, SC$\underline{H}_3$), 2.15 (s, ext. Ar'-C$\underline{H}_3$), 2.14 (s, ext. Ar'-C$\underline{H}_3$), 1.84 (s), 0.40 (s, int. Ar'-C$\underline{H}_3$), 0.39 (s, int. Ar'-C$\underline{H}_3$); **IR (KBr disc), cm^{-1}**, 510 (m), 608 (m), 718 (s), 789 (s), 1193 (m), 1373 (m), 1422 (s), 1435 (s), 1455 (s), 1468 (m), 1479 (m), 2888 (s), 2912 (s), 2962 (s); **MS (CI), *m/e* (%)**, 343 (M+1, 21), 295 (13), 247 (19), 199 (6), 183 (20), 171 (7), 165 (8), 153 (9), 147 (11), 139

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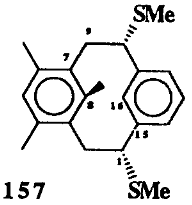
a) The addition took about 10 min. and the colour of the resultant mixture was dark brown.

b) Ar' stands for the penta-substituted phenyl ring and Ar for the less substituted one.

(11), 138 (16), 126 (7), 125 (100), 111 (6), 91 (13), 85 (15), 71 (19).



157

The major isomer **157**[a] was obtained by chromatography of the mixture of isomers **156** through a long column (2.5 x 70 cm) of silica gel using petroleum ether and dichloromethane (5:1) as eluent. Recrystallization from hexane gave colourless crystals of **157**. **mp:** 112°C; **^{1}H NMR (360 MHz)**, δ, 7.68 (dd, $J_{12/14,\ 13}$ = 7.6 Hz, $J_{12/14,\ 16}$ = 1.7 Hz, 2H, H-12, 14), 7.28 (t, $J_{13,\ 12/14}$ = 7.65 Hz, 1H, H-13), 6.87 (s, 1H, H-5), 3.92 (br s, 1H, H-16), 3.36 (dd, $J_{1/10,\ 2/9(ax.)}$ = 12.8 Hz, $J_{1/10,\ 2/9(eq.)}$ = 3.4 Hz, 1H, H-1/10 (ax.)), 3.24 (dd, $J_{2/9\ (eq.),\ 2/9\ (ax.)}$ = 11.3 Hz, $J_{2/9\ (eq.),\ 1/10}$ = 3.3 Hz, 2H, H-2/9 (eq.)), 2.37 (t, J = 12.0 Hz, 2H, H-2/9 (ax.)), 2.36 (s, 6H, ext. Ar-C$\underline{H}_3$), 2.14 (s, 6H, SC$\underline{H}_3$), 0.40 (s, 3H, int. Ar-C$\underline{H}_3$); **^{13}C NMR (90.6 MHz), δ**, 141.8 (C-8), 136.1, 134.6, 132.9 (C-3/7, 4/6, 11/15), 135.2, 129.8, 128.0 (C-5, 13, 16), 124.9 (C-12/14), 54.7 (C-1/9), 38.9 (C-2/9), 19.3 (ext. Ar-$\underline{C}H_3$), 16.0 (int. Ar-$\underline{C}H_3$), 15.5 (S$\underline{C}H_3$); **IR (KBr disc), cm^{-1}**, 510 (s), 608 (m), 720 (s), 797 (s), 859 (m), 976 (m), 1023 (m), 1079 (m), 1372 (m), 1413 (s), 1435 (s), 1456 (m), 1479 (s), 2890 (m), 2900 (m), 2914 (s), 2940 (m), 2964 (s); **MS (EI, 70eV), *m/e* (%)**, 342 (M$^+$, 100), 280 (16), 279 (82),

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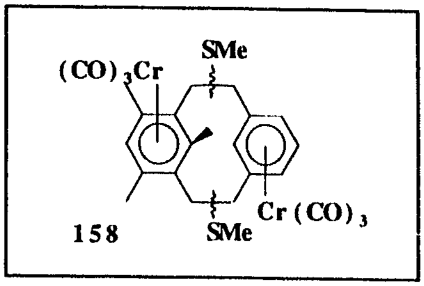
[a] It is estimated from ^{1}H NMR spectrum that this isomer is about 55% of the mixture.

247(32), 232 (15), 231 (58), 197 (13), 181 (38), 147 (12), 135 (12), 131 (17), 114 (12), 91 (18).

Anal.	Calcd. for $C_{21}H_{26}S_2$:	C 73.63,	H 7.65
	Found:	C 73.55,	H 7.56

3. Bis(tricarbonylchromium(0)) complexes of the isomers 158



158

A solution of the isomers **157** (3.68 g, 10.75 mmol) and chromium hexacarbonyl (10.0 g. 45.5 mmol) in dry n-Bu_2O (150 mL) and THF[a] (8 mL) was refluxed under a nitrogen atmosphere for 20 h. After removal of the solvent under reduced pressure, the black residue was dissolved in dichloromethane (250 mL) and filtered. Any remaining black residue was then washed with dichloromethane until the washings were colourless. The golden brown filtrate was evaporated to give a yellow solid **158**, 6.18 g, (93%). A portion was further purified by recrystallization as follows: the compound was dissolved in a minimum of dichloromethane and then hexane was added to precipitate golden yellow crystals of **158**. mp: >224°C (decomp.); **^{1}H NMR**

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[a] A small amount of THF helps to wash off sublimed $Cr(CO)_6$ and therefore prevents blockage of the condenser.

(360 MHz), δ, $\underline{6.16}$[a] (d, J = 6.5 Hz, Ar'-H), 6.02 (dd, J = 6.3 Hz, J = 1 Hz, Ar'-H), $\underline{5.57}$ (d, J = 5.8 Hz, Ar'-H), 5.39 (t, J = 6.6 Hz, Ar'-H), $\underline{5.21}$ (s, Ar-H), $\underline{5.17}$ (t, J = 6.3 Hz, Ar'-H), 5.15 (s, Ar-H), $\underline{4.07}$ (s, int. Ar'-H), $\underline{3.82}$ (d, J = 3.1 Hz, CH-SMe), $\underline{3.74}$ ~ $\underline{3.70}$ (m, CH-SMe), 3.34 (s, int. Ar'-H), 3.31 (dd, J = 13.6 Hz, CH-SMe), $\underline{3.33}$ ~ $\underline{3.27}$ (m, CH_2), $\underline{3.07}$ (dd, J = 12.4 Hz, J = 3.3 Hz, CH_2), 2.98 (dd, J = 11.6 Hz, J = 3.3 Hz, CH_2), $\underline{2.84}$ (dd, J = 14.4 Hz, J = 5.3 Hz, CH_2), $\underline{2.41}$ (s, SCH_3), 2.35 (dd, J = 13.8 Hz, J = 11.7 Hz, CH_2), 2.28 (s, SCH_3), 2.27 (s, ext. CH_3), $\underline{2.26}$ (s, ext. CH_3), $\underline{1.07}$ (s, int. CH_3), 1.05 (s, int. CH_3); **IR (disc), cm^{-1},** 480 (w), 529 (m), 622 (m), 658 (m), 672 (m), 1030 (w), 1388 (m), 1435 (m), 1444 (m), 1856, 1864, 1871 (br. vs), 1951 (br. vs), 2921 (w), 2959 (w); **MS (EI, 70eV), *m/e* (%),** 614 (M$^+$, 20), 558 (19), 530 (49), 478 (43), 474 (28), 422 (46), 395 (37), 394 (100), 248 (28), 332 (24), 331 (71), 330 (29), 282 (47), 80 (61).

Anal.	Calcd. for $C_{27}H_{26}O_6S_2Cr_2$:	C 52.77,	H 4.26
	Found:	C 52.79,	H 4.24

The bis(tricarbonylchromium) complex **159** of the isomer **157** was prepared using the same procedure. **mp:** >280°C (decomp.); **^{1}H NMR (360 MHz),** δ, 6.02 (dd, J = 6.5 Hz, J = 1.4 Hz, 2H, H-12/14), 5.39 (t, J = 6.6 Hz, 1H, H-13), 5.15

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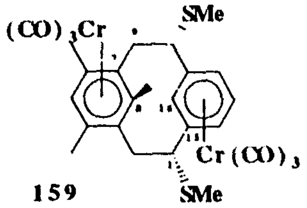
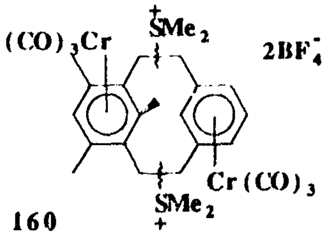
[a] ^{1}H NMR shows that two major isomers are present and they can be assigned separately. Here an underlined number means that peak is from one isomer.



159

(s, H-5), 3.34 (s, 1H, H-16), 3.30 (dd, J = 13.6 Hz, J = 3.4 Hz, 2H, H-1/10), 2.97 (dd, J = 11.7 Hz, J = 3.4 Hz, 2H, H-2/9(eq.)), 2.35 (dd, J = 13.6 Hz, J = 11.7 Hz, 2H, H-2/9(ax.)), 2.28 (s, 6H, $SC\underline{H}_3$ or ext. $C\underline{H}_3$), 2.27 (s, 6H, ext. $C\underline{H}_3$ or $SC\underline{H}_3$), 1.05 (s, 3H, int. $C\underline{H}_3$); **^{13}C NMR (90.6 MHz)**, δ, 233.4, 232.3 ($\underline{C}$=O), 111.7, 107.2, 106.5, 102.2 (C-8), 94.4, 93.1 (C-12/14), 91.3, 86.9 (aromatic $\underline{C}$), 53.4 (C-1/10), 38.4 (C-2/9), 21.6 (int $\underline{C}H_3$), 19.2 (ex. $\underline{C}H_3$), 16.1 ($S\underline{C}H_3$); **IR (disc), cm^{-1}**, 480 (m), 528 (m), 622 (s), 653 (s), 673 (s), 1379 (m), 1389 (m), 1435 (m), 1444 (m), 1828, 1855, 1870 1876, 1879 (br. vs), 1939, 1952 (br. vs); **MS (EI), *m/e* (%)**, 614 (M$^+$, 3), 530 (7), 474 (6), 394 (7), 233 (5), 136 (9), 80 (6), 52 (100).

4. Bis(sulfonium) salts of bis(tricarbonylchromium) complexes 158

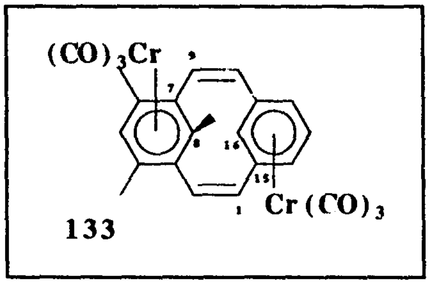


160

Borch reagent$^{121)}$ [$(CH_3O)_2CHBF_4$] (420 mg, ~80% as oil, 1.8 mmol) was added to the solution of bis-chromium complexes **158** (480 mg, 0.78 mmol) in nitrogen purged dichloromethane (20 mL) at room temperature. The mixture was stirred under nitrogen for 4 h.

The solvent was then decanted and nitrogen purged ethyl acetate (10 mL) was added. The mixture was further stirred at room temperature for another 4 h. The mixture was filtered to collect the salts **160** (599 mg, 94%) as a fine yellow powder, **mp**: >300°C (decomp.); **IR (KBr disc), cm^{-1}**, 522 (m), 615 (m), 648 (m), 661 (m), 1038 , 1051 (br. s), 1057, 1062(br. s), 1388 (w), 1432(w), 1908 (br. vs), 1965 (br. vs).

5. (η^6,η^6-*anti*-4,6,8-Trimethyl[2_2](1,3)cyclophane-1,9-diene)-bis(tricarbonylchromium(0)) 133

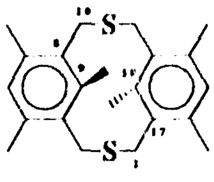


133

The sulfonium salts **160** (595 mg, 0.73 mmol) were added to nitrogen purged dimethylformamide and THF (16 mL, 1:1) under a nitrogen atmosphere at 0°C, followed by addition of potassium t-butoxide (330 mg, 2.94 mmol). After stirring under nitrogen for two min, aqueous HCl (~0.5 M, 10 mL) was added to the resultant dark brown mixture and then diethyl ether (200 mL). The organic layer was separated, washed, dried and concentrated. The crude product was preabsorbed and chromatographed on silica gel under a nitrogen atmosphere using petroleum ether and dichloromethane (2:1) as eluent to yield **133** as a red solid, 302 mg (80%), **mp**: >300°C (decomp.); **^{1}H NMR (360 MHz), δ,** 6.63 (d, $J_{1/10,\ 2/9}$ = 11.1 Hz, 2H, H-1/10 or 2/9), 6.28 (d, $J_{2/9,\ 1/10}$ = 11.1 Hz, 2H, H-2/9 or 1/10), 5.51 ~ 5.29 (AB_2 multiplet, 3H, H-12, 13, 14), 5.33 (s, 1H, H-5), 5.18 (s, 1H, H-16), 2.17 (s, 6H, ext. $C\underline{H}_3$), 1.58 (s, 3H, int. $C\underline{H}_3$); **^{13}C NMR (90.6 MHz), δ,** 233.6, 232.7 ($\underline{C}$=O), 131.4, 131.0 (C-1/10, 2/9), 112.3, 108.8, 106.8 (C-4/6, 3/7, 11/15), 96.0 (C-8), 95.3, 89.6, 84.4, 83.9 (C-5, 12/14, 13, 16), 24.8 (int. Ar-$\underline{C}H_3$), 19.2 (ext. Ar-$\underline{C}H_3$); **IR (disc), cm^{-1}**, 464 (w), 472 (w), 483 (w), 525 (m), 535 (w), 606 (m), 617 (m), 640 (w), 659 (s), 668 (s), 750 (m), 797 (w), 1380 (w), 1387 (w), 1869 (s), 1879 (s), 1908 (s), 1943 (s), 1980 (s); **MS (CI), m/e (%)**, 521 (19), 520 (48), 519 (M+1, 100), 518 (49), 517 (10), 516 (4), 462 (4), 435 (7), 384 (4), 383 (14), 382 (8).

Anal.	Calcd. for $C_{25}H_{18}Cr_2O_6$:	C 57.92,	H 3.50
	Found:	C 57.82,	H 3.53

6. *anti*-5,7,9,14,16,18-Hexamethyl-2,11-dithia[3_2](1,3)cyclophane 162



162

A solution of 1,3-bis (chloromethyl)mesitylene **153** (5.09 g, 24 mmol) and its corresponding dithiol (5.21 g, 24 mmol) in nitrogen purged 95% ethanol (800 mL) and benzene (600 mL) was added dropwise over about 30 h to a well stirred solution[a] of potassium hydroxide (4.04 g, 72 mmol) in nitrogen purged 95% ethanol (1200 mL) and water (30 mL) at room temperature under a nitrogen atmosphere. The solvent was then evaporated and the residue was preabsorbed on silica gel and filtered through a column (3 x 20 cm) of silica gel using benzene and petroleum ether (1:1) as eluent to yield the dithiacyclophane **162** as a white solid, 3.25 g, (38%). Recrystallization from benzene gave colourless crystals. **mp**: 260-262°C (lit. 260-261°C)[117]; **^{1}H NMR (360 MHz), δ**, 6.80 (s, 2H, H-6/15), 3.73 (d, J = 13.8 Hz, 4H, H-1/3/10/12 (eq.)), 3.66 (d, J = 13.8 Hz, 4H, H-1/3/10/12 (ax.)), 2.44 (s, 12H, ext. C$\underline{H}_3$), 1.18 (s, 6H, int. C$\underline{H}_3$); **^{13}C NMR (90.6 MHz), δ**, 139.6 (C-9/18), 136.8 (C-4/8/13/17), 131.0 (C-5/7/14/16), 130.0 (C-6/15), 18.8 ($\underline{C}H_2$), 20.5 (ext. $\underline{C}H_3$), 15.0 (int. $\underline{C}H_3$); **IR (disc), cm^{-1}**, 657 (m), 741 (m), 761 (w), 791 (w), 869 (s), 1011 (m), 1031 (m), 1202 (m), 1229 (w), 1367 (m), 1412 (m), 1441 (s), 1463 (s), 2860 (m), 2910 (m), 2969 (m), 1995 (m); **MS (CI), *m/e* (%)**, 358 (4), 357 (M+1, 19), 356 (11), 311 (14), 179 (15), 178 (11), 177 (67), 175 (14), 148 (10), 147 (100), 146 (26), 145 (72).

7. Bis(sulfonium) salt of dithiacyclophane 162

Borch reagent (3.6 g, 80% as oil, 18 mmol) was added to

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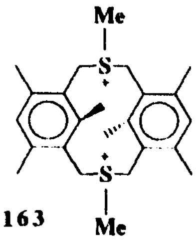
a) The solution was made by dissolving KOH in water and then diluting with ethanol.

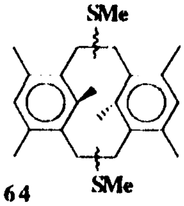
the suspension of the dithiacyclophane **162** (2.14 g, 6 mmol) in dichloromethane (50 mL) at room temperature and then was stirred for 5 h. The mixture was then filtered and ethyl acetate was added to the solid. The resultant suspension was stirred overnight. The bis(sulfonium) salt **163** as a fine powder was obtained by filtration, 3.09 g, (99%). **mp**: >230°C (decomp.); **IR (disc), cm^{-1}**, 522 (m), 869 (m), 992 (m), 1038, 1054, 1058, 1061, 1065 (v br, vs), 1385 (m) 1390 (m), 1406 (m), 1423 (m), 1463 (s), 2928 (w), 2942 (w), 2973 (w), 2980 (w), 3009 (w), 3030 (m).



163

8. Stevens rearrangement of the sulfonium salt 163

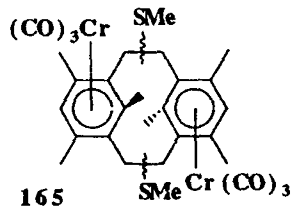
Potassium t-butoxide (6.30 g, 56.1 mmol) was added to a suspension of the bis(sulfonium) salt **163** (7.20 g, 14 mmol) in dry THF (300 mL) with stirring at room temperature. After the mixture was stirred for 10 min., aqueous HCl solution (100 mL, ~1 M) and dichloromethane (200 mL) were added to the resultant clear solution. The organic layer was separated, washed, dried and evaporated. The residue was preabsorbed and filtered through a column (3 x 25 cm) of



164

silica gel using petroleum ether and dichloromethane (3:1) as eluent to yield a mixture of stereoisomers of **164** as a white solid, 5.10 g (95%). **^{1}H NMR (360 MHz),** δ, 6.70 ~ 6.54 (6 singlets, 2H, Ar-$\underline{H}$), 4.92 ~ 4.80, 3.75 ~ 3.61 (m, 2H, C$\underline{H}$-SMe), 3.38 ~ 3.19 (m, 2H, C$\underline{H}_2$-CH), 3.04 ~ 2.79 (m, 2H, C$\underline{H}_2$-CH), 2.57 2.19 (18 singlets, ext. C$\underline{H}_3$ and SC$\underline{H}_3$), 0.89 ~ 0.49 (8 singlets, int. C$\underline{H}_3$); **IR (disc), cm^{-1}**, 793 (w), 855 (m), 960 (m), 1010 (m), 1025 (m), 1278 (w), 1370 (m), 1450 (br, s), 2880 (m), 2910 (m), 2960 (m); **MS (CI), *m/e* (%)**, 385 (M+1, 4), 384 (2), 337 (13), 289 (6), 113 (2), 101 (6), 73 (100).

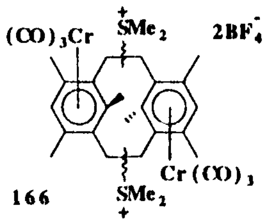
9. Bis(tricarbonylchromium) complex of the stereoisomers 164



165

A solution of the stereoisomers **164** (2.0 g, 5.21 mmol) and chromium hexacarbonyl (6.9 g, 31.4 mmol) in dry n-Bu$_2$O (125 mL) and THF (8 mL) was refluxed with magnetic stirring under nitrogen for 18 h. After removing the solvent under reduced pressure, the solid was dissolved in dichloromethane (300 ml) and filtered. The residue was then washed with dichloromethane until the dichloromethane is nearly colourless. The filtrate was evaporated to yield the bis-chromium complex **165** as a yellow solid, 3.15 g (92%). **mp:** >210°C (decomp.); **^{1}H NMR (360 MHz),** δ, 5.02, 4.96, 4.91, 4.88, 4.87 (s, Ar-$\underline{H}$), 4.58 (d, J = 5.3 Hz, -C$\underline{H}$-SMe), 3.63 (d of d, J = 11.5 Hz, J = 2.2 Hz, -C$\underline{H}$-SMe), 3.49 (m, C$\underline{H}$-SMe), 3.31 ~ 3.16 (m, -C$\underline{H}_2$-CH-), 2.88 ~ 2.67 (m, C$\underline{H}_2$-C$\underline{H}_2$), 2.53 ~ 2.23 (17 singlets, ext. Ar-C$\underline{H}_3$ and -SC$\underline{H}_3$), 1.62 ~ 0.80 (14 singlets, int. Ar-C$\underline{H}_3$); **IR (disc), cm^{-1},** 482 (m), 536 (m), 620 (s), 670 (s), 1006 (w), 1030 (w), 1378 (m), 1432 (m), 1860 (v br, vs), 1950 (v br, vs), 2924 (w), 2970 (w), 2992 (w); **MS (CI), *m/e* (%)**, 658 (24), 657 (M+1, 51), 656 (27), 551 (40), 522 (34), 521 (100), 520 (67), 473 (20), 389 (14), 315 (40), 192 (42), 174 (18).

10. Bis(sulfonium) salt of the bis(tricarbonylchromium) complex 165



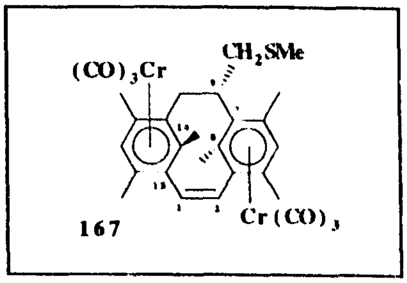
166

Borch reagent (4.37 g, ~80% as oil, 19.9 mmol) was added to the suspension of the bis-chromium complex **165** (5.67 g, 8.64 mmol) in nitrogen purged dichloromethane (200 mL) under a nitrogen atmosphere. After stirring at room temperature for 5 h, the mixture was filtered. The collected solids were then added to nitrogen purged ethyl acetate (60 mL) and the suspension was stirred for 4 h. The solvent was removed by filtration to yield the salt **166** as a yellow solid, 7.31 g (98%). **mp:** >170°C (decomp.); **IR (disc), cm^{-1},** 476 (m), 830 (m), 615 (m), 622 (m), 664(s), 731 (m), 1050 (v br, s), 1270 (w), 1284 (w), 1380 (m), 1435 (m), 1450 (m), 1880 (v br, vs), 1960 (v br, vs), 2960 (w), 2980 (w), 3036 (w).

11. Hofmann elimination of the bis(sulfonium) salt of the complex 166

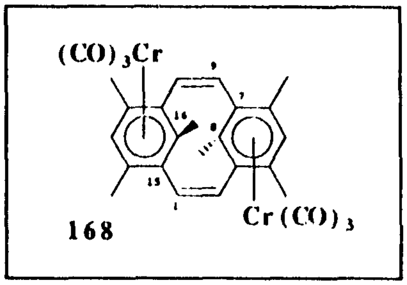
Potassium t-butoxide (235 mg, 2.1 mmol) was added to a solution of the bis-chromium complex **166** (380 mg, 0.44 mmol) in nitrogen purged DMSO and t-butanol (1:1, 16 mL) at room temperature under nitrogen. After the mixture was stirred for 5 min, the aqueous HCl and diethyl ether (50 mL) were added. The organic layer was separated, washed, dried, and evaporated. The residue was preabsorbed and chromatographed through a column (2 x 40 cm) of silica gel using petroleum ether and dichloromethane (2:1) as eluent. The first fraction eluted was the dimethyldihydropyrene **121**, 31.2 mg (25%). **^{1}H NMR (360 MHz), δ**, 8.55 (s, 4H, H-4/5/9/10), 7.79 (s, 2H, H-2/7), 3.15 (s, 12H, ext. C$\underline{H}_3$), -4.03 (s, 6H, int. C$\underline{H}_3$).

Eluted next was the cyclophanene mono-chromium complexes, 56 mg (27%), **^{1}H NMR (90 MHz), δ**, 7.04 (d, J = 11 Hz, 1H, olefinic), 6.67 (s, 1H, Ar-$\underline{H}$(uncompl.)), 6.38 (d, J = 11 Hz, olefinic), 5.09 (s, 1H, Ar-$\underline{H}$(compl.)), 3.88 ~ 3.68 (m, 5H, C$\underline{H}_2$, C$\underline{H}$), 2.28, 2.14 (s, ext. C$\underline{H}_3$), 1.20 (s, 3H, int. C$\underline{H}_3$ (uncompl.)), 0.73 (s, 3H, int. C$\underline{H}_3$(compl.)).



167

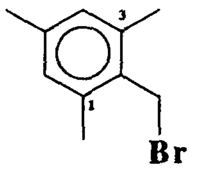
Eluted lastly was the bis-chromium complex of the cyclophanene **167**, 30 mg (11%), **mp:** >210°C (decomp.); **^{1}H NMR (360 MHz), δ,** 6.67 (AB, J = 11.0 Hz, 2H, H-1/2), 5.22 (s, 1H, H-5), 5.03 (s, 1H, H-13), 3.60 ~ 3.53 (m, 3H, H-9, $C\underline{H}_2$SMe), 2.81 (d, J = 13.0 Hz, 1H, H-10(eq.)), 2.42 (dd, 1H, J = 16.4 Hz, J = 10.1 Hz, H-10(ax.)), 2.22, 2.13, 2.10 (s, ext. $C\underline{H}_3$, SCH_3), 1.33 (s, 3H, int. $C\underline{H}_3$), 1.30 (s, 3H, int. $C\underline{H}_3$); **^{13}C NMR (90.6 MHz), δ,** 233.9, 233.8 ($\underline{C}$O), 131.7, 130.7 (C-1, 2), 122.7, 120.0, 115.0, 113.5, 112.9, 109.5, 107.5, 105.8, 101.1, 95.8 (C-3, 4, 6, 7, 8, 11, 12, 14, 15, 16), 89.8, 83.7 (C-5, 13), 43.9, 40.7, 37.7 (C-9, 10, $\underline{C}H_2$SMe), 24.6, 20.8, 19.6, 18.8, 18.8 (int. & ext. $\underline{C}H_3$, $S\underline{C}H_3$); **MS (EI), m/e (%)**, 562 (3), 560 (15), 426 (12), 424 (100), 422 (7), 168 (25), 100 (4).



168

In this fraction, a trace (~1 mg) of the diene bis(tricarbonylchromium) complex **168**, was also found, which was separated by a subsequent careful chromatography. **^{1}H NMR (360 MHz), δ,** 6.60 (s, 2H, H-/1/2/9/10), 5.17 (s, 2H, H-5/13), 2.15 (s, 12H, ext. $C\underline{H}_3$), 1.30 (s, 6H, int. $C\underline{H}_3$); **^{13}C NMR (90.6 MHz), δ,** 234.0 ($\underline{C}$O), 130.2 (C-1/2/9/10), 114.5, 109.0 (C-4/6/12/14, C-3/7/11/15), 94.4 (C-8/16), 90.9 (C-5/13), 26.5 (int. $\underline{C}H_3$), 19.2 (ext. $\underline{C}H_3$).

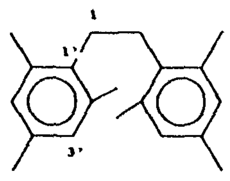
12. 2-Bromomethyl-1,3,5-trimethylbenzene 69c



69c

A mixture of mesitylene (120 g, 1 mol), trioxane (30 g, 1 mol), aqueous hydrobromic acid (500 mL, 48%) and myristyltrimethylammonium bromide (5 g, 15 mmol) was heated at 80~90°C with vigorous mechanical stirring for 8 h. While the reaction mixture was still warm, petroleum ether (50 mL, 30~60°C) was added carefully. The mixture was left open and cooled without stirring overnight. The white solid which formed on the top, was collected by filtration. The solid was washed thoroughly with water and dried. Recrystallization from petroleum ether (30~60°C) gave the bromide **69c** as white crystals, 182 g (85%). **mp**:49~50°C (lit. 49.5~50.5°C)$^{122)}$; **^{1}H NMR (250 MHz), δ**, 6.84 (br s, 2H, Ar-$\underline{H}$), 4.55 (s, 2H, Ar-$C\underline{H}_2$-Br), 2.36 (s, 6H, Ar-$C\underline{H}_3$), 2.25 (s, 3H, Ar-$C\underline{H}_3$); **^{13}C NMR (62.9 MHz), δ**, 138.5 (C-5 or 2), 137.4 (C-1/3), 131.1 (C-2 or 5), 129.2 (C-4/6), 29.6 (-$\underline{C}H_2$-Br), 21.0 ($\underline{C}H_3$-C_5), 19.1 ($\underline{C}H_3$-$C_{1/3}$); **IR (disc), cm^{-1}**, 473 (m), 526 (s), 605 (s), 731 (m), 771 (m), 858 (s), 1029 (w), 1194 (s), 1219 (m), 1375 (m), 1417 (m), 1440 (m), 1461 (m), 1479 (w), 1575 (w), 1608 (m), 2854 (w), 2897 (w), 2907 (w), 2911 (w), 2916 (w), 2941 (w), 2968 (w); **MS (EI), *m/e* (%)**, 214 (M^+, 6), 212 (M^+, 6), 134 (11), 133 (100), 131 (3), 118 (5), 117 (10), 116 (3). 115 (10), 105 (8), 91 (12).

13. 1,2-Bis(2',4',6'-trimethylphenyl)ethane 70c

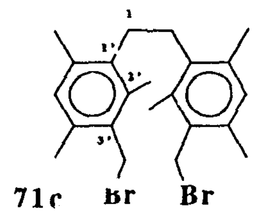


70c

About 5 mL of a solution of the bromide **69c** (106 g, 0.5 mol) in dry THF (400 mL) was added to magnesium (6.03 g, 0.5 mol) in dry THF (500 mL) under nitrogen. After the reaction was initiated by warming the reaction mixture, the remainder of the solution of the bromide **69c** was added at such a rate that kept a gentle reflux of the mixture. After the addition, the reaction mixture was further heated at reflux for 2 h. Removing the solvent yielded a white solid. The solid was dissolved in ether (800 mL) and water (400 mL). The organic layer was separated, washed thoroughly, dried and evaporated to give the dimer **70c** as a white fluffy solid, 66 g (99%). A portion was recrystallized from hexane as a white solid, **mp**:113~114°C; **^{1}H NMR (250 MHz),** δ, 6.86 (s, 4H, H-3'/5'), 2.77 (s, 4H, H-1/2), 2.36 (s, 12H, Ar-C$\underline{H}_3$), 2.26 (s, 6H, Ar-C$\underline{H}_3$); **^{13}C NMR (62.9 MHz), δ,** 136.3 (C-2'/4'), 135.7, 135.2 (C-1', 4'), 129.1 (C-3'/5'), 29.0 (C-1/2); 20.8 ($\underline{C}H_3$-C$_4$'), 20.1 ($\underline{C}H_3$-C$_{2'/6'}$); **IR (disc), cm^{-1},** 570(s), 734 (w), 853 (s), 1010 (m), 1026 (m). 1374 (m), 1467 (s), 1481 (s), 2856 (w), 2906 (m), 2954 (s), 3001 (w); **MS (EI), *m/e* (%),** 266 (M$^+$, 4), 134 (9), 133 (100), 117 (3), 115 (2), 91 (9).

Anal.	Calcd. for $C_{20}H_{26}$:	C 90.16,	H 9.84
	Found:	C 90.26,	H 9.67

14. 1,2-Bis(3'-bromomethyl-2',4',6'-trimethylphenyl)ethane 71c



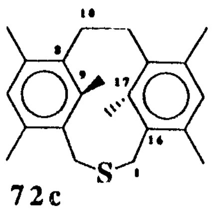
71c

A mixture of the dimer **70c** (133 g, 0.5 mol), trioxane (33 g, 0.55 mol), aqueous hydrobromic acid (300 mL, 48%), myristyltrimethylammonium bromide (4 g) and heptane (250 mL) was heated at reflux with vigorous stirring for 20 h. After the reaction mixture was cooled, the solid was collected by filtration, washed thoroughly with water, and then dried to give the dibromide **71c**, 193 g (85%). A small portion was recrystallized from benzene to give white crystals, **mp**:244-246°C; **^{1}H NMR (360 MHz),** δ, 6.85 (s, 2H, H-5'), 4.57 (s, 4H, $-C\underline{H}_2$-Br), 3.47 (s, 4H, H-1/2), 2.35 (s, 6H, Ar-$C\underline{H}_3$), 2.33 (s, 6H, Ar-$C\underline{H}_3$), 2.26 (s, 6H, Ar-$C\underline{H}_3$); **^{13}C NMR (90.6 MHz),** δ, 137.3, 136.9, 136.1, 135.1, 132.1 (C-1', 2', 3', 4', 6'), 130.6 (C-5'), 30.9, 29.4 ($-\underline{C}H_2-$, $-\underline{C}H_2$-Br), 20.5, 19.2, 15.1 (Ar-$\underline{C}H_3$); **IR (disc), cm^{-1}**, 452 (w), 524 (m), 553 (m), 661 (m), 668 (m), 692 (m), 810 (m), 864 (m), 1008 (w), 1028 (w), 1190 (s), 1218 (m), 1374 (m), 1442 (m), 1463 (m), 2910 (w), 2915 (w) 2921 (w), 2942 (m), 2952 (m), 2969 (m), 2999 (m); **MS (CI), *m/e* (%)**, 451 (M+1, weak), 374

(23), 373 (M-Br, 95), 372 (25), 371 (M-Br, 100), 242 (5), 241 (45), 240 (5), 239 (47), 147 (11), 146 (17), 131(6).

Anal.	Calcd. for $C_{22}H_{28}Br_2$:	C 58.43,	H 6.24
	Found:	C 58.50,	H 6.03

15. 5,7,9,13,15,17-Hexamethyl-2-thia[3,2](1,3)cyclophane 72c



72c

A solution[a)] of sodium sulfide (26.4 g, 0.11 mol) in nitrogen purged water (440 mL) and 95% ethanol (760 mL) was added dropwise over about 48 h to a well stirred suspension of the dibromide **71c** (45.2 g, 0.1 mol) in nitrogen purged benzene (560 mL), 95% ethanol (1425 mL) and water (200 mL) under nitrogen. The mixture was then further stirred for 4 h. The solvent was removed under reduced pressure and the resulting residue was dissolved in dichloromethane (1200 mL) and water (600 mL). The organic layer was separated, washed, dried and evaporated. The residue was preabsorbed onto silica gel and filtered through a column (12 x 30 cm) of silica gel using petroleum ether and dichloromethane (3:1) as eluent to yield the monothiacyclophane **72c** as a white solid, 23.8 g (72%). A sample was recrystallized from hexane to give colourless

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a) This solution was prepared by dissolving Na_2S in water first and then diluting with ethanol.

crystals, **mp**:208-210°C; **^{1}H NMR (360 MHz), δ**, 6.73 (s, 2H, Ar-$\underline{H}$), 3.82 (d, A of AX, J_{gem} = 13.5 Hz, 2H, H-1/3(eq.)), 3.70 (d, X of AX, J_{gem} = 13.5 Hz, 2H, H-1/3(ax.)), 3.02[a] (m, AA' of AA'XX', J_{AX} = $J_{A'X'}$ = -13.3 Hz, $J_{AX'}$ = $J_{A'X}$ = 4.2 Hz, $J_{AA'}$ = 3.0 Hz, 2H, H-10(eq., A), H-11(eq., A')), 2.51 (m, XX' of AA'XX', $J_{XX'}$ = 12.8 Hz. $J_{XA'}$ = $J_{X'A}$ = 4.2 Hz, J_{XA} = $J_{X'A'}$ = -13.5 Hz, 2H, H-10(ax., X), H-11(ax., X')), 2.39 (s, 6H, ext. Ar-C$\underline{H}_3$), 2.34 (s, 6H, ext. Ar-C$\underline{H}_3$), 0.81 (s, 6H, int. Ar-C$\underline{H}_3$); **^{13}C NMR (90.6 MHz), δ**, 140.1, 135.0, 134.8, 133.1, 130.9 (C-4/16, 5/15, 7/13, 8/12, 9/17), 129.2 (C-6/14), 29.6, 27.9 (-$\underline{C}H_2$-S-, -$\underline{C}H_2$-), 19.9, 19.7 (ext. Ar-$\underline{C}H_3$), 15.0 (int. Ar-$\underline{C}H_3$); **IR (disc), cm^{-1}**, 637 (w), 668 (m), 784 (w), 880 (s), 1013 (w), 1027 (w), 1056 (w), 1200 (w), 1367 (m), 1414 (w), 1422 (w), 1446 (s), 1455 (s), 1461 (s), 1563 (w), 2860 (m), 2904 (m), 2931 (s), 2946 (m), 2963 (m); **MS (CI), *m/e* (%)**, 325 (M+1, 81), 324 (35), 323 (33), 280 (17), 279 (100), 191 (48), 161 (38), 147 (70).

