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ALKYLATION AND OXIDATIONS OF SYMMETRICAL DIMETHYLENEBIPHENYL AND RELATED DIANIONS

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ALKYLATION AND OXIDATIONS OF SYMMETRICAL DIMETHYLENEBIPHENYL AND RELATED DIANIONS

by

James Jeffrey White

A Dissertation Submitted to the Faculty of the

DEPARTMENT OF CHEMISTRY

In Partial Fulfillment of the Requirements
For the Degree of

Doctor of Philosophy

In the Graduate College

THE UNIVERSITY OF ARIZONA

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GRADUATE COLLEGE

As members of the Final Examination Committee, we certify that we have read the dissertation prepared by James Jeffrey White

entitled ALKYLATION AND OXIDATIONS OF SYMMETRICAL DIMETHYLENEBIPHENYL AND RELATED DIANIONS

and recommend that it be accepted as fulfilling the dissertation requirement for the Degree of Doctor of Philosophy.

	6/19/86 Date
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Final approval and acceptance of this dissertation is contingent upon the candidate's submission of the final copy of the dissertation to the Graduate College.

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SIGNED James J. White

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Abstract

Bis-benzyl dianions were prepared from the three symmetrical dimethylbiphenyls in yields of 79-86%, and shown to react with a variety of electrophiles on the benzylic carbons. Electrophiles included dimethyl and diethyl sulfate, isopropyl bromide, t-butyl iodide, allyl chloride, trimethylsilyl chloride, trimethylgermyl bromide, and trimethyltin chloride. Reaction of the dianions with α,ω-dihalides provides an excellent route to [n.0]-and [n.0.n.0]cyclophanes. An X-ray study on [14.0]paracyclophane showed it to have a conformation different from that observed in solution by NMR; MM2 calculations were used in determining what the solution conformation is likely to be. Oxidation of the dianions produced the monomer dihydrophenanthrene from the ortho isomer, dimer [2.0.2.0]metacyclophane from the meta isomer, and polymer from the para isomer. An X-ray study on [2.0.2.0]metacyclophane showed it to have the same conformation in the crystal as is observed in solution by NMR. An NMR method for determining the angle of twist in a biphenyl based on the chemical shift of the ortho hydrogens was developed.

Many oxidizing agents were evaluated for the oxidation of the dianion from 2,3-dimethyl-1,3-butadiene to 1,2,5,6-tetramethylenecyclooctane; cupric bromide was found to be the best.

It was discovered that zinc and cadmium enolates can act as vinyl cation equivalents in their reaction with carbanions; other metals tried gave none of this reaction.

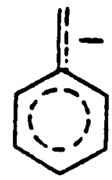
The primary-tertiary allyl anion obtained by adding *n*-butyllithium to 2,3-dimethyl-1,3-butadiene was shown to react quantitatively with ethylene at the tertiary carbon, confirming a postulated step in a complex mechanism proposed earlier.

CHAPTER 1

INTRODUCTION

Allylic and benzylic anions, characterized by having an all carbon skeleton with delocalization of charge, are known to be excellent synthons [1]. The simplest examples are allyl anion 1 and benzyl anion 2 [2,3].

1



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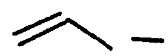
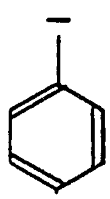
This charge delocalization can be visualized through resonance structures 1a and 1b for allyl anion and resonance structures 2a-e for benzyl anion.

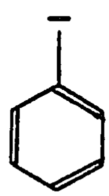
1a



1b



2a



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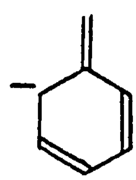

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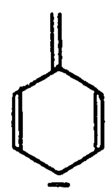

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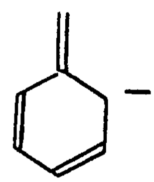


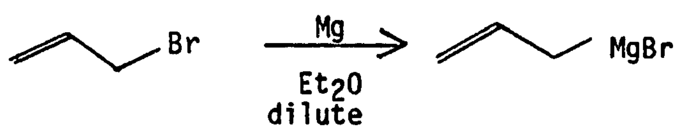
2e

A number of general methods have been developed to synthesize these anions[4,5]. Each will be discussed briefly. The method we used, proton abstraction, will be discussed last and in greater detail.

The oldest general method is the reduction of organic halides to metal salts of carbanions:

$$RX + 2M \longrightarrow RM + MX$$

All Group I and Group II metals as well as zinc metal will reduce halides to carbanions. Lithium, magnesium and zinc metals are the most often employed, because in the case of the other metals Wurtz coupling is a major side reaction. Grignard reagent preparations are the best known examples of this type of reaction, with ethers usually required as solvents. When benzylic and allylic Grignard reagents are prepared, careful control of the reaction conditions is necessary to avoid Wurtz coupling[6].

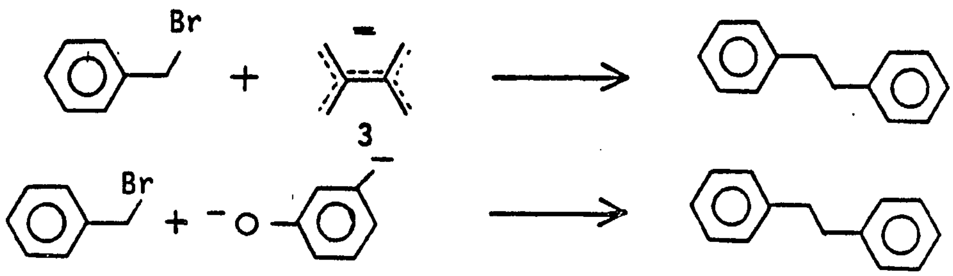


Lithium metal reacts with organic halides without ether solvents; however, preparation of allyllithium and benzyllithium by this route leads to Wurtz coupling[7]. Nevertheless, the reaction of lithium metal with allyl phenyl ether generates allyllithium and lithium phenoxide in good yield[8].

The reaction of organometallics with organic halides creates an equilibrium involving halogen metal exchange, favoring the more stable carbanion:

$$RX + R'M \rightleftharpoons RM + R'X$$

This method is generally used to prepare vinyllithiums and aryllithiums. Benzyl anion is probably an intermediate in the production of bibenzyl in the reactions of benzyl chloride and benzyl bromide with 2,3-dimethylenebutadiene dianion(3)[9,10] and the cresol dianions[11]:

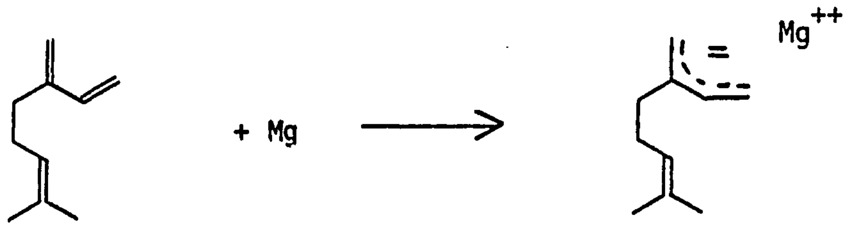


Whether the halogen-metal exchange is concerted or via single electron transfer (SET) is open to question [12,13]. The author favors the SET route in the cases involving allylic and benzylic anions, citing CIDNP evidence in the reactions of alkyllithiums with alkyl and benzyl halides[14,15].

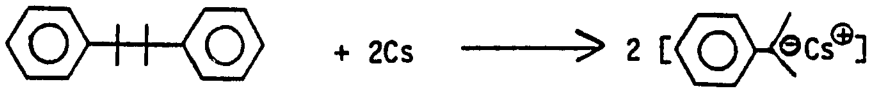
Another general route to allylic and benzylic anions is the reduction of unsaturated compounds with active metals:

$$>C=C< \; + 2M \longrightarrow M-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-M$$

This method involves the reduction of a π-system[16], sometimes with cleavage of a σ-bond[17,18]:



$$(Ph_2CH)_2 + 2K \longrightarrow 2[Ph_2CH^{\ominus}\ K^{\oplus}]$$



Transmetalation is another method to generate allylic and benzylic anions:

$$RM + M' \longrightarrow RM' + M$$

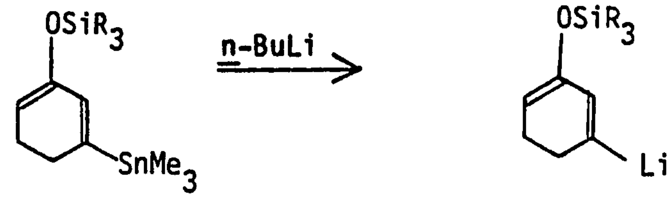
These reactions usually involve organomercury or organic Group IV compounds reacting with Group I metals. An example is the generation of benzyllithium from dibenzylmercury and lithium:

$$(PhCH_2)_2Hg + 2Li \longrightarrow 2PhCH_2Li + Hg$$

Metal exchange involving two organometallics is another way to prepare allyl anions:

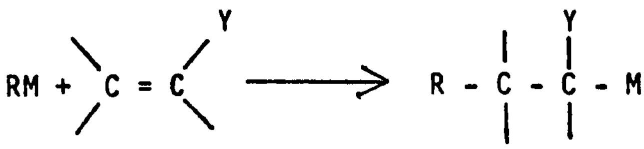
$$RM + R'M' \rightleftharpoons RM' + R'M$$

This method most commonly involves the reaction of organotin compounds with organolithiums[19] as shown in the example below.

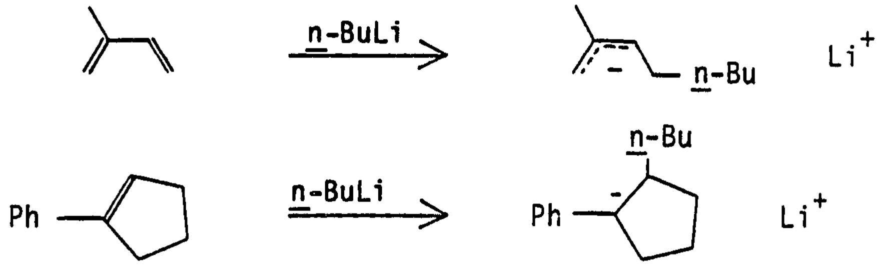


Similarly, allyl anions may be generated in situ for reaction with carbonyl compounds by reacting tetrabutylammonium fluoride with allyltrimethylsilane[20]. Instead of a metal ion the gegenion is a quaternary ammonium ion:

Addition of a carbanion to a conjugated system can result in the formation of a new stabilized carbanion:



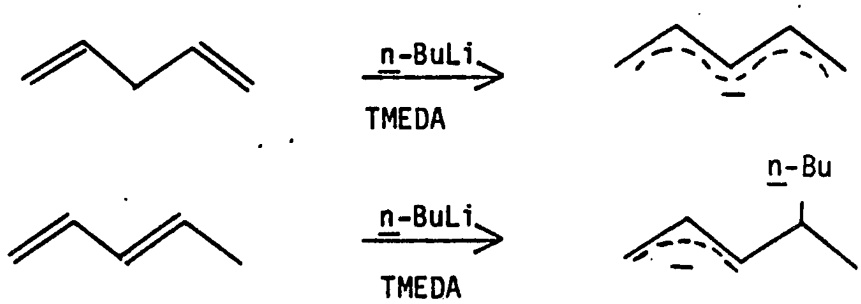
The addition of organolithiums to conjugated olefins and styrenes yields allylic and benzylic anions respectively[21,22,23].



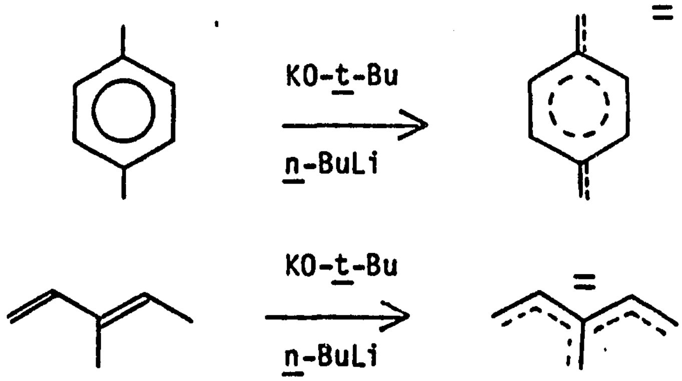
The most important method of allylic and benzylic anion generation is proton abstraction from the parent hydrocarbon:

$$RH + R'M \longrightarrow RM + R'H$$

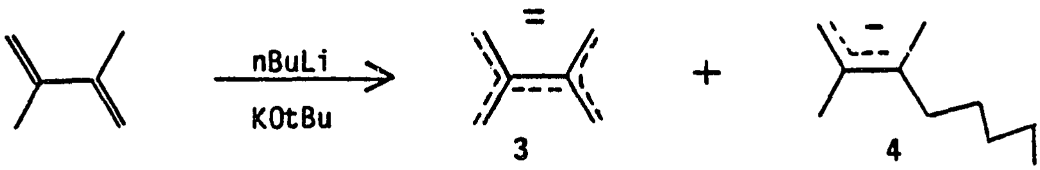
Unstabilized carbanions such as butyllithiums are generally used in proton abstractions of this sort. However, n-butyllithium by itself generally does not metalate these hydrocarbons. Although this process is favored thermodynamically, it is not kinetically. The use of N,N,N,N-tetramethylethylenediamine (TMEDA) with n-butyllithium, with the lithium cation coordinated to the diamine, results in a base capable of metalating benzylic and non-conjugated allylic systems. Reaction of n-butyllithium and TMEDA with conjugated olefins results in the addition of butyl anion to give substituted allyl anions[21,22]:



Activation of n-butyllithium with tertiary alkoxides gives even more potent metalating systems. Lochmann's base (n-butyllithium/potassium t-butoxide in an alkane solvent) readily generates benzylic and allylic anions including those from conjugated olefins[10,24,25,26,27]. Lochmann's base also reacts much faster than n-butyllithium/TMEDA, requiring reaction times of often under two hours versus days or even weeks. This is an especially good method for dianions [10,24,27].