Anal.	Calcd. for $C_{22}H_{28}S$:	C 81.42,	H 8.70
	Found:	C 81.09,	H 8.63

16. *anti*-4,6,8,12,14,16-Hexamethyl-1-methylthio[2$_2$](1,3) cyclophane 92c

A solution of LDA freshly prepared from n-butyllithium

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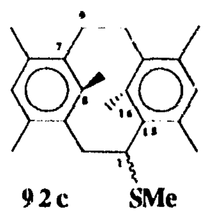
[a] The coupling constants of the AA'XX' system are refined from the simulated spectrum.



92c

(48 mmol in hexane 32 mL) and di-*i*-propylamine (7.0 mL, 50 mmol) in dry THF (100 mL) was added to a solution of the thiacyclophane **72c** (13.0 g, 40 mmol) in dry THF (600 mL) under nitrogen atmosphere with stirring over 30 min. After the reaction mixture was further stirred for 30 min, iodomethane (3.2 mL, 52 mmol) was added to the resulting brown mixture until the colour disappeared, followed by addition of aqueous HCl solution and diethyl ether (500 mL). The organic layer was separated, washed[a], dried and evaporated. The residue was filtered through a short colunm of silica gel using petroleum ether and dichloromethane (3:1) to yield a white solid **92c**, 13.4 g (99%). **mp:**114~132°C; **^1H NMR (360 MHz)**, δ, $\underline{6.65}$, $\underline{6.64}$[b] (s, 2H, H-5/13), 6.58, 6.56 (s, 2H, H-5/13), $\underline{4.88}$ (dd, $J_{1(eq.), 2(ax.)}$ = 6.5 Hz, $J_{1(eq.), 2(eq.)}$ = 1.0 Hz, 1H, H-1(eq.)), 3.68 (dd, $J_{1(ax.), 2(ax.)}$ = 11.3 Hz, $J_{1(ax.), 2(eq.)}$ = 2.6 Hz, 1H, H-1(ax.)), $\underline{3.40}$ (dd, $J_{2(eq.), 2(ax.)}$ = 14.5 Hz, $J_{2(eq.), 1(eq.)}$ = 1.4 Hz, 1H, H-2(eq.)), 3.25 (dd, $J_{2(eq.), 2(ax.)}$ = 12.9 Hz, $J_{2(eq.), 1(ax.)}$ = 2.7 Hz, 1H, H-2(eq.)), 3.12~3.04 (m, 6H, -C$\underline{H}_2$-C$\underline{H}_2$- of both isomers), $\underline{2.93}$ (dd, $J_{2(ax.), 2(eq.)}$ = 14.7 Hz, $J_{2(ax.), 1(eq.)}$ = 6.9 Hz, 1H, H-2(ax.)), 2.85 (dd, $J_{2(ax.), 2(eq.)}$ = 12.6 Hz, $J_{2(ax.), 1(ax.)}$ = 11.8 Hz, 1H, H-2(ax.)), 2.56, 2.34,

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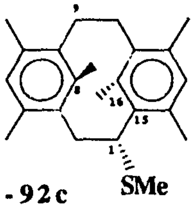
a) If the extract is yellow due to the presence of iodine, it needs to be washed with $Na_2S_2O_3$ solution.

b) Underlined numbers are chemical shifts of the pseudo-axial isomer. The ratio of two isomers is 72:28 (eq:ax) determined from the ^1H nmr spectrum.

2.33, 2.31 (s, ext. Ar-$C\underline{H}_3$), $\underline{2.52}$, $\underline{2.36}$ (s, ext. Ar-$C\underline{H}_3$), 2.41 (m, -$C\underline{H}_2$-$C\underline{H}_2$-), 2.25 (s, $SC\underline{H}_3$), $\underline{2.21}$ (s, $SC\underline{H}_3$), $\underline{0.79}$, $\underline{0.41}$ (s, 6H, int. Ar-$C\underline{H}_3$), 0.57, 0.56 (s, 6H, Ar-$C\underline{H}_3$); **IR (disc), cm^{-1}**, 553 (w), 625 (m), 790 (w), 809 (w), 826 (m), 863 (m), 877 (s), 957 (m), 1011 (m), 1028 (m), 1054 (w), 1150 (w), 1180 (w), 1190 (w), 1319 (w), 1366 (m), 1444(s), 1457 (s), 1555 (w), 1560 (w), 1577 (w), 2858 (m), 2909 (s), 2953 (s); **MS (CI), *m/e* (%)**, 339 (M+1, 26), 338 (23), 292 (19), 291 (100), 193 (11).

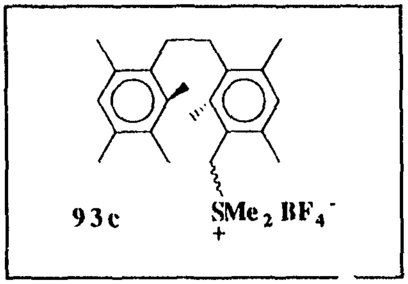
The two isomers of the product **92c** could not be separated by chromatography. Fortunately the pure pseudo-equitorial isomer was obtained as the by-product of elimination of the sulfonium salts of **93c**. Recrystalization from hexane and methanol gave the equitorial isomer **eq-92c** as white plates, **mp**: 142~143°C; **^{1}H NMR (360 MHz)**, δ, 6.58 (s, 1H, H-13), 6.57 (s, 1H, H-5), 3.68 (dd, $J_{1(ax.), 2(ax.)}$ = 11.4 Hz, $J_{1(ax.), 2(eq.)}$ = 2.7 Hz, 1H, H-1(ax.)), 3.25 (dd, $J_{2(eq.), 2(ax.)}$ = 12.9 Hz, $J_{2(eq.), 1(ax.)}$ = 2.7 Hz, 1H, H-2(eq.)), 3.10~3.03 (m, 2H, H-9(eq.), H-10(eq.)), 2.85 (dd, $J_{2(ax.), 2(eq.)}$ = 12.7 Hz, $J_{2(ax.), 1(ax.)}$ = 11.7 Hz, 1H, H-2(ax.)), 2.57 (s, 3H, ext. $C\underline{H}_3$-C_{14}), 2.40 (m, 2H, H-9(ax.), H-10(ax.)), 2.34, 2.33, 2.31 (s, 9H, ext. Ar-$C\underline{H}_3$), 2.25 (s, 3H, S-$C\underline{H}_3$), 0.57 (s, 3H, int. $C\underline{H}_3$-C_{16}), 0.56 (s, 3H, int. $C\underline{H}_3$-C_8); **^{13}C NMR (90.6 MHz)**, δ, 142.4, 141.9, 134.6, 134.5,



eq-92c

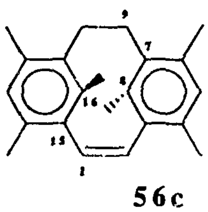
133.6, 133.5, 132.7, 131.4 (C-3, 4, 6, 7, 8, 11, 12, 14, 15, 16), 130.5, 127.9 (C-5, 13), 52.0 (C-1), 37.4 (C-2), 29.9, 29.6 (C-9, 10), 21.1, 19.2, 17.2, 15.7 (ext. & int. $\underline{C}H_3$); **IR (disc), cm^{-1}**, 626 (w), 857 (w), 866 (w), 957 (w), 1008 (w), 1026 (w), 1149 (w), 1180 (w), 1280 (w), 1315 (w), 1370 (m), 1442 (m), 1455 (m), 1565 (m), 2876 (m), 2920 (s), 2984 (s); **MS (EI), *m/e* (%)**, 339 (M+1, 25), 338 (M$^+$, 100), 324 (21), 323 (90), 189 (54), 177 (57), 166 (44), 162 (36), 161 (61), 147 (52), 146 (15), 145 (22), 131 (32), 129 (26), 128 (23), 115 (31), 105 (18), 91 (45).

17. *anti*-4,6,8,12,14,16-Hexamethyl-1-methylthio[2$_2$](1,3)-cycylophane-sulfonium tetrafluoroborate 93c


93c

Borch reagent (10 g, ~80% as oil, 50 mmol) was added to a stirred solution of the stereoisomers **92c** (13.5 g, 40 mmol) in dichloromethane (120 mL) at -30°C. The mixture was then stirred without further cooling for 4 h. Ethyl acetate (60 mL) was added and the mixture was stirred at room temperature for additional 4 h. The bulk of solvent was removed and petroleum ether (100 mL) was added to wash the residue. The solid product was collected by filtration to give the salts **93c** as a pinkish powder, 16.5 g (94%), which were used directly in the following elimination.

18. *anti*-4,6,8,12,14,16-Hexamethyl[2_2](1,3)cyclophan-1-ene 56c



56c

Potassium t-butoxide (2.3 g, 20.5 mmol) was added to a suspension of the sulfonium salts **93c** (4.53 g, 10.3 mmol) in dimethylformamide and t-butanol (60 mL, 1:1) at 0°C. After stirring for 30 min, cold water was added to the resultant mixture and then diethyl ether and petroleum ether (250 mL, 1:3). The organic layer was separated, washed, dried and evaporated. The residue was preabsorbed and chromatographed on silica gel using petroleum ether as eluant. Eluted first was the monoene **56c**, 1.56 g (52%). A portion was recrystalized from petroleum ether and methanol to give **56c** as white crystals, **mp**: >220°C (decomp.); **^{1}H NMR (360 MHz)**, δ, 6.68 (s, 2H, H-5/13), 6.64 (s, 2H, H-1/2), 3.06[a] (m, AA' of AA'XX', $J_{AA'}$ = 4.0 Hz, J_{AX} = $J_{A'X'}$ = -13.1 Hz, $J_{AX'}$ = $J_{A'X}$ = 3.0 Hz, 2H, H-9(eq., A), H-10(eq., A')), 2.28 (s, 6H, ext. $C\underline{H}_3$), 2.22 (s, 6H, ext. $C\underline{H}_3$), 2.17 (m, XX' of AA'XX', $J_{XX'}$ = 12.0 Hz, 2H, H-9(ax., X), H-10(ax., X')), 0.63 (s, 6H, int. $C\underline{H}_3$); **^{13}C NMR (90.6 MHz)**, δ, 139.5, 135.3, 133.9, 132.6, 131.5 (C-3/15, 4/14, 6/12, 7/11, 8/16), 129.8, 129.2 (C-5/13, 1/2), 33.0 (C-9/10), 19.16, 19.13 (ext. $\underline{C}H_3$),

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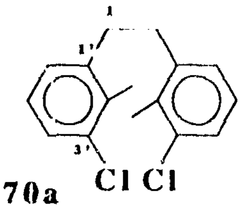
a) The chemical shifts and coupling constants of the AA'XX' system are refined from the simulated spectrum.

17.8 (int. $\underline{C}H_3$); **IR (disc), cm^{-1}**, 473 (m), 483 (m), 598 (m), 653 (s), 742 (m), 772 (s), 824 (s), 855 (s), 956 (m), 1008 (m), 1029 (m), 1190 (m), 1372 (s), 1416 (m), 1441 (s), 1460 (s), 2856 (m) 2899 (s), 2953 (s), 2999 (m); **MS (CI), *m/e* (%)**, 319 (M+29, 5), 292 (M+2, 21), 291 (M+1, 100), 290 (48), 289 (22), 275 (7); **UV, λ_{max}(CH$_3$CN)(ϵ)**, 205(43000), 217 (44,000), 260(29,000), 309(2400).

Anal.	Calcd. for $C_{22}H_{26}$:	C	90.98,	H	9.02
	Found:	C	90.91,	H	8.76

Eluted next was the pseudo-equitorial isomer **92c**, 0.88 g (26%) (see Experiment 16 for its characterization).

19. 1,2-Bis(3'-chloro-2'-methylphenyl)ethane 70a



70a

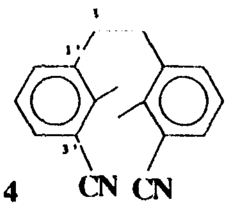
The mixture of 2-chloro-6-hydroxymethyltoluene[123)] (30.2 g, 0.2 mol) in benzene (150 mL) and hydrobromic acid (60 mL, as 48% aq. solution) was refluxed with stirring for 16 h. The organic layer was separated, washed thoroughly with water, and dried by azeotropic distillation. After the bulk of benzene was removed, the concentrated solution of the bromide **69a** was used directly for the coupling reaction.

Several mL of the solution of the bromide **69a** obtained from above (30 mL) in dry THF (150 mL) was added to magnesium (2.43 g, 0.1 mol) in dry THF (200 mL) under nitrogen. After the reaction was initialized by warming the reaction mixture, the remainder of the solution of the bromide **69a** was added slowly to maintain the reaction mixture close to a room temperature. After the addition, the mixture was further stirred at room temperature for 6 h. Then water and dichloromethane (250 mL) were added. The organic layer was separated, washed, dried, and evaporated to yield the dichloride **70a** as white powder, 26.1 g (95%). A portion was recrystallized from hexane to give while crystals, **mp**:108-109°C; **^{1}H NMR (250 MHz), δ**, 7.24 (dd, J = 7.5 Hz, J = 1.7 Hz, 2H, H-4′), 7.05 (t, J = 7.5 Hz, 2H, H-5′), 7.00 (dd, J = 7.6 Hz, J = 1.7 Hz, 2H, H-6′), 2.87 (s, 4H, H-1/2), 2.35 (s, 6H, $C\underline{H}_3$); **^{13}C NMR (62.9 MHz), δ**, 141.6, 135.1, 133.9 (C-1′, 2′, 3′), 127.6, 127.3 126.6 (C-4′, 5′, 6′) 35.1 (C-1/2), 15.8 ($\underline{C}H_3$); **IR (disc), cm^{-1}**, 626 (m), 713 (s), 780 (s), 849 (m), 1008 (s), 1116 (s), 1176 (m), 1370 (w), 1440 (s), 1465 (m), 1566 (m), 2880 (w), 2954 (w), 3060 (w); **MS (EI), *m/e* (%)**, 280 (M+2, 2), 278 (M^+, 3), 142 (3), 141 (32), 140 (10), 139 (100), 104 (8), 103 (24), 102 (5).

Anal.	Calcd. for $C_{16}H_{16}Cl_2$:	C	68.83,	H	5.78
	Found:	C	68.71,	H	5.61

20. 1,2-Bis(3′-cyano-2′-methylphenyl)ethane 84

Copper(I) cyanide (20.0 g, 0.26 mol) was added to a hot



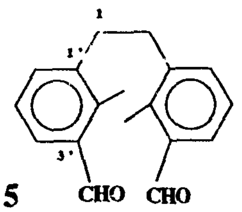
84

solution (~100°C) of the dichloride **70a** (27.9 g, 0.1 mol) in N-methyl-2-pyrrolidi-none (70 mL) and the mixture was refluxed with mechanical stirring for 10 h. The mixture was cooled to ~100°C, and a further portion of copper(I) cyanide (13 g, 0.17 mol) was added and the mixture was then heated at reflux for an additional 14 h. While the mixture was still hot (~100°C), an aqueous solution of ethylene diamine (50 mL + 100 mL H_2O) was added and mixture was vigorously stirred for 15 min. The solid was collected by filtration, washed with dilute ethylene diamine solution twice, then washed thoroughly with water. The solid residue was extracted with dichloromethane (800 mL) and the extract was washed, dried and evaporated. The residue was preabsorbed and chromatographed on silica gel to yield the dicyanide **84** as a white solid, 21,9 g (84%). A portion was recrystallized from hexane to give white crystals, **mp.** 04 ~ 205°C; **^{1}H NMR (360 MHz),** δ, 7.49 (dd, J = 7.3 Hz, J = 1.8 Hz, 2H, H-4'), 7.22 (dd, J = 7.8 Hz, J = 1.8 Hz, 2H, H-6'), 7.18 (t, J = 7.4 Hz, 2H, H-5'), 2.89 (s, 4H, H-1/2), 2.48 (s, 6H, C$\underline{H}_3$); **^{13}C NMR (90.6 MHz),** δ, 140.4, 139.6 (C-1, 2), 133.4, 131.0 126.5 (C-4, 5, 6), 118.4 (C-3), 113.7 ($\underline{C}$N), 33.7 (C-1/2)17.3 ($\underline{C}H_3$); **IR (disc), cm^{-1},** 720 (s), 803 (s), 1140 (w), 1162 (w), 1232 (m), 1380 (s), 1455 (s), 1580 (m), 2224 (s), 2880 (w), 2944 (w), 3010 (w); **MS (CI), *m/e* (%)**, 301 (M+41, 2), 290

(2), 289 (M+29, 18), 262 (20), 261 (M+1, 100), 145 (3), 144 (37), 131 (6), 130 (60), 103 (5), 79(4).

Anal.	Calcd. for $C_{18}H_{16}N_2$:	C 83.05,	H 6.19,	N 10.76
	Found:	C 82.98,	H 6.20,	N 10.69

21. 1,2-Bis(3′-formyl-2′-methylphenyl)ethane 85

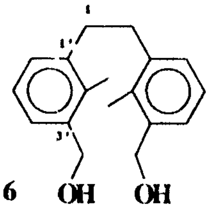


85

Di-isobutylaluminium hydride (0.25 mol in hexane 200 mL) was added dropwise under nitrogen to a solution of the dicyanide **84** (26.0 g, 0.1 mol) in dry benzene (350 mL) at room temperature. After the addition, the mixture was stirred overnight and then was decomposed by slow additions of methanol (100 mL) (using ice-bath cooling) and then aqueous HCl solution (400 mL, 1:1). The mixture was then extracted with dichloromethane (~ 1 L) and the organic layer was separated, washed, dried and evaporated. The residue was preabsorbed and filtered through a column (6 x 15 cm) of silica gel using petroleum ether and dichloromethane (1:1) as eluent to give the dialdehyde **85** as a yellowish powder, 22.3 g (84%). The sample for elemental analysis was obtained by recrystallization from acetone and hexane. **mp**:116~117°C; **^{1}H NMR (360 MHz)**, δ, 10.29 (s, 2H, -C$\underline{H}$O), 7.67 (dd, J = 6.5 Hz, J = 2.7 Hz, 2H, H-4′), 7.30 ~ 7.26 (m, 4H, H-5′, 6′), 2.94 (s, 4H, H-1/2), 2.61 (s, 6H, -C$\underline{H}_3$); **^{13}C NMR (90.6 MHz),** δ, 192.9 (-$\underline{C}$HO), 141.0, 138.2, 134.6 (C-1', 2', 3'), 134.7, 130.5, 125.9 (C-4', 5', 6'), 33.8 (C-1/2), 14.0 (-$\underline{C}H_3$); **IR (disc), cm^{-1}**, 684 (m), 696 (m), 720 (s), 758 (w), 795 (s), 888 (m), 904 (m), 1090 (w), 1141 (w), 1218 (s), 1232 (m), 1260 (m), 1375 (m), 1460 (m), 1578 (m), 1590 (m), 1688 (s), 2768 (w), 2880 (w), 2950 (w); **MS (CI), *m/e* (%)**, 307 (M+41, 3), 295 (M+29, 11), 268 (11), 267 (M+1, 100), 266 (1), 253 (2), 99 (1).

Anal.	Calcd. for $C_{18}H_{18}O_2$:	C	81.17,	H	6.81
	Found:	C	81.32,	H	6.89

22. 1,2-Bis(3'-hydroxymethyl-2'-methylphenyl)ethane 86



86

A solution of the dialdehyde 85 (43.6 g, 164 mmol) in THF (450 mL) was added dropwise to a stirred suspension of sodium borohydride (4.0 g, 100 mmol) in THF (150 mL) and water (10 mL) at room temperature. After 20 h, the aqueous HCl solution (60 mL + 120 mL H_2O) was added slowly to decompose the reaction mixture. The first batch of product was collected by filtration.[a] The aqueous was extracted with dichloromethane until it becomes clear. The organic layer was combined, dried, and evaporated to give

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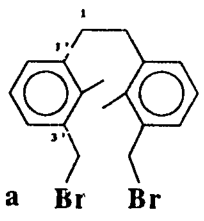
a) The diol xx is less soluble in most solvents.

second batch of the product. Two batches of the product were combined and dried under vacuum to yield the diol **86** as a white powder, 43.5 g (98%). **mp**: 156-158°C (lit. 158-160°C); **^{1}H NMR (360 MHz)**, δ, 7.26 ~ 7.15 (m, ABC system, 6H, H-4', 5', 6'), 4.72 (d, J = 4.0 Hz, 4H, $-C\underline{H}_2OH$), 2.89 (s, 4H, H-1/2), 2.30 (s, 6H, $-C\underline{H}_3$), 1.58 (br s, 2H, $-O\underline{H}$); **^{13}C NMR (90.6 MHz)**, δ, 140.7, 139.0, 134.4 (C-1', 2', 3'), 129.0, 126.2, 125.9 (C-4', 5', 6'), 64.3 ($-\underline{C}H_2OH$), 34.8 (C-1/2), 14.1 ($\underline{C}H_3$).

23. 1,2-Bis(3'-bromomethyl-2'-methylphenyl)ethane 71a

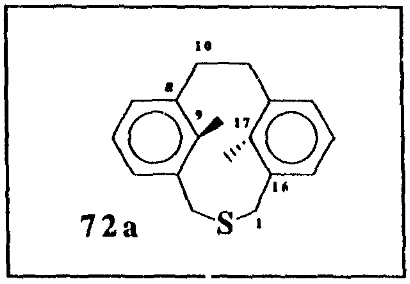
A suspension of the diol in benzene (100 mL) and HBr (60 mL, as 48% aq. solution) and conc. H_2SO_4 (0.5 mL) was refluxed for 24 h. The organic layer was separated and the aqueous was extracted with dichloromethane. The organic layers was combined, washed thoroughly with water, $NaHCO_3$ solution, and water again, dried and evaporated. The residue was preabsorbed on silica gel and filtered through a column (5 x 15 cm) of silica gel using petroleum ether/dichloromethane as eluent to yield the dibromide **71a** as a white solid, 11.95 g, (93%). **mp**: 140-142°C (lit. 142-143°C)$^{40)}$; **^{1}H NMR (250 MHz)**, δ, 7.21 ~ 7.09 (m, ABC system, 6H, H-4', 5', 6'), 4.54 (s, 4H, $-C\underline{H}_2Br$), 2.88 (s, 4H, H-1/2), 2.31 (s, 6H,



71a

-C$\underline{H}_3$); **^{13}C NMR (90.6 MHz),** δ, 140.9, 136.1, 135.3 (C-1′, 2′, 3′), 130.1, 128.3, 126.1 (C-4′, 5′, 6′), 34.7, 33.4 (C-1/2, -$\underline{C}H_2$Br), 14.3 (-$\underline{C}H_3$).

24. anti-9,17-Dimethyl-2-thia[3,2](1,3)cyclophane 72a



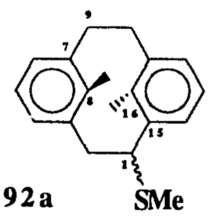
72a

A solution of sodium sulfide (3.7 g, 15 mmol) in nitrogen purged water (120 mL) and 95% ethanol (380 mL) was added dropwise over 48 h to a well stirred suspension of the dibromide **71a** (5.55 g, 14 mmol) in nitrogen purged 95% ethanol (618 mL) and water (182 mL) under nitrogen. After the addition the reaction mixture was further stirred for 2 h. The solvent was removed and the resultant solid residue was dissolved in dichloromethane (500 mL) and water. The organic layer was separated, washed, dried and evaporated. The residue was preabsorbed and chromatographed on silica gel using petroleum ether/dichloromethane (3:1) as eluent to give the monothiacyclophane **72a** as white crystals, 2.32 g (66%). A portion was recrystallized from hexanes to give colourless crystals, **mp:** 171~173°C; **^{1}H NMR (360 MHz),** δ, 7.13 ~ 7.10 (m, 4H, H-5/15, 7/13), 6.98 (t, J = 7.5 Hz, 2H, H-6/14), 3.85 (d, J_{gem} = 13.9 Hz, 2H, H-1/3(eq.)), 3.73 (d,

J_{gem} = 13.8 Hz, 2H, H-1/3(ax.)), 2.94[a] (m, AA′ of AA′XX′, $J_{AA'}$ = 2.6 Hz, J_{AX} = $J_{A'X'}$ = -12.6 Hz, $J_{AX'}$ = $J_{A'X}$ = 4.5 Hz, 2H, H-10(eq., A), H-11(eq., A′)), 2.64 (m, XX′ of AA′XX′, $J_{XX'}$ = 12.4 Hz, J_{XA} = $J_{X'A'}$ = -12.6 Hz, $J_{XA'}$ = $J_{X'A}$ = 4.5 Hz, 2H, H-10(ax., X), H-11(ax., X′)), 0.85 (s, 6H, int. C<u>H</u>$_3$); **^{13}C NMR (90.6 MHz)**, δ, 139.7, 137.6, 135.1 (C-4/16, 8/12, 9/17), 129.1, 128.7, 125.6 (C-5/15, 6/14, 7/13), 35.6, 34.1 (C-1/3, 10/11), 14.3 (-<u>C</u>H$_3$); **IR (disc), cm^{-1}**, 720 (s), 738 (s), 784 (s), 805 (m), 850 (m), 1071 (m), 1168 (w), 1196 (m), 1217 (m), 1415 (m), 1454 (s), 2870 (w), 2930 (w), 2965 (w), 2998 (w); **MS (EI), *m/e* (%)**, 268 (M$^+$, 69), 235 (60), 234 (71), 221 (17), 219 (20), 149 (15), 135 (32), 134 (13), 119 (100), 118 (19), 117 (58), 115 (38), 105 (12), 91 (45).

Anal.	Calcd. for $C_{18}H_{20}S$:	C	80.55,	H	7.51
	Found:	C	79.73,	H	7.24

25. *anti*-8,16-Dimethyl-1-methylthio [2$_2$](1,3)cyclophane 92a



92a

n-Butyllithium (5 mmol in hexane 2 mL) was added using a syringe to a solution of the monothiacyclophane **72a** (1.07 g, 4 mmol) in dry THF (120 ml) under nitrogen at room temperature. After 5 min, methyl iodide

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[a] The chemical shifts and coupling constants of the AA′XX′ system were obtained from the simulated spectrum.

(0.34 mL, 5.5 mmol) was added, then aqueous HCl solution and petroleum ether (300 mL). The organic layer was separated, washed, dried and evaporated to give a mixture of two isomers of **92** as a yellowish semi-solid, 1.14 g (100%). A portion (130 mg) was carefully chromatographed through a column (2 x 80 cm) of silica gel using petroleum ether as eluent. Eluted first was the pseudo-equitorial isomer **eq-92a** as a white solid, 113.2 mg (91%). **mp:** 95 ~ 96°C; **^{1}H NMR (360 MHz),** δ, 7.70[a] (br d, J = 7.3 Hz, 1H, H-14), 7.17 (d, J = 7.4 Hz, 1H, H-12), 7.13(t(dd)[b], J = 7.7 Hz, 2H, H-4/6), 6.97 (t(dd), J = 7.4 Hz, 1H, H-13), 6.84 (t(dd), J = 7.3 Hz, 1H, H-5), 4.02 (dd, J = 11.3 Hz, J = 4.2 Hz, 1H, H-1(ax.)), 3.18 (dd, J = 12.5 Hz, J = 4.2 Hz, 1H, H-2(eq.)), 2.98 ~ 2.94 (m, 2H, H-9(eq.), H-10(eq.)), 2.76 ~ 2.70 (m, 2H, H-9(ax.), H-10(ax.)), 2.64 (t(dd), J = 11.9 Hz, 1H, H-2(ax.)), 2.12 (s, 3H, -SC$\underline{H}_3$), 0.59 (s, 3H, int. C$\underline{H}_3$), 0.57 (s, 3H, int. C$\underline{H}_3$); **^{13}C NMR (90.6 MHz),** δ, 143.0, 142.5, 137.2, 136.4, 135.6, 135.1 (C-3, 7, 8, 11, 15, 16), 128.1, 127.6, 127.3, 124.7 124.4, 124.2 (C-4, 5, 6, 12, 13, 14), 52.3 (C-1), 43.2 (C-2), 36.3, 36.1 (C-9, 10), 15.5, 14.9, 14.8 (int. -$\underline{C}H_3$ and -S$\underline{C}H_3$); **IR (disc), cm^{-1},** 714 (s), 764 (s), 803 (m), 988 (m), 1027 (m), 1058 (m), 1141 (m), 1154 (m), 1171 (m), 1372 (w), 1433 (m), 1451 (m), 2853 (w), 2927 (m), 2964 (w), 3048 (w); **MS (CI), *m/e* (%),** 323 (M+41, 2), 312 (2), 311 (M+29, 9), 284

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a) These assignments are made on the basis of COSY spectrum.

b) These triplets are in fact overlapped doublets of doublets, which have nearly the same coupling constants.

(14), 283 (M+1, 64), 282 (30), 281 (4), 263 (7), 179 (4), 119 (3).

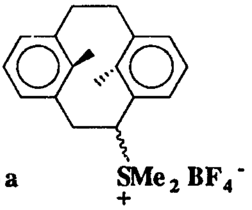
Anal. Calcd. for $C_{19}H_{22}S$: C 80.80, H 7.85

Found: C 81.10, H 7.76

Eluted next was the pseudo-axial isomer **ax-92a** as a white solid, 11.5 mg (9%). **mp:** 156 ~ 157°C; **^{1}H NMR (360 MHz), δ,** 7.26 (d, J = 7.2 Hz, 1H, Ar-$\underline{H}$), 7.16 (d, J = 7.2 Hz, 1H, Ar-$\underline{H}$), 7.15 (d, J = 7.2 Hz, 1H, Ar-$\underline{H}$), 7.07 (d, J = 7.3 Hz, Ar-$\underline{H}$), 6.88 (t, J = 7.3 Hz, 1H, Ar-$\underline{H}$), 6.83 (t, J = 7,3 Hz, 1H, Ar-$\underline{H}$), 4.41 (br d, J = 5.8 Hz, 1H, H-1(eq.)), 3.28 (dd, J = 14.0 Hz, J = 6.9 Hz, 1H, H-2(eq.)), 3.04 (br d, J = 14.0 Hz, 1H, H-2(ax.)), 2.96 ~ 2.81, 2.78 ~ 2.70 (m, 4H, H-9, H-10), 2.18 (s, 3H, -SC$\underline{H}_3$), 0.88 (s, 3H, C_{16}-C$\underline{H}_3$), 0.53 (s, 3H, C_8-C$\underline{H}_3$); **^{13}C NMR (90.6 MHz), δ,** 144.3, 142.3, 137.1, 136.9, 134.7. 134.0 (C-3, 7, 8, 11, 15, 16), 128.8, 128.7, 128.5, 128.1, 124.0, 123.9 (C-4, 5, 6, 12, 13, 14), 57.6 (C-1), 41.1 (C-2), 36.2, 36.0 (C-9, 10), 17.2, 14.7, 14.4 (-S$\underline{C}H_3$, int. $\underline{C}H_3$); **MS (CI), *m/e* (%),** 311 (M+29, 3), 284 (6), 283 (M+1, 27), 282 (30), 281 (3), 269 (4), 263 (9), 236 (20), 235 (100), 233 (5), 179 (5), 165 (3), 119 (3).

26. *anti*-8,16-Dimethyl-1-methylthio [2$_2$](1,3)cyclophanesulfonium tetrafluoroborate 93a

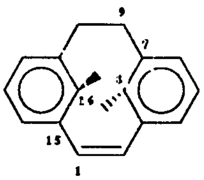
Borch reagent (0.88 g, ~80% as oil, 5.4 mmol) was added to a stirred solution of stereoisomers of **92a** (1.02 g, 3.6 mmol) in dichloro-methane (20 mL) at -30°C. The mixture was then stirred at -30°C for 4 h. After removal of the solvent under reduced pressure, ethyl acetate (10 mL) was added and the mixture was stirred at room temperature for 4 h. The solid product was collected by filtration to give the sulfonium salts **93a** as a pale powder, 1 24 g (90%). **^{1}H NMR (250 MHz)**, δ, 7.47 (t, J = 8.0 Hz, H-12, 14), 7.30 (t, J = 7.0 Hz, H-4, 6), 7.12 (t, J = 7.5 Hz, H-13), 6.97 (t, J = 7.4 Hz, H-5), 4.59 (dd J = 11.4 Hz, J = 4.1 Hz, H-1), 3.56 (dd, J = 12.0 Hz, J = 4.0 Hz, H-2(eq.)), 3.36 (s, -S(C$\underline{H}_3$)), 3.32 ~ 3.07 (m, -C$\underline{H}_2$-), 3.04 (s, S(C$\underline{H}_3$)), 2.98 ~ 2.81 (m, -C$\underline{H}_2$-), 0.82 (s, int. C$\underline{H}_3$(ax.)), 0.73 (br s, int. C$\underline{H}_3$(eq.)), 0.62 (s, int. C$\underline{H}_3$(ax.)).



93a

27. *anti*-8,16-Dimethyl [2$_2$](1,3)cyclophan-1-ene 56a

Potassium t-butoxide (0.62 g, 5.5 mmol) was added to a solution of the sulfonium salt **93a** (1.1 g, 2.87 mmol) in dimethylformamide and t-butanol (26 mL, 1:1) at room temperature. After 30 min, cold water and then petroleum ether (300 mL) was added to the resultant mixture. The



56a

organic layer was separated, washed, dried and evaporated. The residue was preabsorbed and filtered though a short column of silica gel using petroleum ether as eluent to give the cyclophanene **56a** as a white solid, 0.62 g (92%). A portion was recrystallized from methanol and hexane to give white crystals, **mp:** 148-150°C (lit. 151-152°C)[65b]; **^{1}H NMR (360 MHz), δ,** 6.97 (m, 4H, H-4/14, 6/12), 6.86(m, 2H, H-5/13), 6.59 (s, 2H, H1/2), 2.89[a] (m, AA' of AA'XX', $J_{AA'}$ = 2.8 Hz, J_{AX} = $J_{A'X'}$ = -12.2 Hz, $J_{AX'}$ = $J_{A'X}$ = 3.9 Hz, 2H, H-9(eq., A), H-10(eq., A')), 2.50 (m, XX' of AA'XX', $J_{XX'}$ = 12.1 Hz, J_{XA} = $J_{X'A'}$ = -12.2 Hz, $J_{XA'}$ = $J_{X'A}$ = 3.9 Hz, 2H, H-9(ax., X), H-10(ax., X')), 0.76 (s, 6H, int. C$\underline{H}_3$); **^{13}C NMR (90.6 MHz), δ,** 140.4, 138.5, 135.9 (C-3/15, 7/11, 8/16), 132.1, 128.1, 125.8, 123.7 (C-4/14, 5/13, 6/12, 1/2), 39.2 (C-9/10), 17.3 (int. C$\underline{H}_3$); **MS (CI), *m/e* (%)**, 263 (M+29, 5), 236 (19), 235 (M^+, 100), 234 (10), 233 (2), 219 (4); **UV, λ_{max}(CH_3CN)(ε)**, 212 (36,000), 255 (24,300), 307 (1980).

28. *anti*-8,16-Dimethyl-1-phenylthio $[2_2]$(1,3)cyclophane 169

A nitrogen-purged solution of anthranillic acid (343 mg, 2.5 mmol) in 1,2-dichloroethane (25 mL) was added dropwise under nitrogen over 4 h to a hot solution of the monothiacyclophane **72a** (537 mg, 2 mmol) and *iso*-amylnitrite

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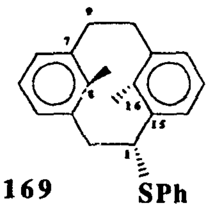
[a] The chemical shifts and coupling constants of this AA'XX'system are refined from the simulated spectrum.

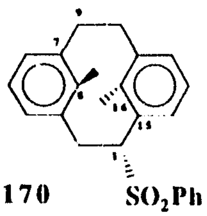


169

(1.05 g, 9 mmol) in 1,2-dichloroethane (25 mL). After the addition, the mixture was refluxed for 15 min. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel using petroleum ether and dichloromethane (3:1) to give **169** as a white semi-solid, 528 mg (77%). Recrystallization from pentane gave the pure pseudo-equitorial isomer of **169** as white crystals. **^{1}H NMR (360 MHz)**, δ, 7.74 (dd, J = 6.7 Hz, J = 1.0 Hz, 1H, H-14), 7.32 ~ 7.29 (m, 2H, H-12, H-4), 7.21 ~ 7.07 (m, 6H, H-6, Ph-$\underline{H}$), 6.93 (t(dd), J = 7.5 Hz, 1H, H-13), 6.85 (t(dd), J = 7.3 Hz, 1H, H-5), 4.48 (dd, $J_{1,\ 2(ax.)}$ = 11.4 Hz, $J_{1,\ 2(eq.)}$ = 4.2 Hz, 1H, H-1(ax)), 3.33 (dd, $J_{2(eq.),\ 2(ax.)}$ = 12.5 Hz, $J_{2(eq.),\ 1}$ = 4.2 Hz, 1H, H-2(eq.)), 2.99 ~ 2.93 (m, 2H, H-9/10(eq.)), 2.79 (t(dd), J = 11.8 Hz, 1H, H-2(ax.)), 2.80 ~ 2.67 2H, H-9/10(ax.)), 0.65 (s, 3H, int. $C\underline{H}_3$), 0,59 (s, 3H, int. $C\underline{H}_3$); **^{13}C NMR (62.9 MHz)**, δ, 142.7, 142.2, 137.1, 137.0, 136.6, 136.3, 135.0, (aromatic quarternary $\underline{C}$), 129.3, 128.8, 128.2, 127.7, 127.5, 125.9, 124.8, 124.6, 124.5 (aromatic ternary $\underline{C}$), 52.1 (C-1), 43.3 (C-2), 36.3, 36.1 (C-9, 10), 14.8 (int. $\underline{C}H_3$); **IR (disc), cm^{-1}**, 689 (s), 702 (m), 718 (s), 734 (s), 742 (m), 765 (s), 804 (m), 1025 (m), 1089 (m), 1430 (m), 1459 (m), 1479 (m), 1582 (m), 2860 (w), 2914 (w), 2960 (w), 3060 (w); **MS (CI), *m/e* (%)**, 346 (5), 345 (M+1, 23), 344 (5), 271 (10), 235 (25), 187 (19), 163 (5), 135 (42), 86 (25), 85

(100), 84 (26), 71 (55).

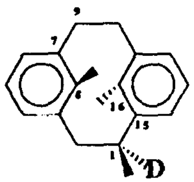
29. *anti*-1-(benzenesulfonyl)-8,16-dimethyl [2$_2$](1,3) cyclophane 170



170

Hydrogen peroxide (12 mL, 30%) was added to a warm solution of the sulfide **169** (345 mg, 1 mmol) in acetic acid (20 mL) and benzene (40 mL). The mixture was refluxed for 4 h. Then the solvent was removed under reduced pressure. The residue was preabsorbed and filtered through a short column of silica gel using dichloromethane to give the sulfone **170** as a white solid, 308 mg (82%). A portion was recrystallized from a mixture of acetone and hexanes to give white crystals, **mp:** 248-250°C; **^{1}H NMR (360 MHz),** δ, 8.03 (dd, J = 7.8 Hz, J = 1.1 Hz, 1H, H-14), 7.99 ~ 7.92 (m, 2H, -SO$_2$Ph-$\underline{H}$(ortho)), 7.57 ~ 7.45 (m, 3H, -SO$_2$Ph-$\underline{H}$), 7.16 (d, J = 7.4 Hz, 1H, H-12), 7.11 (t(dd), J = 7.2 Hz, 2H, 4, 6), 6.94 (t(dd), J = 7.6 Hz, 1H, H-13), 6.84 (t(dd), J = 7.4 Hz, 1H, H-5), 4.20 (dd, $J_{1,2(ax.)}$ = 11.3 Hz, $J_{1,\,2(eq.)}$ = 3.4 Hz, 1H, H-1), 3.64 (dd, $J_{2(eq.),\,2(ax.)}$ = 12.3 Hz, $J_{2(eq.),\,1}$ = 3.3 Hz, 1H, H-2(eq.)), 3.20 (t(dd), J = 12.2 Hz, J = 11.5 Hz, 1H, H-2(ax.)), 2.94 ~ 2.87 (m 2H, H-9/10(eq.)), 2.76 ~ 2.58 (m, 2H, H-9/10(ax.)), 0.66 (s, 3H, int. C$\underline{H}_3$), 0.41 (s, 3H, int. C$\underline{H}_3$); **^{13}C NMR (62.9 MHz),** δ, 143.4, 142.8, 139.3, 137.7, 137.2, 133.2, 129.2 (aromatic quarternary C), 133.5, 129.0 (Ph-C), 128.9, 128.4 (Ph-C), 128.0, 127.5, 125.6, 125.1, 124.7, (aromatic ternary C), 69.3 (C-1), 36.3, 36.1, 35.9 (C-2, 9, 10), 15.3, 14.9 (int. CH_3); **IR (disc), cm^{-1}**, 603 (s), 694 (m), 718 (m), 735 (s), 751 (m), 771 (m), 1088 (m), 1139 (s), 1150 (m), 1291 (s), 1306 (m), 1448 (m), 2946 (w), 2970 (w), 3055 (w); **MS (EI), *m/e* (%)**, 376 (M^+, 2), 236 (18), 235 (M-$PhSO_2$, 100), 219 (22), 183 (3), 179 (8), 141 (8), 125 (38), 79 (4).

30. Deprotonation of the sulfone 170

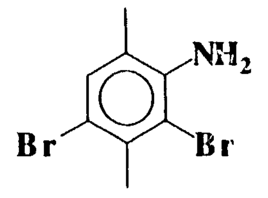


171

n-Butyllithium (0.25 mmol in hexane 0.1 mL) was added to the suspension of the sulfone **170** (38 mg, 0.1 mmol) in dry THF (5 mL) at -78°C under nitrogen. The mixture was stirred without further cooling for 30 min. The resultant dark-brown mixture was quenched with D_2O (~0.5 mL)(finally colorless). The mixture was extracted with dichloromethane. The organic extract was washed, dried and evaporated. The residue was preabsorbed and chromatographed on silica gel to give the deuterated sulfone **171** as a white solid, 33 mg (87%). **^{1}H NMR (250 MHz), δ**, 8.03 (dd, J = 7.7 Hz, J = 1.0 Hz, 2H, H-14), 7.99 ~ 7.94 (m, 2H, SO_2Ph-H(ortho)), 7.55 ~ 7.45 (m, 3H, SO_2Ph-H), 7.17 ~ 7.10 (m, 3H, H-4, 6, 12), 6.94

(t(dd), J = 7.6 Hz, 1H, H-13), 6.83 (t(dd), J = 7.4 Hz, 1H, H-5), 3.63 (d, $J_{2(eq.), 2(ax.)}$ = 12.3 Hz, 1H, H-2(eq.)), 3.20 (d, $J_{2(ax.), 2(eq.)}$ = 12.3 Hz, 1H, H-2(ax.)), 2.94 ~ 2.88 (m, 2H, H-9/10(eq.)), 2.72 ~ 2.62 (m, 2H, H-9/10(ax.)), 0.66 (s, 3H, int. $C\underline{H}_3$), 0.41 (s, 3H, int. $C\underline{H}_3$).

31. 2,4-Dibromo-3,5-dimethylaniline 76[124)]

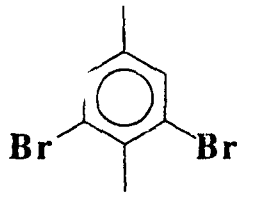


76

A rapid stream of air saturated with bromine vapor (500 g, 3.12 mol) was introduced by applying suction into a stirred solution of aniline (189 g, 1.56 mol) in 95% ethanol (1.7 L) and water (1.4 L) at room temperature under darkness (4~6 h). The solid was collected by filtration and washed thoroughly with a large quantity of water until the washings were nearly neutral. The pinkish product was not dried, but was used directly in the deamination reaction. A small amount of wet product was dried for the purpose of calculation of the yield, 394 g (dry weight) (94%). **^{1}H NMR (90 MHz)**, δ, 7.22 (s, 1H, H-5), 3.37 (br s, 2H, $N\underline{H}_2$), 2.51 (s, 3H, $-C\underline{H}_3$), 2.15 (s, 3H, $-C\underline{H}_3$).

32. 2,6-Dibromo-*p*-xylene 77[125)]

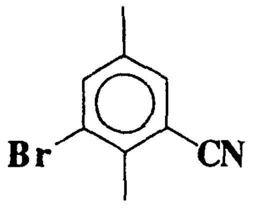
Concentrated H_2SO_4 (200 mL) was added to a solution of



77

the crude 2,4-dibromo-3,5-dimethylaniline (372 g, 1.33 mol) (from experiment 31) in 95% ethanol (1.7 L) and benzene (400 mL). While the mixture was hot, sodium nitrite (200 g) was added in small portions as quickly as the violence of the reaction permitted (~1 h). After the addition, the mixture was refluxed for 3 h and then was kept warm overnight. After the mixture was cool, dilute H_2SO_4 (200 mL + 1.4 L H_2O) and petroleum ether (1.5 L) were added. The organic layer was separated, washed with water, $NaHCO_3$ solution, water again, dried and evaporated. The dark residue was distilled under vacuum (133~136°C/13 tor) to give the dibromide as yellowish solid, 262 g (75%). **mp:** 58~59°C (lit. 61°C); **^{1}H NMR (90 MHz),** δ, 7.32 (s, 2H, H-3/5), 2.47 (s, 3H, C_1-$C\underline{H}_3$), 2.22 (s, 3H, C_4-$C\underline{H}_3$).

33. 1-Bromo-3-cyano-2,5-dimethylbenzene 78



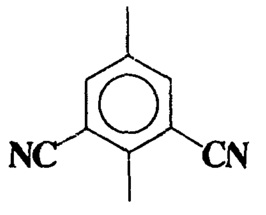
78

Copper(I) cyanide (29.5 g, 33 mmol) was added to a hot solution (~80°C) of 2,6-dibromotoluene **77** (174 g, 0.66 mol) in dimethylformamide (100 mL). The mixture was then heated at gentle reflux with a mechnical stirring for 4 h. When the mixture was still hot, the mixture was decomposed by additions of aqueous solution of ethylene diamine (80 mL + 240 mL H_2O) and dichloromethane (400 mL). The resultant mixture was stirred for 30 min and then was filtered to remove copper powder. The organic layer was separated, washed, dried and evaporated. The residue was preabsorbed and chromatographed on silica gel using petroleum ether first as eluent. After unreacted dibromide was eluted off the column, 92.1 g (53%), the column was eluted with petroleum ether and dichloromethane (3:1) to give the monocyanide as white solid, 60.6 g (44%). **mp:** 74~75°C; **^{1}H NMR (360 MHz),** δ, 7.57 (s, 1H H-4), 7.35 (s, 1H, H-6), 2.56 (s, 3H, C_2-$C\underline{H}_3$), 2.31 (s 3H, C_5-$C\underline{H}_3$); **^{13}C NMR (90.6 MHz),** δ, 138.4, 137.9 (C-2, 5), 137.6, 132.1 (C-4, 6), 125.5 (C-1), 117.6 (C-3), 114.0 (-$\underline{C}$N), 21.1, 20.3 (-$\underline{C}H_3$); **IR (disc), cm^{-1},** 704 (m), 799 (s), 873 (s), 1000 (m), 1115 (w), 1220 (w), 1258 (m), 1380 (w), 1450 (w), 1468 (m), 1545 (w), 2132 (m), 2928 (w), 3060 (w); **MS (CI), *m/e* (%),** 240 (M+29, 6), 238 (M+29, 5), 213 (8), 212 (M+1, 85), 211 (15), 210 (M+1, 100), 209 (6), 172 (7), 171 (50), 130 (4);

Anal. Calcd. for C_9H_8BrN: C 51.46, H 3.84, N 6.67
Found: C 51.10, H 3.81, N 6.51

Eluted last was the dicyanide **172** as white solid, 2.6 g (3%), **mp:**171~172°C; **^{1}H NMR (360 MHz),** δ, 7.61 (s, 2H, H-3/5), 2.69 (s, 3H, C_1-$C\underline{H}_3$), 2.38 (s, 3H, C_4-$C\underline{H}_3$); **^{13}C NMR (90.6 MHz),** δ, 142.4, 137.6 (C-1, 4), 136.9 (C-3/5), 116.4

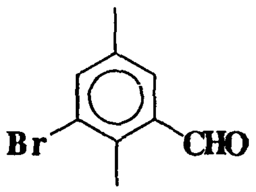
(C-2/6), 114.5 ($\underline{C}N$), 20.3 (C_1-$\underline{C}H_3$), 18.9 (C_4-$C\underline{H}_3$); **IR (disc), cm^{-1}**, 887 (s), 1012 (m), 1039 (m), 1284 (m), 1385 (s), 1450 (br, s), 1600 (w), 1820 (w), 2220 (s), 3050 (w); **MS (CI), *m/e* (%)**, 197 (M+41, 2), 185 (M+29, 9), 158 (9), 157 (M+1, 100), 156 (5).



172

When one equivalent of copper cyanide was used, the same reaction afforded 16~17% of the unreacted dibromide, 50~52% of the monocyanide **78**, and 22~24% of the dicyanide **172**.

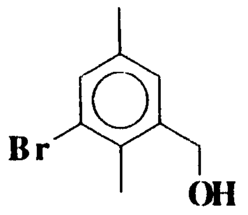
34. 3-Bromo-2,5-dimethylbenzaldehyde 79



79

Di-isobutylaluminium hydride (75 mmol in hexane 60 mL) was added dropwise over 1.5 h under nitrogen to a solution of 1-bromo-3-cyano-2,5-dimethylbenzene (10.5 g, 50 mmol) in dry benzene (60 mL) at room temperature. After the addition, the mixture was stirred overnight under nitrogen. The mixture was decomposed by slow additions of methanol (15 mL) and then aqueous methanol (40 mL, 1:1), followed by aqueous HCl solution (120 mL, 1:2(H_2O)). The resultant mixture was filtered and the organic layer was separated. The aqueous layer was extracted with diethyl ether (100 mL x 2). The organic layers were combined, washed, dried and evaporated to give the aldehyde **79** as a yellowish liquid, 10.33 g (97%). The product could be further purified by vacuum distillation to give a colourless liquid, 10.3 g (97%). **bp:**116 ~ 117°C/2.5 mmHg; **^{1}H NMR (250 MHz), δ**, 10.19 (s, 1H, C$\underline{H}$O), 7.59 (s, 1H, H-6), 7.54 (s, 1H, H-4), 2.66 (s, 3H, C_2-C$\underline{H}_3$), 2.34 (s, 3H, C_5-C$\underline{H}_3$); **MS (CI), *m/e* (%)**, 215 (M+1 93), 214 (7), 213 (M+1, 100), 125 (17).

35. 1-Bromo-2,5-dimethyl-3-hydroxybenzene 80

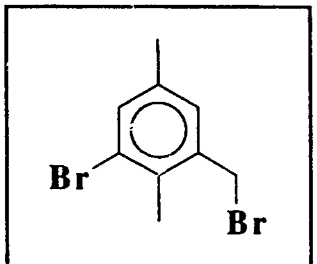


80

A solution of the aldehyde **79** (30.0 g, 140 mmol) in THF (350 mL) was added dropwise to a stirred suspension of sodium borohydride (2.65 g, 70 mmol) in THF (300 mL) at room temperature. After stirring for 20 h, the mixture was decomposed by additions of aqueous HCl solution (180 mL, 1:2(H_2O)) and diethyl ether (250 mL). The organic layer was separated and the aqueous layer was extracted with diethyl ether (200 mL x 2). The organic layers were combined, washed, dried and evaporated to give the alcohol **80** as a white solid, 30.3 g (100%), **mp:** 89~90°C; **^{1}H NMR (360 MHz), δ**, 7.33 (s, 1H, H-6), 7.11 (s, 1H, H-4), 4.67 (d, J = 5.7 Hz, 2H, -C$\underline{H}_2$OH), 2.36 (s, 3H, -C$\underline{H}_3$), 2.29 (s, 3H, -C$\underline{H}_3$), 1.54 (t, J = 5.8 Hz, 1H, -O$\underline{H}$); **^{13}C NMR (90.6 MHz), δ**, 140.1, 137.0, 132.5 (C-2, 3, 5), 132.4, 127.7 (C-4, 6), 125.9 (C-1); **IR (disc), cm^{-1}**, 608 (m), 692 (m), 743 (m), 810 (m), 851 (s), 993 (m), 1046 (s), 1116 (s), 1250 (m), 1272 (w), 1360 (m), 1460 (br, m), 1606 (m), 2860 (w), 2920 (w), 3240 (v br, s); **MS (EI), *m/e* (%)**, 216 (4), 215 (M+1, 13), 214 (4), 213 (M+1, 15), 200 (9), 199 (M-H_2O, 95), 198 (14), 197 (M-H_2O, 100), 187 (36), 185 (39), 149 (14), 121 (12), 119 (9).

Anal.	Calcd. for $C_9H_{11}BrO$:	C	50.26,	H	5.15
	Found:	C	50.20,	H	5.15

36. 1-Bromo-3-Bromomethyl-2,5-dimethylbenzene 69b



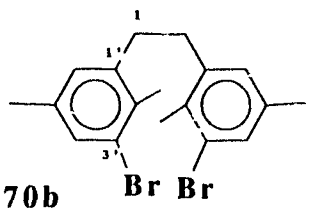
69b

A mixture of the alcohol **80** (28.8 g, 134 mmol) in benzene (120 mL) and aqueous HBr (100 mL, 48%) was refluxed with stirring for 40 h. The organic layer was separated, washed with water, $NaHCO_3$ solution, water, dried and evaporated. The residue was preabsorbed and filtered through a short column of silica gel using petroleum ether as eluent to give the bromide **69b** as white solid, 36.3 g (97%). A portion was recrystallized from pentane to give colorless crystals, **mp:** 51~52° ; **^{1}H NMR (360 MHz), δ**, 7.34 (s, 1H, H-6), 7.05 (s, 1H, H-4), 4.47 (s, 2H, -C$\underline{H}_2$Br), 2.41 (s, 3H, -C$\underline{H}_3$), 2.26 (s, 3H, -C$\underline{H}_3$); **^{13}C NMR (90.6 MHz), δ**, 137.2, 137.1, 133.8 (C-2, C-3, C-5), 133.7, 130.0 (C-4, C-6), 126.2 (C-1), 32.8 (-

$\underline{C}H_2Br$), 20.4, 18.3 ($-\underline{C}H_3$); **IR (disc), cm^{-1}**, 624 (m), 720 (s), 813 (m), 858 (s), 953 (m), 1005 (m), 1140 (m), 1203 (s), 1230 (w), 1264 (m), 1379 (m), 1445 (br, m), 1468 (m), 1605 (w), 2920 (w), 2990 (w); **MS (CI), *m/e* (%)**, 281 (M+4+1, 7), 279 (M+2+1, 15), 277 (M+1, 8), 227 (2), 225 (2), 200 (9), 199 (M-Br, 97), 198 (10), 197 (M-Br, 100), 147 (4), 133 (12).

Anal. Calcd. for $C_9H_{10}Br_2$: C 38.75, H 3.97
Found: C 39.02, H 3.62

37. 1,2-Bis(3′-bromo-2′,5′-dimethylphenyl)ethane 70b

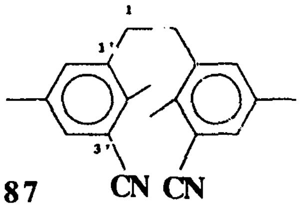


70b

A solution of the dibromide **69b** (21.5 g, 7.7 mmol) in dry diethyl ether (50 mL) and magnesium (0.95 g, 3.9 mmol) was warmed up to reflux under nitrogen. Once the reaction was initialized, anhydrous ferric chloride (50 mg, 0.3 mmol) was added quickly and the reaction reacted vigorously. After the reaction subsided 20 min later, the mixture was further refluxed for 1 h. Then cold water was added, followed by aqueous HCl, dichloromethane (200 mL). The organic layer was separated, washed, dried and evaporated to give the dibromide **70b** as white powder, 14.2 g (93%). A portion was recrystallized from ethyl acetate to give white crystals, **mp:** 169~170°C; **^{1}H NMR (360 MHz),** δ, 7.26 (br s, 2H, H-6′), 6.85 (br s, 2H, H-4′), 2.79 (s, 4H, H-1/2), 2.34 (s, 3H, -C$\underline{H}_3$), 2.25 (s, 3H, -C$\underline{H}_3$); **^{13}C NMR (90.6 MHz), δ**, 141.4, 136.9, 132.3, (C-1′, 2′, 5′), 131.1, 129.1 (C-4′, 6′), 125.9 (C-3′), 35.7 (C-1/2), 20.5, 18.6 (-$\underline{C}H_3$); **IR (disc), cm^{-1}**, 716 (m), 805 (s), 850 (s), 948 (m), 998 (m), 1224 (m), 1468 (br, m), 1545 (br, w), 1605 (m), 2874 (w), 2920 (w), 2950 (w); **MS (CI), *m/e* (%)**, 397 (2), 396 (2), 395 (M+1, 3), 141 (3), 239 (3), 214 (10), 213 (93), 212 (11), 211 (100), 199 (6), 197 (7), 133 (12), 102 (8), 100 (6), 86 (5).

Anal.	Calcd. for $C_{18}H_{20}Br_2$:	C 54.57,	H 5.09
	Found:	C 54.83,	H 5.06

38. 1,2-Bis(3′-cyano-2′,5′-dimethylphenyl)ethane 87

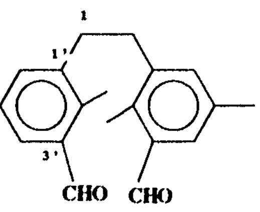


87

Copper(I) cyanide (26.9 g, 0.3 mol) was added to a hot solution of the dibromide **70b** (39.6 g, 0.1 mol) in N-methyl-2-pyrrolidinone (150 mL) and the mixture was refluxed with mechanical stirring for 20 h. While the reaction mixture was still hot (~80°C), aqueous ethylene diamine (280 mL, 1:3 (H_2O)) was added and the mixture was vigorously stirred for 30 min. The solid was collected by filtration and the filtrate was extracted with dichloromethane (100 mL x 2). Then the solid was dissolved in dichloromethane (~800 mL) and was filtered. The organic layers were combined, washed, dried and evaporated. The residue was preabsorbed and filtered through a column of silica gel using petroleum ether and dichloromethane (1:1) as eluent to give the dicyanide **87** as a yellowish solid, 27.6 g (96%). A portion was recrystallized from acetone to give white crystals, **mp:** 206~207°C; **^{1}H NMR (360 MHz), δ**, 7.28 (s, 2H, H-4′), 7.05 (s, 2H, H-6′), 2.80 (s, 4H, H-1/2), 2.43 (s, 6H, $C_{2'}$-C$\underline{H}_3$), 2.28 (s, 6H, $C_{5'}$-C$\underline{H}_3$); **^{13}C NMR (90.6 MHz), δ**, 140.4, 136.5, 136.3 (C-1′, 2′, 5′), 134.4, 131.1 (C-4′, 6′), 118 (C-3′), 113.5 (-$\underline{C}$N), 33.9 (C-1/2), 20.6, 16.9 (-$\underline{C}H_3$); **IR (disc), cm^{-1}**, 727 (s), 864 (s), 1022 (br, m), 1042 (m), 1207 (w), 1298 (m), 1384 (w), 1470 (br, s), 1607 (m), 2223 (s), 2880 (w), 2930 (w), 2960 (m); **MS (CI), *m/e* (%)**, 329 (M+41, 2), 317 (M+29, 12), 290 (21), 289 (M+1, 100), 158 (3), 144 (17).

Anal.	Calcd. for $C_{20}H_{20}N_2$:	C 83.30,	H 6.99,	N 9.71
	Found:	C 83.23,	H 7.16,	N 9.56

39. 1,2-Bis(3′-formyl-2′,5′-dimethylphenyl)ethane 88



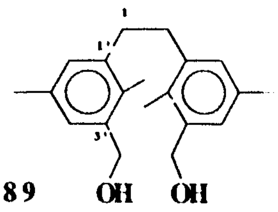
88

Di-*iso*-butylaluminium hydride (0.25 mol in hexane 200 mL) was added dropwise under nitrogen to a solution of the dicyanide **87** (28.84 g, 0.1 mol) in dry benzene (500 mL) at room temperature. After the addition, the mixture was stirred overnight and then was decomposed by slow additions of methanol (100 mL) and then aqueous HCl (400 mL, 1:1) under nitrogen. Dichloromethane (800 mL) was added and the mixture was filtered. The solid residue was washed with dichloromethane twice. The organic layers were combined, washed, dried and evaporated. The residue was preabsorbed and chromatographed on silica gel using petroleum ether and dichloromethane/ethyl acetate (5.5:4:0.5) as eluent to give the dialdehyde **88** as a yellowish solid, 24.2 g (82%). A portion was recrystallized from acetone to give white crystals, **mp:**142-144°C; **^{1}H NMR (360 MHz), δ**, 10.28 (s, 2H, $\mathrm{C\underline{H}O}$), 7.49 (s, 2H, H-4'), 7.13 (s, 2H, H-6'), 2.86 (s, 4H, H-1/2), 2.57 (s, 6H, $\mathrm{C_{2'}\text{-}C\underline{H}_3}$), 2.33 (s, 6H, $\mathrm{C_{5'}\text{-}C\underline{H}_3}$); **^{13}C NMR (90.6 MHz), δ**, 193.3 ($\mathrm{\underline{C}HO}$), 141.2, 135.6, 135.3, 134.6 (C-1', 2', 3', 5'), 135.7, 130.9 (C-4', 6'), 34.1 (C-1/2), 20.7, 13.7 ($\mathrm{\underline{C}H_3}$); **IR (disc), cm^{-1}**, 673 (m), 721 (m), 763 (m), 874 (s), 900 (s), 980 (m), 1040 (m), 1120 (m), 1195 (m), 1258 (m), 1292 (s), 1378 (m), 1405 (w), 1467 (m), 1604 (m), 1670 (s, br), 2766 (w), 2880 (w), 2880 (w), 2920 (w), 2940 (w); **MS (CI), *m/e* (%)**, 295 (M+1, 100), 161 (15), 147 (9), 133 (13)

Anal.	Calcd. for $C_{20}H_{22}O_2$:	C 81.60,	H 7.53
	Found:	C 81.44,	H 7.68

40. 1,2-Bis(3'-hydroxymethyl-2',5'-dimethylphenyl)ethane 89

A solution of the dialdehyde **88** (21.0 g, 71.3 mmol) in



89

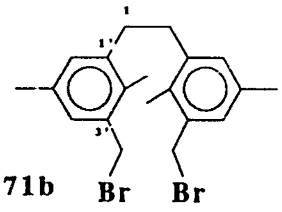
THF (500 mL) was added dropwise to a suspension of sodium borohydride (1.90 g, 50.0 mmol) in THF (75 mL) and water (5 mL) at room temperature. After 24 h, the mixture was decomposed by addition of HCl solution (90 mL, 1:2(H_2O)). The first batch of product was collected by filtration. The aqueous layer was extracted with diethyl ether (200 mL x 3). The extract was washed, dried and evaporated to give a second batch of the diol **89** as a white solid, 20.2 g (95%). A portion was recrystallized from acetone to give colorless crystals, **mp:** 174~175°C; **^{1}H NMR (360 MHz),** δ, 7.04 (s, 2H, H-4' or H-6'), 6.98 (s, 2H, H-6'or H-4'), 4.68 (d, J = 5.7 Hz, 4H, C$\underline{H}_2$OH), 2.81 (s, 4H, H-1/2), 2.30 (s, 6H, C$\underline{H}_3$), 2.27 (s, 6H, C$\underline{H}_3$), 1.48 (t, J = 5.8 Hz, 1H, -O$\underline{H}$); **IR (disc), cm^{-1},** 674 (br, m), 748 (m), 860 (s), 1005 (v br, s), 1124 (w), 1345 (w), 1475 (br, s), 1612 (w), 2876 (w), 2920 (w), 2996 (w), 3330 (v br, s); **MS (EI), *m/e* (%),** 283 (9), 282 (M+1-OH, 100), 280 (19), 150 (17), 134 (11), 130 (11), 112 (32), 100 (23), 98 (16), 92 (14), 88 (15), 86 (29).

Anal.	Calcd. for $C_{20}H_{26}O_2$:	C 80.50,	H 8.78
	found:	C 79.86,	H 8.24

41. 1,2-Bis(3'-bromomethyl-2',5'-dimethylphenyl)ethane 71b

A mixture of the diol **89** in benzene (200 mL) and HBr

(120 mL, 48%) was refluxed for 36 h. When the mixture was cooled, some of the product was crystallized out. The first batch of the product was collected by filtration, washed thoroughly and dried. The organic layer of the filtrate was separated, washed, dried and evaporated. The solid residue was preabsorbed and filtered through a short column of silica gel using petroleum ether/dichloromethane (2:1) to give second batch of the dibromide **71b** as a white solid, 25.7 g (total, 95%). A portion was recrystallized twice from acetone to give white crystals, **mp:** 178~179°C; **^{1}H NMR (360 MHz), δ**, 7.03 (s, 2H, H-4′ or H-6′), 6.96 (s, 2H, H-6′ or H-4′), 4.51 (s, 4H, C$\underline{H}_2$Br), 2.81 (s, 4H, H-1/2), 2.28 (s, 6H, C$\underline{H}_3$); **^{13}C NMR (90.6 MHz), δ**, 141.0, 135.9, 135.5, 132.1 (C-1′, 2′, 3′, 5′), 130.9, 128.9 (C-4′, 6′), 34.9, 33.6 ($\underline{C}H_2$Br, C-1/2), 20.8, 13.9 ($\underline{C}H_3$); **IR (disc), cm^{-1}**, 596 (s), 644 (m), 737 (s), 864 (s), 908 (m), 1220 (s), 1295 (w), 1375 (m), 1450 (br, m), 1464 (m), 1608 (w), 2880 (w), 2920 (w), 2942 (w); **MS (CI), *m/e* (%)**, 346 (14), 345 (M-Br, 80), 344 (18), 343 (M-Br, 100), 227 (56), 225 (66), 147 (22), 133 (12), 132 (51), 131 (9), 119 (9), 117 (19).

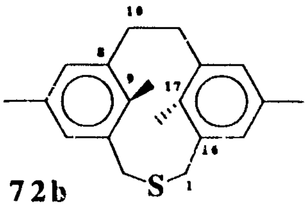


71b

Anal.					
	Calcd. for $C_{20}H_{24}Br_2$:	C	56.63,	H	5.70
	Found:	C	56.64,	H	5.57

42. *anti*-6,9,14,17-Tetramethyl-2-thia[3,2](1,3)cyclophane

72b



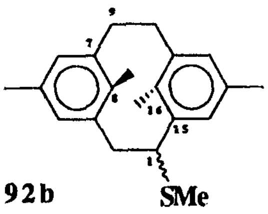
72b

A solution of sodium sulfide (2.64 g, 11 mmol) in nitrogen purged water (60 mL) and 95 % ethanol (250 mL) and benzene (50 mL) was added dropwise over 20 h to a well stirred suspension of the dibromide **71b** (4.24 g, 10 mmol) and Cs_2CO_3 (0.65 g) in nitrogen purged benzene (150 mL) and 95% ethanol (800 mL) and water (140 mL) under nitrogen. After the addition, the mixture was further stirred for 2 h. The solvent was removed and the wet solid residue was dissolved in dichloromethane (500 mL) and the mixture was filtered to remove sulphur. The organic layer was separated, washed, dried and evaporated. The residue was preabsorbed and chromatographed through a column (40 x 4 cm) of silica gel using petroleum ether/dichloromethane (4:1) to give **72b** as a white solid, 2,46 g (83%). A portion was recrystallized from hexanes to give white crystals, **mp:** 175~176°C; **^{1}H NMR (360 MHz),** δ, 6.92 (s, 2H, H-5/15), 6.91 (s, 2H, H-7/13), 3.80 (d, J_{gem} = 13.9 Hz, 2H, H-1/3 (eq.)), 3.70 (d, J_{gem} = 13.8 Hz, 2H, H-1/3(ax.)), 2.85 (m, AA′ of AA′XX′, $J_{AA'}$ = 2.7 Hz, J_{AX} = $J_{A'X'}$ = -12.5 Hz, $J_{AX'}$ = $J_{A'X}$ = 4.4 Hz, 2H, H-10(eq., A), H-11(eq., A′)), 2.60 (m, XX′ of AA′XX′, $J_{XX'}$ = 12.5 Hz, J_{XA} = $J_{X'A'}$ = -12.5 Hz, $J_{XA'}$ = $J_{X'A}$ = 4.4 Hz, 2H, H-10(ax. X), H-11(ax., X′)), 2.24 (s, 6H, ext. C<u>H</u>$_3$), 0.84 (s, 6H, int.

C$\underline{H}_3$); **^{13}C NMR (90.6 MHz)**, δ, 137.6, 136.7, 134.9, 134.5 (C-4/12, 6/14, 8/12, 9/17), 129.8, 129.3 (C-5/15, 7/13), 35.5 (C-1/2), 34.2 (C-10/11), 20.6 (ext. $\underline{C}H_3$), 13.9 (int. $\underline{C}H_3$); **IR (disc), cm^{-1}**, 746 (m), 848 (m), 846 (s), 1030 (m), 1063 (w), 1180 (m), 1260 (w), 1372 (m), 1410 (w), 1460 (s, br), 1606 (m), 2860 (w), 2920 (m), 2960 (w); **MS (CI), *m/e* (%)**, 337 (M+41, 1), 325 (M+29, 7), 299 (6), 298 (23), 297 (M+1, 100), 296 (25), 295 (17), 265 (11), 251 (30), 194 (11), 193 (21), 133 (7), 85 (16).

Anal.	Calcd. for $C_{20}H_{24}S$:	C	81.03,	H	8.16
	Found:	C	81.13,	H	8.02

43. *anti*-1-Methylthio-5,8,13,16-tetramethyl [2$_2$] (1,3) cyclophane 92b



92b

A solution of LDA freshly prepared from n-butyllithium (6 mmol in hexane 4.0 mL) and di-*i*-propylamine (0.85 mL, 6 mmol) in dry THF (10 mL) was added using a syringe to a solution of the thiacyclophane **72b** (1.19 g, 4 mmol) in dry THF (120 mL) under nitrogen at room temperature. After 30 min, iodomethane (0.4 mL, 6.5 mmol) was added to the resultant yellow mixture, followed by additions of dilute HCl solution and diethyl ether. The organic layer was separated, washed, dried and evaporated. The residue was preabsorbed and filtered through a column of silica gel using petroleum ether and dichloromethane (4:1) as eluent to give a mixture of two isomers of the sulfide **92b** as a semi-solid (solidified on standing), 1.24 g (100%) (^{1}H NMR spectrum shows the ratio of two isomers is 91:9). **^{1}H NMR (360 MHz), δ**, 7.47 (s, Ar-$\underline{H}$), $\underline{7.15}$,[a] $\underline{7.86}$ (s, Ar-$\underline{H}$), 6.96, 6.93, 6.90 (s, Ar-$\underline{H}$), $\underline{4.34}$ (d, H-1), 3.99 (dd, J = 11.3 Hz, J = 4.1 Hz, H-1), 3.11 (dd, J = 12.4 Hz, J = 4.2 Hz, H-2), 2.90 ~ 2.67 (m, H-9/10), 2.61 (t, J = 11.8 Hz, H-2), 2.26, 2.24, 2.20, 2.16, 2.12, (s, ext. C$\underline{H}_3$, and SC$\underline{H}_3$), $\underline{0.89}$, $\underline{0.54}$ (s, int. C$\underline{H}_3$), 0.61, 0.59 (s, int. C$\underline{H}_3$); **MS (CI), *m/e* (%)**, 312 (26), 311 (M+1, 98), 310 (35), 309 (12), 264 (23), 263 (M-SMe, 100), 138 (8), 71 (12).

A portion (100 mg) was chromatographed through a long column (2 x 65 cm) of silica gel using petroleum ether and dichloromethane (10:1) as eluent. Eluted first was the pseudo-equitorial isomer **eq-92b** as a white solid, 90 mg (91%). Recrystallization from diether ether gave white crystals, **mp:** 114~115°C; **^{1}H NMR (360 MHz), δ**, 7.47 (s, 1H, H-14), 6.96, 6.93, 6.90 (s, 3H, H-4, 6, 12), 3.99 (dd, $J_{1,2(ax.)}$ = 11.3 Hz, $J_{1,2(eq.)}$ = 4.3 Hz, 1H, H-1), 3.11 (dd, $J_{2(eq.),1}$ = 4.2 Hz, $J_{2(eq.),2(ax.)}$ = 12.4 Hz, 1H, H-2(eq.)), 2.90 ~ 2.85 (m, 2H, H-9/10(eq.)), 2.64 ~ 2.58 (m, 2H, H-9/10(ax.)), 2.61 (t(dd), J = 11.9 Hz, 1H, H-2(ax.)), 2.26 (s, 3H, ext. -

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[a] Assignments for each isomer are made whenever possible and the underlined numbers are peaks of the pseudo-axial isomer.

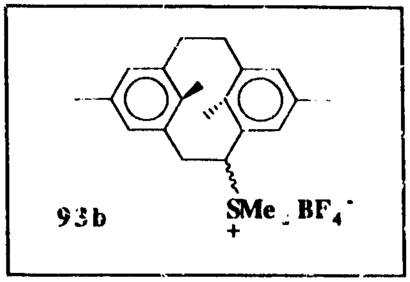
$C\underline{H}_3$), 2.20 (s, 3H, ext. -$C\underline{H}_3$), 2.13 (s, 3H, $SC\underline{H}_3$), 0.60 (s, 3H, int. -$C\underline{H}_3$), 0.58 (s, 3H, int. -$C\underline{H}_3$); **^{13}C NMR (90.6 MHz), δ**, 140.4, 139.9, 137.3, 137.0, 135.6, 135.1, 133.6, 133.2 (C-3, 5, 7, 8, 11, 13, 15, 16), 128.9, 128.3, 120.1, 124.8 (C-4, 6, 12, 14), 52.3 (C-1), 43.2 (C-2), 36.2, 36.0 (C-9, C-10), 20.9, 20.6 (ext. $\underline{C}H_3$), 14.[illegible], 14.5 (int. $\underline{C}H_3$); **IR (disc), cm^{-1}**, 720 (s), 800 (m), 840 (s), 863 (m), 882 (w), 988 (w), 1040 (m), 1180 (s), 1358 (w), 1440 (br, s), 1594 (m), 2860 (m), 2920 (s), 2960 (m).