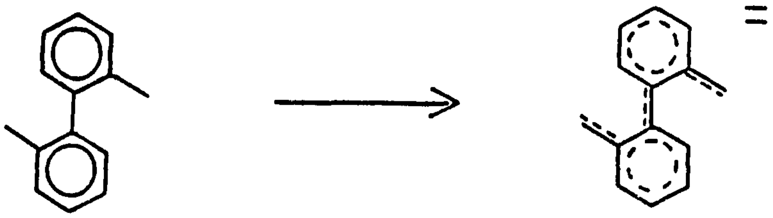


This metalating system was therefore the primary choice for generating the dianions of interest in this work. 2,3-Dimethylenebutadiene dianion 3 was generated from 2,3-dimethyl-1,3-butadiene in approximately 80% yield from this method with monoanion 4 being formed in ~12% yield as a result of addition as a side reaction[9,10,24].



3 4

It was expected that the three symmetrical dimethylenebiphenyl dianions (5-7) could be easily prepared in this manner from the corresponding dimethylbiphenyls (8-10). Dianion 5 has recently been prepared from 8 by Raston and coworkers using n-butyllithium and TMEDA; the analogous difunctional Grignard reagent was also generated in the same study[28,29].



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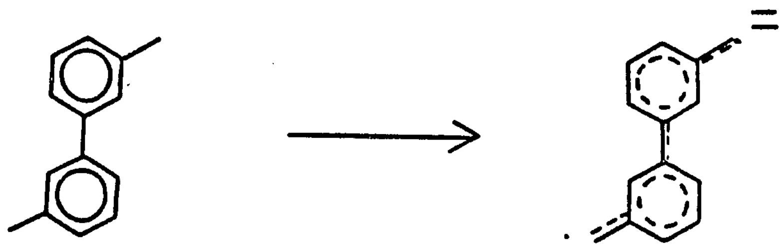

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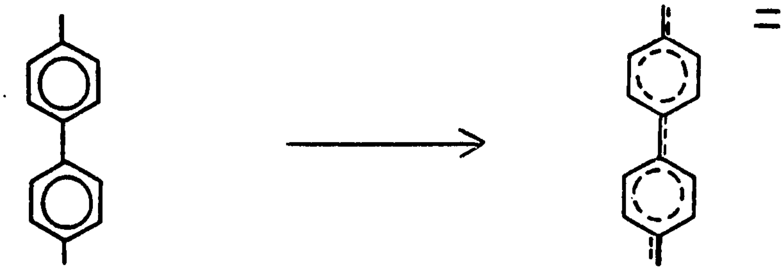


10 7

The relative stabilities of a number of allylic and benzylic anions have been calculated[30]. These have been expressed in terms of resonance energy per atom (REPA). The REPA's of mono- and dianions are given in Table 1 with units in terms of the Huckel parameter β.

Dianions 3 [10,24], 16 and 17 [21] can be thought of as two allyl anions, linked through a σ bond, middle to middle (3), end to end (16), and middle to end (17). Relative to allyl anion (1), the stability of these dianions is a function of the degree of π-delocalization across this bond. Dianions 3 and 17 are more stable than 1, while dianion 16 is less stable than 1.

Symmetrical dimethylenebiphenyl dianions 5-7 can be considered analogous to xylylene dianions 22-24. Dianions 5-7 are more stable than the ortho- (22) or para-xylylene (24) dianions, but less stable than the meta isomer (23). In the case of the xylylene dianions the meta

Table 1. REPA's of Selected Carbanions (in β units)

Monoanions:

1

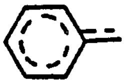
0.055

11

0.053

12

0.133



2

0.092[a]

13

0.039

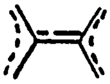
Dianions:

14
0.068

15
-0.040

16
0.028

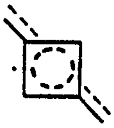
17
0.065



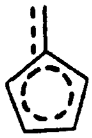
3
0.062

18
0.010

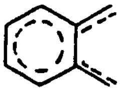
19
-0.035



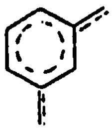
20
0.032



21
0.092

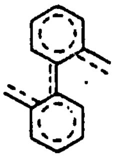


22
0.065

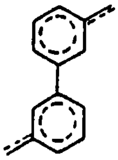


23
0.077

24
0.061



5
0.068[a]



6
0.067[a]

7
0.070[a]

[a] [31]

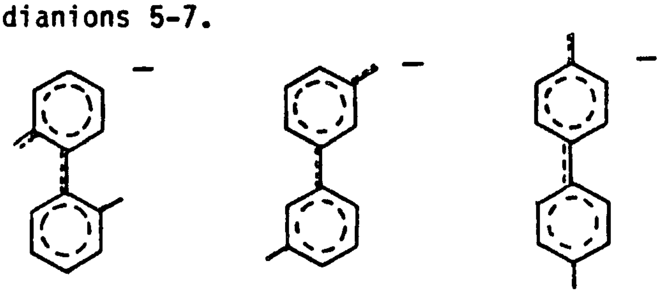
isomer (23) is the most stable while the para isomer (24) is the least stable. The opposite is calculated to be true of 5-7: The para isomer (7) is the most stable, while the meta isomer (6) is the least stable; the meta isomer is calculated to have very little π-delocalization across the σ-bond connecting the two phenyl rings. The differences in energy among 5-7 are, however, calculated to be quite small.

REPA's can only be used to make qualitative comparisions in the stabilities of these anions. For example, cyclopentadienyl anion, 12, which has an REPA of 0.133β and benzyl anion, 3, which has an REPA of 0.092β have pKa values of 16.25 and 41.2 as cesium salts in cyclohexylamine (CHA)[32,33]. Thermodynamic acidities of cesium and lithium salts measured in CHA match up very well with those measured in THF [34]. Allyl anion, 1, is approximately 2-3 pK units less acidic than 2 [35,36], but has an REPA of only 0.055. Clearly there is not a good correlation between REPA's and thermodynamic acidies. Nevertheless, these anions and dianions have pK values in the range of 36 to 46 where only a few quantitative determinations have been made. The REPA's provide at least a basis for qualitative comparison of the stabilities and hence the reactivities of these anions and dianions.

Formation of 3 must proceed via intermediate monoanion 25. However, when one equivalent of base is reacted with 2,3-dimethyl-1,3-butadiene, no monoanion 25 is found, but instead half an equivalent of dianion 3 is formed. Monoanion 25 is very similar to isoprene anion 13 and would be expected to have an REPA very close to that of 13 for its π-system. In terms of REPA dianion 3 is 0.024β more stable than monoanion 25, and would be expected to disproportionate to the parent diene and dianion 3 before it could build up to high concentrations. This is consistent with what is observed[9,10,24].

25

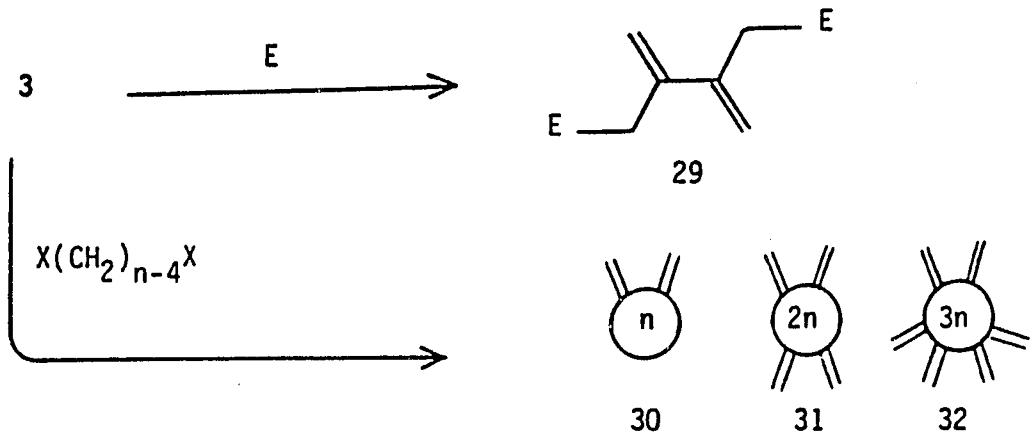
Dianions 5-7 are calculated to be considerably less stable than benzyl anion 2. Monoanions 26-28 would be expected to be even more stable than 2 due to increased π-delocalization and the absence of destabilizing coulombic interactions present in the dianions. The pKa of p-methylbiphenyl has been measured to be 38.57 in THF as its cesium salt[34] and the pKa of m-methylbiphenyl has been measured to be 39.95 as a lithium salt in CHA (p-methylbiphenyl's pKa = 38.73 as Li salt in CHA while toluene's pKa is 40.91[33]). Unlike 25, monoanions 26-28 would be expected to form in high concentrations before further metalation to dianions 5-7.



26 27 28

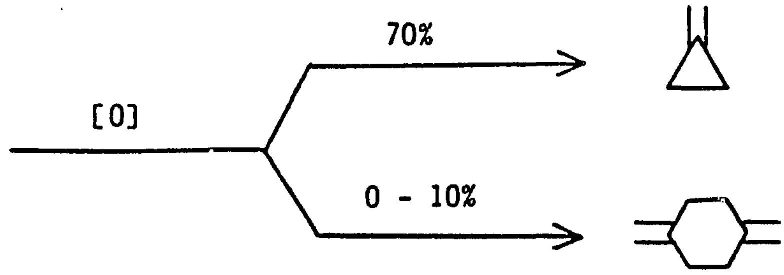
Dianion 3 has been reacted with numerous electrophiles to give symmetrical 2,3-disubstituted-1,3-butadienes (29) in good yield

[9,10,22,24]. 3 has also been reacted with α,ω-dihaloalkanes generating 1,2-dimethylenecycloalkanes (30), dimers (31), and trimers (32)[9,10,22].



Oxidation of dianion 3 would be expected to produce 1,2-dimethylenecyclobutane, 30,n=4, high yield analogously to the oxidation of isobutylene dianion 14 to methylenecyclopropane 33 in 70% yield [37], possibly accompanied by dimeric product 31,n=4. Oxidation of 14 under a variety of conditions gave a maximum of 10% yield of the analogous dimer 34[37,38]. 31,n=4 was isolated as a side product in varying yields from reactions of dianion 3 with t-butyl bromide, t-butyl iodide, dibromomethane, and 1,3-dibromopropane, but surprisingly not from 1,2-dibromoethane[9,10]. 30,n=4 has not been found in any of the reactions involving dianion 3. We wished to investigate the reactions of 3 with various oxidizing agents to be able to generate 30,n=4 and/or 31,n=4 in high yield.

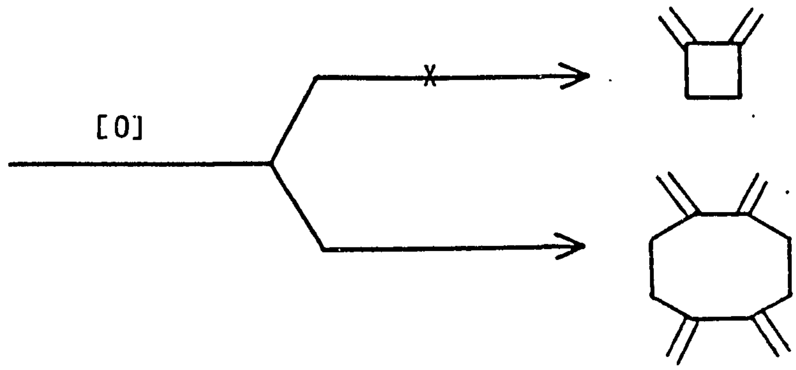
14



33

34

3



30,n=4

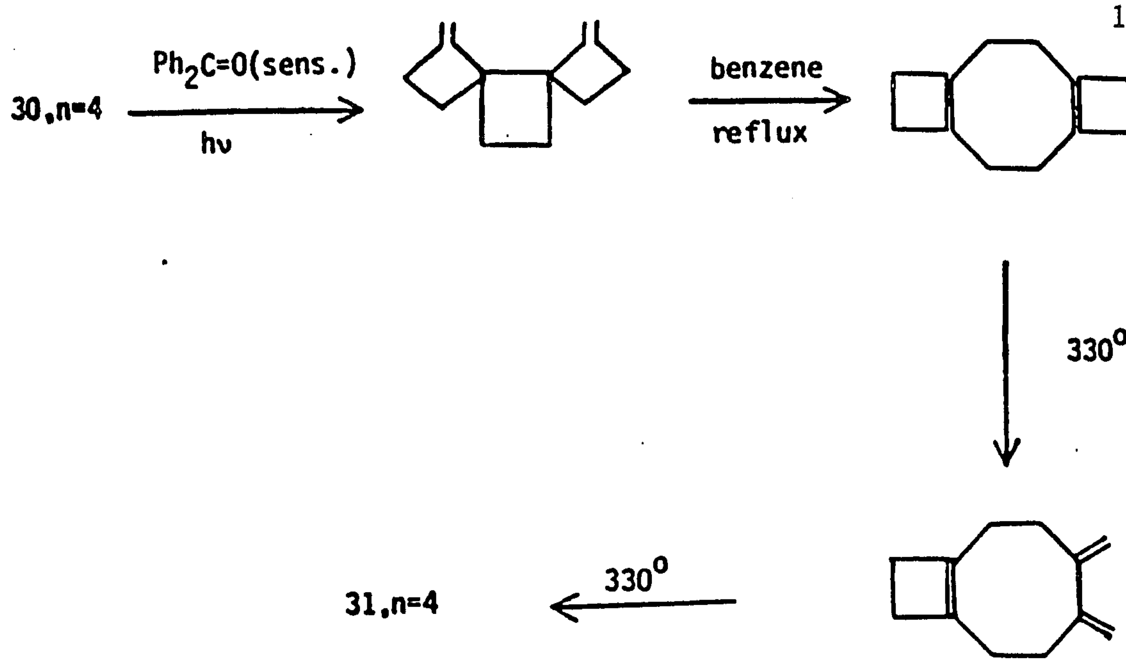
31,n=4

30,n=4 has long been known (along with its 1,3-isomer 35) as a dimer of allene 36 [39,40].