Anal. Calcd. for $C_{21}H_{26}S$: C 81.23, H 8.44

Found: C 81.32, H 8.38

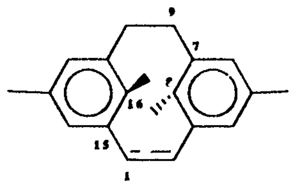
Eluted next was the pseudo-axial isomer **ax-92b** as a white solid, 9.0 mg (9%), **mp:** 176~177°C; **^{1}H NMR (360 MHz), δ**, 7.05 (s, 1H, H-14), 6.94 (s, 2H, H-4, 6), 6.86 (s, 1H, H-12), 4.34 (dd, $J_{1,\,2(eq.)}$ = 7.0 Hz, $J_{1,\,2(ax.)}$ = 0.8 Hz, 1H, H-1), 3.26 (dd, $J_{2(eq.),\,2(ax.)}$ = 14.0 Hz, $J_{2(eq.),\,1}$ = 7.1 Hz, 1H, H-2(eq.)), 2.97 (dd, $J_{2(ax.),\,2\,(eq.)}$ = 13.9 Hz, $J_{2(ax.),\,1}$ = 0.8 Hz, 1H, H-2(ax.)), 2.88 ~ 2.69 (m, 4H, H-9/10), 2.23 (s, 3H, ext. $C\underline{H}_3$), 2.20 (s, 3H, ext. $C\underline{H}_3$), 2.16 (s, 3H, $SC\underline{H}_3$), 0.89 (s, 3H, C_{16}-$C\underline{H}_3$), 0.54 (s, 3H, int. C_8-$C\underline{H}_3$); **^{13}C NMR (90.6 MHz), δ**, 141.7, 139.7, 137.0, 136.9, 134.6, 133.79, 132.77 (C-3, 5, 7, 8, 11, 13, 15, 16), 129.5, 129.3, 129.2, 128.7 (C-4, 6, 12, 14), 57.5 (C-1), 41.0 (C-2), 36.2, 35.9 (C-9, 10), 20.7, 20.5 (ext. $C\underline{H}_3$), 17.1 ($SC\underline{H}_3$), 14.4, 14.1 (int. $C\underline{H}_3$).

44. *anti*-1-Methylthio-5,8,13,16-tetramethyl[2_2](1,3)cyclophane-sulfonium fluoroborate 93b


93b

Borch reagent (2.0 g, ~80% as oil, 10 mmol) was added to a stirred solution of isomers of **92b** (2.48 g, 8 mmol) in dichloromethane (25 mL) at -30°C. After stirring for 4 h, ethyl acetate (40 mL) was added and the mixture was further stirred overnight. The bulk of solvent was removed and petroleum ether was added. The solid was collected by filtration to give the sulfonium salts **93b** as dark grey powder, 3.28 g (99%).

45. *anti*-5,8,13,16-Tetramethyl [2_2](1,3)cyclophan-1-ene 56b

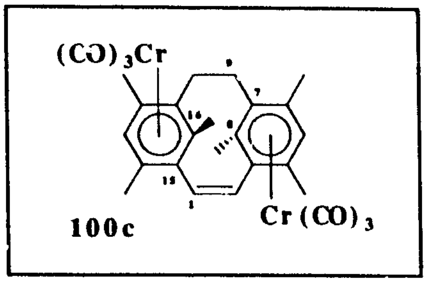

56b

Potassium t-butoxide (1.6 g, 14.3 mmol) was added to a solution of the sulfonium salts **93b** (2.35 g, 5.7 mmol) in dimethylformamide and t-butanol (50 mL, 1:1) at room temperature. After stirring for 40 min, cold water was added, followed by additions of diethyl ether and petroleum ether (300 mL, 1:1). The organic layer was separated, washed thoroughly, dried and evaporated. The residue was preabsorbed and chromatographed on silica gel using petroleum ether as eluent to give the monoene **56b** as yellowish solid, 1.08 g (72%). A portion was recrystallized from methanol to give nearly white crystals, **mp:** 151~152°C; **^{1}H NMR (360 MHz),** δ, 6.77 (s, 2H, H-4/14), 6.66 (s, 2H, H-6/12), 6.54 (s, 2H, H-1/2), 2.81 (m, AA′ of AA′XX′, $J_{AA'}$ = 2.8 Hz, J_{AX} = $J_{A'X'}$ = -12.1 Hz, $J_{AX'}$ = $J_{A'X}$ = 3.9 Hz, 2H, H-9(eq., A), H-10(eq., A′)), 2.48 (m, XX′ of AA′XX′, $J_{XX'}$ = 12.2 Hz, 2H, H-9(ax., X), H-10(ax., X′)), 2.22 (s, 6H, ext. $C\underline{H}_3$), 0.73 (s, 6H, int. $C\underline{H}_3$); **^{13}C NMR (90.6 MHz),** δ, 138.4, 138.0, 135.9, 134.8 (C-3/15, 5/13, 7/11, 8/16), 132.1 (C-1/2), 128.8, 124.2 (C-4/14, 6/12); **IR (disc), cm^{-1},** 625 (s), 696 (m), 715 (m), 784 (m), 846 (s), 874 (s), 1373 (m), 1435 (m), 1441 (m), 1461 (s), 2853 (m), 2912 (m), 2924 (m), 2948 (m), 2958 (w), 3000 (w); **MS (CI), *m/e* (%),** 264 (20), 263 (M+1, 100), 262 (49), 261 (17), 247 (16), 107 (2); **UV, λ_{max}(CH_3CN)(ε),** 203 (42,000), 214 (37,000), 260 (28,000), 301 (1900).

46. Preparations of the tricarbonylchromium(0) complexes of the cyclophanenes

A) Tricarbonylchromium(0) complexes of *anti*-4,6,8,12,14,16-Hexamethyl[2$_2$](1,3)cyclophan-1-ene

A stirred solution of the monoene **56c** (87 mg, 0.3 mmol) and tricarbonylchromium naphthalene complex (164 mg, 1 mmol)



100c

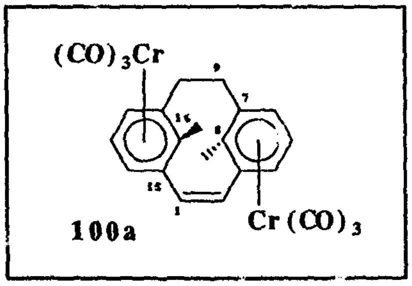
in nitrogen purged diether ether (1 mL) and THF (0.2 mL) in a small heavy-wall vial with a screw cap was heated with an oil bath to 60°C for 20 h. The insoluble bis-chromium complex was collected by filtration, and recrystallization from hexane and dichloromethane gave **100c** as an orange-red solid, 110.6 mg (66%), **mp:** 267-268 (sealed tube, decomp.); **^{1}H NMR (360 MHz), δ,** 6.69 (s, 2H, H-1/2), 5.06 (s, 2H, H-5/13), 3.12 (m, 2H, H-9/10(eq.)), 2.23 (s, 6H, ext. C$\underline{H}_3$), 2.17 (m, 2H, H-9/10(ax.)), 2.13 (s, 6H, ext. C$\underline{H}_3$), 1.11 (s, 6H, int. C$\underline{H}_3$); **^{13}C NMR (90.6 MHz), δ,** 233.8 ($\underline{C}$O), 130.5 (C-1/2), 115.7, 113.2, 108.5, 107.2, 98.0 (C-3/15, 4/14, 6/12, 7/11, 6/16), 90.8 (C-5/13), 32.5 (C-9/10), 24.4, 19.0 (ext. & interanl $\underline{C}H_3$); **IR (disc), cm^{-1},** 616 (m), 622 (s), 670 (s), 755 (w), 1380 (m), 1388 (m), 1433 (w), 1445 (w), 1457 (w), 1873 (br, v s), 1950 (br, v s), 2956 (w), 2976 (w), 2983 (w); **MS (CI), m/e (%),** 563 (M+1, w).

Anal.	Calcd. for $C_{28}H_{26}O_6Cr_2$:	C	59.79,	H	4.66
	Found:	C	59.57,	H	4.71

The mother liquor was evaporated and the residue was preabsorbed and chromatographed on silica gel under nitrogen using petroleum ether and dichloromethane as eluent to give the mono-chromium complex **99c** as a red solid, 20 mg (16%). **^{1}H NMR (360 MHz), δ,** 6.95 (d, J = 11.4 Hz, 1H, H-1), 6.72 (s, 1H, H-13), 6.36 (d, J = 11.2 Hz, 1H, H-2), 5.10 (s, 1H, H-5), 3.24~ 3.19 (m, 1H, H-10(eq.)), 2.97~2.90 (m, 1H, H-9(eq.), 2.48~ 2.38 (m, 1H, H-10(ax.)), 2.26, 2.24, 2.22, 2.10 (s, 12H, ext. C$\underline{H}_3$), 1.97~1.86 (m, 1H, H-9(ax.)), 1.11 (s, 3H, int. C$\underline{H}_3$-C_{16}), 0.49 (s, 3H, int. C$\underline{H}_3$-C_8); **^{13}C NMR (90.6 MHz), δ**, 235.0 ($\underline{C}$O), 138.9, 135.3, 134.2, 133.2, 131.5 (C-3, 4, 6, 7, 8), 134.3 (C-2), 130.4 (C-1), 125.2 (C-5), 116.8, 114.6, 107.3, 105.9, 100.5 (C-11, 12, 14, 15, 16), 91.2 (C-13), 33.2, 32.1 (C-9, 10), 21.1, 21.0, 19.1, 18.9 (ext. & int. $\underline{C}H_3$) ; **IR (disc), cm^{-1}**, 623 (m), 653 (w), 672 (m), 741 (w), 763 (w), 820 (w), 1378 (w), 1435 (w), 1450 (w), 1860 (br, s), 1960 (br, s), 2960 (w); **MS (CI), *m/e* (%)**, 428 (37), 427 (M+1, 100), 426 (75), 265 (57), 264 (36), 230 (59), 229 (34), 216 (50), 130 (80).

B) Tricarbonylchromium(0) complexes of *anti*-8,16-Dimethyl [2$_2$](1,3)cyclophan-1-ene

The method used for the preparation of these complexes was the same as A). The reaction of the cyclophanene **56a** (70 mg, 0.3 mmol) and tricarbonylchromium(0) naphthalene complex (130 mg, 0.79 mmol) afforded the orange red bis-chromium complex **100a**, 87 mg (57%) and the red mono-chromium complex **99a**, 42 mg (38%).



100a

Bis(tricarbonylchromium(0)) complex 100a, mp: >245°C (decomp.); **^{1}H NMR (250 MHz), δ**, 6.65 (s, 2H, H-1/2), 5.45 ~ 5.28 (m, 6H, H-4/14, 5/13, 6/12), 2.03 ~ 2.92 (m, 2H, H-9/10(eq.)), 2.57 ~ 2.47 (m, 2H, H-9/10(ax)), 1.20 (s, 6H, int. $C\underline{H}_3$); **^{13}C NMR (90.6 MHz), δ**, 233.2 ($\underline{C}$O), 131.8 (C-1/2), 118.3, 97.2 (quartary $\underline{C}$), 95.9, 93.0, 85.5 (C-4/14, 5/13, 6/12), 37.7 (C-9/10), 24.2 (int. $\underline{C}$); **IR (disc), cm^{-1}**, 622 (w), 668 (m), 1381 (w), 1386 (w), 1435 (w), 1455 (w), 1855 (v s), 1942 (v s), 1955 (v s); **MS (CI), *m/e* (%)**, 507 (M+1, 6), 373 (7), 372 (29), 371 (89), 370 (40), 263 (6), 236 (18), 235 (100), 234 (31), 219 (20), 207 (11), 179 (10).

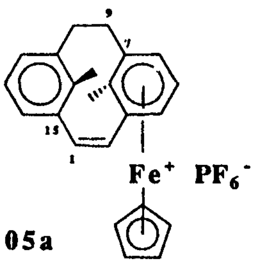
Tricarbonyl-chromium(0) complex 99a, **mp.** 178~179°C; **^{1}H NMR (360 MHz), δ**, 7.03~6.96 (m, 3H, H-12, 13, 14), 6.88 (d, J = 11.1 Hz, 1H, H-1), 6.35 (d, J = 11.1 Hz, 1H, H-2), 5.44 ~5.22(m, 3H, H-4, 5, 6), 3.15~3.05 (m, 1H, H-10(eq.)), 2.85~2.74 (m, 2H, H-10(ax), H-9(eq)), 2.25~2.15 (m, 1H, H-9(ax)), 1.31 (s, 3H, C_{16}-$C\underline{H}_3$), 0.51 (s, 3H, C_8-$C\underline{H}_3$); **^{13}C NMR (90.6 MHz), δ**, 234.4 ($\underline{C}$O), 136.5 (C-2), 139.7, 137.3, 134.6 (C-3, 7, 8), 129.2, 126.6, 125.0 (C-5,6,4,1), 119.6, 118.0, 99.6 (C-11, 15, 16), 94.9, 91.9, 86.5 (C-12, 13, 14), 39.4, 37.1 (C-9, 10), 20.9, 20.5 (int. $\underline{C}H_3$); **IR (disc), cm^{-1}**, 627 (s), 660 (s), 670 (m), 718 (m), 740 (m), 752 (m), 807 (s), 878 (m), 1045 (w), 1140 (w), 1183 (w), 1372 (w), 1383 (m), 1410 (m), 1440 (m), 1855 (v br, s), 1936 (vs), 1953 (vs), 2940 (w); **MS (CI), *m/e* (%)**, 372 (33), 371 (M+1, 100), 370 (34), 369 (5), 368 (2), 315 (2), 314 (2), 235 (4), 149 (2).

47. Preparations of (η^5-cyclopentadienyl)iron(I) complexes of the cyclophanenes

General Procedure:

The solution of the *p*-chlorotoluene-iron complex **104** (1 eq.) and the cyclophanene (1 eq.) in nitrogen purged dichloromethane (35 mL) was irradiated using a floor lamp (150 W) for 1.5 h. Another equivalent of **104** was added and the mixture was further irradiated for 2 h. The solvent was removed, and the residue was preabsorbed and then chromatographed on aluminia oxide using dichloromethane and petroleum ether and methanol (5.5:4:0.5) as eluent to give the corresponding product.

A). The CpFe(I) complex of the cyclophanene 105a



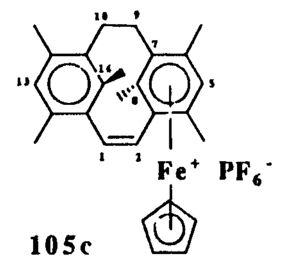
105a

The reaction of the cyclophanene **56a** (106 mg, 0.45 mmol) and *p*-chlorotoluene iron(I) complex **104** (176 x 2 mg, 0.9 mmol) yielded after column chromatography the brown complex **105a**, 176 mg (78%). **mp:** >265°C (decomp.); **^{1}H NMR (360 MHz, in CD_2Cl_2)**; δ, 7.15 (m, 3H, H-12, 14), 7.13 (d, J = 10.9 Hz, 1H, H1), 7.04 (t, J = 4.8 Hz, 1H, H-13), 6.66 (t, J = 6.2 Hz, 1H, H-5), 6.53 (d, J = 11.1 Hz, 1H, H-2), 5.96(d, J = 6.0 Hz, 1H, H-4), 5.69 (d.

J = 6.2 Hz, 1H, H-6), 4.77 (s, 5H, Cp-H), 3.11 (dt, J = 13.1 Hz, J = 3.5 Hz, 1H, H-10(eq.)), 3.00 (dt, J = 12.4 Hz, J = 3.4 Hz, 1H, H-9(eq)), 2.58 (td, J = 12.9 Hz, J = 3.5 Hz, 1H, H-10(ax)), 2.42 (td, J = 12.2 Hz, J = 3.9 Hz, 1H, H-9(ax.)), 0.92 (s, 3H, C_{16}-$C\underline{H}_3$), 0.67 (s, 3H, C_8-$C\underline{H}_3$); **^{13}C NMR (62.9 MHz, in CD_2Cl_2)**, δ, 139.7, 137.6, 134.7, 130.2, 128.1, 125.4 (C-1, 2, 11, 12, 13, 14, 15, 16), 117.7, 115.2, 89.3, 85.8, 81.6 (C-3, 4, 5, 6, 7, 8), 76.7 (Cp), 38.4, 37.4 (C-9, 10), 22.3, 20.9 (int. $\underline{C}H_3$); **IR (disc), cm^{-1}**, 560 (s), 716 (w), 748 (m), 805 (w), 840 (br, vs), 860 (s), 874 (s), 1040 (w), 1140 (w), 1184 (w), 1380 (w), 1405 (m), 1415 (m), 1440 (m), 2840 (w), 2860 (w), 3120 (m).

Anal.	Calcd. for $C_{23}H_{23}PF_6Fe$:	C	55.22,	H	4.63
	Found:	C	55.03,	H	4.64

B). The CpFe(I) complex of the cyclophanene 105c

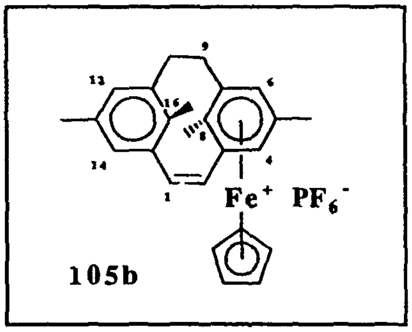


105c

The reaction of the cyclophanene **56c** (130 mg, 0.45 mmol) and *p*-chlorotoluene iron(I) complex **104** (176 x 2 mg, 0.9 mmol) gave after column chromatography the brown-red complex **105c**, 205 mg (82%). **mp:** >250°C (decomp.); **^{1}H NMR (360 MHz)**, δ, 7.24 (d, J = 11.3 Hz, 1H, H-1), 6.83 (s, 1H, H-13), 6.58 (d, J = 11.3 Hz, 1H, H-2), 6.47 (s, 1H, H-5), 4.62 (s, 5H, Cp), 3.25~3.21 (m, 1H, H-10(eq)), 3.16-3.12 (m, 1H, H-9(eq.)), 2.38, 2.29, 2.26, 2.25 (s, 12H, ext. $C\underline{H}_3$), 2.20 ~ 2.16 (m, 2H, H-9, 10(ax.)), 0.83 (s, 3H, C_{16}-$C\underline{H}_3$), 0.48 (s, 3H, C_8-$C\underline{H}_3$); **^{13}C NMR (62.9 MHz, in CD_2Cl_2), δ**, 138.2 (C-1), 131.8 (C-2), 139.0, 136.9, 134.3, 133.9, 131.5, (C-11, 12, 14, 15, 16), 123.0 (C-13), 115.5, 112.5, 97.2, 94.7, 88.5 (C-3, 4, 6, 7, 8), 85.5 (C-5), 76.8 (Cp), 32.6, 32.4 (C-9, 10), 22.5, 21.1, 19.2, 19.1, 18.9 (ext. & int. $\underline{C}H_3$); **IR (disc), cm^{-1}**, 560 (s), 740 (w), 770 (w), 840 (br, vs), 1378 (m), 1414 (w), 1445 (m), 2920 (w), 2960 (w), 3100 (w).

Anal. Calcd. for $C_{27}H_{31}PF_6Fe$: C 58.29, H 5.61
Found: C 58.18, H 5.69

C) The CpFe(I) complex of the cyclophanene 105b



105b

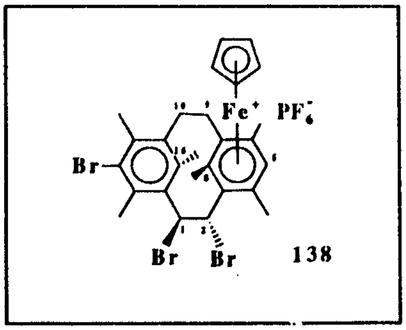
The reaction of the cyclophanene **56b** (105 mg, 0.4 mmol) and the iron complex **104** (79 x 2 mg, 0.8 mmol) gave the complex **105b** as a brown solid, 99.2 mg (47%). **mp:** >220°C (decomp.); **^{1}H NMR (360 MHz, in CD_2Cl_2), δ**, 7.08 (d, J = 11.1 Hz, 1H, H-1), 6.95 (s, 1H, H-14), 6.84 (s, 1H, H-12), 6.49 (d, J = 11.1 Hz, 1H, H-2), 5.89 (s, 1H, H-4), 5.61 (s, 1H, H-6), 4.66 (Cp), 3.05 (dt, J = 12.9 Hz, J = 3.4 Hz, 1H, H-10(eq)), 2.95 (dt, J = 12.0 Hz, J = 3.2 Hz, 1H, H-9(eq.)), 2.64 (s, 3H, C_{13}-$C\underline{H}_3$), 2.54 (td, J

= 12.4 Hz, J = 3.4 Hz, 1H, H-10(ax)), 2.42 (td, J = 11.9 Hz, J = 3.8 Hz, 1H, H-9(ax)), 2.27 (s, 3H, C_5-C$\underline{H}_3$), 0.90 (s, 3H, C_{16}-C$\underline{H}_3$), 0.62 (s, 3H, C_8-C$\underline{H}_3$); **^{13}C NMR (90.6 MHz), δ,** 139.8 (C-1), 138.0, 137.4, 137.0, 134.5 (C-11, 13, 15, 16), 125.8, 124.5 (C-12, 14), 116.5, 114.1, 96.8, 87.5 (C-3, 5, 7, 8), 86.5, 82.2 (C-4, 6), 77.0 (Cp), 38.2, 37.0 (C-9, 10), 22.1, 20.7, 20.4, 20.2 (ext. & int. $\underline{C}H_3$); **IR (disc), cm^{-1},** 558 (s), 623 (w), 668 (w), 712 (w), 763 (w), 785 (w), 827 (vs), 842 (vs), 870 (m), 879 (m), 1383 (w), 1419 (w), 1436 (w), 1456 (w), 2920 (w).

Anal.	Calcd. for $C_{25}H_{27}PF_6Fe$:	C	56.84,	H	5.15
	Found:	C	56.52,	H	5.36

48. Electrophilic addition to the double bond of the cyclophanene-iron complexes

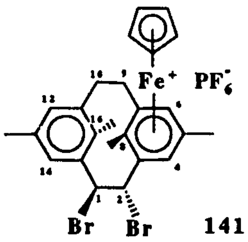
A) The reaction of Br_2 with the cyclophanene-iron complex 105c



138

Bromine (~10 equivalent) was added to the solution of the cyclophanene-iron complex **105c** (167 mg, 0.3 mmol) in dry dichloromethane (~2 mL). The mixture was kept under dark for two days. The adduct was collected by simply decaning the solvent and washed with small amount of dichloromethane. The solid was dried under vacumn to give the bromine adduct **138** as a red solid, 201 mg (94%). **^{1}H NMR (360 MHz, in CD_3CN),** δ, 6.45 (br s, 1H, H-1), 6.39 (s, 1H, H-5), 6.24 (br s, 1H, H-2), 4.75 (s, 5H, Cp), 3.50 ~ 3.40 (m, 1H, H-10(eq.)), 3.31 ~ 3.22 (m, 1H, H-9(eq.)), 2.65 ~ 2.54 (m, 2H, H-9, 10(ax.)), 2.66 (s, 3H, ex. $C\underline{H}_3$), 2.64 (s, 3H, ex. $C\underline{H}_3$), 2.60 (s, 3H, ex. $C\underline{H}_3$), 2.43 (s, 3H, ex. $C\underline{H}_3$), 1.28 (s, 3H, C_{16}-$C\underline{H}_3$), 0.74 (s, 3H, C_8-$C\underline{H}_3$); **^{13}C NMR (90.6 MHz, in CD_3NO_2),** δ, 143.3, 140.2, 137.2, 136.9, 130.4, 127.9 (C-11, 12, 13, 14, 15, 16), 115.1, 110.2, 101.8, 100.9, 95.1 (C-3, 4, 6, 7, 8), 86.0 (C-5), 79.4 (Cp), 54.2, 51.1 (C-1, C-2), 32.3, 30.3 (c-9, 10), 22.1, 21.9, 21.4, 21.3, 21.2, 19.8 (ext. & int. $\underline{C}H_3$).

B). The reaction of Br_2 with the cyclophanene-iron complex 105b



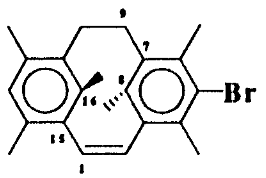
141

One drop of bromine was added to the solution of the iron complex **105b** in CD_2Cl_2 in 5 mm NMR tube under dark. After 10 min, the spectrum was recorded and showed that the bromine adduct **141** was formed as a single product. **^{1}H NMR (360 MHz),** δ, 7.15 (s, 1H, H-14), 7.04 (s, 1H, H-12), 6.41 (s, 1H, H-4), 6.10 (s, 1H, H-6), 5.57 (d, J = 4.9 Hz, 1H, H-1), 5.23 (d, J = 5.0 Hz, 1H, H-2), 4.76

(Cp), 3.14 ~ 2.64 (m, 4H, H-9, 10), 2.68 (s, 3H, C_{13}-C$\underline{H}_3$), 2.26 (s, 3H, C_5-C$\underline{H}_3$), 1.01 (s, 3H, C_{16}-C$\underline{H}_3$), 0.92 (s, 3H, C_8-C$\underline{H}_3$).

49. Attempted dehydrobromination of the bromine adduct 138

Sodium amide (100 mg, 2.6 mmol) was added to the suspension of the bromine adduct **138** (215 mg, 0.3 mmol) in dry THF (50 mL) and the mixture was refluxed for 30 min. After the mixture was cooled, dichloromethane (100 mL) was added. The organic layer was washed thoroughly with water, dried and evaporated. The residue was preabsorbed and filtered through a column of silica gel using petroleum ether and dichloromethane (4:1) to give the bromocyclophanene **139** as white solid. **^{1}H NMR (360 MHz), δ,** 6.69 (s, 1H, H-13), 6.68 (AB, J = 11.4 Hz, 2H, H-1, H-2), 3.19 ~ 3.05 (m, 2H, H-9, 10(eq)), 2.48, 2.40, 2.27, 2.21 (s, 12H, ext. C$\underline{H}_3$), 2.31 ~ 2.12 (m, 2H, H-9, 10(ax)), 0.83, 0.67 (s, 6H, int. C$\underline{H}_3$); **MS, (EI), *m/e* (%),** 368 (M^+, 14), 353 (12), 338 (17), 275 (17), 274 (100), 273 (39), 272 (64), 258 (62).

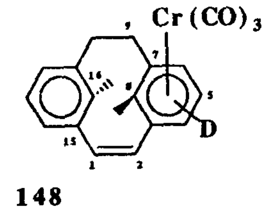


139

The dehydrobromination reactions were also tried under the following conditions: (1) using $NaOCH_3$ as a base in refluxing methanol; (2) using t-BuOK in t-BuOH and dioxane; (3) using DBU as the base and solvent; (4)

irradiation with UV light in acetonitrile. Under all these conditions, the products obtained were characterized as the same compound as above.

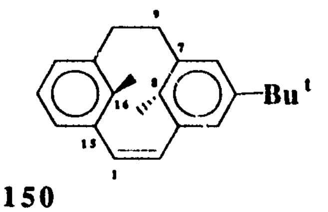
50. Deprotonation of the cyclophanene-chromium (0) complex 99a



148

n-Butyllithium (0.30 mmol in hexane 0.2 mL) was added to the solution of the complex **99a** (78 mg, 0.21 mmol) in dry THF (10 mL) at - 78°C and the resultant mixture was stirred at that temperature for 1 h. D_2O (~1 mL) was then added slowly to decompose the mixture at -78°C. The mixture was warmed up gradually to room temperature. The solvent was removed and the residue was preabsorbed on neutral Al_2O_3 and chromatographed under nitrogen using petroleum ether and dichloromethane (3:1) to yield the deuterated complex **148** as red solid, 68 mg (87%). **^{1}H NMR (360 MHz),** δ, 7.05 ~ 6.93 (m, 3H, H-13, 14, 15), 6.87 (d, J = 11.1 Hz, 1H, H-1), 6.35 (d, J = 11.0 Hz, 1H, H-2), 5.44 ~ 5.38 (m, 1.5H, H-4, 6), 5.22 ~ 5.20 (m, 0.6H, H-5), 3.10 ~ 3.04 (m, 1H, H-10 (eq.)), 2.84 ~ 2.74 (m, 2H, H-10(ax.), H-9(eq.)), 2.23 ~ 2.15 (m, 1H. H-9(ax.)), 1.31 (s, 3H, C_{16}-$C\underline{H}_3$), 0.51 (s, 3H, C_8-$C\underline{H}_3$); **^{2}H NMR (??? MHz),** δ, 5.43 (br s, D-4, 6), 5.24 (s, D-5).

51. Nucleophilic substitution of the cyclophanene-chromium complex

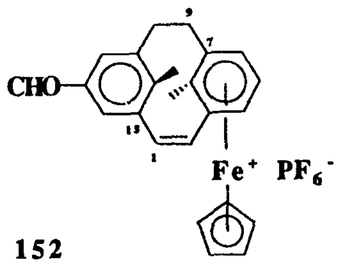


150

t-Butyllithium (0.11 mmol in hexane 0.1 mL) was added to the solution of the cyclophanene-chromium complex **99a** (37 mg, 0.1 mmol) in dry THF (5 mL) at -78°C. After stirring for 1 h, Fe(III)-DMF complex (195 mg) was added to decompose the mixture. The mixture was extracted with diethyl ether (50 mL) and the organic layer was washed, dried and evaporated. The residue was chromatographed on silica gel using petroleum ether as eluent to give the decomplexed substitution product **150** as an oil, 18 mg (62%). **^{1}H NMR (360 MHz)**, δ, 7.17 ~ 6.88 (m, Ar-H), 6.61 (s, H-1, 2), 2.95 ~ 2.87 (m, H-9, 10), 2.53 ~ 2.39 (m, H-9, 10), 1.36 (s, Bu^t), 0.76, 0.61 (s, int. $C\underline{H}_3$).

52. Electrophilic substitution of the cyclophanene-iron complex

$TiCl_4$ (0.05 mL, 0.45 mmol) was added to the solution of the cyclophanene-iron complex **105a** (100 mg, 0.2 mmol) and $ClCH_2OCH_3$ (35 mg, 0.3 mmol) in dry dichloromethane (10 mL) at 0°C. The mixture was stirred at room temperature for 3 h. The mixture was poured into ice-water. The organic layer was



152

separated and the aquous layer was extracted with dichloro-methane until colorless. The organic was dried, evaporated and the residue was chromatographed on silica gel using petroleum ether and dichloromethane and methanol (4:5:1) as eluent. The first fraction was the unreacted starting material, 32 mg. The second fraction gave **152**, 2 mg. **^{1}H NMR (360 MHz, in CD_3CN)**, δ, 9.88 (s, 1H, C<u>H</u>O), 7.69 (s, 1H, H-14), 7.59 (s, 1H, H-12), 7.19 (d, J = 11.0 Hz, 1H, H-1), 6.69 (d, J = 11.1 Hz, 1H, H-2), 6.64 (t, J = 6.1 Hz, 1H, H-5), 6.00 (d, J = 6.1 Hz, 1H, H-4), 5.75 (d, J = 6.3 Hz, 1H, H-6), 3.27 ~ 3.20 (m, 1h, H-10(eq.)), 3.05 ~ 2.98 (m, 1H, H-9(eq.)), 2.68 ~ 2.60 (m, 1H, H-10(ax.)), 2.48 ~ 2.40 (m, 1H, H-9(ax.)), 0.87 (s, 3H, C_{16}-C$\underline{H}_3$), 0.75 (s, 3H, C_8-C$\underline{H}_3$).

53. Attempted Electrophilic addition to the bridge double bonds of the cyclophanenes

A) Bromine or pyridinium hydrobromide perbromide additions

Pyridinium bromide perbromide (32 mg, 0.1 mmol) was added to the solution of the cyclophanene **56c** (29 mg, 0.1 mmol) in dichloromethane (10 mL) at 0°C. The mixture was stirred for 20 min. The resultant green solution was washed thoroughly, dried and evaporated. The residue was chromatographed on silica gel using petroleum ether to give a green fraction which was the hexamethyldihydropyrene **121** mixed with a small amount (<10%) of the bromopyrene **122**, 30 mg.

The bromine addition to the cyclophanene **56c** was tried at -78°C and it also gave the hexamethyldihydropyrene **121** as major product.

B) Phenylselenenyl chloride (PhSeCl) or phenylselenenyl trichloride (PhSeCl$_3$) additions

The cyclophanene **56c** (29 mg, 0.1 mmol) was added to the suspension of the phenylselenenyl trichloride (263 mg, 0.1 mmol) in diethyl ether (2 mL) at 0°C. The mixture was stirred for 15 min, petroleum ether (30 mL) was added. The organic layer was separated, washed, dried and evaporated. The residue was chromatographed on silica gel using petroleum ether as eluent to give the green hexamethyldihydropyrene **121** as the product, 26 mg (90%).

The reaction of the cyclophanene **56c** with the phenylselenenyl chloride in dichloromethane at 0°C after 2.5 h yielded a mixture of the hexamethyldihydropyrene and unreacted cyclophanene.

C) Photoaddition of benzeneselenosulfonate to the cyclophanene

The mixture of the cyclophane **56b** (58 mg, 0.2 mmol) and the benzeneselenosulfonate **131** (63 mg, 0.2 mmol) in tetrachloromethane (~1 mL) was irradiated for 1.5 h. After the irradiation, diethyl ether (30 mL) was added and the organic layer was separated, washed, dried and evaporated. The residue was chromatographed on silica gel using petroleum ether and dichloromethane (1:1) as eluent to give a green fraction which was the hexamethyldihydropyrene and unreacted cyclophanene.

54. Attempted cyclopropanations of the cyclophanenes

A) Simmons-Smith reaction

The suspension of the freshly prepared Zinc-Copper dust[126)] (~350 mg) and the cyclophanene **56a** (94 mg, 0.4 mmol) in diethyl ether (5 mL) was warmed up. Diiodomethane (?? mL, 0.8 mmol) was added slowly and then the mixture was refluxed for 20 h. Diethyl ether (50 mL) was added to the resultant dark brown-purple solution. The organic layer was separated, washed, dried and evaporated. The ^{1}H NMR of the residue was recorded and found that there was no cyclopropanation product except the unreacted cyclophanene.

B) Titanium(IV) chloride catalyzed cyclopropanation

The zinc dust (1.75 g, 26.7 mmol), copper(I) chloride (270 mg, 2.7 mmol), diethyl ether (5 mL), dibromomethane (3.4 g, 20 mmol), and the cyclophanene **56a** (94 mg, 0.4 mmol) were added in this order. With stirring the titanium(IV) chloride (3 drops) was added and the mixture was refluxed for 1.5 h. After the mixture was cooled, the saturated aqueous ammonium chloride (15 mL) was added. The resultant mixture was extracted with diethyl ether. The extract was washed with NaOH solution (10%, 3 x 15 mL) and saturated NaCl solution, dried. The solvent was removed to give a yellow sticky residue. ^{1}H NMR and tlc of the residue indicated that it is the unreacted cyclophanene **56a**.

C) Cyclopropanation of the cyclophanene with dichlorocarbene

The mixture of the cyclophanene **56a** (70 mg, 0.3 mmol), sodium trichloroacetate (1.10 g, 6 mmol), and benzyl triethylammonium chloride (5 mg) in dry chloroform (2 mL) was refluxed for 8 h. Petroleum ether (50 mL) and water were added. The organic layer was separated, washed, dried, and evaporated. ^{1}H NMR and tlc indicated that it is the unreacted cyclophanene and there is no cyclopropanation product.

The reaction of the cyclophanene **56c** with CCl_2 in the same condition yielded a mixture which could not be separated by column chromatography and hence could not be characterized.

55. Photoisomerization of the cyclophanenes

The solution of the cyclophanene (~1.2 x 10^{-4} M) in acetonitrile was placed in a UV cell which has a stopcock. The solution was degassed thoroughly with argon for 15 min, then was sealed by closing the stopcock. The cell was first placed in the thermostated cell holder of the UV spectrometer. After the equilibrium was reached, the sample was irradiated using an ultraviolet lamp (~254 nm) for 1-2 min. Then the rate of the disapperance of the tetrahydropyrene was measured by continuously monitoring the absorption at its long wavelength band (~328 nm). In each case, the rates were measured at four or five different temperatures.

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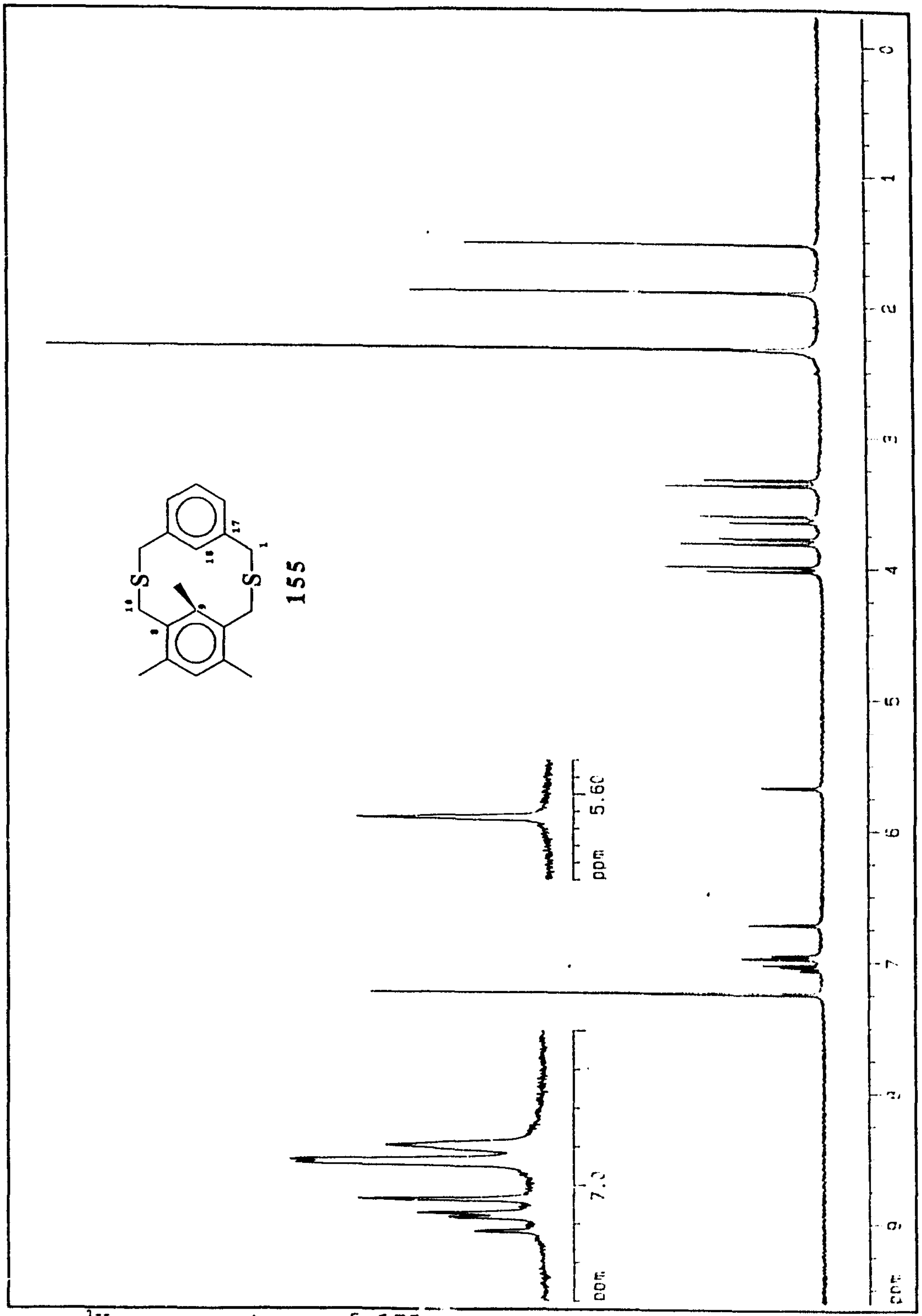
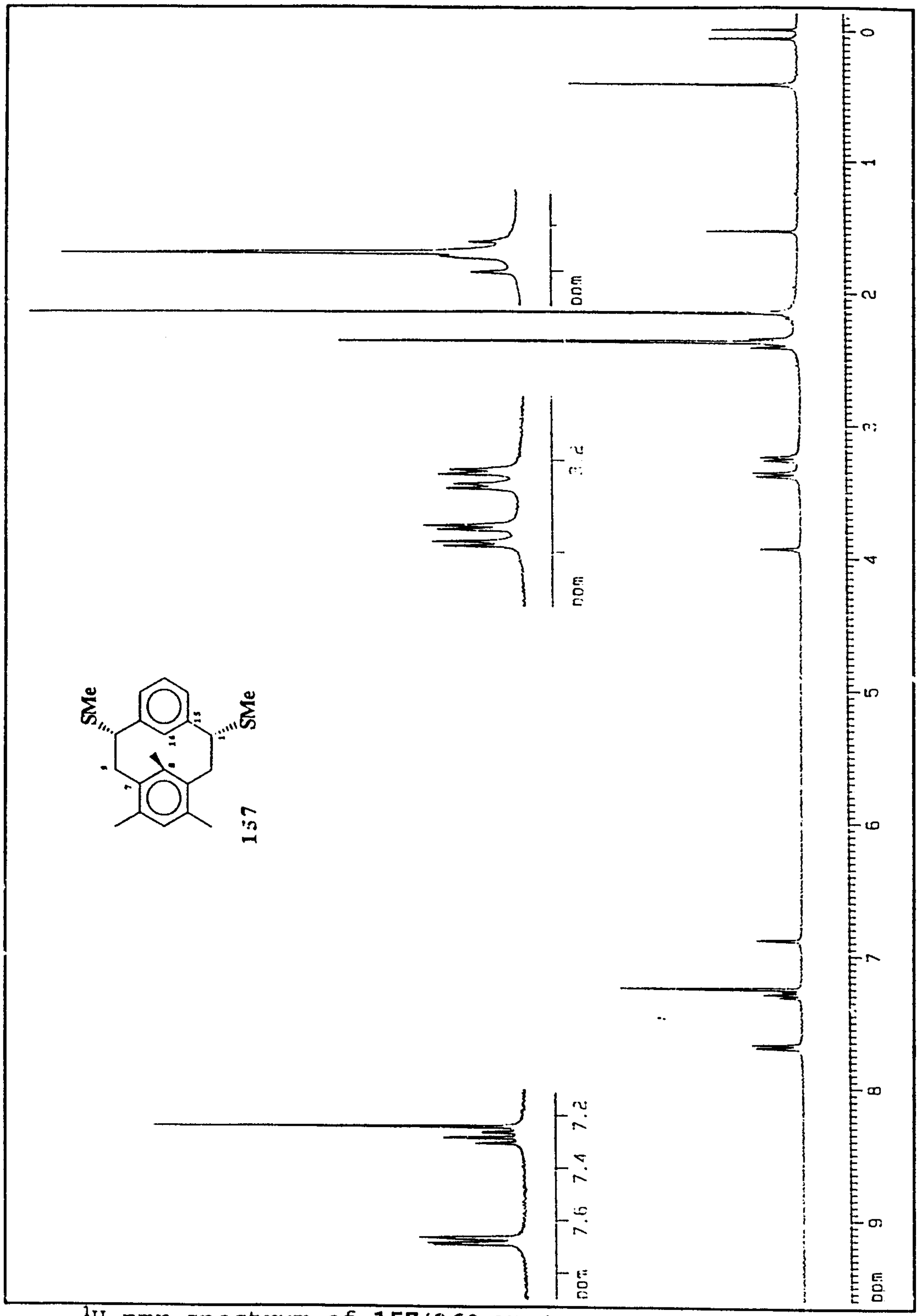


^{1}H nmr spectrum of **155** (360 MHz)



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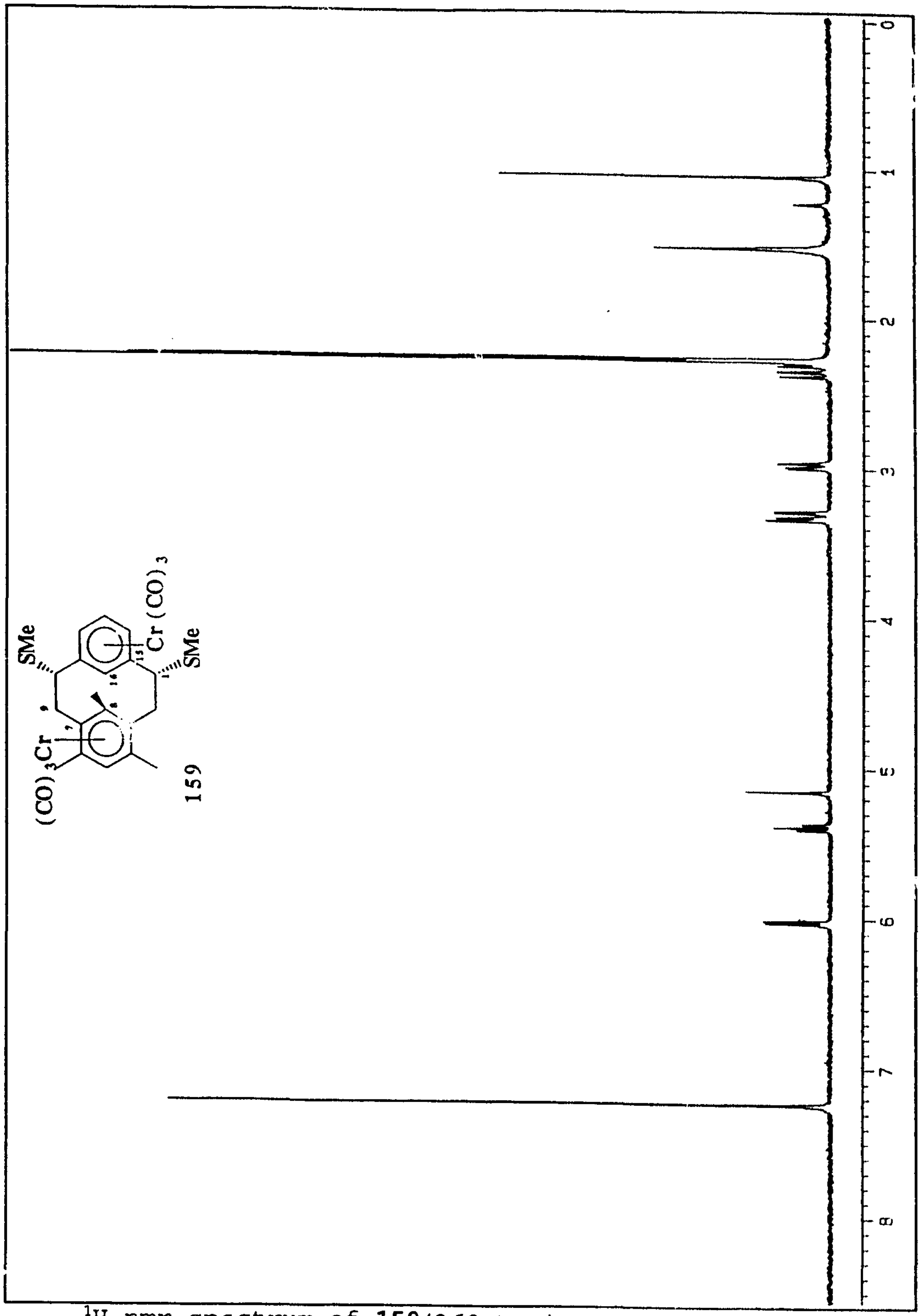
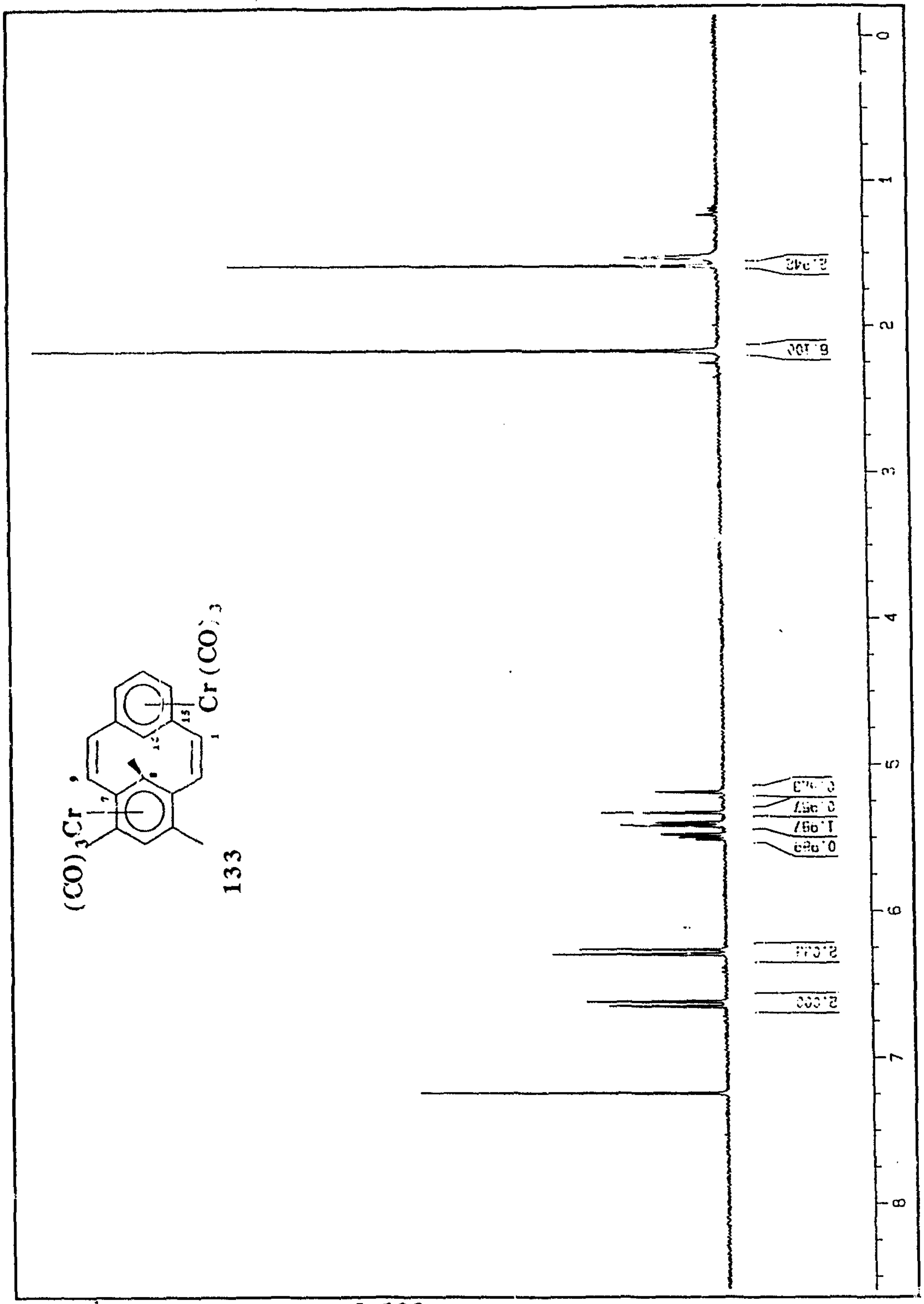
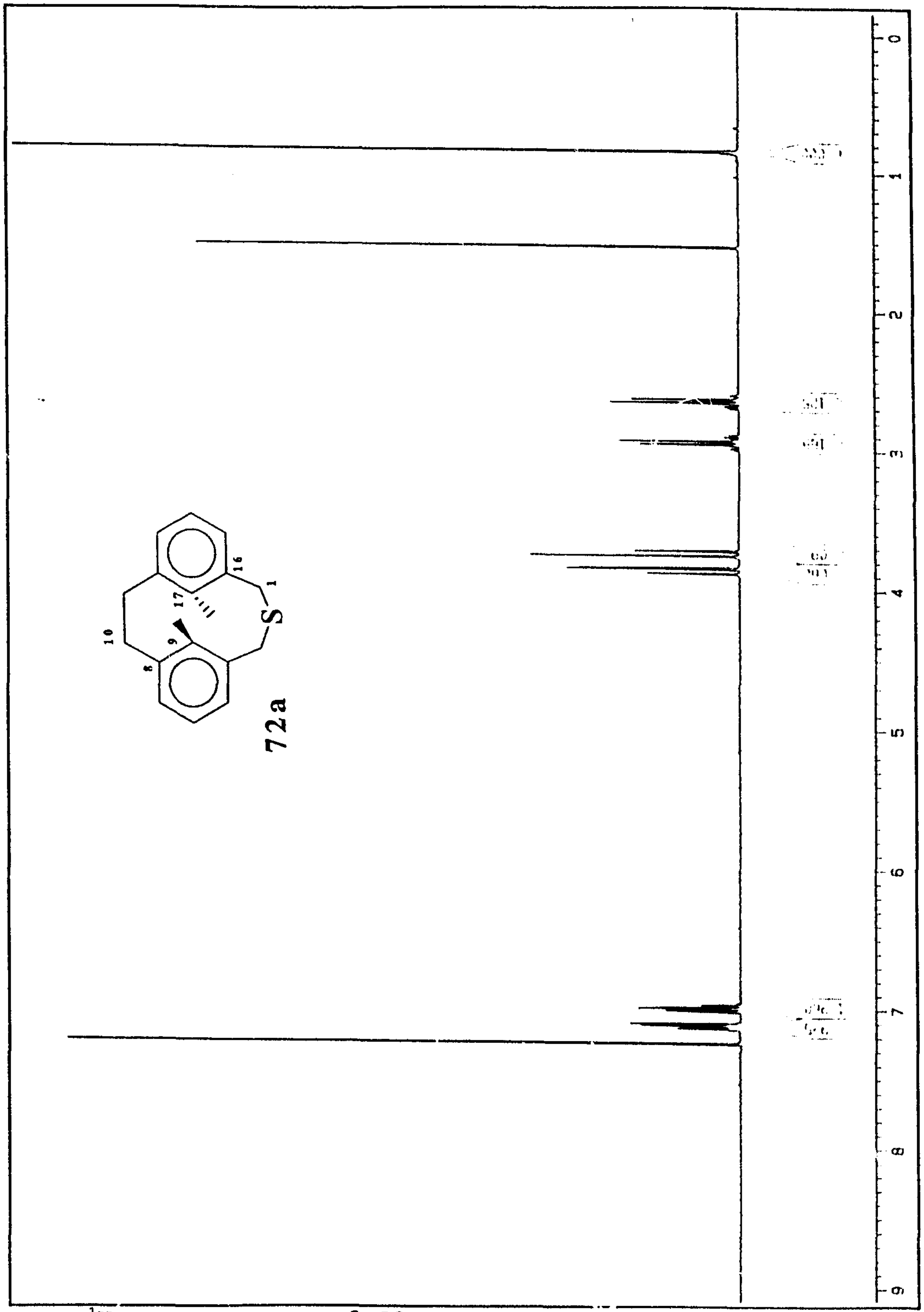


^{1}H nmr spectrum of **159**(360 MHz)

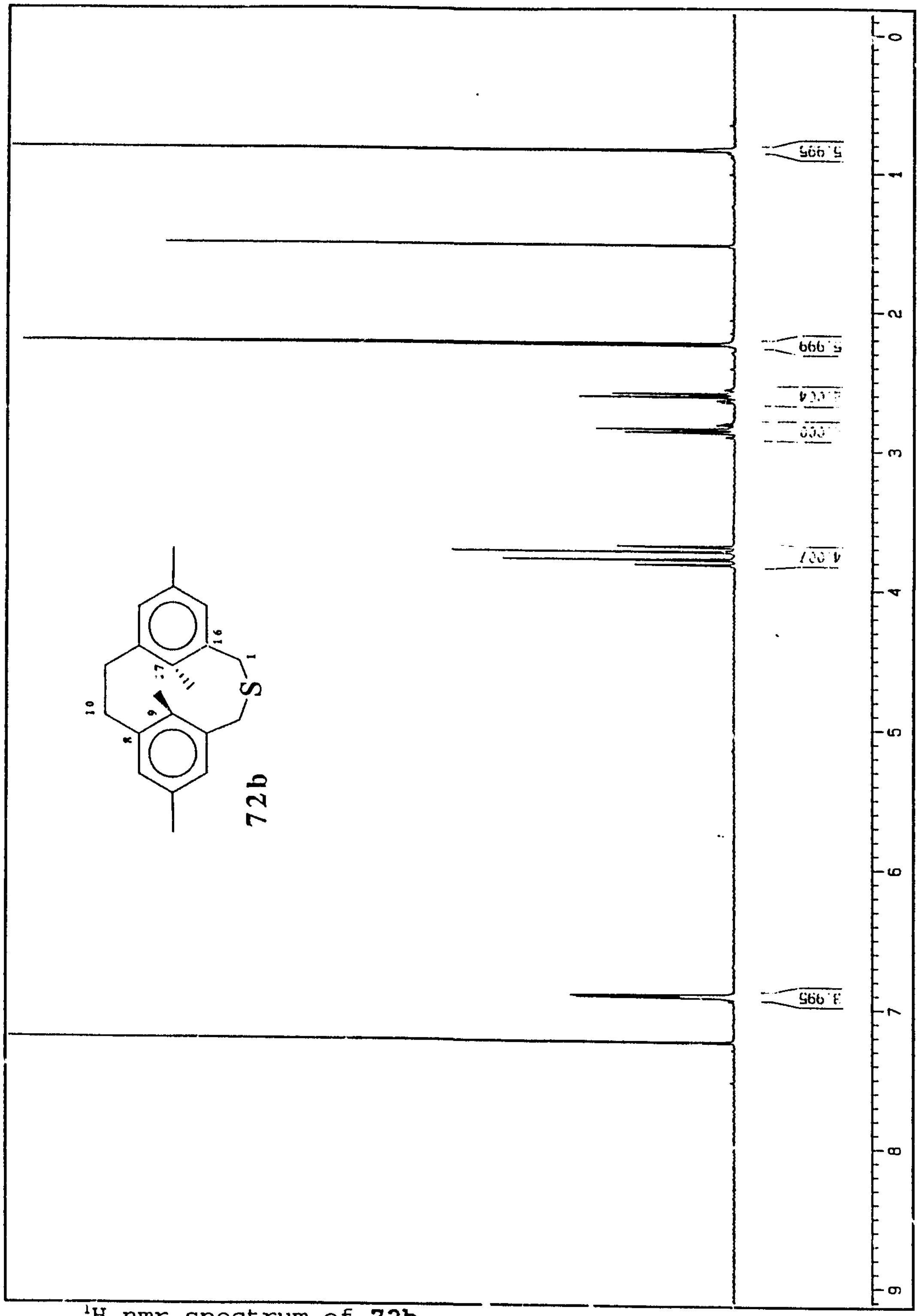


133

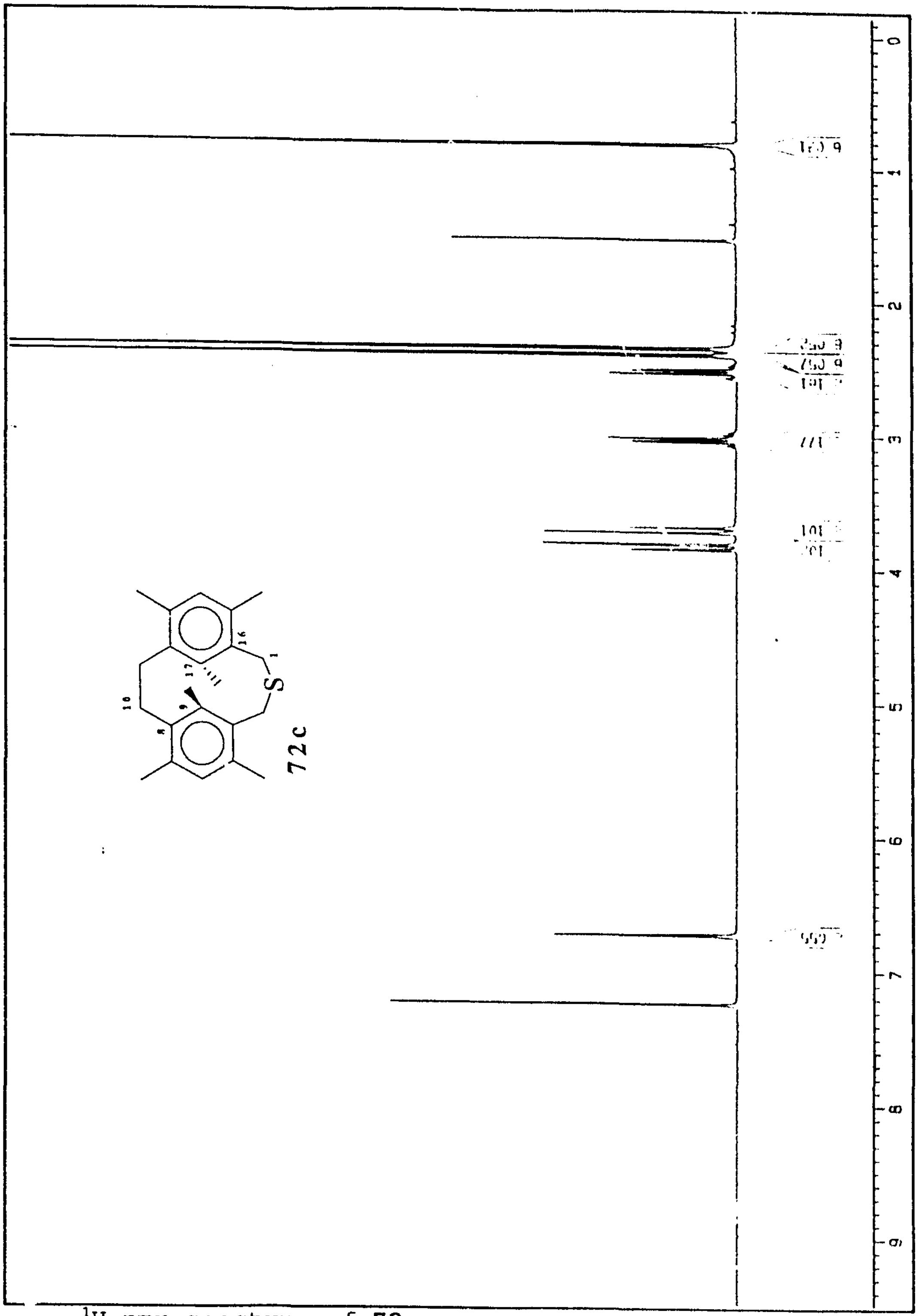
^{1}H nmr spectrum of **133**(360 MHz)



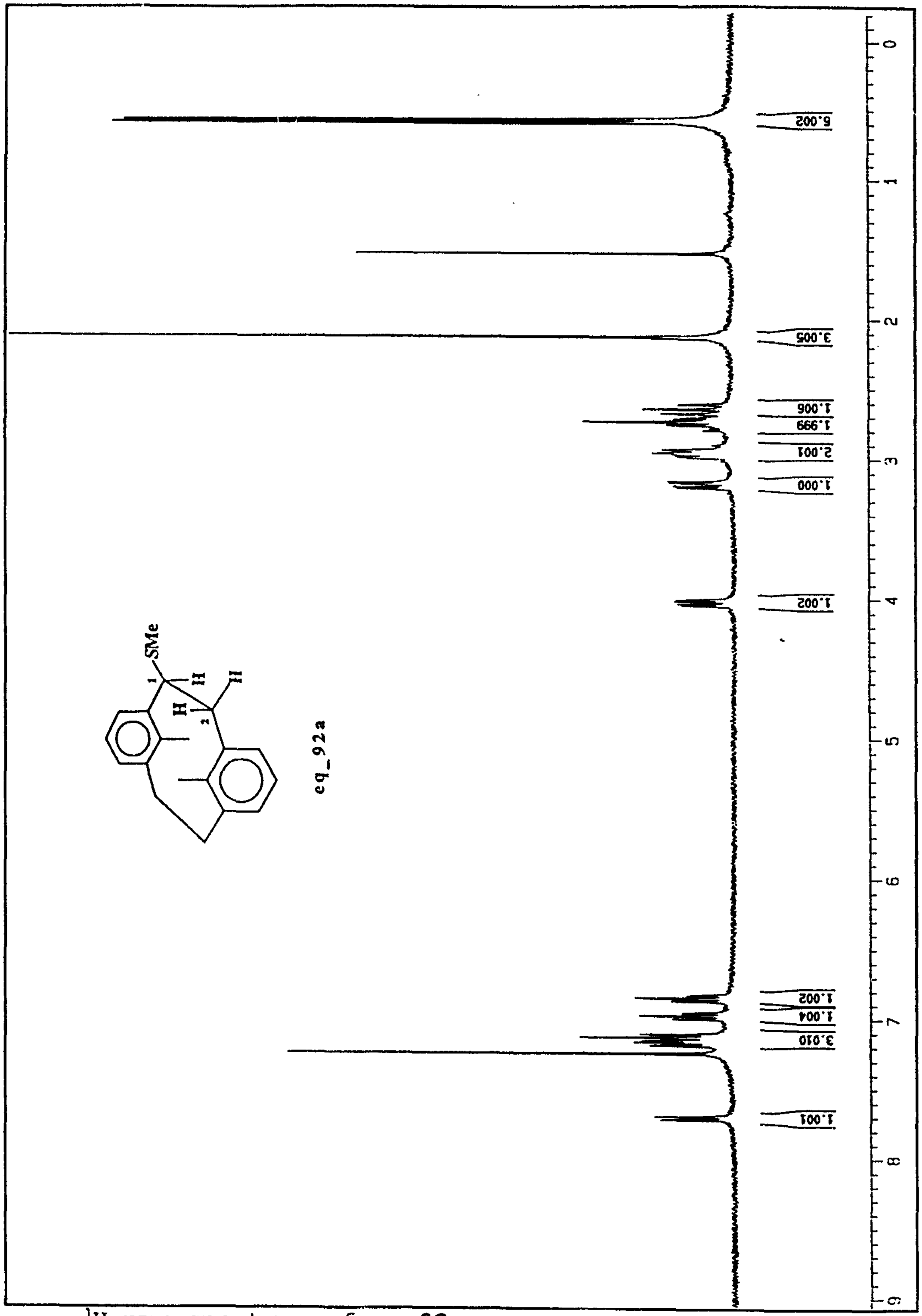
^{1}H nmr spectrum of **72a** (360 MHz)



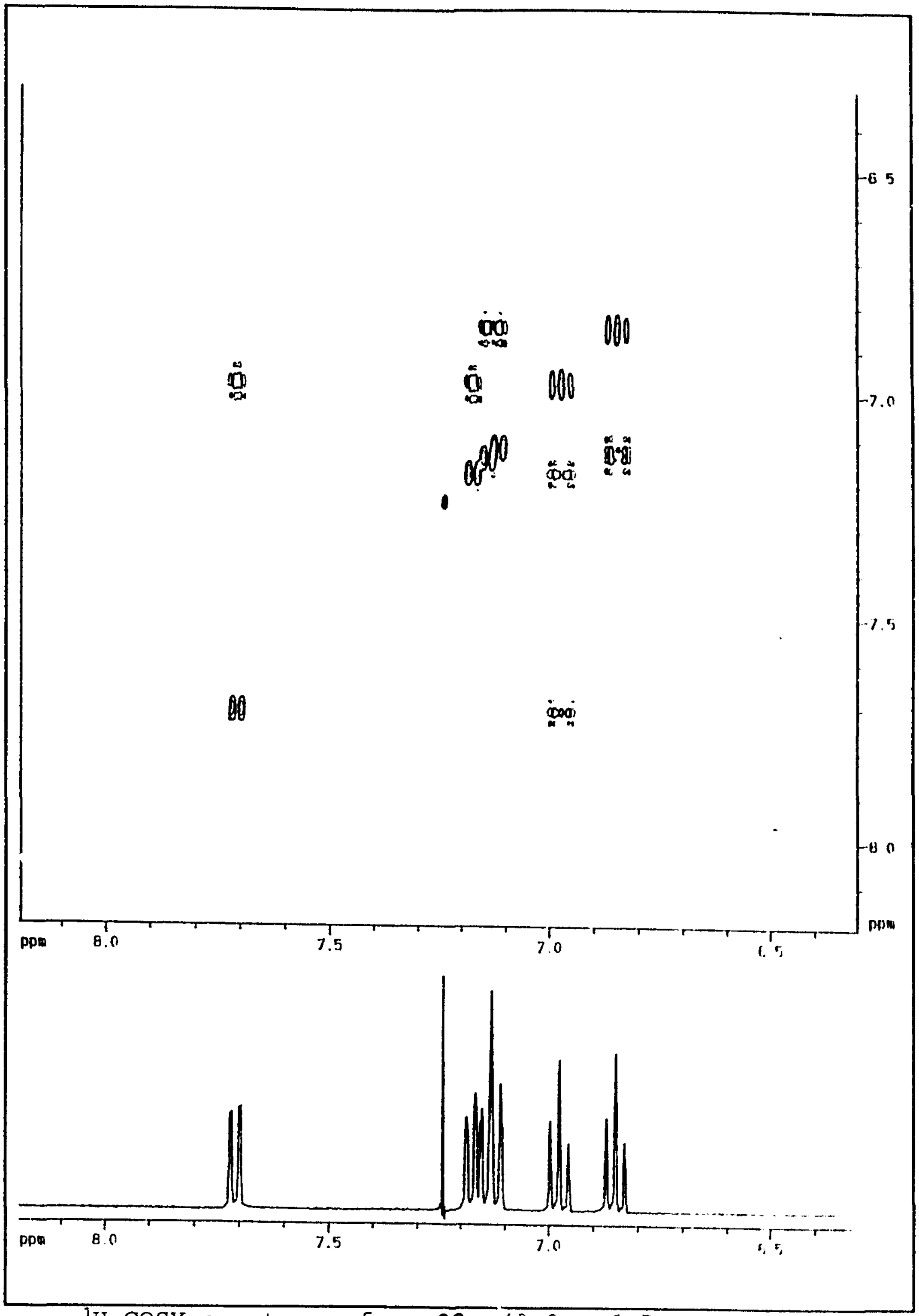
^{1}H nmr spectrum of **72b** (360 MHz)



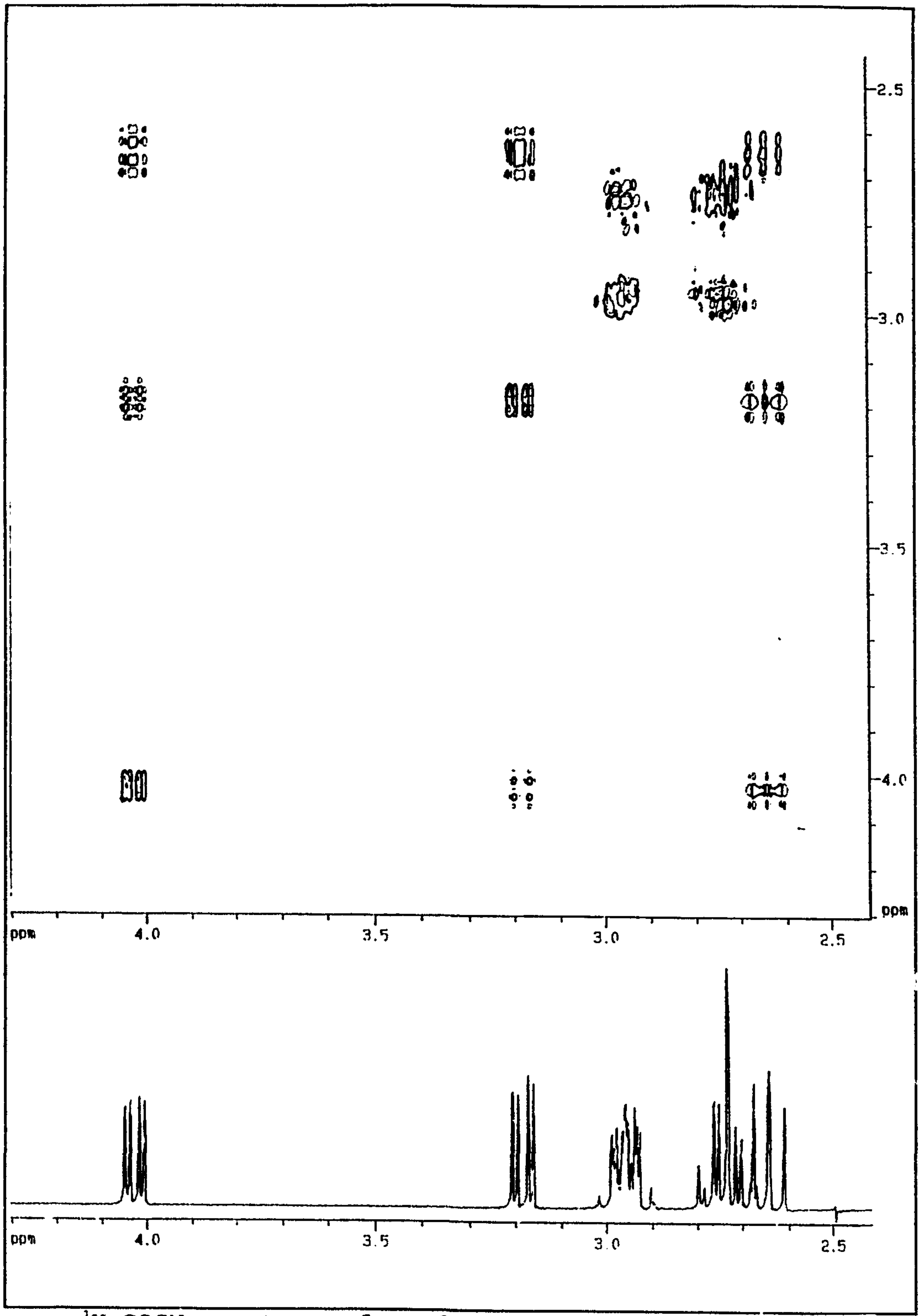
^{1}H nmr spectrum of **72c** (360 MHz)