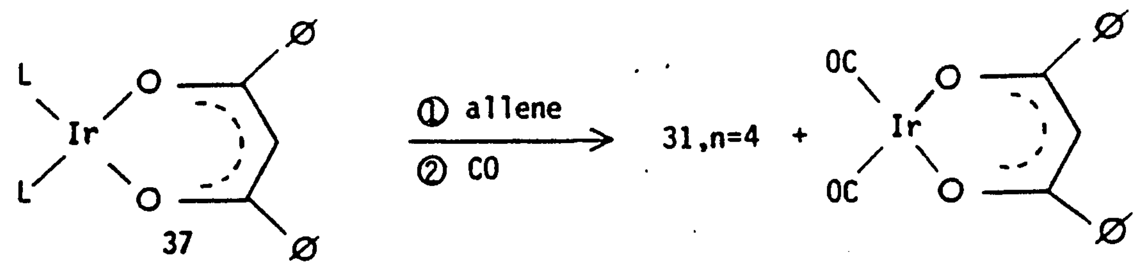
35

36

1,2,5,6-Tetramethylenecyclooctane, 31,n=4, had been sought as a precursor to [2.2.2]propellane[41,42]. 31,n=4 has been prepared by the dimerization of 30,n=4 in 51% yield using the following scheme[41,43]:

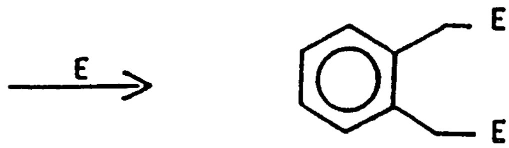


31,n=4 has also been generated in very good yield by the reaction of allene with organo-iridium complex 37 and subsequent reaction with carbon monoxide [44,45]. The rhodium complex has also been reacted in the same way to form 31,n=4 [46].

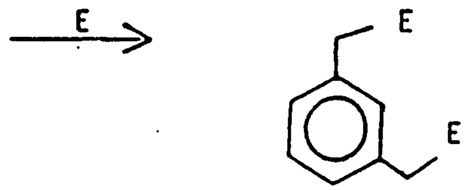


L = cyclooctene

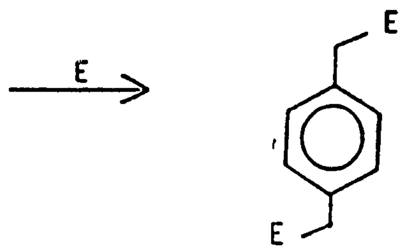
Xylylene dianions (22-24) have been reacted with various electrophiles to create symmetrically disubstituted benzenes (38-40) in good yields [27,47].

22 

38

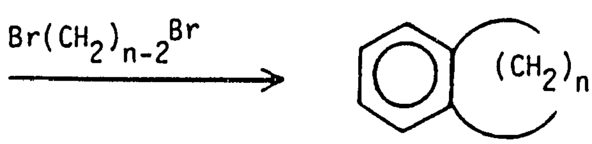
23 

39

24 

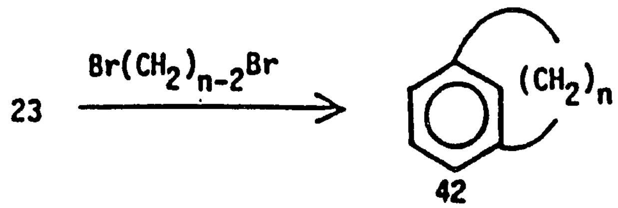
40

Dianions 22-24 have also been reacted with α,ω-dibromoalkanes to generate the corresponding ortho-, meta- and para-[n]-cyclophanes (41-43) in low to moderate yields [27,47]. These syntheses of cyclophanes were superior to previous literature syntheses.

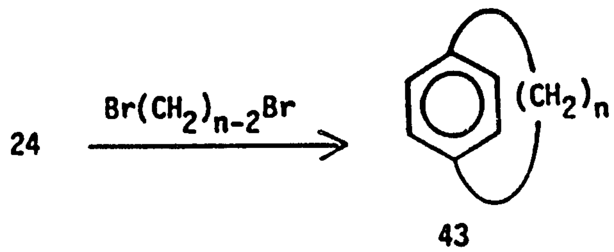
22 

41

n	%
5	11
6	7
7	0
8	0
9	7

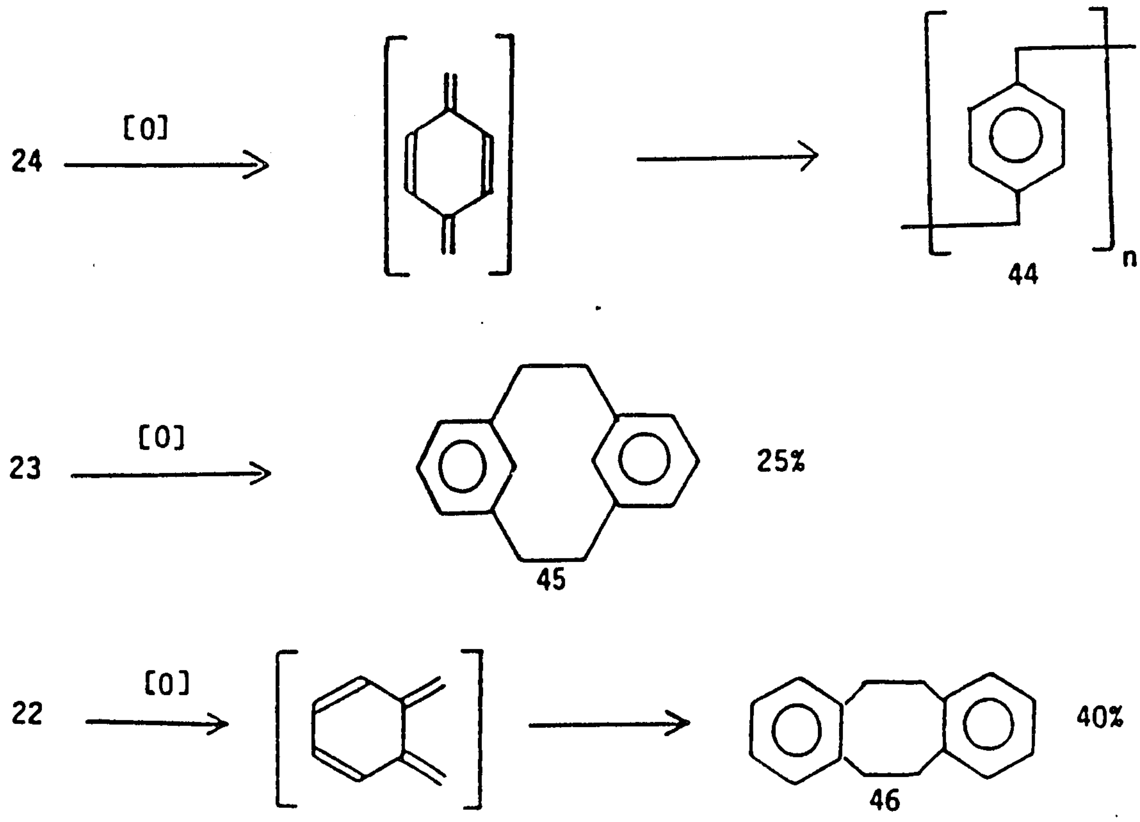


7	trace
8	10
9	26
10	27



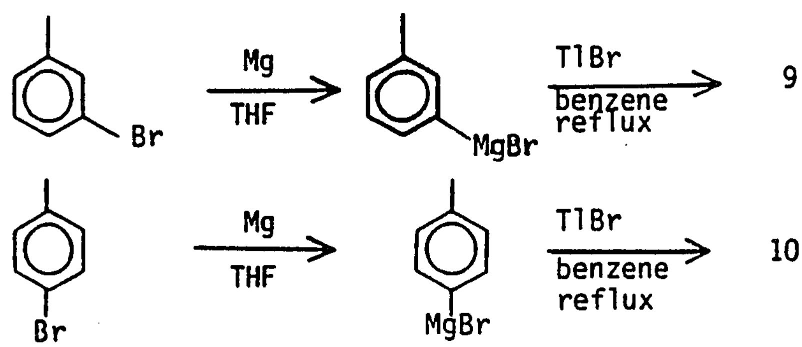
9	5
10	7
11	7

Oxidation of these dianions gave the expected products: 24 produced polymer, 44; 23 generated [2.2]metacyclophane, 45; and 22 yielded dimeric product 46 [27,47].

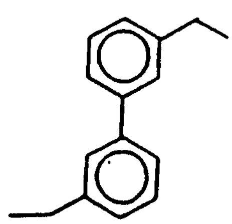


We hoped to be able to successfully perform these reactions with the symmetrical dimethylenebiphenyl dianions to generate symmetrically substituted biphenyls, [n.0]cyclophanes and oxidation products. We expected that the syntheses of these compounds would be in most cases superior to methods previously reported in the literature.

The best procedure for preparation of 9 and 10 involves the coupling of the Grignard reagents formed from the appropriate bromotoluenes with thallium bromide [48,49] as shown on the following page:

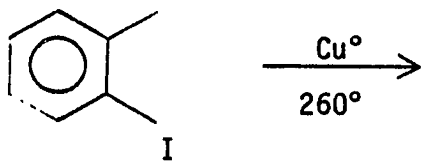


3,3′-Diethylbiphenyl, 47, was prepared in 80% yield using the same procedure [48]. 47 would be the expected product of dimethylation of dianion 6.



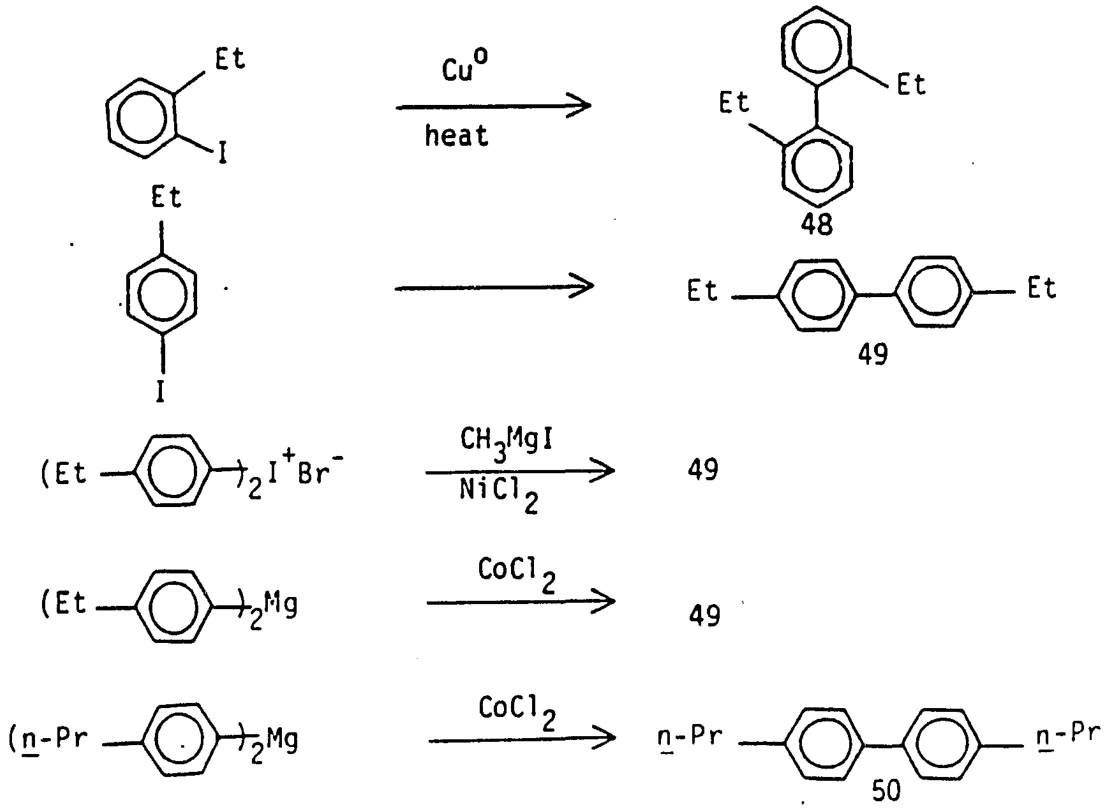
47

8 cannot be prepared in this manner, and the Ullman reaction is commonly used as shown below with o-iodotoluene [50]:



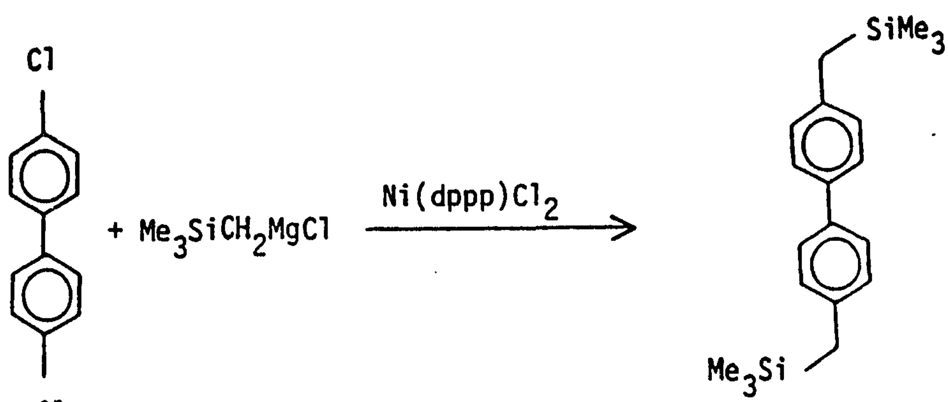
8

2,2′-Diethylbiphenyl, **48**, and its 4,4′-analog, **49**, which would be expected from methylation of dianions **5** and **7** respectively, are also generated by the Ullman reaction, each in about 60% [51]. **49** is also generated in 79% yield from the $NiCl_2$ catalyzed reaction of methyl magnesium iodide with di-p-ethylphenyliodonium bromide in ether [52]. **49** has also been prepared in 61% yield from cobalt catalyzed coupling of di-p-ethylphenylmagnesium. 4,4′-Dipropylbiphenyl, **50** was prepared in 47% yield using the same procedure [53].