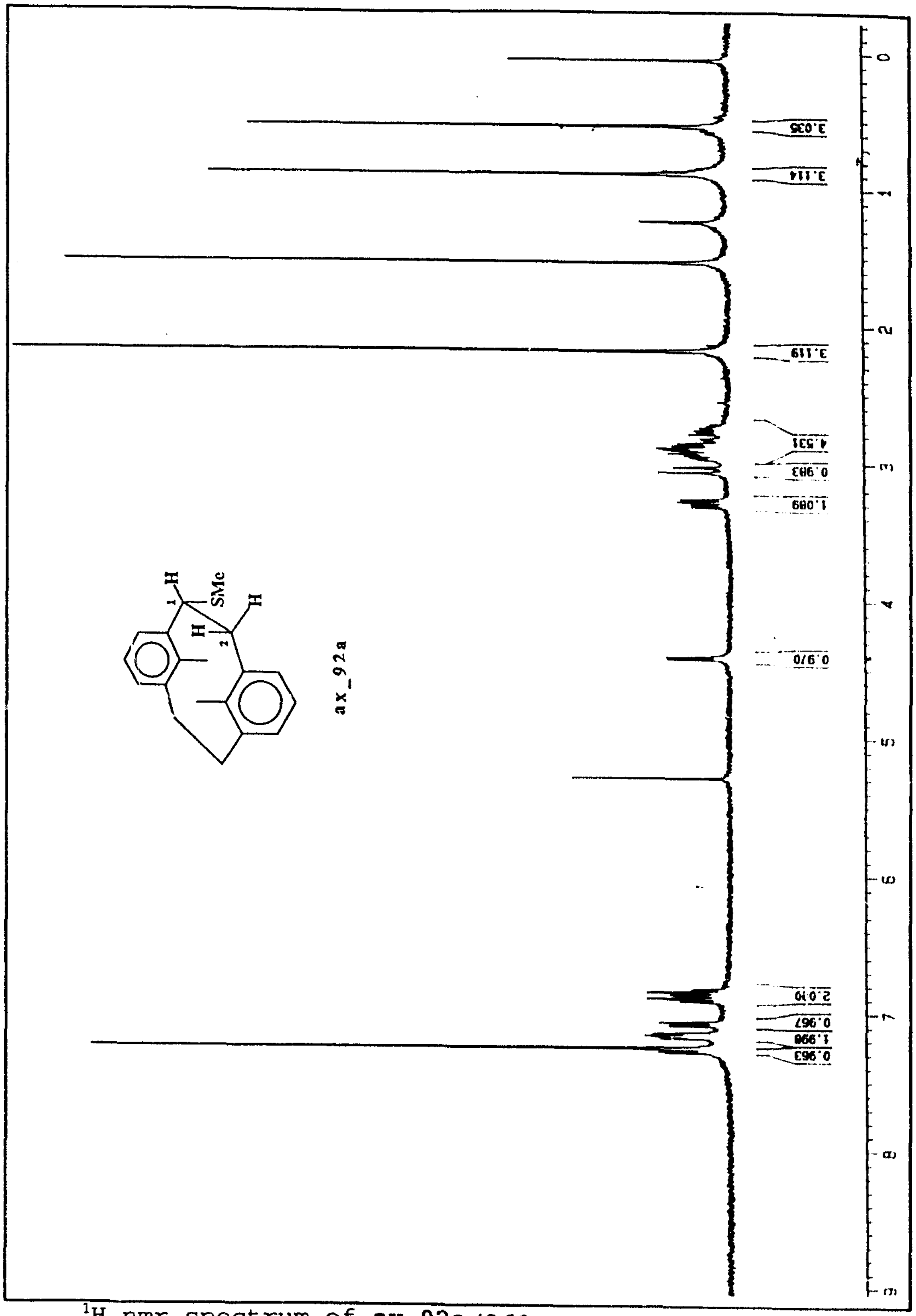
^{1}H nmr spectrum of **eq-92a** (360 MHz)



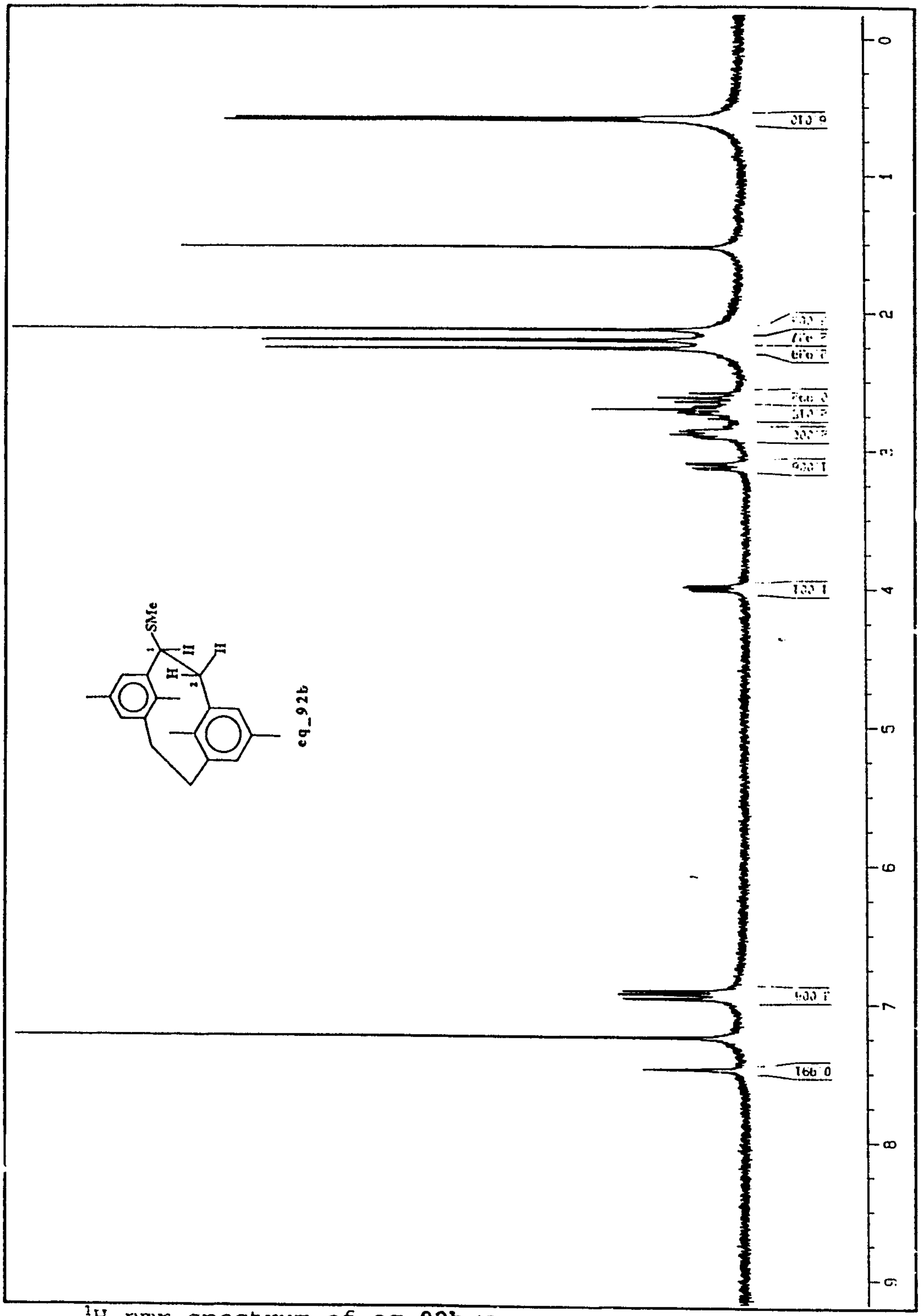
^{1}H COSY spectrum of **eq-92a** (8.0 - 6.5 ppm) (360 MHz)



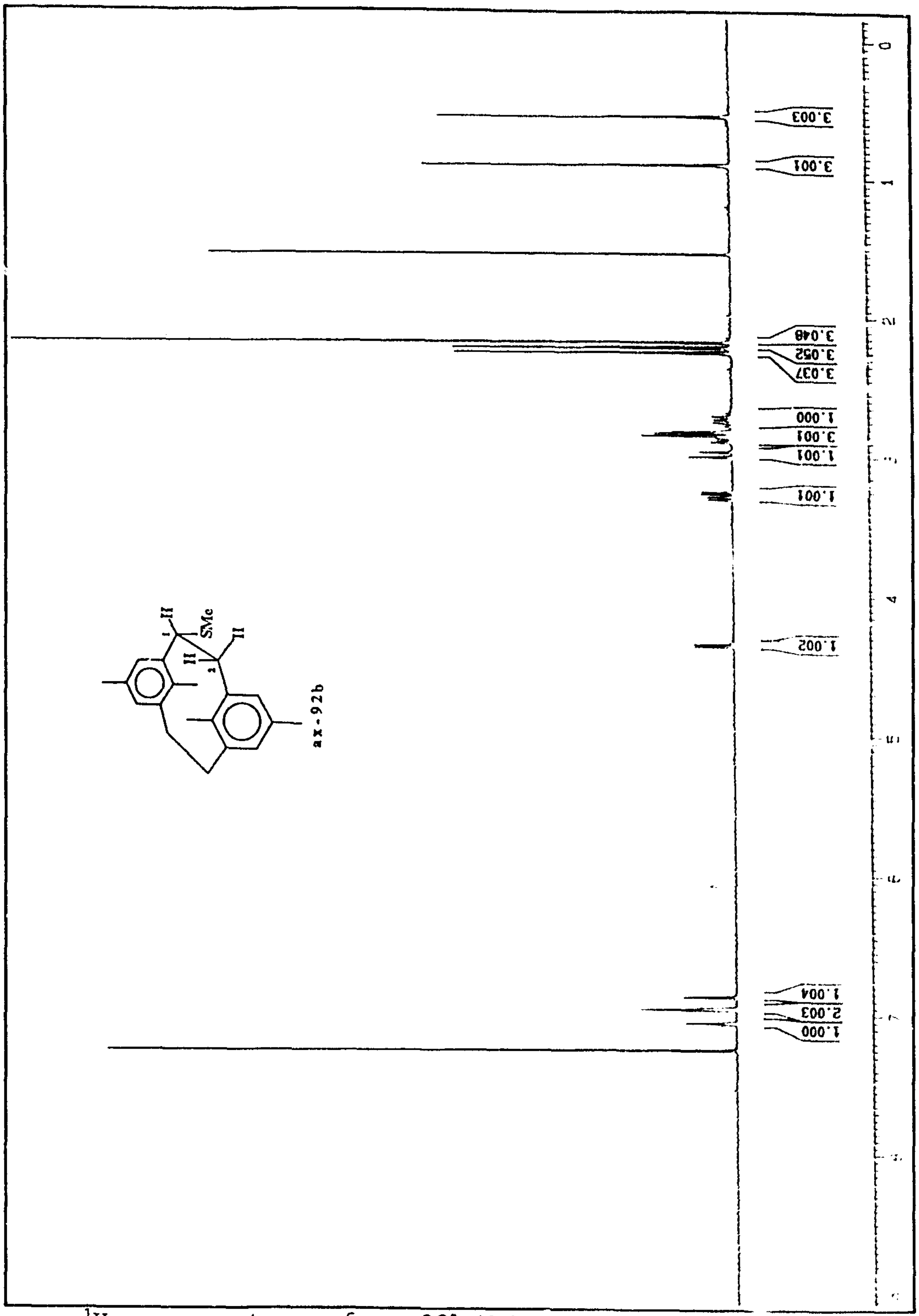
^1H COSY spectrum of **eq-92a** (4.5 - 2.5 ppm)(360 MHz)



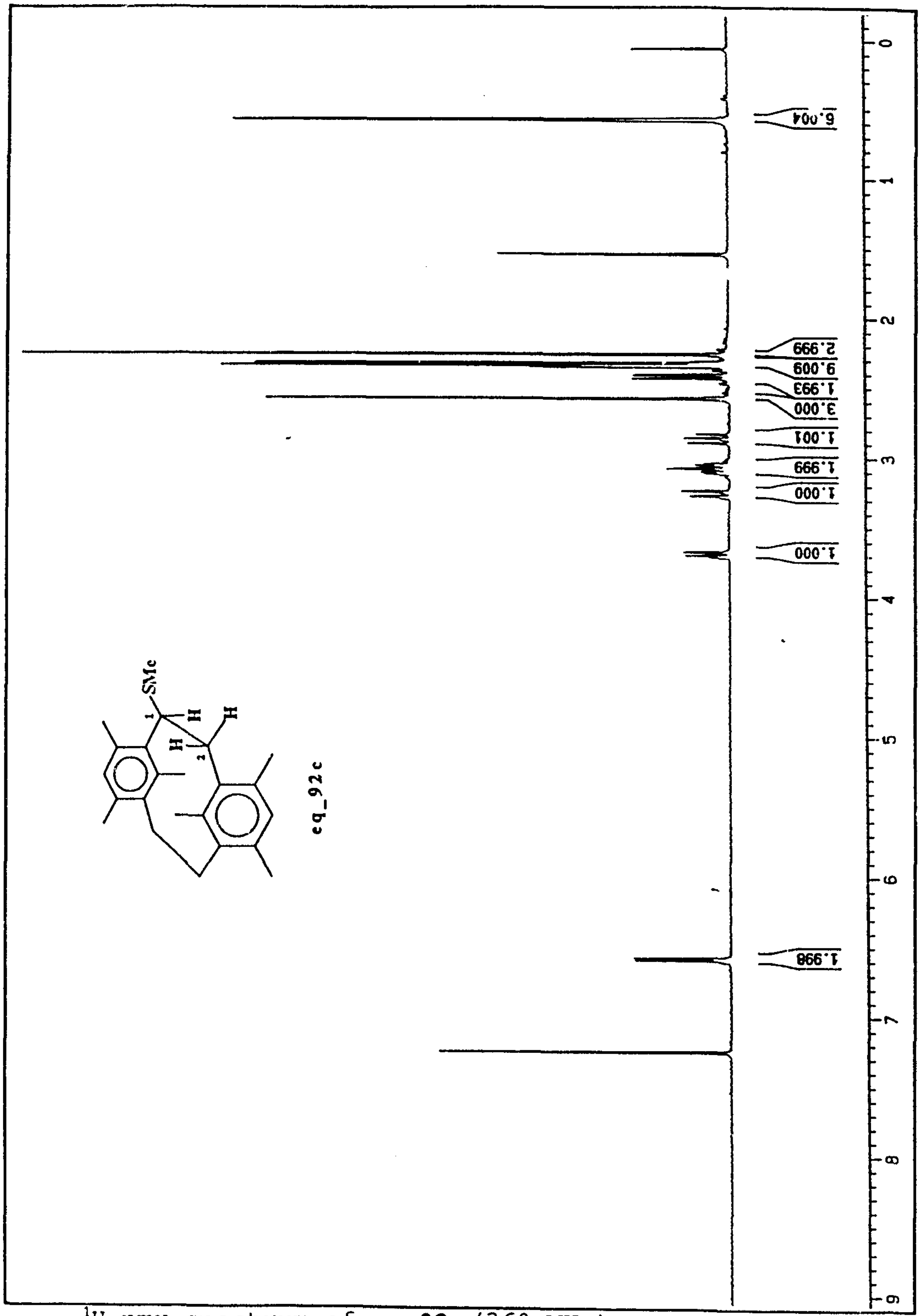
^{1}H nmr spectrum of **ax-92a** (360 MHz)



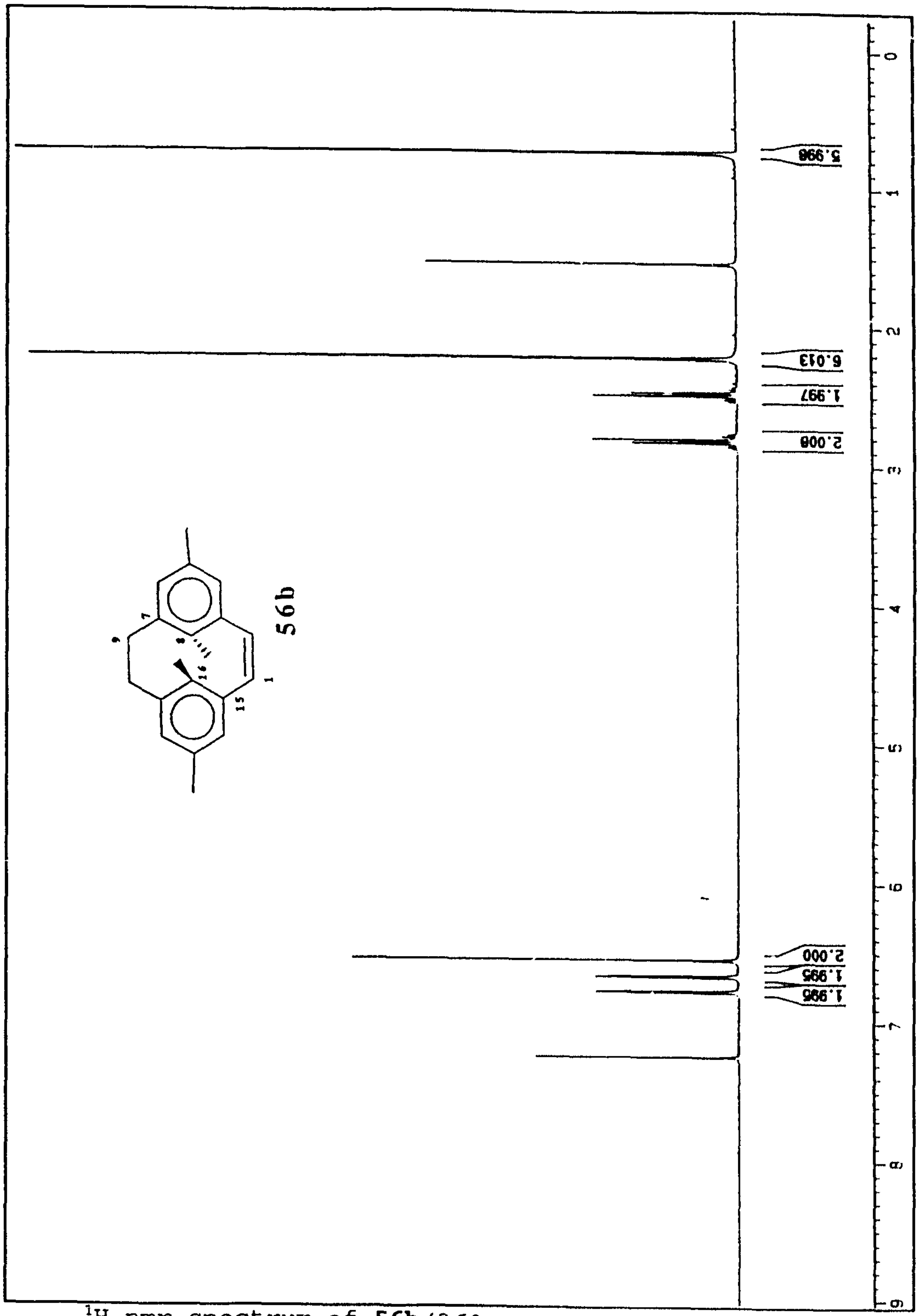
^{1}H nmr spectrum of **eq-92b** (360 MHz)



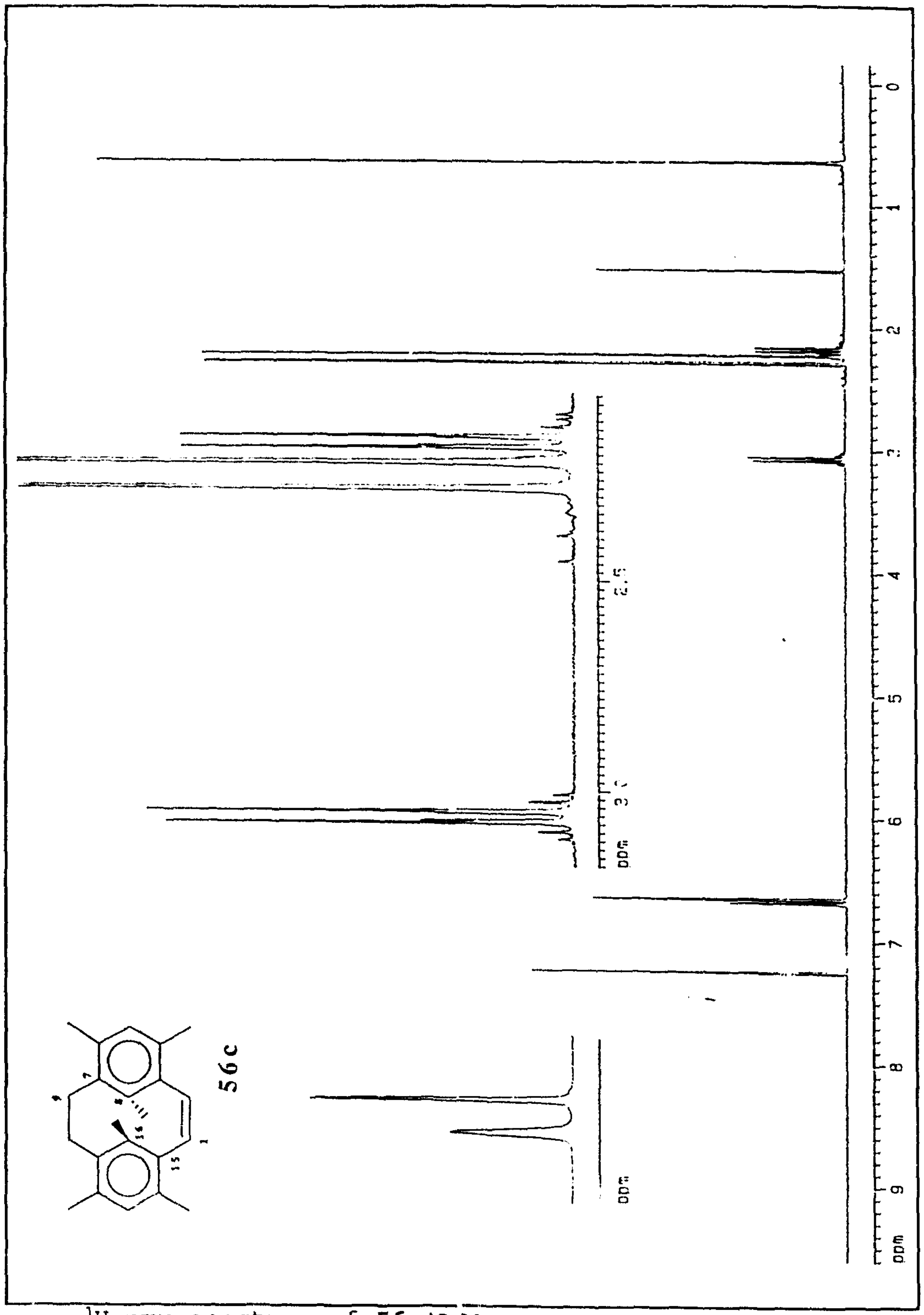
^{1}H nmr spectrum of **ax-92b** (360 MHz)



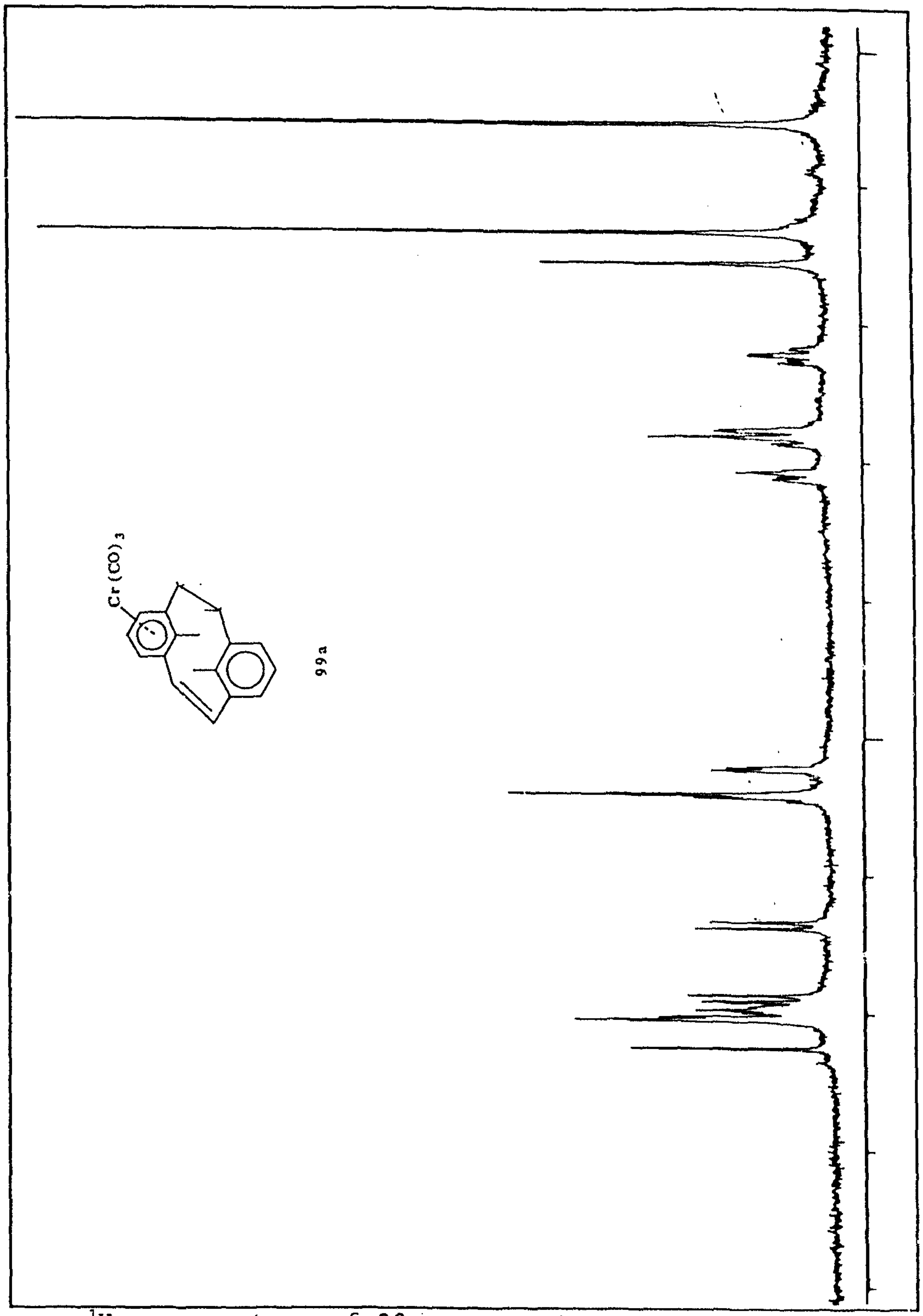
^{1}H nmr spectrum of **eq-92c** (360 MHz)



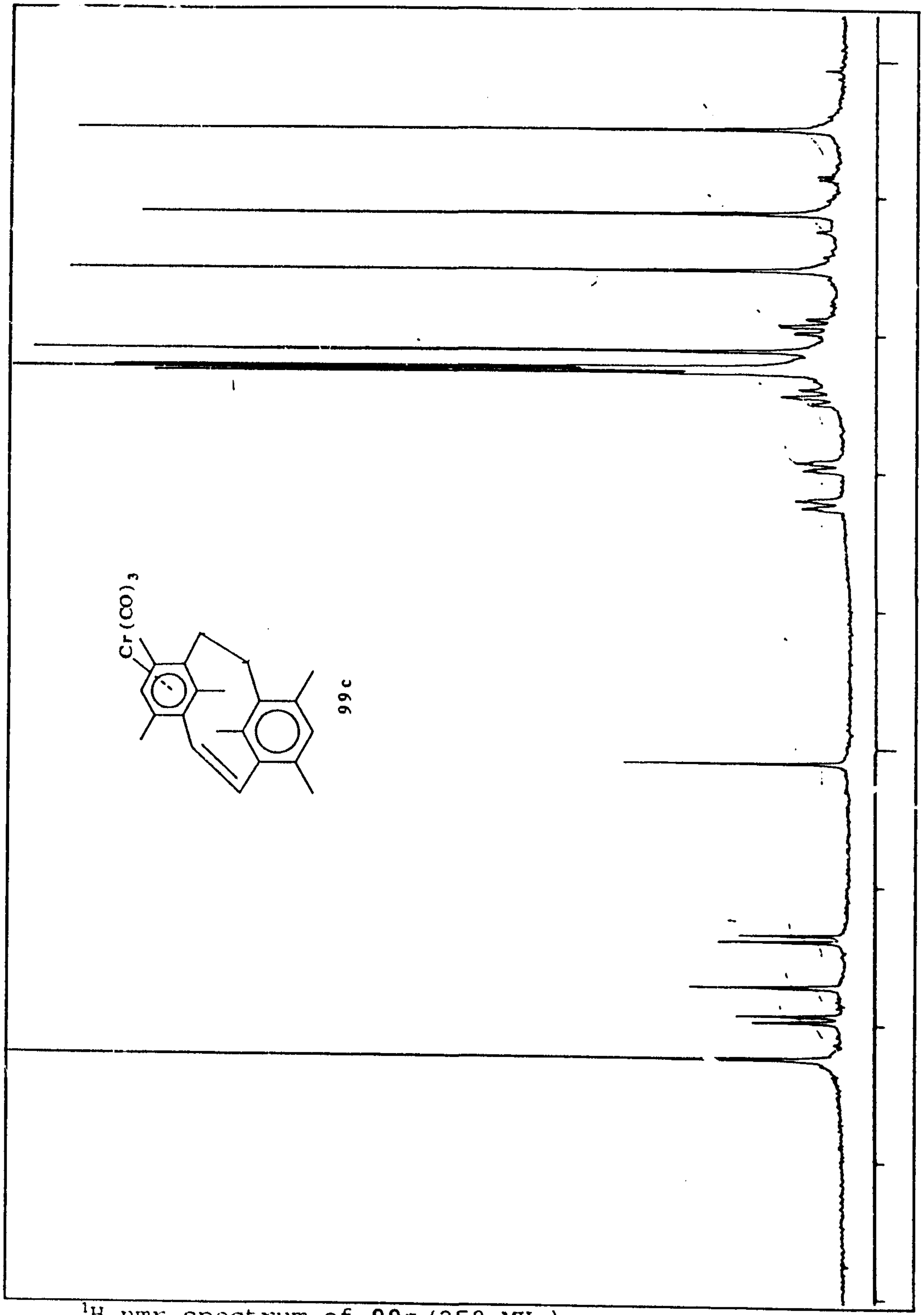
^{1}H nmr spectrum of **56b** (360 MHz)



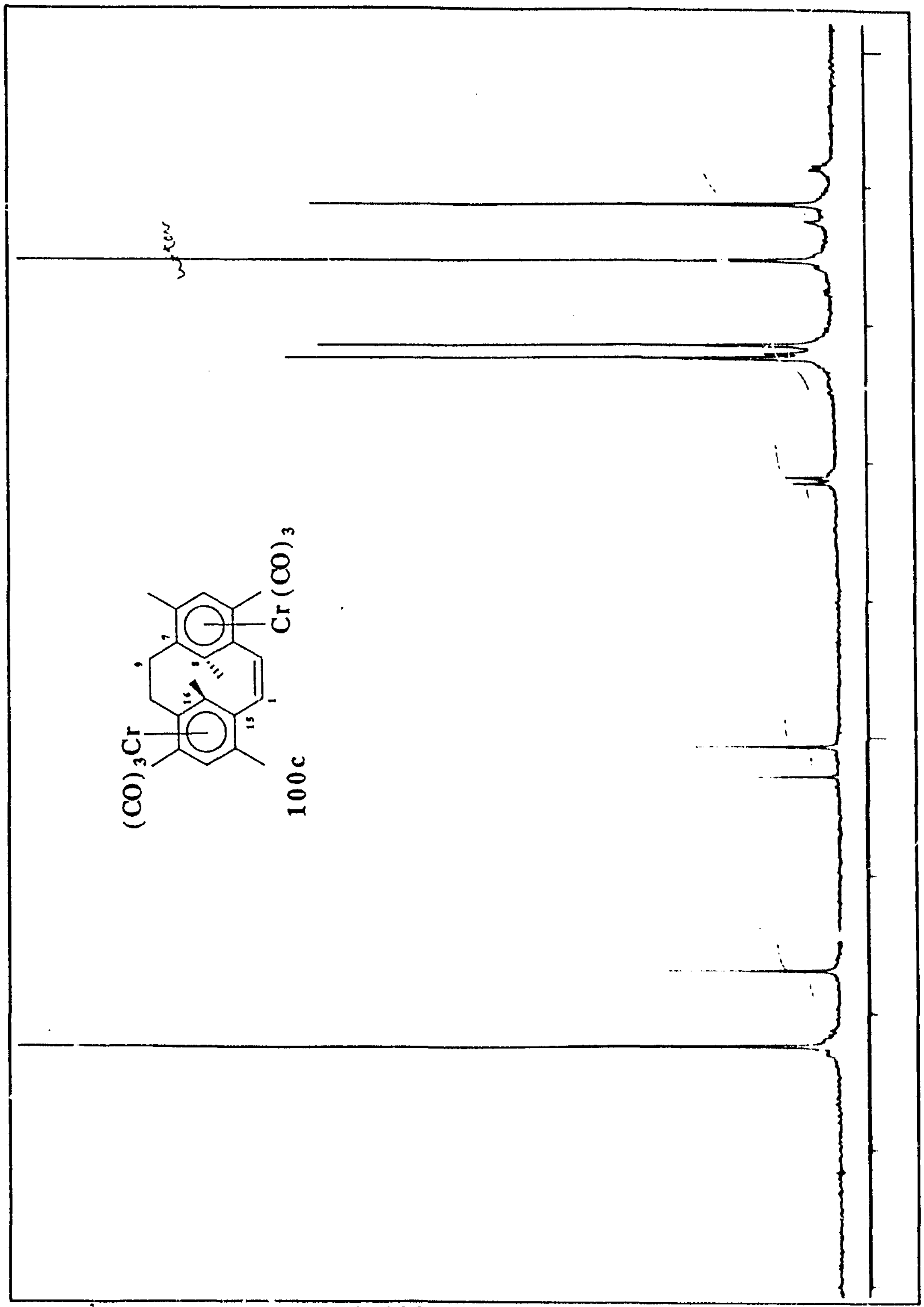
^{1}H nmr spectrum of **56c**(360 MHz)



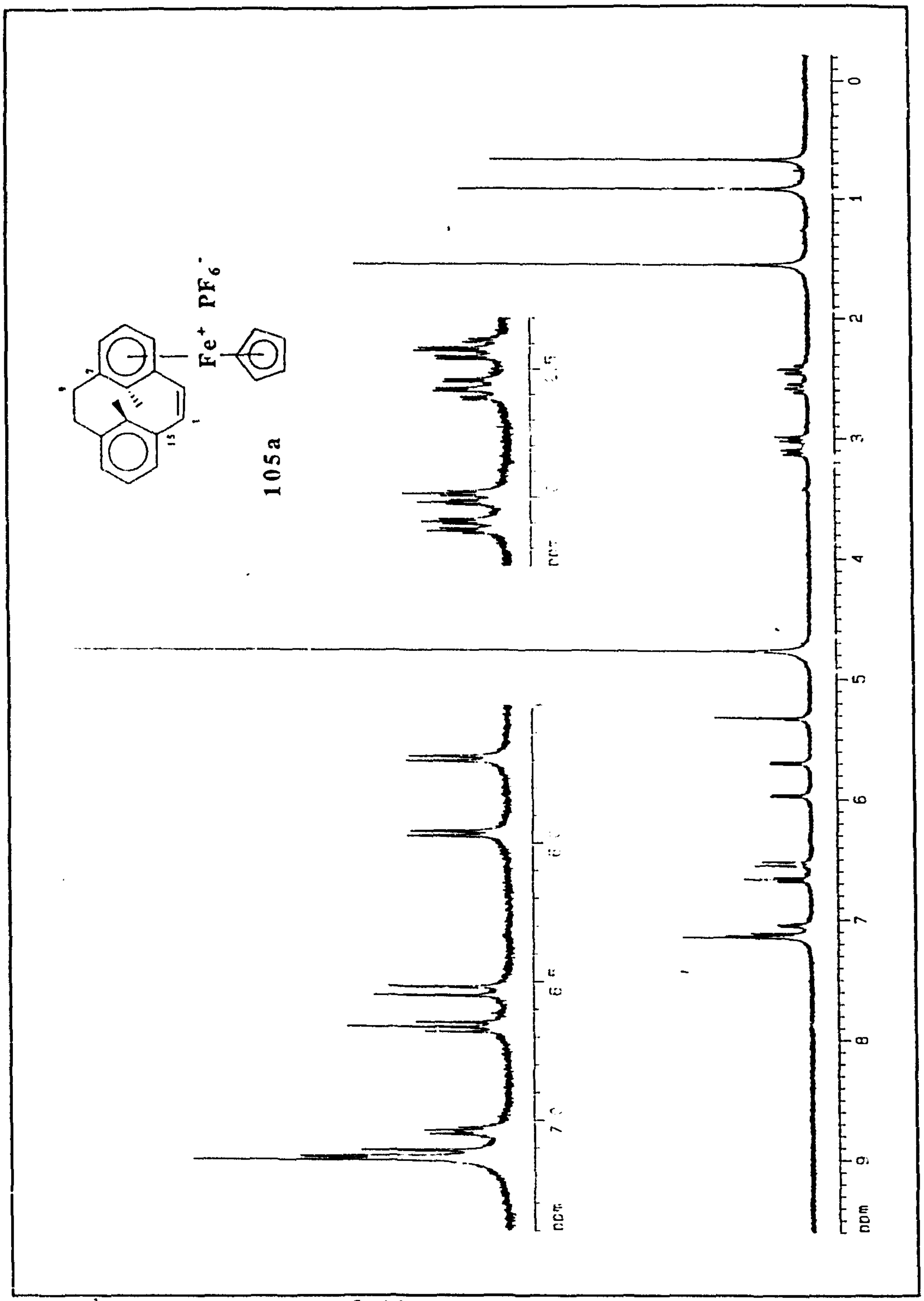
^{1}H nmr spectrum of **99a** (250 MHz)