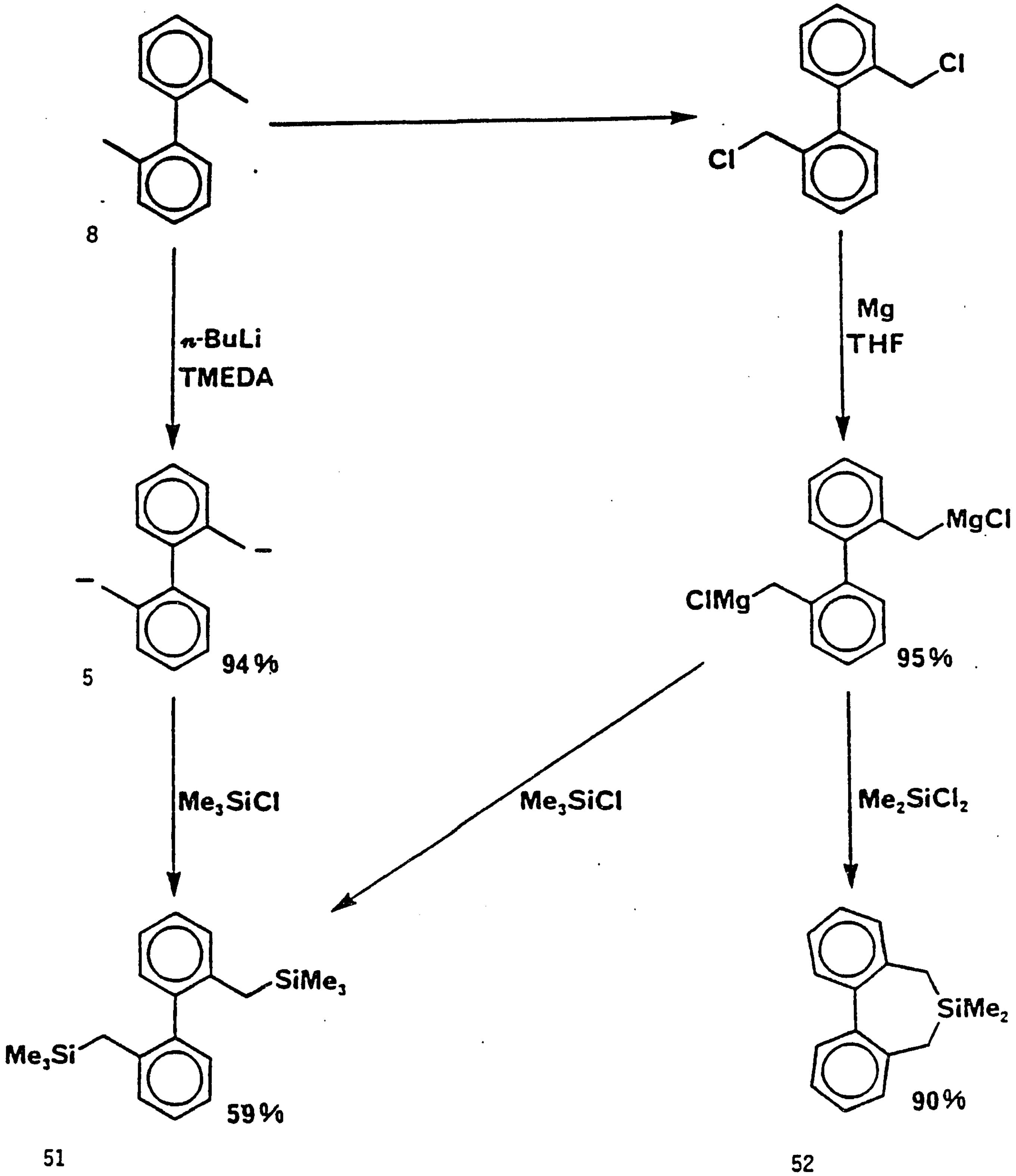
Dianion **5**, as its Li/TMEDA salt, and its di-Grignard analog have been reacted with trimethylsilyl chloride to give 2,2′-bis(trimethylsilylmethyl)biphenyl, **51**, in 59% yield and reacted with dimethylsilyl dichloride to give dibenzosilepin **52** in 90% yield (see following page) [28,29].

4,4′-Bis(trimethylsilylmethyl)biphenyl, **53**, which is expected from the reaction of 7 with trimethylsilyl chloride, has been synthesized in 65% yield from the nickel-catalyzed reaction of 4,4′-dichlorobiphenyl with trimethylsilylmethylmagnesium chloride as shown below [54]:

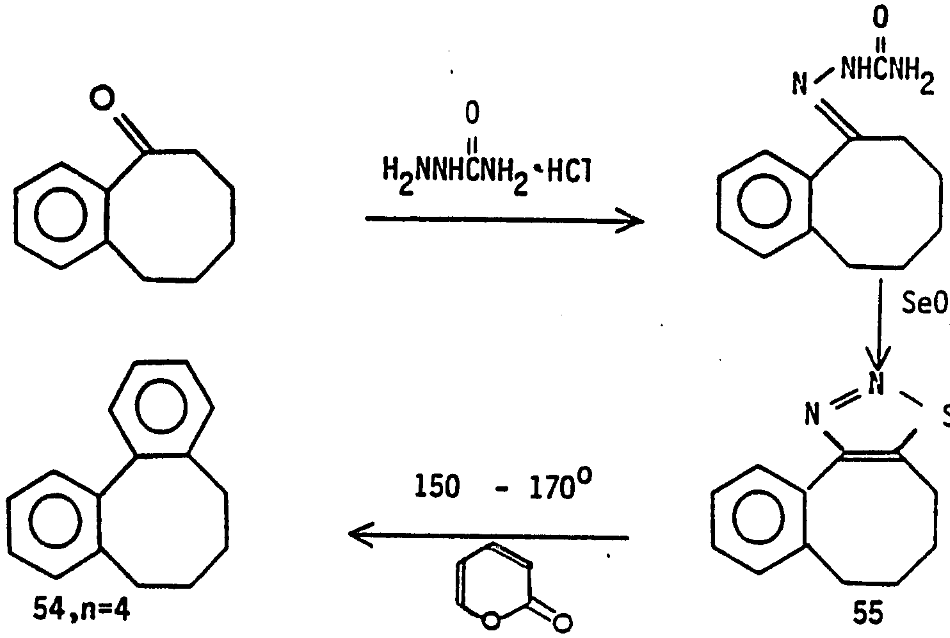


53

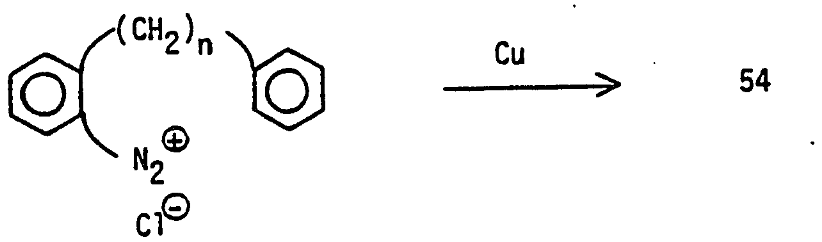
Reaction of dianion **5** with α,ω-dihaloalkanes would be expected to produce [n,0]orthocyclophanes, **54**. [3.0]Orthocyclophane, **54,n=3**, has been prepared by other methods; in each case the overall yield from a readily available starting material is about 20% at best and a minimum of several steps are required [55,56,57]. [4.0]Orthocyclophane, **54,n=4**, has been generated in several ways [58,59,60], the


Cl
Cl
8
n-BuLi
TMEDA
Mg
THF
MgCl
ClMg
5
94%
95%
Me3SiCl
Me3SiCl
Me2SiCl2
SiMe3
Me3Si
SiMe2
59%
90%
51
52

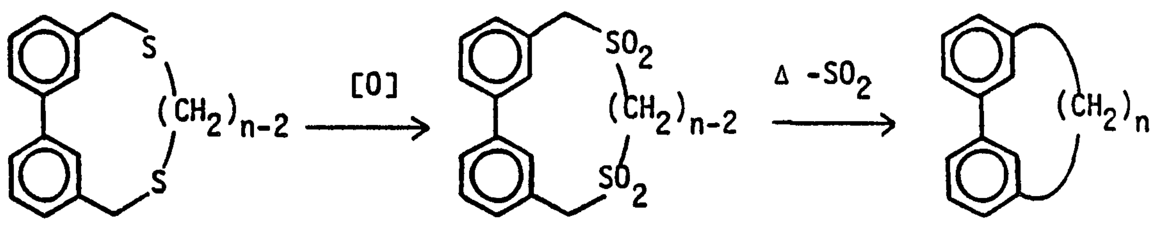
most elegant being from 1,2,3-selenadiazole, **55**, and α-pyrone in 58% yield as shown below [59,61,62]. This series has been generated in



low yields from the Pschorr reaction. The yields for **54,n=1-6** were 7.1, 31.7, 8.8, 3.1, 1.7 and 2.7% respectively [60]:

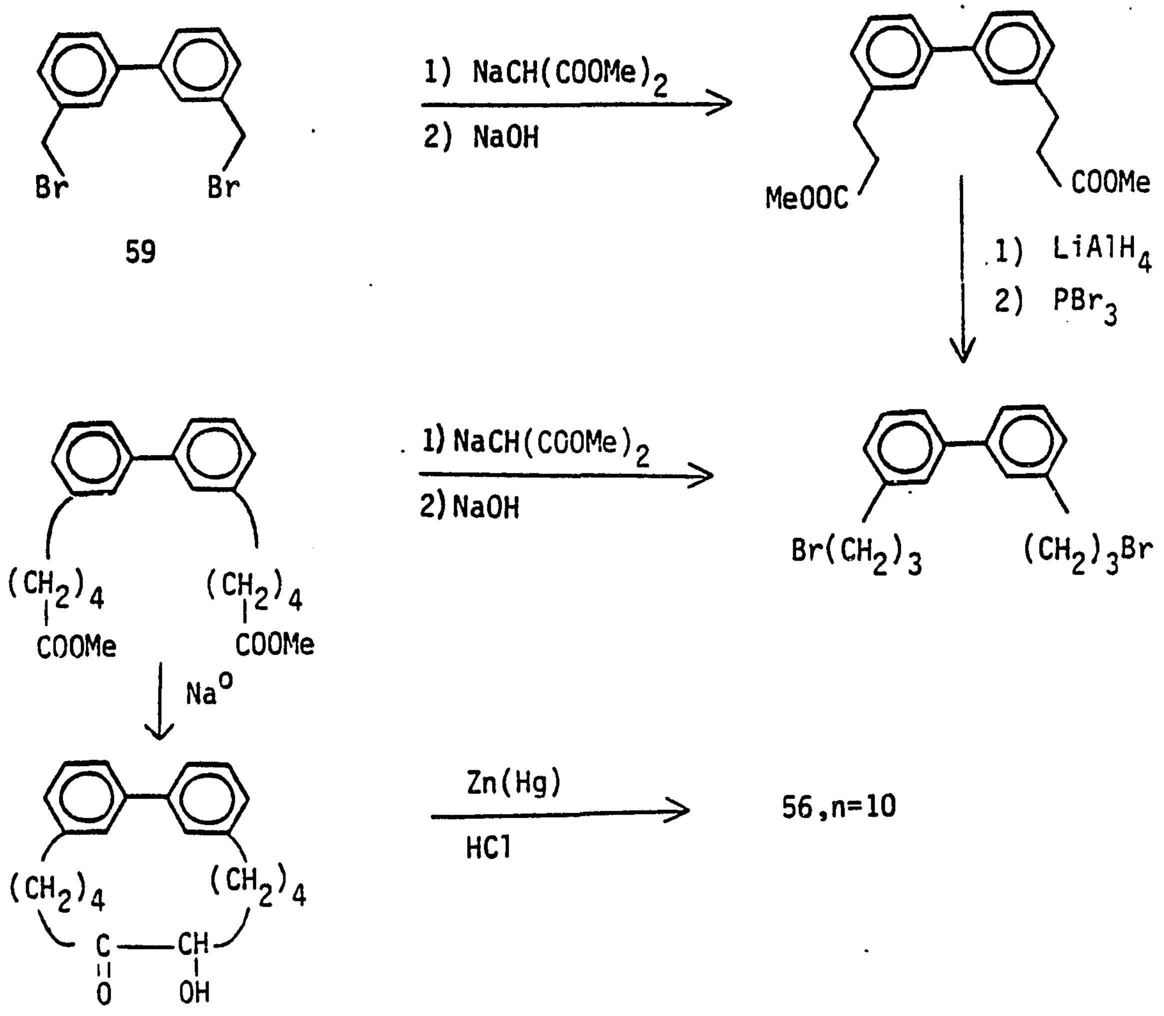


[n.0]Metacyclophanes, **56**, which would be expected from the reaction of **6** with α,ω-dibromoalkanes, have been synthesized in two ways. The highly strained form **56,n=6,7** have been formed from the corresponding sulfide **57** which is oxidized to the disulfone **58**, which is pyrolyzed, eliminating sulfur dioxide to give the desired product [63]:



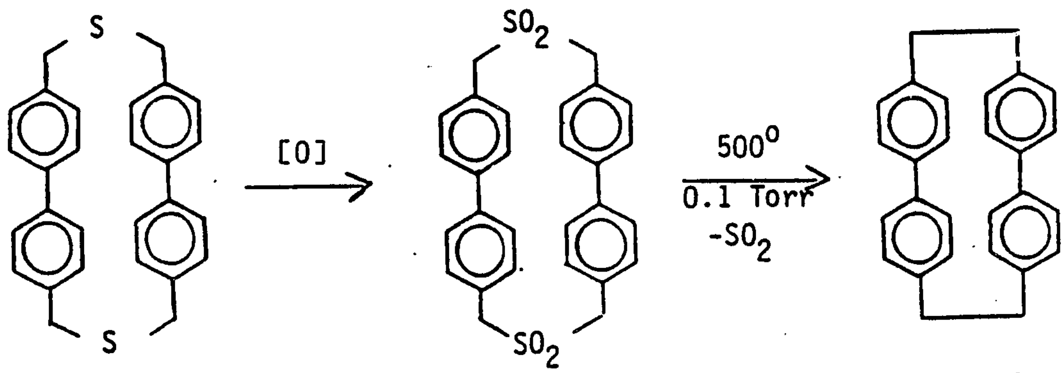
57 58 56,n=6,7

56,n=10 was prepared in the multistep synthesis shown below from 3,3′-bis(bromomethyl)biphenyl 59 with the last two steps resulting in a conversion of only 10%. 56,n=8 was synthesized similarly, the major difference being the replacement of the aromatic rings with cyclohexyl rings and the addition of a ring-aromatization (dehydrogenation) step at the end [64].

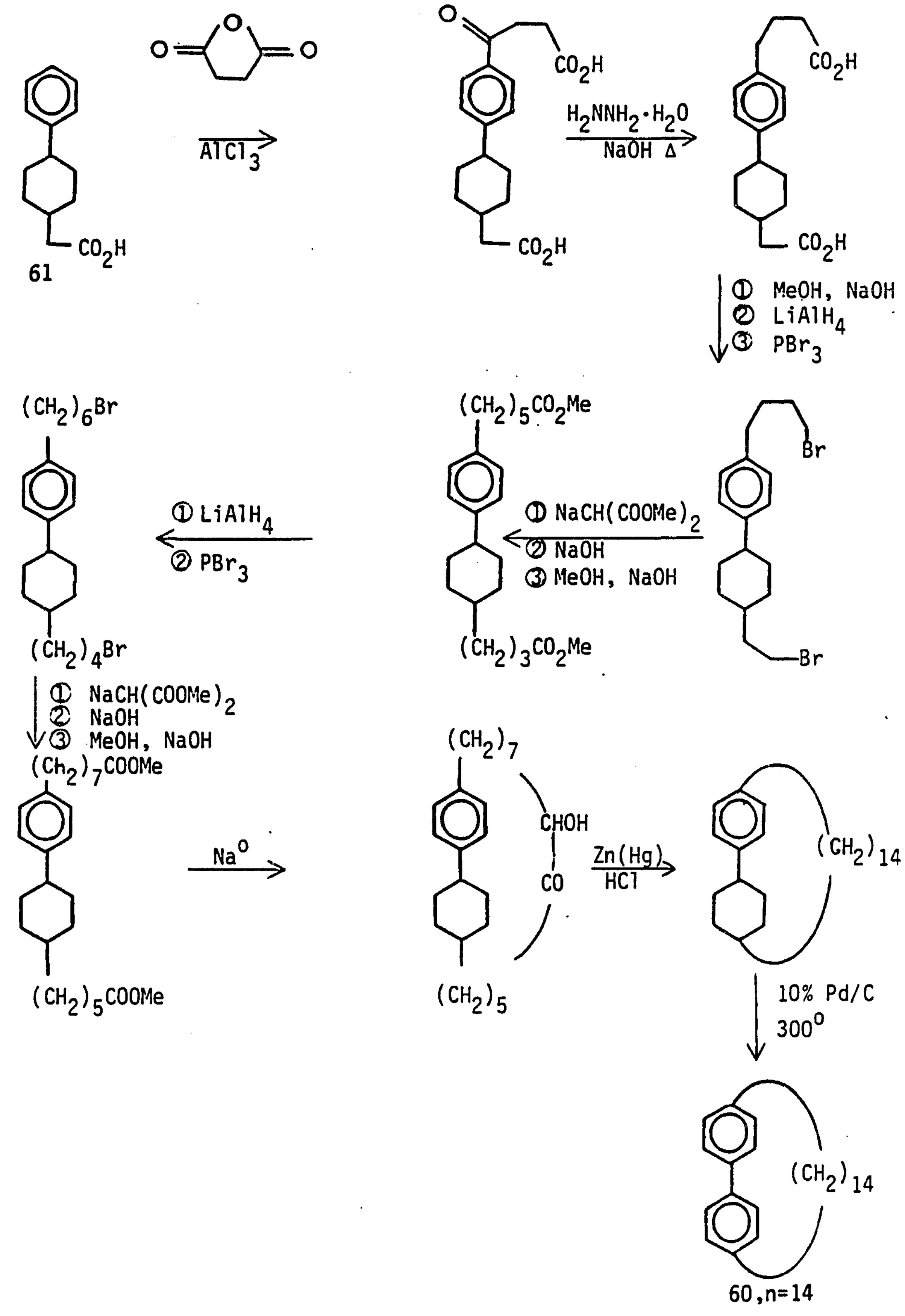


[n.0]paracyclophanes, **60**, would be the expected products from the reaction of dianion **7** with appropriately long α,ω-dibromoalkanes. **60,n=11-16** have been prepared in low yields via multistep syntheses [65]. An example is shown on the following page for **60,n=14** starting from 4-phenylcyclohexylacetic acid, **61** [65,66].

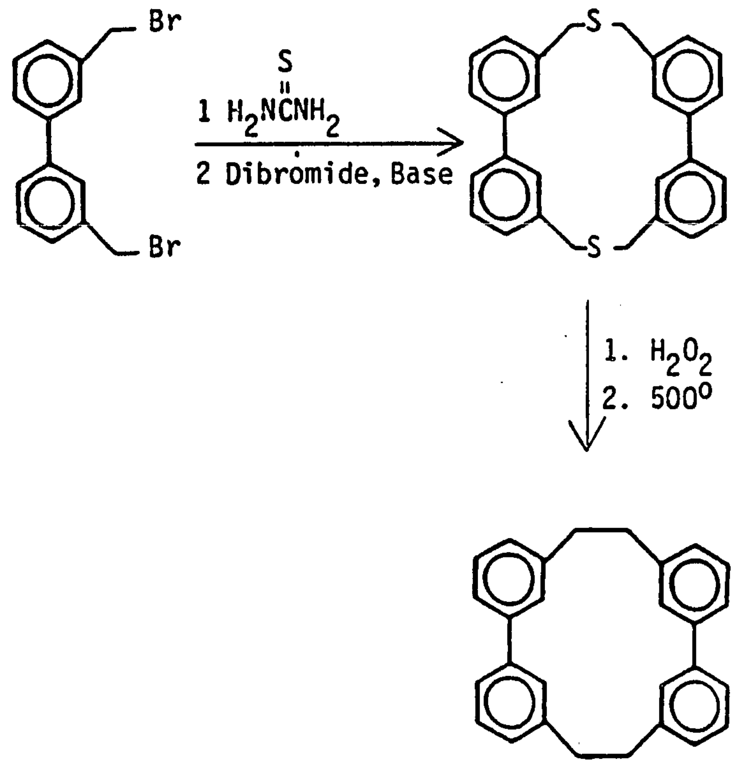
[2.0.2.0]Paracyclophane, **62,n=2**, which might be obtained from the oxidation of dianion **7**, has been made from the oxidation of sulfide **63** to sulfone, **64**, which pyrolytically eliminates sulfur dioxide to give **62,n=2** in 47% yield [67,68].



[2.0.2.0]Metacyclophane, **65,n=2**, which might be expected from the oxidation of dianion **6**, was first generated from oxidation of the analogous Grignard reagent with cupric chloride in 3% yield [69]. **65,n=2** has been generated in 45% overall yield from 3,3′-bis(bromomethyl)biphenyl in the increasingly familiar sulfone-pyrolysis scheme shown below [70]:

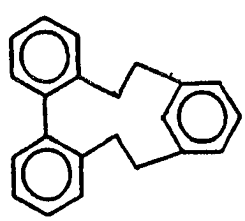


AlCl3
CO2H
H2NNH2·H2O
NaOH Δ
61
MeOH, NaOH
LiAlH4
PBr3
(CH2)6Br
(CH2)5CO2Me
Br
NaCH(COOMe)2
NaOH
MeOH, NaOH
(CH2)4Br
(CH2)3CO2Me
(Ch2)7COOMe
(CH2)7
CHOH
CO
Na0
Zn(Hg)
HCl
(CH2)14
(CH2)5COOMe
(CH2)5
10% Pd/C
3000
60,n=14

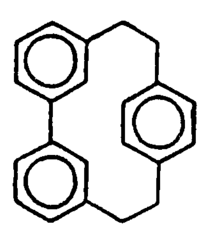


65,n=2

Cyclophanes **66** and **67**, which might be obtained from dianions **5** and **6**, respectively, reacting with the appropriate α,α′-dibromoxylene, are generated in the same manner (sulfone pyrolysis) as **65,n=2**, in yields of 9 and 25% [71,72].



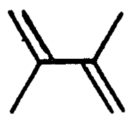
66



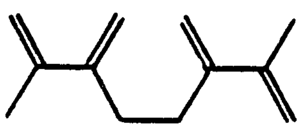
67

RESULTS

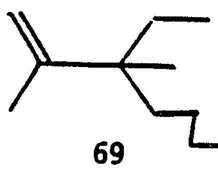
2,3-Dimethylenebutadiene dianion, 3, was prepared from 2,3-dimethyl-1,3-butadiene with Lochmann's base. Dianion 3 has yielded dimeric 31,n=4 as an oxidative side product in reaction with t-butyl bromide and iodide, dibromomethane and to a lesser extent, 1,3-dibromopropane [10]. A number of oxidizing agents were employed in an attempt to optimize the yield of 31,n=4. A summary of yields for the reactions of 4 giving 31,n=4 are listed in Table 2. The reported yields are based on starting material, 2,3-dimethyl-1,3-butadiene, and not on dianion 3 which is obtained from the diene in 73% yield [22,24].

 $\xrightarrow[\underline{n}\text{-BuLi}]{\text{KO-}\underline{t}\text{-Bu}}$ 3 $\xrightarrow{[O]}$ 35

The reaction of 3 with $FeBr_3$ was also found to have generated 68 in 10% yield and 69 in 6% yield. When 3 was reacted with CdI_2 in THF a wide variety of products were characterized: 31,n=4 in 11%, 68 in 2%, 70 in 9%, 71 in 4%, 72 in 5%, 73 in 15%, 69 in 12% and 74 in 2% yield. The reaction of 4 with $ZnBr_2$ yielded the same products in essentially the same proportions, except that oxidative products 31,n=4 and 68 were not found.



68



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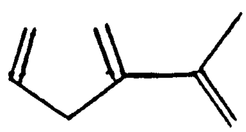
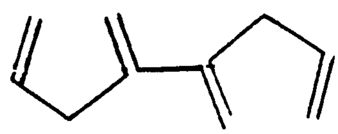


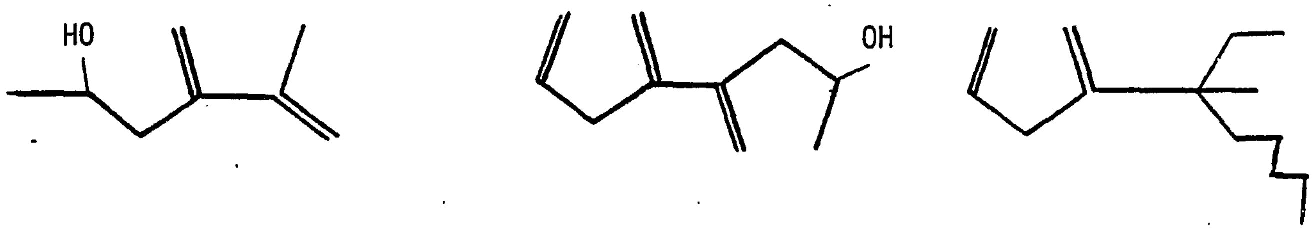
70



71

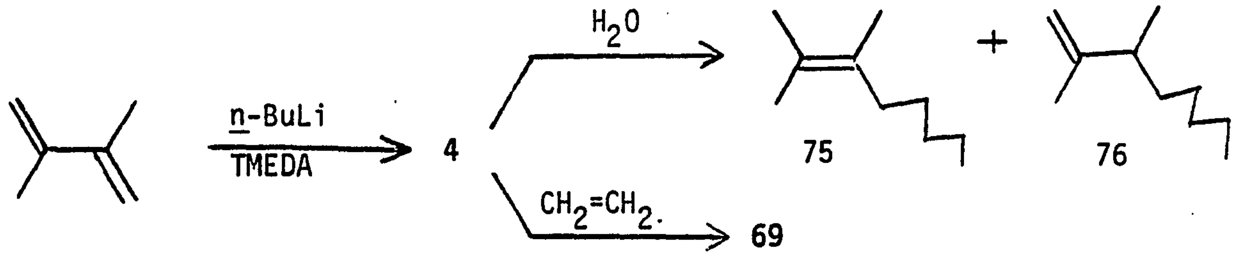
Table 2. Yields of **35** from **3**

Oxidant	% Yield
t-BuI	16 [10]
t-BuBr	15 [9,10]
CH_2Br_2	11 [9,10]
$Br(CH_2)_3Br$	1 [9,10]
$FeBr_3$	8
$NiBr_2$	1
Cu_2Br_2	11
$CuBr_2$	17
$ZnBr_2$	0
CdI_2	11
Cl_3CCCl_3	11
I_2	3

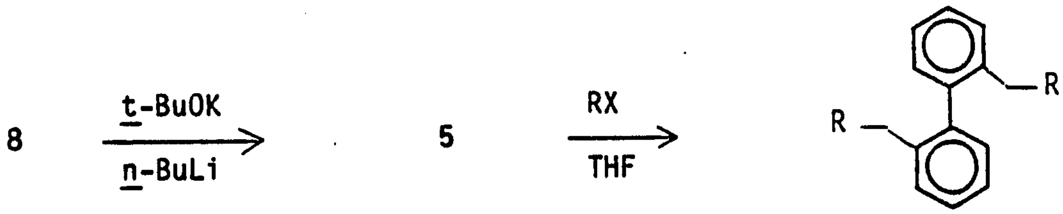


72 73 74

Dianion 4 was generated in 50% yield from 2,3-dimethyl-1,3-butadiene with n-BuLi/TMEDA based on H_2O quench products 75 and 76. Bubbling excess ethylene into the solution containing 4 gave 69 quantitatively upon aqueous workup. Subsequent reactions of 4 with propylene and isobutylene failed to yield analogous products.