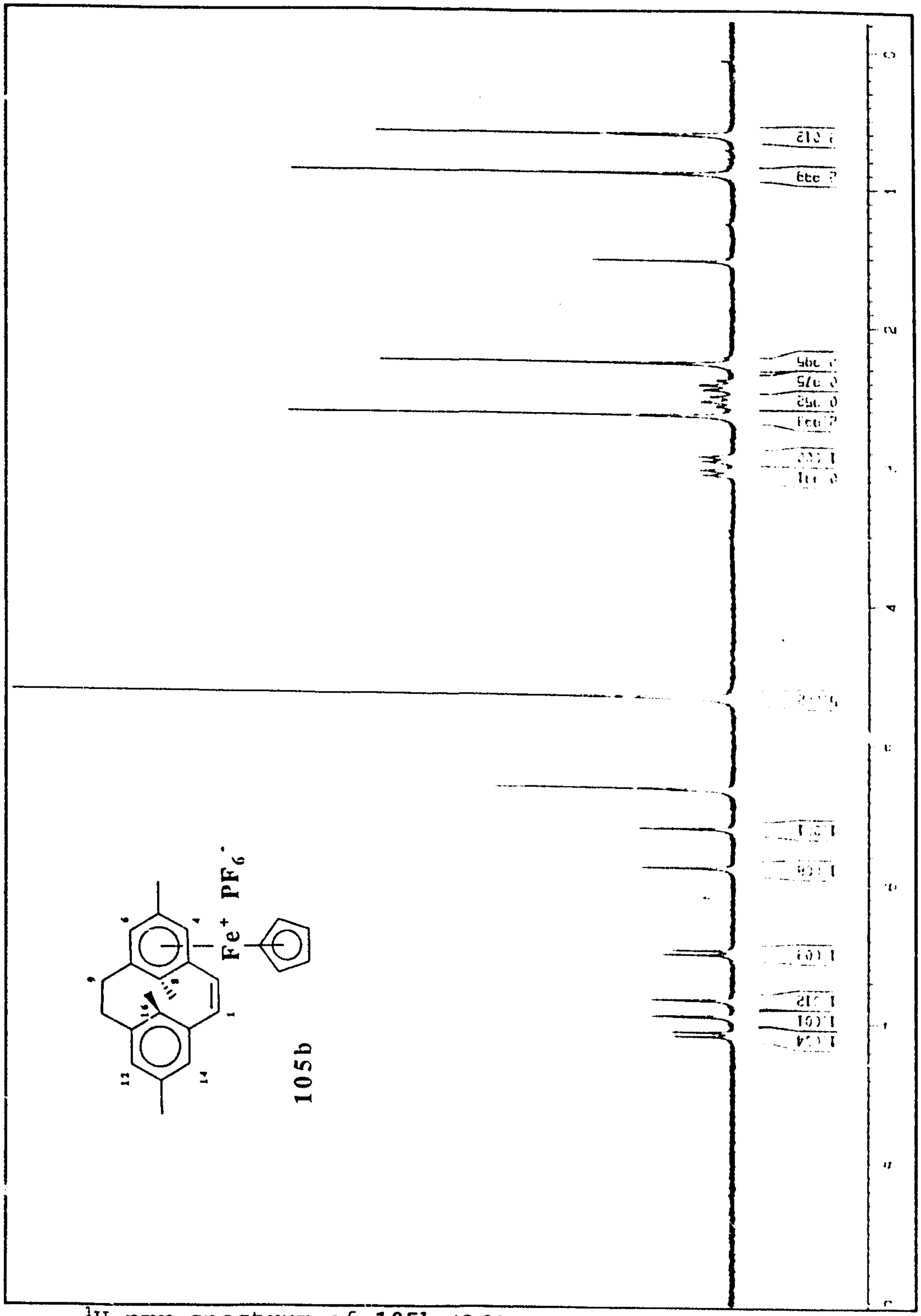
^{1}H nmr spectrum of **99c** (250 MHz)



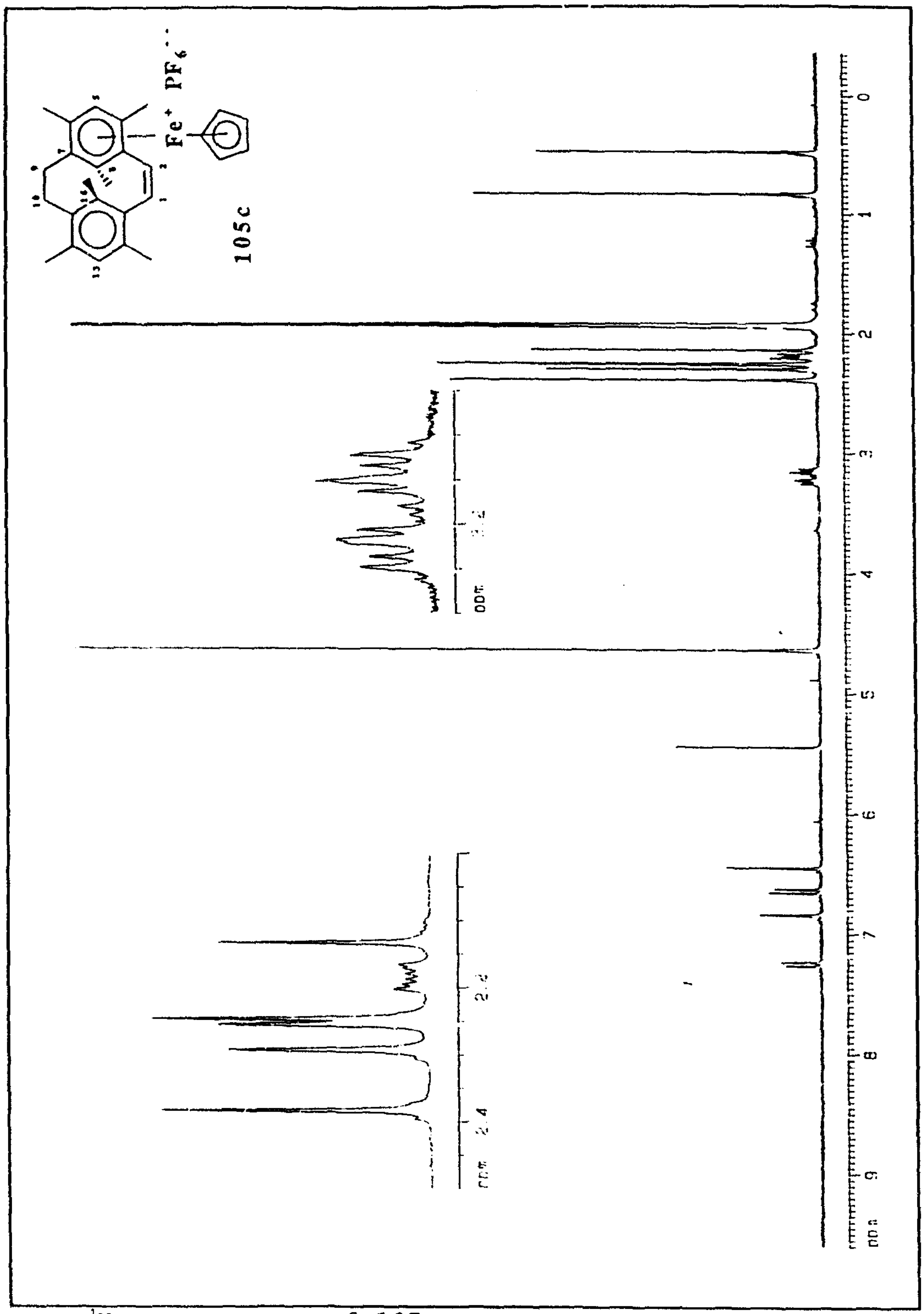
^{1}H nmr spectrum of **100c** (250 MHz)



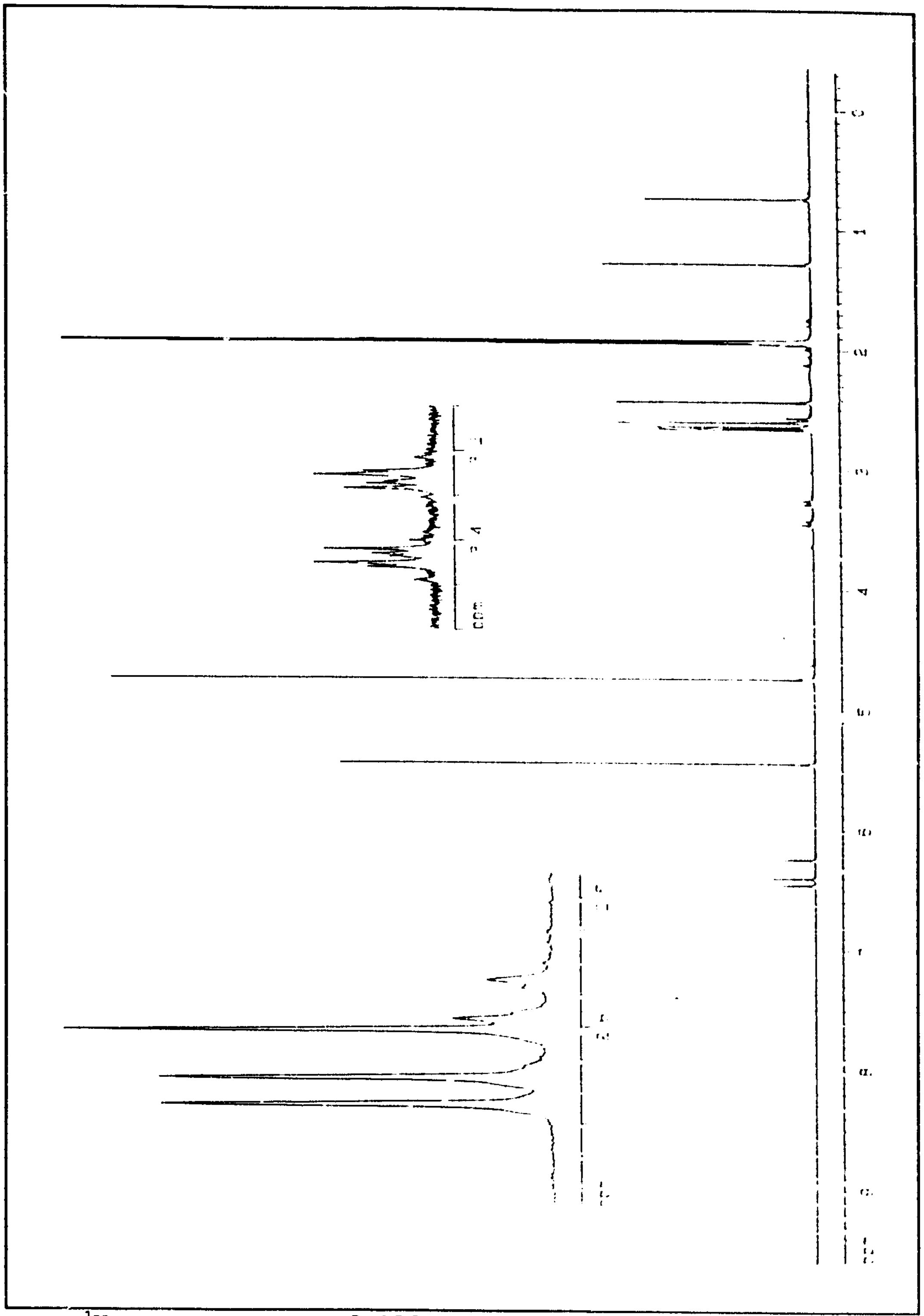
^{1}H nmr spectrum of **105a**(360 MHz)



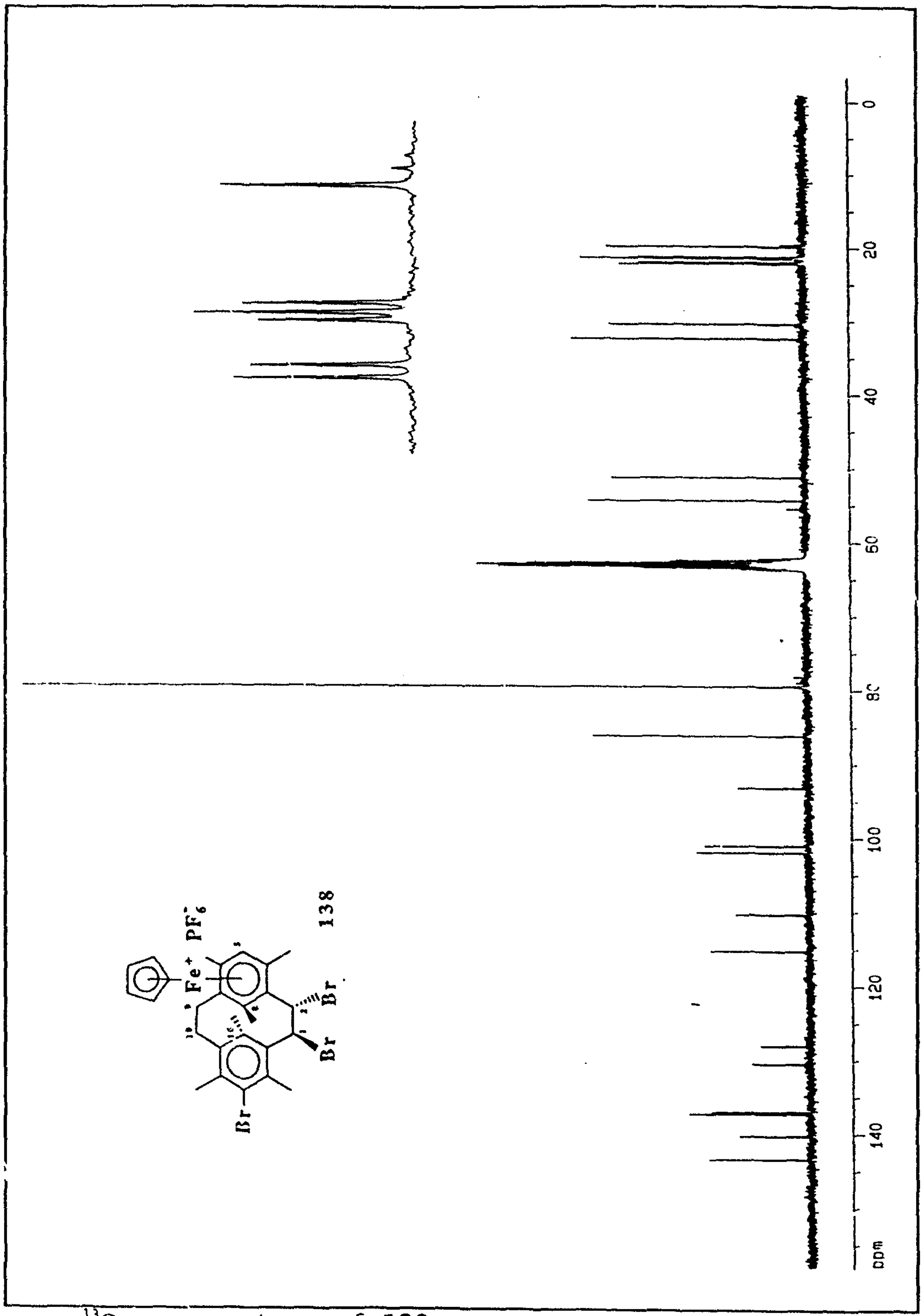
^{1}H nmr spectrum of **105b** (360 MHz)



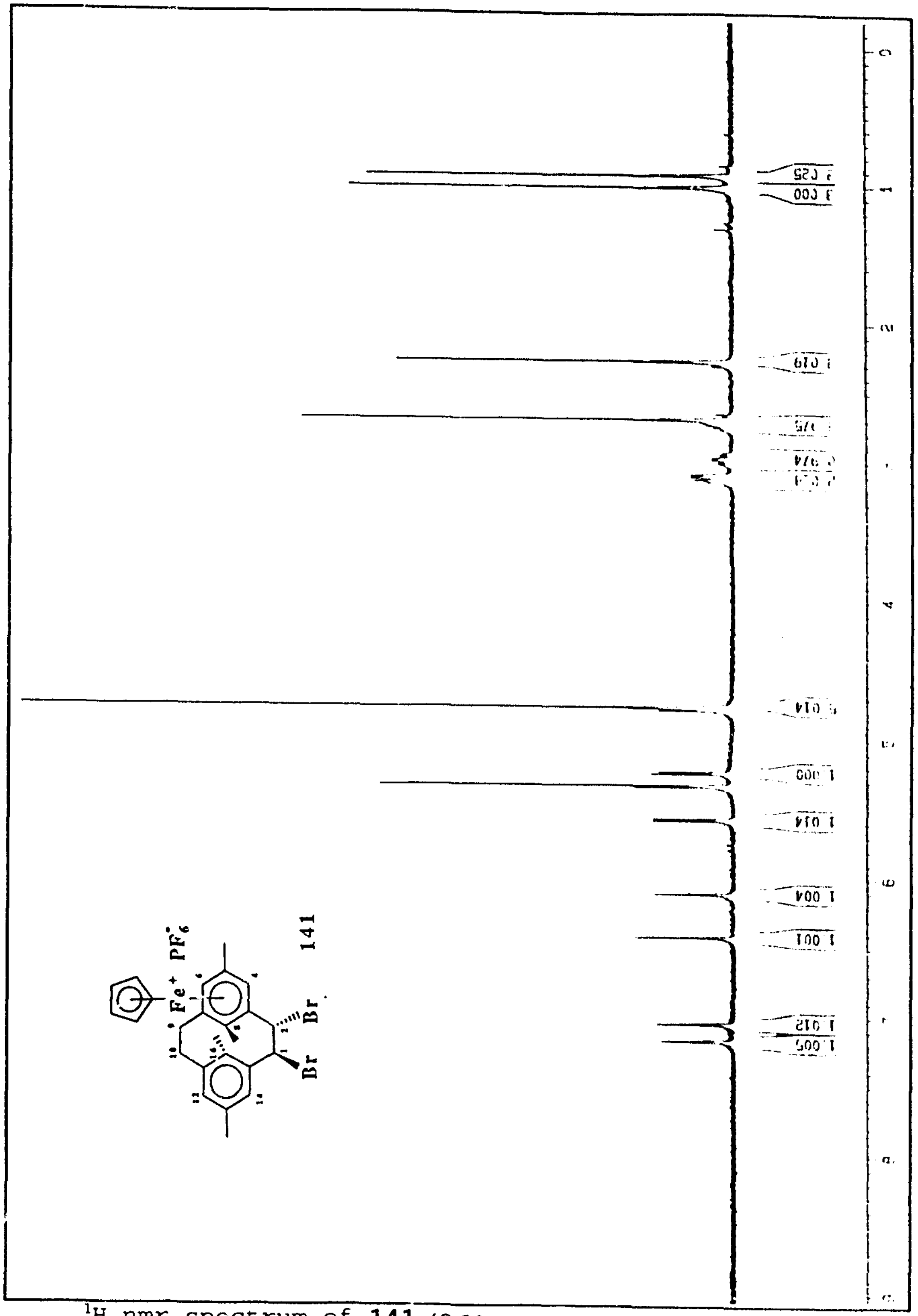
^{1}H nmr spectrum of **105c** (360 MHz)



^{1}H nmr spectrum of **138** (360 MHz)



^{13}C nmr spectrum of **138** (360 MHz)



¹H nmr spectrum of **141** (360 MHz)

Formula	$C_{18}H_{20}S$
Formula Weight	560.9
F(000)	1152.00
Temperature(°C)	20
System	Orthorhombic
Space Group	*Pccn*
a	28.790(6)Å
b	12.922(4)Å
c	7.575(2)Å
α	90°
β	90°
γ	90°
V	2818.3Å
Z	8
D_c	1.265 g cm^{-3}
D_m	1.264 g cm^{-3}
μ	2.06 cm^{-3}
D_c	1.265 g cm^{-3}
D_m	1.264 g cm^{-3}
Crystal dimensions	0.30 x 0.45 x 0.77 x 0.68(mm)
μ	2.06 cm^{-1} (ABSB02)
Standards	404;060;12,0,0
2θ range	0 - 50
No. of reflections	3264
$I=2.5\sigma(I)$	1572
Radiation	Mo·K_α 0.71069Å
Max. shift/esd	0.062(H)
Residual electron density	0.51
R	0.082
R_w	0.078

Fractional atomic coordinates and temperature parameters.

Atom	x/a	y/b	z/c	Ueq
S(2)	22085(5)	61038(12)	51937(21)	443(4)
C(1)	18348(22)	69319(49)	65470(84)	433(17)
C(3)	18487(22)	54411(47)	35512(78)	412(17)
C(4)	16482(19)	44397(40)	42684(68)	333(15)
C(5)	19588(22)	36735(46)	47575(80)	470(18)
C(6)	18125(26)	28182(48)	56853(89)	555(19)
C(7)	13560(28)	27907(47)	62440(87)	549(19)
C(8)	10371(23)	35591(45)	58165(83)	450(17)
C(9)	11836(19)	43421(41)	46178(68)	353(15)
C(10)	5867(24)	35888(57)	67695(**)	611(20)
C(11)	6267(26)	42930(56)	84714(90)	586(20)
C(12)	7708(21)	54005(47)	80168(79)	435(17)
C(13)	4249(23)	60894(59)	75653(92)	581(19)
C(14)	5341(23)	70440(55)	68027(90)	555(19)
C(15)	9907(24)	72704(46)	64785(83)	465(18)
C(16)	13471(19)	66118(42)	69672(72)	369(15)
C(17)	12397(20)	56813(43)	78690(71)	364(15)
C(18)	8332(23)	50585(55)	37856(90)	491(18)
C(19)	16197(23)	50319(48)	86498(82)	445(18)
H(1A)	1835(18)	7531(36)	5923(45)	45(5)'
H(1B)	1991(18)	6983(33)	7395(44)	34(5)'
H(3A)	1587(22)	5974(38)	3264(47)	75(5)'
H(3B)	2129(22)	5412(38)	2939(49)	84(5)'
H(5)	2297(19)	3684(33)	4305(46)	54(5)'
H(6)	2061(18)	2323(36)	6021(47)	59(5)'
H(7)	1267(19)	2275(37)	7390(46)	71(5)'
H(10A)	350(22)	3796(38)	6196(48)	68(5)'
H(10B)	497(19)	2828(37)	7375(47)	70(5)'
H(11A)	762(22)	4056(38)	9426(48)	66(5)'
H(11B)	264(21)	4175(36)	8836(47)	66(5)'
H(13)	83(17)	5882(30)	7771(43)	32(5)'
H(14)	172(22)	7513(42)	6501(49)	99(5)'
H(15)	1142(20)	7739(38)	5911(48)	70(5)'
H(18A)	789(21)	5101(38)	2459(49)	70(5)'
H(18B)	530(22)	4863(37)	4179(48)	66(5)'
H(18C)	787(22)	5748(40)	4558(49)	86(5)'
H(19A)	1534(20)	4698(36)	9641(47)	58(5)'
H(19B)	1998(24)	5404(39)	9002(49)	97(5)'
H(19C)	1731(17)	4501(35)	7708(45)	47(5)'

Estimated standard deviations are given in parentheses.

Coordinates x 10^n where n = 5,5,4 for S,C,H

Temperature parameters x 10^n where n = 4,4,3 for S,C,H
U_{eq} = the equivalent isotropic temperature parameter.
$U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i{}^* a_j (a_i \cdot a_j)$

Primed values indicate that U_{iso} is given

$T = \exp(-8\pi^2 U_{iso} \sin^2\theta/\lambda^2)$

Bond angles (°C).

Atoms	Angle	Atoms	Angle
C(3) -S(2) -C(1)	108.7(3)	C(11) -C(10) -C(8)	110.3(5)
C(16) -C(1) -S(2)	120.6(4)	C(12) -C(11) -C(10)	112.0(5)
C(4) -C(3) -S(2)	111.8(4)	C(13) -C(12) -C(11)	117.6(6)
C(5) -C(4) -C(3)	117.4(5)	C(17) -C(12) -C(11)	121.4(6)
C(9) -C(4) -C(3)	121.3(5)	C(17) -C(12) -C(13)	120.6(6)
C(9) -C(4) -C(5)	120.9(5)	C(14) -C(13) -C(12)	120.7(6)
C(6) -C(5) -C(4)	120.9(5)	C(15) -C(14) -C(13)	118.6(6)
C(7) -C(6) -C(5)	117.9(6)	C(16) -C(15) -C(14)	122.2(6)
C(8) -C(7) -C(6)	122.6(6)	C(15) -C(16) -C(1)	117.9(6)
C(9) -C(8) -C(7)	117.4(6)	C(17) -C(16) -C(1)	122.8(5)
C(10) -C(8) -C(7)	118.8(6)	C(17) -C(16) -C(15)	119.3(5)
C(10) -C(8) -C(9)	123.4(6)	C(16) -C(17) -C(12)	117.9(5)
C(8) -C(9) -C(4)	118.6(5)	C(19) -C(17) -C(12)	121.7(5)
C(18) -C(9) -C(4)	121.1(5)	C(19) -C(17) -C(16)	120.4(5)
C(18) -C(9) -C(8)	120.3(6)		

Estimated standard deviations are given in parentheses.

Bond angles involving H atoms (°C).

Atoms	Angle	Atoms	Angle
H(1A) -C(1) -S(2)	101.9(28)	H(11A)-C(11) -C(12)	113.1(36)
H(1A) -C(1) -C(16)	110.4(34)	H(11B)-C(11) -C(10)	93.2(22)
H(1B) -C(1) -S(2)	99.8(35)	H(11B)-C(11) -C(12)	116.6(26)
H(1B) -C(1) -C(16)	112.6(35)	H(11B)-C(11) -H(11A)	99.7(43)
H(1B) -C(1) -H(1A)	110.7(43)	H(13) -C(13) -C(12)	118.9(24)
H(3A) -C(3) -S(2)	103.9(26)	H(13) -C(13) -C(14)	120.4(23)
H(3A) -C(3) -C(4)	111.3(30)	H(14) -C(14) -C(13)	108.8(26)
H(3B) -C(3) -S(2)	82.4(29)	H(14) -C(14) -C(15)	132.6(26)
H(3B) -C(3) -C(4)	118.2(32)	H(15) -C(15) -C(14)	136.5(39)
H(3B) -C(3) -H(3A)	123.2(39)	H(15) -C(15) -C(16)	101.0(39)
H(5) -C(5) -C(4)	120.7(24)	H(18A)-C(18) -C(9)	122.1(32)
H(5) -C(5) -C(6)	118.0(24)	H(18B)-C(18) -C(9)	108.6(29)
H(6) -C(6) -C(5)	115.4(27)	H(18B)-C(18) -H(18A)	102.1(41)
H(6) -C(6) -C(7)	126.2(27)	H(18C)-C(18) -C(9)	111.4(28)
H(7) -C(7) -C(6)	117.9(30)	H(18C)-C(18) -H(18A)	118.7(37)
H(7) -C(7) -C(8)	117.0(29)	H(18C)-C(18) -H(18B)	86.3(40)
H(10A)-C(10) -C(8)	117.4(34)	H(19A)-C(19) -C(17)	113.4(37)
H(10A)-C(10) -C(11)	107.0(31)	H(19B)-C(19) -C(17)	121.1(25)
H(10B)-C(10) -C(8)	112.3(28)	H(19B)-C(19) -H(19A)	104.5(39)
H(10B)-C(10) -C(11)	100.9(21)	H(19C)-C(19) -C(17)	108.8(24)
H(10B)-C(10) -H(10A)	107.6(44)	H(19C)-C(19) -H(19A)	109.9(36)
H(11A)-C(11) -C(10)	120.2(33)	H(19C)-C(19) -H(19B)	97.8(35)

Estimated standard deviations are given in parentheses.

Interatomic distances (Å).

Atoms	Distance	Atoms	Distance
C(1) -S(2)	1.831(6)	C(10) -C(8)	1.484(9)
C(3) -S(2)	1.832(6)	C(18) -C(9)	1.507(8)
C(16) -C(1)	1.498(8)	C(11) -C(10)	1.582(10)
C(4) -C(3)	1.518(8)	C(12) -C(11)	1.529(9)
C(5) -C(4)	1.385(8)	C(13) -C(12)	1.379(9)
C(9) -C(4)	1.369(7)	C(17) -C(12)	1.402(8)
C(6) -C(5)	1.376(8)	C(14) -C(13)	1.398(10)
C(7) -C(6)	1.381(9)	C(15) -C(14)	1.369(9)
C(8) -C(7)	1.391(9)	C(16) -C(15)	1.384(8)
C(9) -C(8)	1.423(8)	C(17) -C(16)	1.417(8)
		C(19) -C(17)	1.500(8)

Estimated standard deviations are given in parentheses.

Interatomic distances for the hydrogen atoms (Å).

Atoms	Distance	Atoms	Distance
H(1A) -C(1)	0.907(42)	H(11B)-C(11)	1.090(58)
H(1B) -C(1)	0.787(39)	H(13) -C(13)	1.032(46)
H(3A) -C(3)	1.043(56)	H(14) -C(14)	1.227(60)
H(3B) -C(3)	0.931(57)	H(15) -C(15)	0.861(48)
H(5) -C(5)	1.032(51)	H(18A)-C(18)	1.014(36)
H(6) -C(6)	0.992(48)	H(18B)-C(18)	0.957(58)
H(7) -C(7)	1.124(41)	H(18C)-C(18)	1.074(47)
H(10A)-C(10)	0.852(53)	H(19A)-C(19)	0.900(40)
H(10B)-C(10)	1.115(45)	H(19B)-C(19)	1.221(65)
H(11A)-C(11)	0.877(44)	H(19C)-C(19)	1.040(40)

Estimated standard deviations are given in parentheses.

Formula	$(C_{19}H_{22}S_2)_2$
Formula Weight	314.5
$F(000)$	1152.00
Temperature(°C)	20
System	Triclinic
Space Group	$P1$
a	11.856(3)Å
b	14.904(4)Å
c	9.536(2)Å
α	83.37(3)°
β	86.62(3)°
γ	97.42(3)°
V	1655.2 Å
Z	4
D_c	1.262 g cm^{-3}
D_m	1.281 g cm^{-3}
Crystal dimensions	0.190 x 0.108 x 0.632(mm)
μ	2.67 cm^{-1}
Standards	004,600,060
2θ range	0 - 50
No. of reflections	5821
$I=1.5\sigma(I)$	3480
Radiation	Mo·K_α 0.71069Å
Max. shift/esd	2.5(H12), 1.6(H372) 0.06(C37), rest 0.3 or less
Residual electron density	0.36
R	0.0819
R_W	0.0775

Fractional atomic coordinates and temperature parameters.

Atom	x/a	y/b	z/c	Ueq
S(1)	-1783(17)	13191(12)	5059(17)	641(7)
S(2)	3310(19)	32626(12)	65255(18)	702(8)
C(1)	2233(11)	230(7)	2271(11)	85(4)
C(2)	2456(10)	1660(8)	6767(11)	77(4)
C(3)	-1176(7)	1580(6)	4254(9)	61(3)
C(11)	-184(8)	533(4)	2151(7)	57(3)
C(12)	496(5)	876(4)	3316(6)	44(2)
C(13)	1633(6)	714(4)	3368(7)	52(3)
C(14)	2210(7)	982(5)	4490(8)	57(3)
C(15)	1755(6)	1392(4)	5551(6)	48(2)
C(16)	629(5)	1568(4)	5500(5)	39(2)
C(17)	86(8)	2006(5)	6637(8)	62(3)
C(18)	10(5)	1322(4)	4350(5)	38(2)
C(21)	1328(6)	3657(5)	5009(7)	52(3)
C(22)	849(5)	3658(4)	3592(6)	45(2)
C(23)	49(6)	4203(4)	3173(8)	61(3)
C(24)	-382(7)	4183(5)	1875(9)	71(3)
C(25)	-102(6)	3537(5)	1009(7)	58(3)
C(26)	676(5)	2966(4)	1418(6)	42(2)
C(27)	982(6)	2253(4)	536(7)	52(3)
C(28)	1179(5)	3058(4)	2694(6)	38(2)
S(3)	50499(21)	35087(17)	44206(19)	916(10)
S(4)	58521(22)	17398(13)	-17052(22)	861(10)
C(4)	6941(8)	5483(6)	1924(11)	73(4)
C(5)	7339(8)	4057(7)	-2522(9)	68(3)
C(6)	4060(6)	2823(5)	1095(8)	57(3)
C(31)	4787(7)	4238(6)	2824(7)	60(3)
C(32)	5469(5)	4162(4)	1454(6)	44(2)
C(33)	6465(5)	4755(4)	1050(6)	44(2)
C(34)	7048(6)	4696(4)	-228(7)	51(2)
C(35)	6675(5)	4078(4)	-1126(6)	42(2)
C(36)	5691(5)	3475(4)	-723(5)	36(2)
C(37)	5245(7)	2796(5)	-1690(8)	54(3)
C(38)	5083(5)	3501(4)	597(6)	38(2)
C(41)	6953(7)	1764(6)	-452(7)	64(3)
C(42)	6559(5)	1621(4)	1047(7)	47(2)
C(43)	5971(7)	788(5)	1705(11)	78(4)
C(44)	5562(9)	685(7)	3076(11)	91(4)
C(45)	5706(7)	1395(7)	3845(9)	77(4)
C(46)	6273(5)	2239(4)	3262(6)	51(2)
C(47)	6387(7)	3061(5)	4051(8)	63(3)
C(48)	6723(5)	2326(4)	1872(6)	44(2)
H(11)	1906(91)	106(75)	1360(**)	165(47)'
H(12)	1954(**)	-828(98)	2533(**)	194(59)'
H(13)	2862(**)	629(89)	2092(**)	209(66)'
H(21)	3123(70)	1568(53)	6425(83)	74(33)'
H(22)	2710(97)	2321(81)	7208(**)	210(51)'
H(23)	2438(78)	1191(61)	7370(93)	145(39)'

H(31)	-1314(40)	1658(32)	3387(54)	21(14)'
H(32)	-1661(60)	1304(47)	4741(74)	70(26)'
H(33)	-1001(65)	2497(56)	4095(79)	127(27)'
H(111)	-996(51)	396(38)	2411(59)	49(19)'
H(112)	42(62)	-47(53)	1682(77)	108(27)'
H(141)	2950(52)	967(39)	4455(61)	51(20)'
H(171)	-919(74)	1805(54)	6356(82)	122(30)'
H(172)	245(50)	1841(39)	7364(60)	43(20)'
H(211)	2035(44)	3387(33)	5121(51)	31(15)'
H(212)	1698(45)	4308(38)	5093(53)	48(16)'
H(231)	-144(53)	4770(44)	3779(67)	78(21)'
H(241)	-998(53)	4490(40)	1530(61)	56(19)'
H(251)	-414(45)	3446(34)	146(57)	40(16)'
H(271)	1150(52)	2571(40)	-503(70)	72(20)'
H(272)	1671(57)	1874(45)	944(68)	74(23)'
H(281)	1740(40)	2635(32)	3011(48)	27(13)'
H(41)	6370(65)	5965(53)	2123(77)	108(27)'
H(42)	7903(64)	5822(45)	1533(69)	92(23)'
H(43)	6989(69)	5283(54)	2766(84)	99(33)'
H(51)	7702(70)	3648(55)	-2564(84)	99(36)'
H(52)	6980(60)	4251(48)	-3395(78)	86(26)'
H(53)	8107(63)	4726(50)	-2719(73)	100(24)'
H(61)	3247(56)	2999(40)	739(62)	64(19)'
H(62)	4033(79)	2694(63)	2135(99)	149(38)'
H(63)	4057(85)	2442(66)	249(99)	167(41)'
H(311)	4779(47)	4853(40)	2853(56)	53(18)'
H(312)	3835(78)	3904(57)	2876(86)	129(33)'
H(341)	7732(46)	5107(34)	-469(52)	37(15)'
H(371)	5418(49)	3026(39)	-2708(65)	61(19)'
H(372)	4577(73)	2603(55)	-1408(92)	77(33)'
H(411)	7302(44)	1280(36)	-727(52)	39(15)'
H(412)	7585(47)	2403(39)	-812(55)	51(17)'
H(431)	5894(52)	364(44)	1097(65)	61(21)'
H(441)	5251(64)	57(55)	3504(78)	103(27)'
H(451)	5463(64)	1405(49)	4755(81)	92(27)'
H(471)	6545(44)	2878(35)	5103(60)	48(16)'
H(472)	6864(50)	3616(40)	3560(61)	57(19)'
H(481)	7162(41)	2965(33)	1455(48)	33(14)'

Estimated standard deviations are given in parentheses.