The symmetrical dimethylenebiphenyl dianions 5-7 were prepared from the appropriate dimethylbiphenyls (8-10) with Lochmann's base. Dianions 5-7 were reacted a variety of organic halides to yield a number of symmetrically disubstituted biphenyls (78-79). The reported yields of product are based on the appropriate dimethylbiphenyl (8-10) and not on the dianion used.



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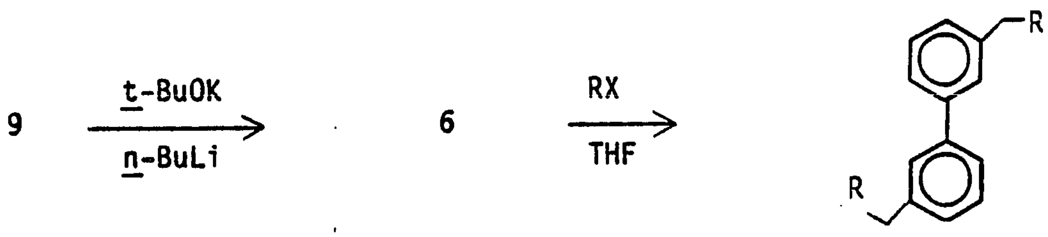
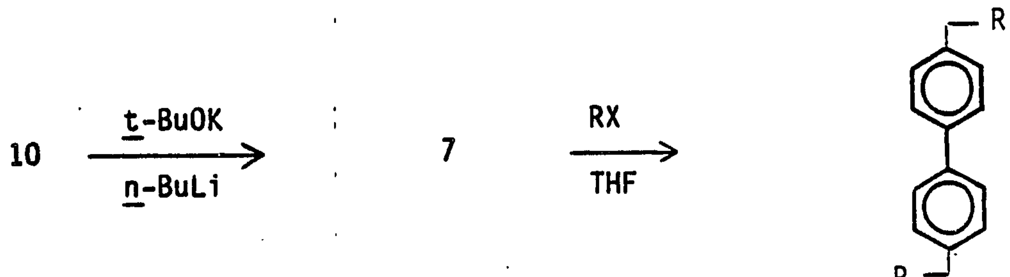


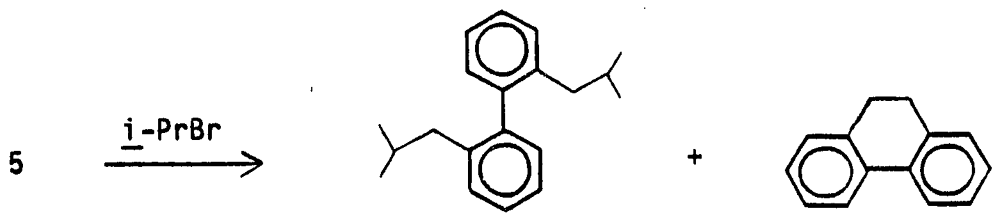
78



79

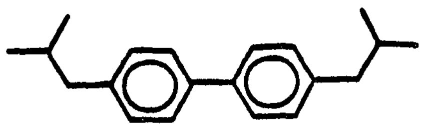
Dianions 5-7 were reacted with dimethyl sulfate to prepare 48, 47, and 49 in 86, 84, and 79% yields, respectively. Diethyl sulfate was reacted with 7 to give an 86% yield of 50.

Isopropyl bromide was reacted with dianions 5 and 7 to generate 2,2′-and 4,4′-diisobutylbiphenyl, 80 and 81, in 50 and 78% yields respectively. A 20% yield of dihydrophenanthrene 54,n=2 was obtained from the reaction with dianion 5:



80

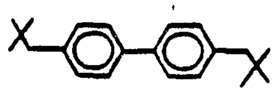
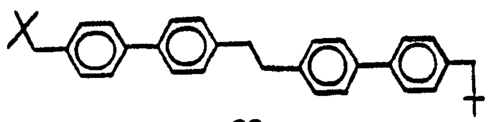
54,n=2

7 $\xrightarrow{\underline{i}\text{-PrBr}}$ 

81

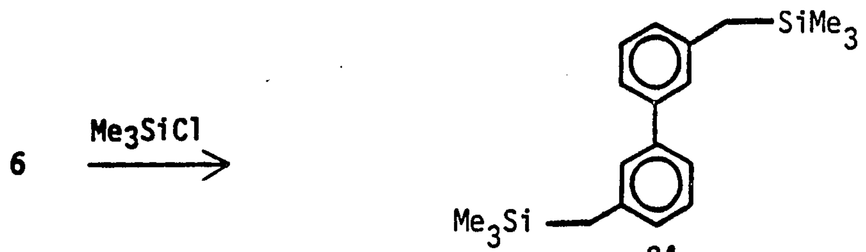
$\underline{t}$-Butyl iodide was reacted with 7 to give a 44% yield of 4,4′-dineopentylbiphenyl 82 and a 20% yield of oxidative side product 83. The reaction of 5 with $\underline{t}$-butyl iodide produced no alkylation products, instead giving a 67% yield of dihydrophenanthrene, 54,n=2.

5 $\xrightarrow{\underline{t}\text{-BuI}}$ 54,n=2

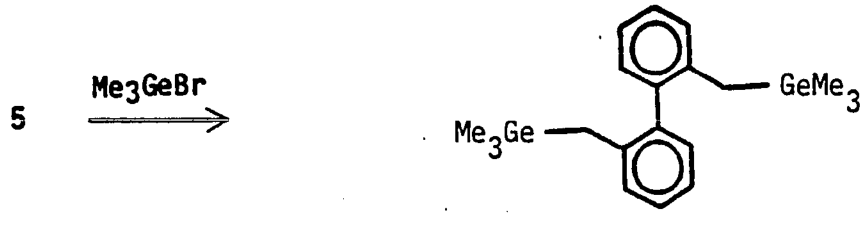
7 $\xrightarrow{\underline{t}\text{-BuI}}$  + 

82 83

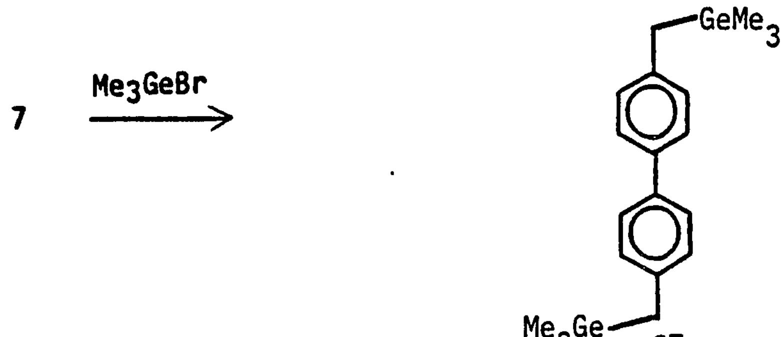
Trimethylsilyl chloride reacted with dianions 5-7 to yield the respective bis(trimethylsilylmethyl)biphenyls 51, 84, and 53 in 44, 69, and 71%. Oxidative coupling product 85 was obtained in ~5% yield from 53 upon 6 months standing. Dianions 5 and 7 reacted in the same manner with trimethylgermyl bromide to yield 2,2′- and 4-4′-bis(trimethylgermylmethyl)biphenyls, 86 and 87, in 39 and 77% yields. When trimethyltin chloride was added to dianion 7 by inverse addition there was essentially no reaction after 3 days; reaction by direct addition generated an unstable mixture of products including some in which an aromatic ring has apparently been trimethylstannylated in addition to the expected product from reaction at the benzylic position.



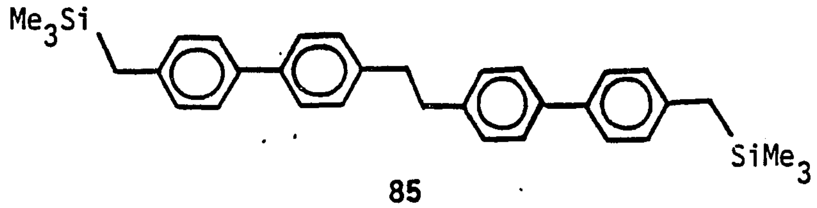
84



86

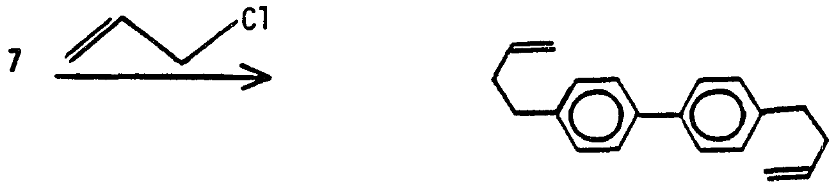


87



85

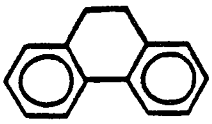
The reaction of dianion 7 with allyl chloride produced 88 in 79% yield which partially oligomerized upon standing.



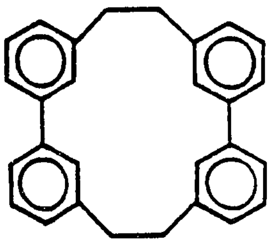
88

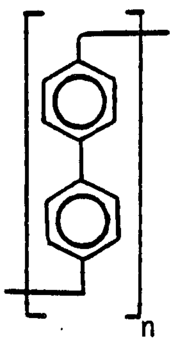
A summary of the reactions of dianion **5** with monofunctional electrophiles is given in Table 3. A similar compilation for dianions **6** and **7** is given in Table 4.

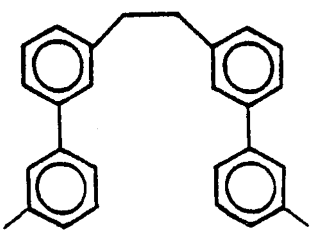
Dianions **5-7** were oxidized using iodine or 1,2-dibromoethane. Attempts to oxidize **7** to [2.0.2.0]paracyclophane, **62**,n=2, failed and only a polymeric mixture was obtained. Reaction of **6** with I_2 gave [2.0.2.0]metacyclophane, **65**,n=2, in 19% yield as well as **89** in 40% yield and **90** in 17% yield. A more efficient reaction of **6** with 1,2-dibromoethane yielded **65**,n=2 in 39% yield. Crystals of **65**,n=2 were grown at 0° from a pentane solution and a crystal structure was obtained by X-ray diffraction. **5** was reacted with dibromoethane to generate **54**,n=2 in 68% yield.

5 $\xrightarrow{[O]}$ 

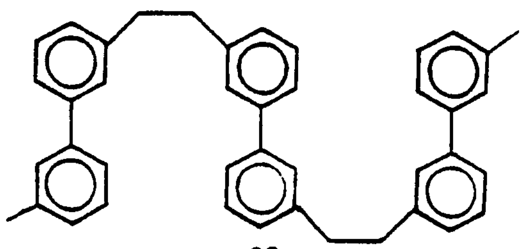
54,n=2

6 $\xrightarrow{[O]}$  65,n=2

7 $\xrightarrow{[O]}$ 



89



90

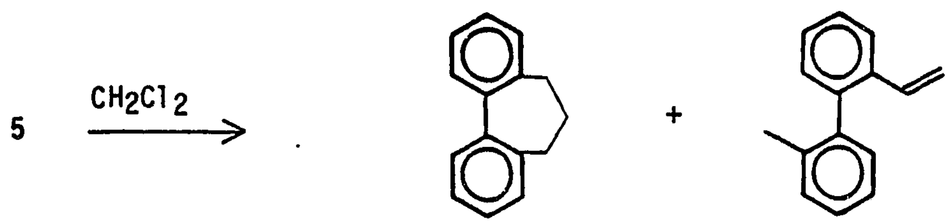
Table 3. Disubstitution Products of Dianion 5

R	X	% yield	Product	% 54,n=2
Me	$MeSO_4$	86	48	0
i-Pr	Br	50	80	20
t-Bu	I	0	-	67
Me_3Si	Cl	44	51	1
Me_3Ge	Br	39	86	2

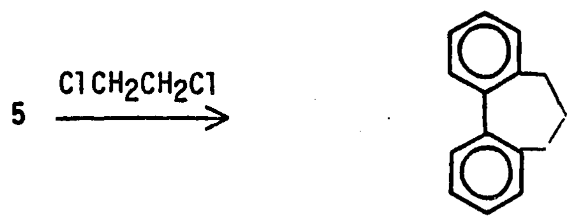
Table 4. Disubstitution Products of Dianions 6 and 7

R	X	Dianion	% yield	Product
Me	$MeSO_4$	6	84	47
Me	$MeSO_4$	7	79	49
Et	$EtSO_4$	7	86	50
i-Pr	Br	7	78	81
t-Bu	I	7	44	82
$H_2C{=}CHCH_2$	Cl	7	79	88
$SiMe_3$	Cl	6	69	84
$SiMe_3$	Cl	7	71	53
$GeMe_3$	Br	7	77	87

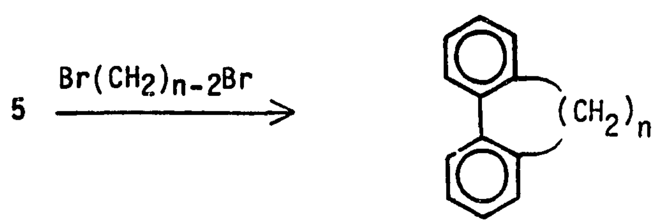
Dianions **5-7** were reacted with various α,ω-dihaloalkanes to generate mostly various [n.0]-ortho-, meta- and paracyclophanes **54**, **56**, and **60**. Dianion **5** was reacted with dichloromethane to yield **54,n=3** in 29% yield and 2-o-tolylstyrene, **91**, also in 29% yield. Reaction of **5** with 1,2-dichloroethane gave **54,n=4** in 5% yield. **54,n=5** was prepared in 31% yield by the reaction of **5** with 1,3-dibromopropane. The reaction of 1,4-dibromobutane with **5** produced **54,n=6** in 41% yield and the analogous reaction with 1,5-dibromopentane yielded **54,n=7** in 26% yield. **54,n=2** was generated as a side product in most of these reactions.



54,n=3 **91**



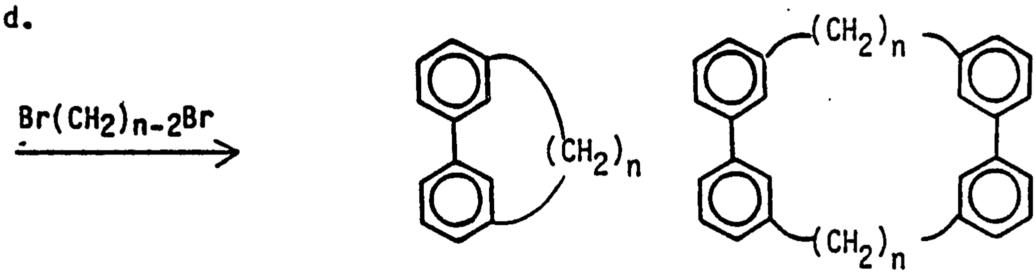
54,n=4



54,n=5,6,7

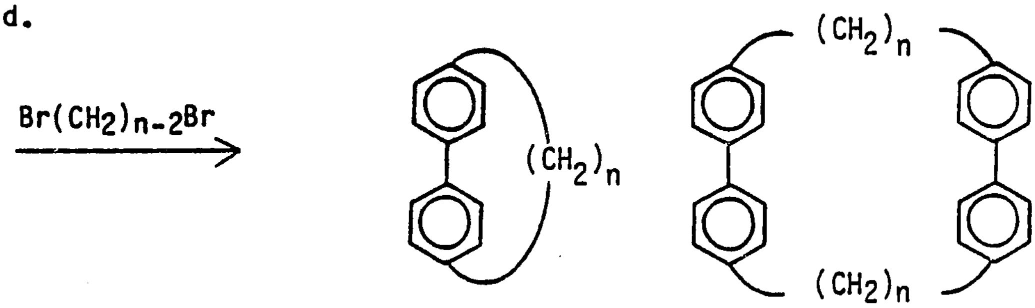
A summary of the reaction of 5 with α,ω-dihaloalkanes is given in Table 5.

Dianion 6 was reacted with 1,8-dibromooctane to generate 56,n=10 in 38% yield and dimeric 65,n=10 in 20% yield. An analogous reaction with 1,7-dibromoheptane yielded 56,n=9 in 7% and its dimer 65,n=9 in 33% yield.

6 

56,n=9,10 65,n=9,10

Dianion 7 was reacted with 1,10-dibromodecane giving only a trace of 60,n=12 but producing dimeric 62,n=12 in 27% yield. The reaction of 1,12-dibromododecane with 7 generated [14.0]paracyclophane 60,n=14 in 14% yield and dimeric 62,n=14 in 20% yield. Crystals of 60,n=14 were grown from pentane at 0°C, and a crystal structure was obtained by X-ray diffraction. The analogous reaction of 7 with 1,14-dibromotetradecane provided 60,n=16 in 5% yield and 62,n=16 in 22% yield.

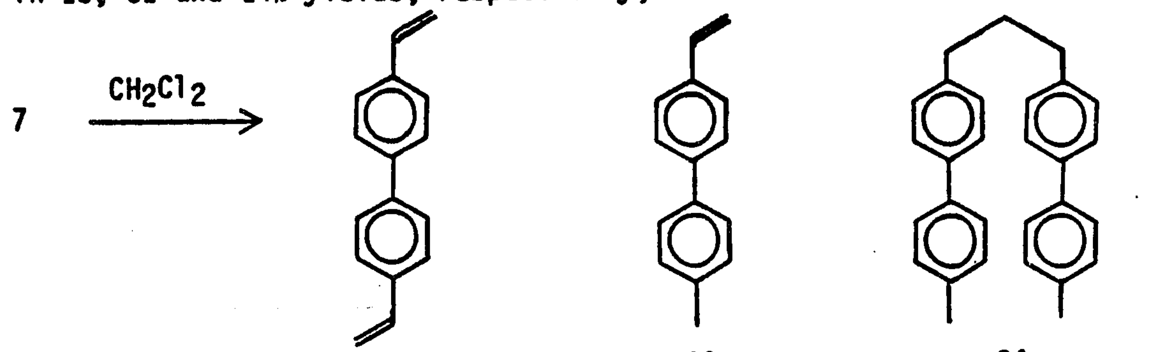
7 

60,n=12,14,16 62,n=12,14,16

Table 5. [0.n] Orthocyclophanes from Dianion 5

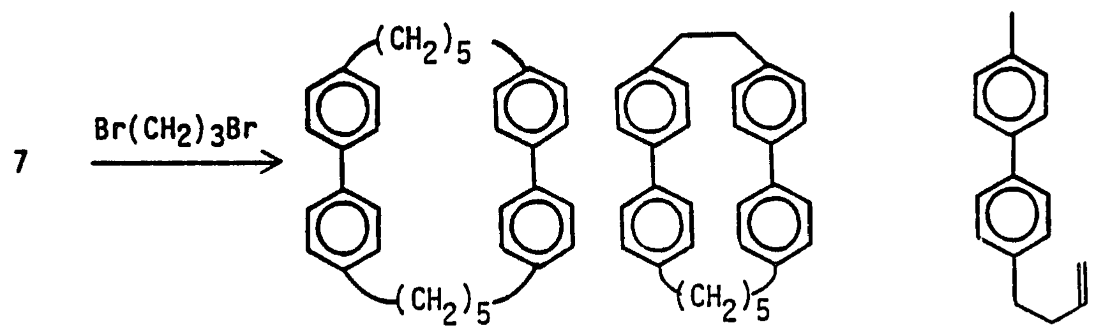
Dihalide	Product	% yield	% 54,n=2
CH_2Cl_2	54,n=3	29	2
$ClCH_2CH_2Cl$	54,n=4	5	1
$Br(CH_2)_3Br$	54,n=5	31	5
$Br(CH_2)_4Br$	54,n=6	41	0
$Br(CH_2)_5Br$	54,n=7	26	1

Dichloromethane was reacted with dianion 7 in an attempt to generate [3.0.3.0]paracyclophane (62,n=3). A mixture of 92, 93 and 94 in 13, 31 and 14% yields, respectively, was obtained.



92 93 94

1,3-Dichloropropane reacted very sluggishly with 7 and not to completion; aqueous workup primarily gave back starting material. Dianion 7 reacted with 1,3-dibromopropane to give a mixture of products including the dsired [5.0.5.0]paracyclophane 62,n=5 in 6% yield along with [2.0.5.0] paracyclophane 95 in 2% yield and 96 in 24% yield.



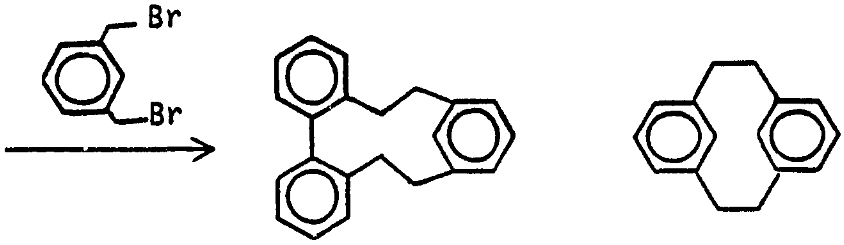
62,n=5 95 96

The reactions of dianions 6 and 7 with α,ω-dihaloalkanes are summarized in Table 6.

Table 6. Meta- and Paracyclophanes from the Reactions of Dianions 6 and 7 with α,ω-Dihaloalkanes.

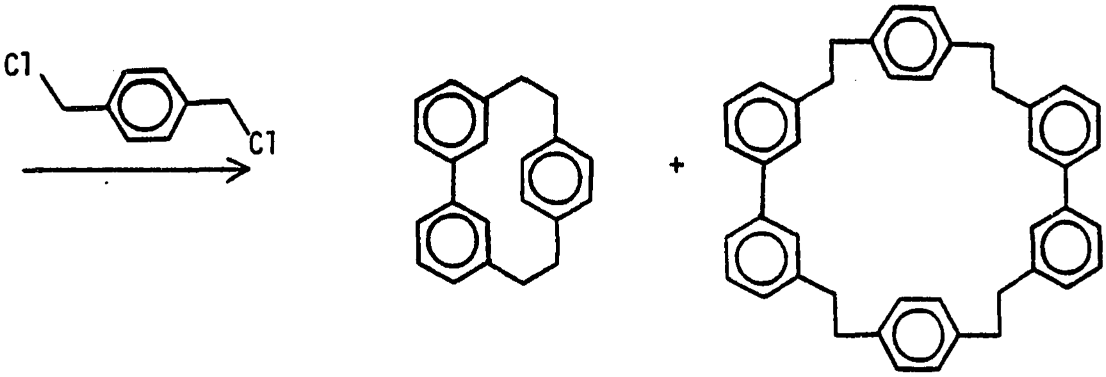
Dihalide	Dianion	Monomeric Cyclophanes	% yield	Dimeric Cyclophanes	% yield
CH_2Cl_2	7	-	-	62,n=3	0
$Cl(CH_2)_3Cl$	7	-	-	62,n=5	0
$Br(CH_2)_3Br$	7	-	-	62,n=5	6
				95	2
$Br(CH_2)_7Br$	6	56,n=9	7	65,n=9	33
$Br(CH_2)_8Br$	6	56,n=10	38	65,n=10	20
$Br(CH_2)_{10}Br$	7	60,n=12	trace	62,n=12	27
$Br(CH_2)_{12}Br$	7	60,n=14	14	62,n=14	20
$Br(CH_2)_{14}Br$	7	60,n=16	5	62,n=16	22

5 was reacted with α,α′-dibromo-m-xylene to generate 66 in 8% yield as well as 54,n=2 in 32% yield and [2.2]metacyclophane, 45, in 4% yield.

5  + 54,n=2

66 45

The reaction of α,α′-dichloro-p-xylene with 6 provided 67 in 4% yield and dimeric 97 in 6% yield.

6 

67 97

DISCUSSION

Substitution reactions involving the studied dianions may result from a number of possible mechanisms. The first mechanism discussed involves the ionization of the electrophile to generate an alkyl cation, which then rapidly couples to the anion (nucleophile, Nu:$^-$). This is the S_N1 mechanism:

S_N1:

$$RX \rightleftharpoons R^+ + X^-$$

$$Nu^- + R^+ \longrightarrow NuR$$

The S_N1 mechanism is favored only when the R group is capable of stabilizing a positive charge; this is not the case for most of the electrophiles reacted. Also, the S_N1 mechanism is not particularly favored in strongly basic systems or in non-polar solvents while the following mechanisms tend to be favored. It is therefore doubtful that the S_N1 mechanism is involved in these reactions.