Coordinates x 10^n where n = 5,5,4 for S,C,H

Temperature parameters x 10^n where n = 4,4,3 for S,C,H
U_{eq} = the equivalent isotropic temperature parameter.
$U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j (a_i \cdot a_j)$

Primed values indicate that U_{iso} is given

$T = \exp(-8\pi^2 U_{iso} \sin^2\theta/\lambda^2)$

Bond angles (°C)

Atoms			Angle
C(27)	-S(1)	-C(11)	107.4(3)
C(21)	-S(2)	-C(17)	106.3(4)
C(12)	-C(11)	-S(1)	117.3(4)
C(13)	-C(12)	-C(11)	118.7(6)
C(18)	-C(12)	-C(11)	121.4(6)
C(18)	-C(12)	-C(13)	119.8(6)
C(12)	-C(13)	-C(1)	123.2(7)
C(14)	-C(13)	-C(1)	119.3(8)
C(14)	-C(13)	-C(12)	117.6(6)
C(15)	-C(14)	-C(13)	124.5(7)
C(14)	-C(15)	-C(2)	121.1(7)
C(16)	-C(15)	-C(2)	120.5(7)
C(16)	-C(15)	-C(14)	118.4(6)
C(17)	-C(16)	-C(15)	120.7(6)
C(18)	-C(16)	-C(15)	119.0(5)
C(18)	-C(16)	-C(17)	120.3(6)
C(16)	-C(17)	-S(2)	118.3(5)
C(12)	-C(18)	-C(3)	121.1(6)
C(16)	-C(18)	-C(3)	118.3(6)
C(16)	-C(18)	-C(12)	120.6(6)
C(22)	-C(21)	-S(2)	116.1(5)
C(23)	-C(22)	-C(21)	122.4(6)
C(28)	-C(22)	-C(21)	119.0(6)
C(28)	-C(22)	-C(23)	118.4(6)
C(24)	-C(23)	-C(22)	121.1(7)
C(25)	-C(24)	-C(23)	120.1(7)
C(26)	-C(25)	-C(24)	119.8(7)
C(27)	-C(26)	-C(25)	121.4(6)
C(28)	-C(26)	-C(25)	118.6(6)
C(28)	-C(26)	-C(27)	119.9(6)
C(26)	-C(27)	-S(1)	113.4(5)
C(26)	-C(28)	-C(22)	121.5(6)
C(47)	-S(3)	-C(31)	107.2(4)
C(41)	-S(4)	-C(37)	106.9(4)
C(32)	-C(31)	-S(3)	118.0(6)
C(33)	-C(32)	-C(31)	119.8(6)
C(38)	-C(32)	-C(31)	119.9(5)
C(38)	-C(32)	-C(33)	120.3(5)
C(32)	-C(33)	-C(4)	123.4(6)
C(34)	-C(33)	-C(4)	117.9(6)
C(34)	-C(33)	-C(32)	118.7(6)
C(35)	-C(34)	-C(33)	122.8(6)
C(34)	-C(35)	-C(5)	120.3(6)
C(36)	-C(35)	-C(5)	120.7(6)
C(36)	-C(35)	-C(34)	119.0(5)
C(37)	-C(36)	-C(35)	120.5(5)
C(38)	-C(36)	-C(35)	119.9(5)
C(38)	-C(36)	-C(37)	119.6(5)

Atoms			Angle
C(36)	-C(37)	-S(4)	119.3(5)
C(32)	-C(38)	-C(6)	119.7(5)
C(36)	-C(38)	-C(6)	121.0(5)
C(36)	-C(38)	-C(32)	119.3(5)
C(42)	-C(41)	-S(4)	116.4(5)
C(43)	-C(42)	-C(41)	122.4(7)
C(48)	-C(42)	-C(41)	120.5(6)
C(48)	-C(42)	-C(43)	117.1(6)
C(44)	-C(43)	-C(42)	121.4(8)
C(45)	-C(44)	-C(43)	120.3(8)
C(46)	-C(45)	-C(44)	121.5(8)
C(47)	-C(46)	-C(45)	123.2(6)
C(48)	-C(46)	-C(45)	117.7(7)
C(48)	-C(46)	-C(47)	119.1(6)
C(46)	-C(47)	-S(3)	114.6(5)
C(46)	-C(48)	-C(42)	122.0(5)

Estimated standard deviations are given in parentheses.

Interatomic distances (Å)

Atoms	Distance
C(11) -S(1)	1.846(6)
C(27) -S(1)	1.829(7)
C(17) -S(2)	1.848(8)
C(21) -S(2)	1.805(7)
C(13) -C(1)	1.531(13)
C(15) -C(2)	1.526(13)
C(18) -C(3)	1.510(11)
C(12) -C(11)	1.509(10)
C(13) -C(12)	1.402(10)
C(18) -C(12)	1.388(8)
C(14) -C(13)	1.373(10)
C(15) -C(14)	1.361(10)
C(16) -C(15)	1.395(9)
C(17) -C(16)	1.485(10)
C(18) -C(1	1.412(8)
C(22) -C(21)	1.496(9)
C(23) -C(22)	1.374(10)
C(28) -C(22)	1.384(9)
C(24) -C(23)	1.369(11)
C(25) -C(24)	1.397(11)
C(26) -C(25)	1.377(10)
C(27) -C(26)	1.497(9)
C(28) -C(26)	1.399(8)
C(31) -S(3)	1.832(7)
C(47) -S(3)	1.828(9)
C(37) -S(4)	1.814(8)
C(41) -S(4)	1.821(8)
C(33) -C(4)	1.516(12)
C(35) -C(5)	1.512(10)
C(38) -C(6)	1.491(8)

Atoms	Distance
C(32) -C(31)	1.518(9)
C(33) -C(32)	1.387(8)
C(38) -C(32)	1.401(8)
C(34) -C(33)	1.384(9)
C(35) -C(34)	1.377(9)
C(36) -C(35)	1.383(7)
C(37) -C(36)	1.513(9)
C(38) -C(36)	1.420(8)
C(42) -C(41)	1.461(9)
C(43) -C(42)	1.402(9)
C(48) -C(42)	1.385(9)
C(44) -C(43)	1.352(14)
C(45) -C(44)	1.354(15)
C(46) -C(45)	1.385(11)
C(47) -C(46)	1.507(11)
C(48) -C(46)	1.385(8)

Estimated standard deviations are given in parentheses.

Interatomic distances for the hydrogen atoms (Å)

Atoms	Distance
H(11) -C(1)	0.998(16)
H(12) -C(1)	1.555(42)
H(13) -C(1)	0.887(21)
H(21) -C(2)	0.871(85)
H(22) -C(2)	1.129(22)
H(23) -C(2)	0.849(86)
H(31) -C(3)	0.850(52)
H(32) -C(3)	0.761(64)
H(33) -C(3)	1.345(83)
H(111)-C(11)	0.969(59)
H(112)-C(11)	1.074(82)
H(141)-C(14)	0.879(63)
H(171)-C(17)	1.244(87)
H(172)-C(17)	0.750(57)
H(211)-C(21)	0.981(55)
H(212)-C(21)	1.027(55)
H(231)-C(23)	1.117(70)
H(241)-C(24)	0.966(65)
H(251)-C(25)	0.939(56)
H(271)-C(27)	1.043(63)
H(272)-C(27)	1.115(71)
H(281)-C(28)	1.011(50)
H(41) -C(4)	1.073(84)
H(42) -C(4)	1.205(70)
H(43) -C(4)	0.831(79)
H(51) -C(5)	0.794(89)
H(52) -C(5)	0.987(75)
H(53) -C(5)	1.249(69)
H(61) -C(6)	1.094(68)
H(62) -C(6)	0.986(98)

Atoms	Distance
H(63) -C(6)	1.038(15)
H(311)-C(31)	0.922(61)
H(312)-C(31)	1.169(88)
H(341)-C(34)	0.951(49)
H(371)-C(37)	0.992(59)
H(372)-C(37)	0.825(82)
H(411)-C(41)	0.932(57)
H(412)-C(41)	1.139(52)
H(431)-C(43)	0.904(68)
H(441)-C(44)	0.992(75)
H(451)-C(45)	0.900(78)
H(471)-C(47)	1.043(57)
H(472)-C(47)	0.990(54)
H(481)-C(48)	1.046(45)

Estimated standard deviations are given in parentheses.

Formula	$C_{23}H_{23}FePF_6$
Formula Weight	500.24
$F(000)$	1023.96
Temperature(°C)	20
System	Monoclinic
Space Group	$P2_1/c$
a	11.636(2)Å
b	12.524(2)Å
c	14.681(3)Å
α	90°
β	90.69(2)°
γ	90°
V	2137.7 Å
Z	4
D_c	1.554 g cm^{-3}
D_m	1.555 g cm^{-3}
Crystal dimensions	0.94 x 0.42 x 0.36(mm)
μ	7.76 cm^{-1} (EMPABS)
Standards	600,060,008
2θ range	0 - 50
No. of reflections	2687
$I=3\sigma(I)$	2027
Radiation	Mo·K_α 0.71069Å
Max. shift/esd	0.166(H)
Residual electron density	0.74
R	0.0689
R_w	0.0746

Fractional atomic coordinates and temperature parameters.

Atom	x/a	y/b	z/c	Ueq
Fe(1)	34754(8)	42689(8)	21723(7)	536(4)
P(1)	69234(23)	22967(24)	333(17)	831(10)
F(1)	6897(8)	2376(6)	1087(4)	149(4)
F(2)	8049(8)	2979(7)	8(6)	184(5)
F(3)	7591(13)	1335(8)	102(6)	254(7)
F(4)	6999(7)	2230(7)	-1031(4)	151(4)
F(5)	6408(14)	3416(12)	-19(7)	312(9)
F(6)	5849(10)	1741(18)	60(7)	349(11)
C(19)	5061(11)	4107(12)	2759(17)	129(7)
C(20)	5173(9)	4363(15)	1851(14)	121(7)
C(21)	4654(12)	5324(15)	1700(10)	120(6)
C(22)	4231(9)	5686(9)	2496(15)	109(6)
C(23)	4463(13)	4951(18)	3164(8)	121(6)
C(1)	2298(11)	833(8)	1558(8)	104(5)
C(2)	3056(8)	1621(8)	1399(7)	81(4)
C(3)	2802(6)	2743(6)	1706(5)	57(3)
C(4)	2635(8)	3566(8)	1060(6)	72(4)
C(5)	2127(8)	4536(8)	1311(7)	77(4)
C(6)	1708(7)	4646(7)	2179(7)	71(4)
C(7)	1879(6)	3852(6)	2842(5)	56(3)
C(8)	2597(5)	2962(5)	2638(4)	46(2)
C(9)	1176(8)	3840(8)	3697(7)	79(4)
C(10)	156(10)	3132(9)	3602(10)	105(5)
C(11)	428(6)	1981(7)	3344(6)	69(3)
C(12)	558(8)	1202(9)	4018(7)	80(4)
C(13)	1047(8)	252(9)	3828(8)	82(4)
C(14)	1553(8)	88(7)	3008(9)	81(4)
C(15)	1453(7)	865(6)	2305(6)	69(3)
C(16)	719(6)	1729(6)	2450(5)	59(3)
C(17)	3117(7)	2282(6)	3388(6)	62(3)
C(18)	204(9)	2344(9)	1642(8)	95(4)
H(11)	2483(80)	13(25)	1382(65)	118(33)'
H(21)	3434(50)	1614(45)	868(43)	35(17)'
H(41)	2970(66)	3380(63)	515(63)	77(27)'
H(51)	2151(61)	5047(65)	858(56)	73(25)'
H(61)	1289(66)	5251(68)	2390(55)	77(24)'
H(91)	1158(77)	4600(77)	3978(65)	107(31)'
H(92)	1732(75)	3619(87)	4260(48)	134(41)'
H(101)	-247(99)	3027(86)	4261(80)	141(41)'
H(102)	-493(99)	3112(99)	3069(99)	305(99)'
H(121)	-5(73)	1334(75)	4523(63)	94(29)'
H(131)	950(67)	-324(70)	4356(61)	90(26)'
H(141)	1992(87)	-543(76)	2847(66)	106(33)'
H(171)	2660(56)	1607(36)	3663(49)	86(26)'
H(172)	3838(52)	1794(62)	3192(65)	120(34)'
H(173)	3444(79)	2867(56)	3866(50)	115(33)'
H(181)	-719(11)	2292(60)	1571(52)	80(24)'
H(182)	829(99)	1991(99)	1195(99)	226(74)'
H(183)	270(94)	3193(21)	1768(82)	146(44)'

Estimated standard deviations are given in parentheses.

Coordinates x 10^n where n = 5,5,4,4,4 for Fe,P,F,C,H

Temperature parameters x 10^n where n = 4,4,3,3,3 for Fe,P,F,C,H

U_{eq} = the equivalent isotropic temperature parameter.

$U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j (a_i \cdot a_j)$

Primed values indicate that U_{iso} is given

$T = \exp(-8\pi^2 U_{iso} \sin^2\theta/\lambda^2)$

Interatomic distances (Å)

Atoms		Distance
C(19)	-Fe(1)	2.038(10)
C(20)	-Fe(1)	2.039(10)
C(21)	-Fe(1)	2.032(9)
C(22)	-Fe(1)	2.033(10)
C(23)	-Fe(1)	2.032(10)
C(3)	-Fe(1)	2.171(7)
C(4)	-Fe(1)	2.087(9)
C(5)	-Fe(1)	2.031(8)
C(6)	-Fe(1)	2.110(8)
C(7)	-Fe(1)	2.175(7)
C(8)	-Fe(1)	2.050(7)
F(1)	-P(1)	1.552(6)
F(2)	-P(1)	1.564(8)
F(3)	-P(1)	1.435(8)
F(4)	-P(1)	1.568(6)
F(5)	-P(1)	1.525(11)
F(6)	-P(1)	1.431(8)
C(20)	-C(19)	1.379(20)
C(23)	-C(19)	1.402(20)
C(21)	-C(20)	1.363(18)
C(22)	-C(21)	1.352(18)
C(23)	-C(22)	1.369(19)
C(2)	-C(1)	1.345(13)
C(15)	-C(1)	1.483(14)
C(3)	-C(2)	1.506(11)
C(4)	-C(3)	1.411(11)
C(8)	-C(3)	1.418(9)
C(5)	-C(4)	1.400(13)
C(6)	-C(5)	1.377(13)
C(7)	-C(6)	1.403(11)

Atoms		Distance
C(8)	-C(7)	1.427(9)
C(9)	-C(7)	1.507(11)
C(17)	-C(8)	1.512(10)
C(10)	-C(9)	1.486(14)
C(11)	-C(10)	1.524(13)
C(12)	-C(11)	1.396(12)
C(16)	-C(11)	1.396(11)
C(13)	-C(12)	1.348(14)
C(14)	-C(13)	1.362(14)
C(15)	-C(14)	1.422(13)
C(16)	-C(15)	1.395(11)
C(18)	-C(16)	1.530(11)

Estimated standard deviations are given in parentheses.

Bond angles (°C)

Atoms			Angle
C(20)	-Fe(1)	-C(19)	39.6(6)
C(21)	-Fe(1)	-C(19)	66.3(5)
C(21)	-Fe(1)	-C(20)	39.1(5)
C(22)	-Fe(1)	-C(19)	66.5(5)
C(22)	-Fe(1)	-C(20)	65.6(5)
C(22)	-Fe(1)	-C(21)	38.9(5)
C(23)	-Fe(1)	-C(19)	40.3(6)
C(23)	-Fe(1)	-C(20)	66.5(5)
C(23)	-Fe(1)	-C(21)	66.0(5)
C(23)	-Fe(1)	-C(22)	39.4(6)
C(3)	-Fe(1)	-C(19)	111.6(5)
C(3)	-Fe(1)	-C(20)	108.9(4)
C(3)	-Fe(1)	-C(21)	134.9(6)
C(3)	-Fe(1)	-C(22)	173.7(5)
C(3)	-Fe(1)	-C(23)	142.6(7)
C(4)	-Fe(1)	-C(19)	134.6(8)
C(4)	-Fe(1)	-C(20)	106.8(5)
C(4)	-Fe(1)	-C(21)	108.6(5)
C(4)	-Fe(1)	-C(22)	138.4(7)
C(4)	-Fe(1)	-C(23)	173.3(5)
C(4)	-Fe(1)	-C(3)	38.6(3)
C(5)	-Fe(1)	-C(19)	165.6(7)
C(5)	-Fe(1)	-C(20)	126.1(7)
C(5)	-Fe(1)	-C(21)	101.5(5)
C(5)	-Fe(1)	-C(22)	109.3(6)
C(5)	-Fe(1)	-C(23)	143.4(8)
C(5)	-Fe(1)	-C(3)	71.0(3)
C(5)	-Fe(1)	-C(4)	39.7(4)
C(6)	-Fe(1)	-C(19)	153.[illegible](8)
C(6)	-Fe(1)	-C(20)	159.2(8)
C(6)	-Fe(1)	-C(21)	121.2(6)
C(6)	-Fe(1)	-C(22)	102.9(4)
C(6)	-Fe(1)	-C(23)	116.5(6)
C(6)	-Fe(1)	-C(3)	81.4(3)
C(6)	-Fe(1)	-C(4)	69.5(4)
C(6)	-Fe(1)	-C(5)	38.8(4)

Estimated standard deviations are given in parentheses.

Interatomic distances for the hydrogen atoms (Å)

Atoms	Distance
H(11) -C(1)	1.080(1)
H(21) -C(2)	0.900(60)
H(41) -C(4)	0.925(86)
H(51) -C(5)	0.923(83)
H(61) -C(6)	0.954(80)
H(91) -C(9)	1.037(96)
H(92) -C(9)	1.0[illegible]
H(101)-C(10)	1.[illegible](18)
H(102)-C(10)	1.0[illegible]1(11)
H(121)-C(12)	1.009(88)
H(131)-C(13)	1.066(90)
H(141)-C(14)	0.971(94)
H(171)-C(17)	1.080(1)
H(172)-C(17)	1.080(1)
H(173)-C(17)	1.080(1)
H(181)-C(18)	1.080(1)
H(182)-C(18)	1.080(4)
H(183)-C(18)	1.080(1)

Estimated standard deviations are given in parentheses.

Formula	$C_{25}H_{18}O_6Cr_2 \bullet \frac{1}{2}(CH_2Cl_2)$
Formula Weight	560.9
$F(000)$	557.97
Temperature(°C)	20
System	Triclinic
Space Group	$P\bar{1}$
a	11.514(5)Å
b	14.513(6)Å
c	7.854(2)Å
α	81.34(3)°
β	90.69(2)°
γ	111.61(4)°
V	1204.2Å
Z	2
D_c	1.547 g cm^{-3}
D_m	1.534 g cm^{-3}
Crystal dimensions	0.496 x 0.123 x 0.287(mm)
μ	9.83 cm^{-1} (ABSB02)
Standards	060,004,600
2θ range	0 - 50
No. of reflections	4246
$I \geq 3\sigma(I)$	3394
Radiation	Mo·K_α 0.71069Å
Max. shift/esd	0.122(H62) otherwise 0.07
Residual electron density	0.96
R	0.0631
R_w	0.0654

Fractional atomic coordinates and temperature parameters.

Atom	x/a	y/b	z/c	Ueq
Cr(1)	75955(7)	17596(6)	5744(10)	382(3)
Cr(2)	26586(6)	28580(6)	21707(9)	337(3)
Cl(1)	-11334(28)	46651(36)	58360(50)	1704(24)
C(17)	415(20)	4590(12)	5725(22)	213(12)
O(21)	3562(4)	4483(3)	4459(5)	62(2)
O(22)	469(4)	1915(4)	4407(5)	69(2)
O(23)	1412(4)	4122(4)	-61(6)	71(2)
O(31)	5785(4)	263(4)	-1568(5)	75(2)
O(32)	8622(7)	169(5)	2023(7)	114(4)
O(33)	9303(5)	2242(4)	-2314(7)	100(3)
C(21)	3233(4)	3852(4)	3572(6)	42(2)
C(22)	1304(4)	2284(4)	3531(6)	46(2)
C(23)	1883(5)	3622(4)	780(7)	47(2)
C(31)	6475(5)	835(4)	-725(7)	46(2)
C(32)	8225(7)	790(5)	1509(8)	68(3)
C(33)	8663(5)	2066(5)	-1176(8)	62(3)
C(1)	5708(5)	1386(4)	4280(7)	46(2)
C(2)	4628(5)	1515(4)	4496(7)	46(2)
C(3)	3944(4)	1952(4)	3086(6)	37(2)
C(4)	2764(4)	1314(4)	2469(7)	40(2)
C(4')	2030(7)	340(5)	3494(12)	61(3)
C(5)	2286(5)	1554(4)	817(7)	42(2)
C(6)	2998(4)	2387(4)	-274(6)	41(2)
C(6')	2534(8)	2537(8)	-2120(8)	65(4)
C(7)	4177(4)	3030(4)	361(6)	37(2)
C(8)	4549(4)	2882(4)	2138(6)	34(2)
C(8')	5654(5)	3675(5)	2948(10)	51(3)
C(9)	5081(5)	3689(4)	-940(7)	49(2)
C(10)	6158(5)	3570(4)	-1135(8)	52(2)
C(11)	6766(4)	2999(4)	111(7)	40(2)
C(12)	8067(5)	3402(4)	518(8)	50(2)
C(13)	8607(5)	3034(5)	2008(9)	54(2)
C(14)	7844(5)	2292(5)	3180(8)	49(2)
C(15)	6521(4)	1875(4)	2830(6)	39(2)
C(16)	6050(4)	2112(4)	1145(6)	34(2)
H(1)	6024(59)	922(49)	5224(86)	71(19)'
H(2)	4260(50)	1299(41)	5594(75)	52(16)'
H(5)	1483(50)	1152(39)	327(66)	42(14)'
H(9)	4818(47)	4124(39)	-1705(69)	42(14)'
H(10)	6580(57)	3911(46)	-2010(82)	61(18)'
H(12)	8557(47)	3999(40)	-5(64)	37(13)'
H(13)	9473(58)	3369(45)	2307(77)	61(17)'
H(14)	8225(54)	2125(43)	4275(78)	56(17)'
H(16)	5277(37)	1799(28)	796(47)	7(9)'
H(41)	2419(52)	-115(44)	3460(70)	46(15)'
H(42)	1303(95)	91(72)	2923(**)	129(39)'

H(43)	2040(67)	386(54)	4572(**)	76(25)'
H(61)	2944(60)	2318(48)	-2888(86)	65(19)'
H(62)	2658(64)	3140(54)	-2345(91)	63(25)'
H(63)	1731(80)	2141(59)	-2343(**)	91(27)'
H(81)	6229(73)	3534(57)	3018(**)	86(27)'
H(82)	5449(60)	3675(48)	4329(89)	71(19)'
H(83)	5742(52)	4212(45)	2559(75)	42(18)'

Estimated standard deviations are given in parentheses.

Coordinates x 10^n where n = 5,5,4,4,4 for Cr,Cl,O,C,H

Temperature parameters x 10^n where n = 4,4,3,3,3 for
Cr,Cl,O,C,H
U_{eq} = the equivalent isotropic temperature parameter.
$U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i \cdot a_j)$

Primed values indicate that U_{iso} is given

$T = \exp(-8\pi^2 U_{iso} \sin^2\theta / \lambda^2)$

Interatomic distances (Å)

Atoms	Distance
C(31) -Cr(1)	1.833(5)
C(32) -Cr(1)	1.836(8)
C(33) -Cr(1)	1.838(7)
C(11) -Cr(1)	2.297(6)
C(12) -Cr(1)	2.236(6)
C(13) -Cr(1)	2.192(6)
C(14) -Cr(1)	2.248(6)
C(15) -Cr(1)	2.327(6)
C(16) -Cr(1)	2.130(6)
C(21) -Cr(2)	1.831(6)
C(22) -Cr(2)	1.845(5)
C(23) -Cr(2)	1.837(6)
C(3) -Cr(2)	2.315(6)
C(4) -Cr(2)	2.265(6)
C(5) -Cr(2)	2.192(6)
C(6) -Cr(2)	2.250(6)
C(7) -Cr(2)	2.290(5)
C(8) -Cr(2)	2.167(5)
C(17) -Cl(1)	1.837(24)
C(17) -C(17)	1.954(42)
C(21) -O(21)	1.160(7)
C(22) -O(22)	1.156(6)
C(23) -O(23)	1.151(8)
C(31) -O(31)	1.151(7)
C(32) -O(32)	1.156(11)
C(33) -O(33)	1.158(9)
C(2) -C(1)	1.355(10)
C(15) -C(1)	1.475(7)
C(3) -C(2)	1.489(8)
C(4) -C(3)	1.416(6)
C(8) -C(3)	1.406(6)
C(4') -C(4)	1.511(8)
C(5) -C(4)	1.399(7)
C(6) -C(5)	1.406(7)
C(6') -C(6)	1.503(8)
C(7) -C(6)	1.422(6)
C(8) -C(7)	1.423(7)
C(9) -C(7)	1.498(7)
C(8') -C(8)	1.523(7)
C(10) -C(9)	1.341(10)
C(11) -C(10)	1.472(9)
C(12) -C(11)	1.412(7)
C(16) -C(11)	1.430(6)
C(13) -C(12)	1.393(9)
C(14) -C(13)	1.399(8)
C(15) -C(14)	1.430(7)
C(16) -C(15)	1.417(7)

Estimated standard deviations are given in parentheses.

Interatomic distances for the hydrogen atoms (Å)

Atoms	Distance
H(1) -C(1)	1.052(70)
H(2) -C(2)	0.960(58)
H(41) -C(4')	0.930(73)
H(42) -C(4')	0.882(95)
H(43) -C(4')	0.857(83)
H(5) -C(5)	0.968(48)
H(61) -C(6')	0.958(81)
H(62) -C(6')	0.827(78)
H(63) -C(6')	0.905(76)
H(81) -C(8')	0.756(95)
H(82) -C(8')	1.135(73)
H(83) -C(8')	0.766(63)
H(9) -C(9)	0.916(57)
H(10) -C(10)	0.863(60)
H(12) -C(12)	0.905(46)
H(13) -C(13)	0.955(58)
H(14) -C(14)	0.962(60)
H(16) -C(16)	0.872(37)

Estimated standard deviations are given in parentheses.

Bond angles (d).

Atoms	Angle	Atoms	Angle
C(32) -Cr(1) -C(31)	87.6(3)	C(5) -Cr(2) -C(21)	167.3(2)
C(33) -Cr(1) -C(31)	86.7(3)	C(5) -Cr(2) -C(22)	95.8(2)
C(33) -Cr(1) -C(32)	87.9(3)	C(5) -Cr(2) -C(23)	104.7(2)
C(11) -Cr(1) -C(31)	100.8(2)	C(5) -Cr(2) -C(3)	65.3(2)
C(11) -Cr(1) -C(32)	165.8(3)	C(5) -Cr(2) -C(4)	36.6(2)
C(11) -Cr(1) -C(33)	104.0(3)	C(6) -Cr(2) -C(21)	143.8(2)
C(12) -Cr(1) -C(31)	132.3(2)	C(6) -Cr(2) -C(22)	128.8(2)
C(12) -Cr(1) -C(32)	139.4(2)	C(6) -Cr(2) -C(23)	86.4(2)
C(12) -Cr(1) -C(33)	87.1(3)	C(6) -Cr(2) -C(3)	76.2(2)
C(12) -Cr(1) -C(11)	36.3(2)	C(6) -Cr(2) -C(4)	65.4(2)
C(13) -Cr(1) -C(31)	166.5(3)	C(6) -Cr(2) -C(5)	36.9(2)
C(13) -Cr(1) -C(32)	104.9(3)	C(7) -Cr(2) -C(21)	109.7(2)
C(13) -Cr(1) -C(33)	98.7(3)	C(7) -Cr(2) -C(22)	161.0(2)
C(13) -Cr(1) -C(11)	66.0(2)	C(7) -Cr(2) -C(23)	97.8(2)
C(13) -Cr(1) -C(12)	36.7(2)	C(7) -Cr(2) -C(3)	63.7(2)
C(14) -Cr(1) -C(31)	141.0(2)	C(7) -Cr(2) -C(4)	76.5(2)
C(14) -Cr(1) -C(32)	89.5(3)	C(7) -Cr(2) -C(5)	66.0(2)
C(14) -Cr(1) -C(33)	132.0(2)	C(7) -Cr(2) -C(6)	36.5(2)
C(14) -Cr(1) -C(11)	76.7(2)	C(8) -Cr(2) -C(21)	89.5(2)
C(14) -Cr(1) -C(12)	65.2(2)	C(8) -Cr(2) -C(22)	138.8(2)
C(14) -Cr(1) -C(13)	36.7(2)	C(8) -Cr(2) -C(23)	129.1(2)
C(15) -Cr(1) -C(31)	106.9(2)	C(8) -Cr(2) -C(3)	36.4(2)
C(15) -Cr(1) -C(32)	102.4(3)	C(8) -Cr(2) -C(4)	66.8(2)
C(15) -Cr(1) -C(33)	163.0(2)	C(8) -Cr(2) -C(5)	80.3(2)
C(15) -Cr(1) -C(11)	64.2(2)	C(8) -Cr(2) -C(6)	67.5(2)
C(15) -Cr(1) -C(12)	76.3(2)	C(8) -Cr(2) -C(7)	37.1(2)
C(15) -Cr(1) -C(13)	65.9(2)	O(21) -C(21) -Cr(2)	178.1(5)
C(15) -Cr(1) -C(14)	36.4(2)	O(22) -C(22) -Cr(2)	178.6(5)
C(16) -Cr(1) -C(31)	86.9(2)	O(23) -C(23) -Cr(2)	178.1(5)
C(16) -Cr(1) -C(32)	133.1(2)	O(31) -C(31) -Cr(1)	178.7(5)
C(16) -Cr(1) -C(33)	138.1(3)	O(32) -C(32) -Cr(1)	176.9(6)
C(16) -Cr(1) -C(11)	37.4(2)	O(33) -C(33) -Cr(1)	177.7(5)
C(16) -Cr(1) -C(12)	67.6(2)	C(15) -C(1) -C(2)	125.1(5)
C(16) -Cr(1) -C(13)	80.8(2)	C(3) -C(2) -C(1)	123.2(5)
C(16) -Cr(1) -C(14)	67.4(2)	C(2) -C(3) -Cr(2)	150.4(4)
C(16) -Cr(1) -C(15)	36.7(2)	C(4) -C(3) -Cr(2)	70.1(3)
C(22) -Cr(2) -C(21)	87.0(2)	C(4) -C(3) -C(2)	117.5(4)
C(23) -Cr(2) -C(21)	87.6(3)	C(8) -C(3) -Cr(2)	66.1(3)
C(23) -Cr(2) -C(22)	91.7(2)	C(8) -C(3) -C(2)	121.2(4)
C(3) -Cr(2) -C(21)	102.0(2)	C(8) -C(3) -C(4)	119.8(4)
C(3) -Cr(2) -C(22)	104.9(2)	C(3) -C(4) -Cr(2)	73.9(3)
C(3) -Cr(2) -C(23)	161.1(2)	C(4') -C(4) -Cr(2)	132.4(5)
C(4) -Cr(2) -C(21)	131.9(2)	C(4') -C(4) -C(3)	122.1(5)
C(4) -Cr(2) -C(22)	85.7(2)	C(5) -C(4) -Cr(2)	68.9(3)
C(4) -Cr(2) -C(23)	140.1(2)	C(5) -C(4) -C(3)	119.5(4)
C(4) -Cr(2) -C(3)	36.0(2)	C(5) -C(4) -C(4')	118.3(5)

C(4)	-C(5)	-Cr(2)	74.5(3)
C(6)	-C(5)	-Cr(2)	73.8(3)
C(6)	-C(5)	-C(4)	120.7(4)
C(5)	-C(6)	-Cr(2)	69.3(3)
C(6')	-C(6)	-Cr(2)	132.7(6)
C(6')	-C(6)	-C(5)	119.1(5)
C(7)	-C(6)	-Cr(2)	73.3(3)
C(7)	-C(6)	-C(5)	119.3(4)
C(7)	-C(6)	-C(6')	121.5(5)
C(6)	-C(7)	-Cr(2)	70.2(3)
C(8)	-C(7)	-Cr(2)	66.7(3)
C(8)	-C(7)	-C(6)	119.2(4)
C(9)	-C(7)	-Cr(2)	148.0(5)
C(9)	-C(7)	-C(6)	117.4(4)
C(9)	-C(7)	-C(8)	122.0(4)
C(3)	-C(8)	-Cr(2)	77.5(3)
C(7)	-C(8)	-Cr(2)	76.2(3)
C(7)	-C(8)	-C(3)	118.4(4)
C(8')	-C(8)	-Cr(2)	121.2(5)
C(8')	-C(8)	-C(3)	120.7(4)
C(8')	-C(8)	-C(7)	120.7(4)
C(10)	-C(9)	-C(7)	122.2(5)
C(11)	-C(10)	-C(9)	125.9(5)
C(10)	-C(11)	-Cr(1)	146.8(4)
C(12)	-C(11)	-Cr(1)	69.5(4)
C(12)	-C(11)	-C(10)	120.2(4)
C(16)	-C(11)	-Cr(1)	65.0(3)
C(16)	-C(11)	-C(10)	121.5(4)
C(16)	-C(11)	-C(12)	117.5(5)
C(11)	-C(12)	-Cr(1)	74.2(3)
C(13)	-C(12)	-Cr(1)	69.9(4)
C(13)	-C(12)	-C(11)	121.3(5)
C(12)	-C(13)	-Cr(1)	73.4(4)
C(14)	-C(13)	-Cr(1)	73.8(4)
C(14)	-C(13)	-C(12)	119.7(5)
C(13)	-C(14)	-Cr(1)	69.4(4)
C(15)	-C(14)	-Cr(1)	74.8(3)
C(15)	-C(14)	-C(13)	120.7(5)
C(1)	-C(15)	-Cr(1)	149.7(4)
C(14)	-C(15)	-Cr(1)	68.8(3)
C(14)	-C(15)	-C(1)	119.0(4)
C(16)	-C(15)	-Cr(1)	64.1(3)
C(16)	-C(15)	-C(1)	122.9(4)
C(16)	-C(15)	-C(14)	117.2(4)
C(11)	-C(16)	-Cr(1)	77.6(3)
C(15)	-C(16)	-Cr(1)	79.2(4)
C(15)	-C(16)	-C(11)	119.4(4)

Estimated standard deviations are given in parentheses.

Bond angles involving H atoms (°C)

Atoms			Angle
H(1)	-C(1)	-C(2)	118.9(39)
H(1)	-C(1)	-C(15)	116.0(39)
H(2)	-C(2)	-C(1)	119.5(39)
H(2)	-C(2)	-C(3)	117.3(38)
H(41)	-C(4')	-C(4)	108.4(32)
H(42)	-C(4')	-C(4)	107.1(59)
H(42)	-C(4')	-H(41)	104.3(86)
H(43)	-C(4')	-C(4)	113.1(45)
H(43)	-C(4')	-H(41)	104.2(69)
H(43)	-C(4')	-H(42)	118.9(85)
H(5)	-C(5)	-Cr(2)	126.2(40)
H(5)	-C(5)	-C(4)	123.4(29)
H(5)	-C(5)	-C(6)	115.8(29)
H(61)	-C(6')	-C(6)	112.0(41)
H(62)	-C(6')	-C(6)	106.2(49)
H(62)	-C(6')	-H(61)	111.7(66)
H(63)	-C(6')	-C(6)	113.8(49)
H(63)	-C(6')	-H(61)	99.7(72)
H(63)	-C(6')	-H(62)	113.5(78)
H(81)	-C(8')	-C(8)	110.0(58)
H(82)	-C(8')	-C(8)	108.4(29)
H(82)	-C(8')	-H(81)	105.2(71)
H(83)	-C(8')	-C(8)	114.2(41)
H(83)	-C(8')	-H(81)	116.1(70)
H(83)	-C(8')	-H(82)	101.9(61)
H(9)	-C(9)	-C(7)	116.7(34)
H(9)	-C(9)	-C(10)	120.6(35)
H(10)	-C(10)	-C(9)	117.4(50)
H(10)	-C(10)	-C(11)	116.3(48)
H(12)	-C(12)	-Cr(1)	141.9(42)
H(12)	-C(12)	-C(11)	121.8(35)
H(12)	-C(12)	-C(13)	115.2(32)
H(13)	-C(13)	-Cr(1)	133.2(46)
H(13)	-C(13)	-C(12)	119.0(35)
H(13)	-C(13)	-C(14)	120.5(35)
H(14)	-C(14)	-Cr(1)	133.9(44)
H(14)	-C(14)	-C(13)	117.8(31)
H(14)	-C(14)	-C(15)	121.1(32)
H(16)	-C(16)	-Cr(1)	123.9(32)
H(16)	-C(16)	-C(11)	118.1(24)
H(16)	-C(16)	-C(15)	121.4(23)

Estimated standard deviations are given in parentheses.