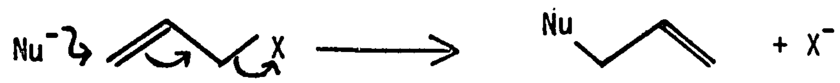
The next mechanism involves backside attack by the anion (nucleophile, Nu:$^-$) on the alkyl halide with simultaneous expulsion of a halide ion. This is the well-known, concerted, S_N2 mechanism:

S_N2:

$$Nu:^- \; R{-}X \longrightarrow NuR + X^-$$

When the electrophile is an allyl halide then γ-attack via an S_N2' mechanism is also a possibility [73]:

S_N2':



The S_N2 and S_N2' mechanisms involve transfer of two electrons, but single electron transfer (SET) is also possible. SET provides a number of possible pathways leading the desired as well as other products. The nine steps involved in the SET mechanisms to be discussed are listed below:

1. $Nu{:}^- + RX \longrightarrow Nu\cdot + [RX]^{\overline{\cdot}}$

2. $[RX]^{\overline{\cdot}} \longrightarrow R\cdot + X^-$

3. $Nu{:}^- + R\cdot \longrightarrow [NuR]^{\overline{\cdot}}$

4. $[NuR]^{\overline{\cdot}} + RX \longrightarrow NuR + [RX]^{\overline{\cdot}}$

5. $Nu{:}^- + Nu\cdot \longrightarrow [NuNu]^{\overline{\cdot}}$

6. $[NuNu]^{\overline{\cdot}} + RX \longrightarrow NuNu + [RX]^{\overline{\cdot}}$

7. $Nu\cdot + R\cdot \longrightarrow NuR$

8. $Nu\cdot + Nu\cdot \longrightarrow NuNu$

9. $R\cdot + R\cdot \longrightarrow RR$

The radicals formed in the first two steps may react in two ways, by radical-radical coupling (RRC) or by radical-anion coupling (RAC). Steps 1, 2, 7, 8 and 9 are those involved in RRC. Step 2 is believed to be very rapid when X=halide, thus if R• is formed while still in the vicinity of, or while entrapped in a solvent "cage" with $Nu:^-$, then step 7 will be favored and NuR will predominate as the product. If R• is formed away from or escapes the solvent "cage" or vicinity of $Nu:^-$, steps 8 and 9 become important and NuNu and RR are formed in greater amounts.

When steps 3, 4, 5 and 6 are occurring then RAC is involved. The $S_{RN}1$ reaction as described by Bunnett [74,75,76] is well known in the reactions of aryl halides with anions. This is a chain mechanism where step 1 is the slow initiation step and steps 2, 3 and 4 are the more rapid propagation steps. The termination steps are 7, 8 and 9 while steps 5 and 6 are negligible propagation steps. $S_{RN}1$ gives primarily NuR as a product. When the rate of step 1 becomes competitive with the propagation steps 3 and 4 then steps 5 and 6 become important and more dimeric Nu-Nu results. Also, the concentration of radicals increases thereby raising the importance of termination steps 7, 8 and 9, and resulting in more RRC. We will term the mechanisms where step 1 is competitive with steps 3 and 4 but where RAC is still favored over RRC as $S_{RN}1'$ mechanisms.

We now have the two extreme cases of RRC in a "cage" and the $S_{RN}1$ mechanism, each giving NuR as a product and a continuum of mechanisms in between, yielding NuNu or RR as side products labeled loosely as $S_{RN}1'$. The RRC mechanism is a non-chain process, while the "pure" $S_{RN}1$ involves a very long chain and the intermediate $S_{RN}1'$ mechanisms have shorter chain lengths.

The $S_{RN}2$ mechanism (steps 2 and 3 of $S_{RN}1$ merged, as shown below) is unlikely in SET reactions as it requires a negatively charged anion to attack an also negatively charged anion radical. The resulting coulombic repulsion makes this mechanism improbable and it has been ruled out in aryl halide reactions [75]. Additionally, step 2 is believed to be very rapid when X=halide, so it is unlikely that the anion radical would wait for a collison with another negatively charged species before splitting into R• and X^-.

$S_{RN}2$:

$$Nu:^- + [RX]^{\overline{\cdot}} \longrightarrow [NuR]^{\overline{\cdot}} + X^-$$

The last mechanistic possibility to be considered is that of substitution by halogen-metal exchange (HME) [12,13] followed by subsequent S_N2 reactions, as given below. HME may be concerted or stepwise involving SET. HME involves equilibria favoring the thermodynamically most stable product. It is unlikely for simple alkyl halides reacting with resonance-stabilized anions, because the anion resulting from the exchange would be so much less stable than the resonance stabilized anions equilibrating with them. In cases where the resulting anion is also resonance stabilized, this mechanism may be important. In addition to substitution products, coupling of the electrophile with its conjugate anion to R-R would be expected.

HME:

$$\mathrm{Nu:^-} + \mathrm{RX} \longrightarrow \mathrm{NuX} + \mathrm{R:^-}$$

$$\mathrm{R:^-}\ \mathrm{Nu{-}X} \longrightarrow \mathrm{RNu} + \mathrm{X^-}$$

$$\mathrm{R:^-}\ \mathrm{R{-}X} \longrightarrow \mathrm{RR} + \mathrm{X^-}$$

$$\mathrm{Nu:^-}\ \mathrm{Nu{-}X} \longrightarrow \mathrm{NuNu} + \mathrm{X^-}$$

Bordwell and Clemens [78,79] have given some rules involving factors that determine whether the reactions of carbanions with electrophiles will tend to go by S_N2 or SET mechanisms. The factors which favor an SET mechanism over an S_N2 mechanism are:

1. A poor leaving group, X
2. Steric hindrance in RX
3. A strong electron acceptor in R
4. Increasing basicity in the reacting anion

The REPA's of the anions are an excellent measure of the basicity of anions, with a lower REPA indicating a stronger base. Although factors may favor one mechanism or the other, it is likely that in some reactions two (or more) mechanisms are competing.

It is difficult to assess in SET reactions whether RAC is involved or not. CIDNP effects were shown when some reactions of primary alkyl iodides with alkyllithiums were monitored by 'H NMR [14,15]. CIDNP effects show products to have been formed from radicals; products from radical anions in general do not exhibit this effect. This technique is quite sensitive and even small amounts of RRC are detectable, but it is not easily quantitated. Therefore, it does not differentiate between RRC and the mechanisms termed $S_{RN}1$ which involve some RRC. Although the reactions between unstabilized alkyl anions and alkyl halide are probably purely RRC, in cases where stabilized anion-radicals can be formed, the author favors RAC involvement because the concentration of anions is very high in these reactions and the concentration of radicals is generally quite low. There are also no coulombic constraints for RAC. Therefore, any radical formed has a very much greater probability of colliding with an anion than with another radical.

Oxidations can be imagined to be achieved by either SET or HME followed by S_N2. An example shown for iodine is as follows:

SET:

$$Nu:^- + I_2 \longrightarrow Nu\cdot + I\cdot + I^-$$

HME:

$$Nu:^- + I_2 \longrightarrow NuI + I^-$$

$$Nu:^- + Nu\text{-}I \longrightarrow NuNu + I^-$$

The HME mechanism is unlikely in these reactions because no brominated or iodinated compounds have been found as side products in any of the oxidations.

SET mechanisms also appear to be involved in the oxidation of these anions. The oxidation of dianion 3 to 31,n=4 may go via a number of pathways involving RRC and/or RAC as shown in Figure 1. For the same

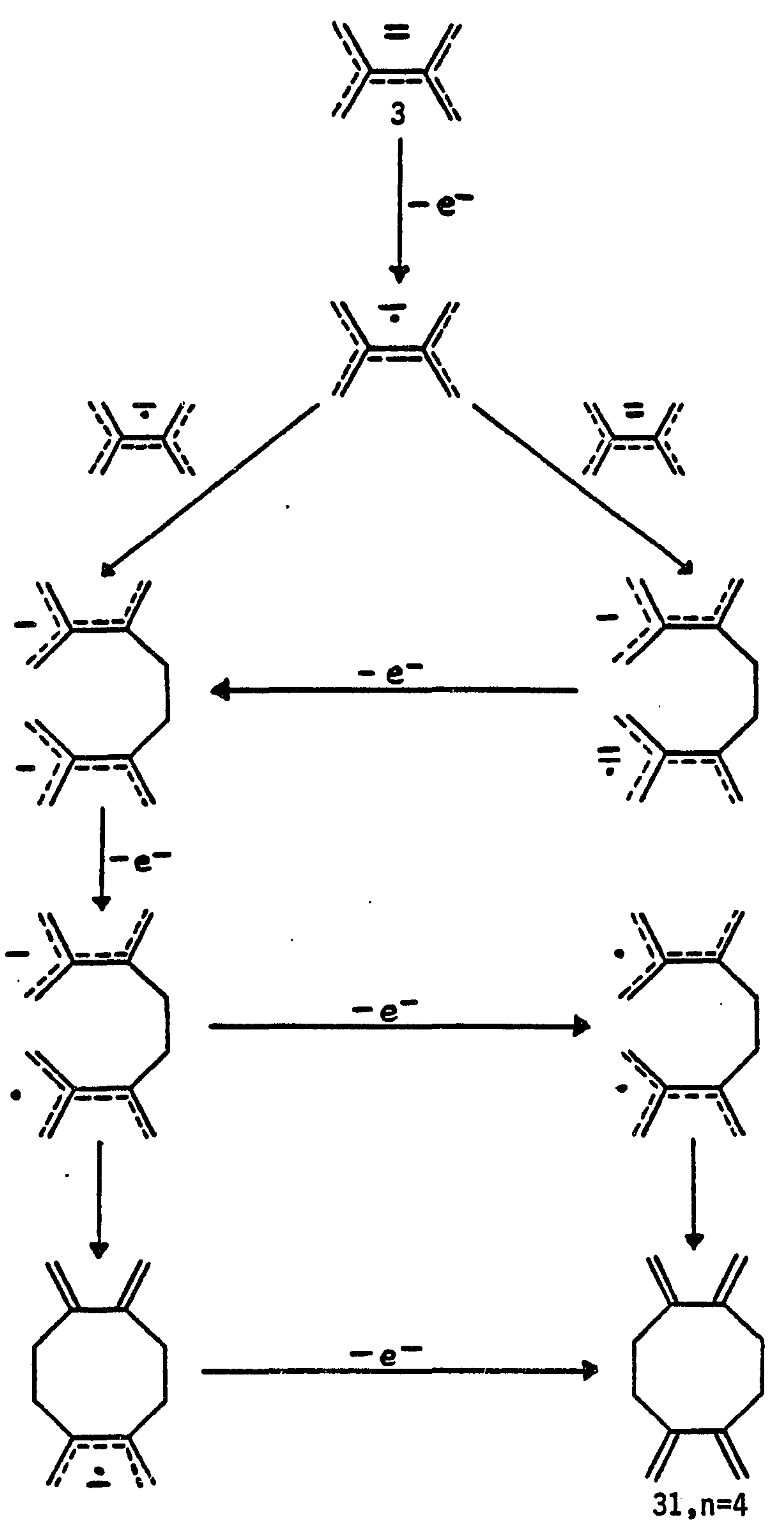
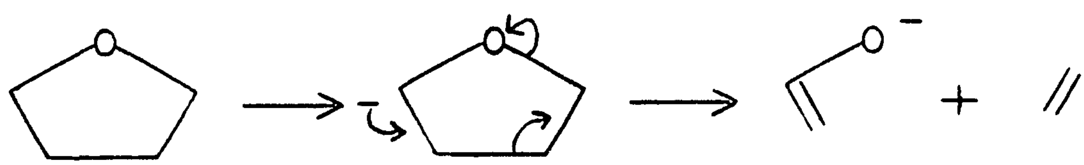


Fig. 1. Mechanism of formation of 31,n=4

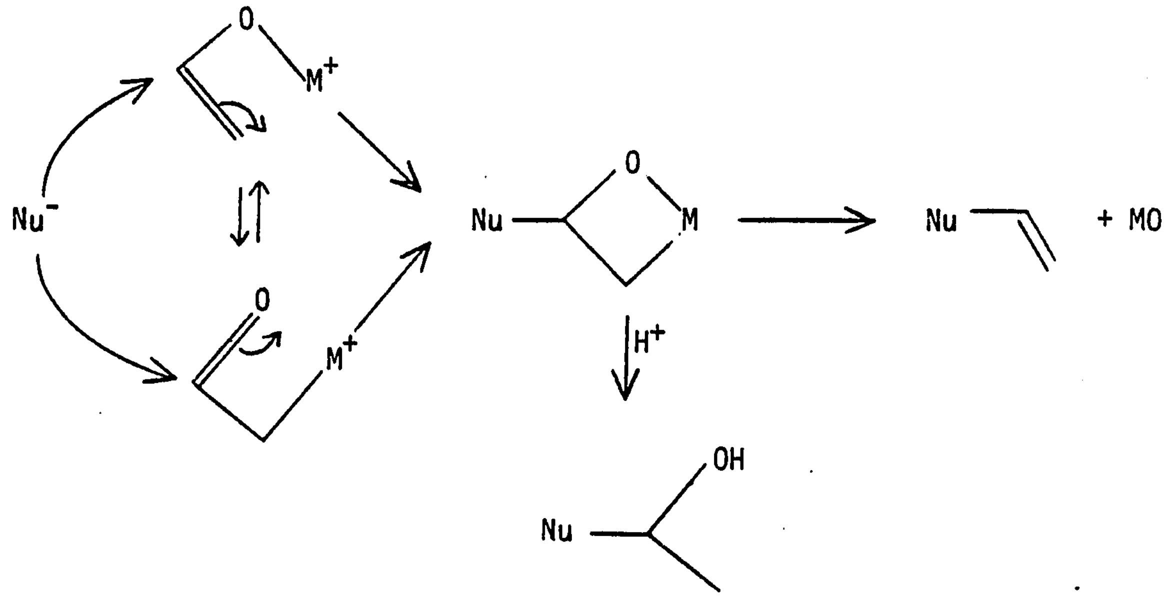
reasons as above, RAC is again more likely than RRC, espeically in the cyclization step as a resonance stabilized anion radical is formed.

Why is **31,n=4** formed from **3** and not **30,n=4**, while **33** and not dimeric **34** is generated from **14**? Angle strain would lead us to expect the opposite. Both **3** and **14** give resonance stabilized anion radicals. RRC involving these radical anions is upon simple examination of resonance structures not particularly favored or disfavored to any great extent. However, RAC of **14** and its conjugate radical anion is strongly disfavored as the resultant trianion radical is unstabilized, while RAC of 3 and its conjugate radical anion leads to a trianion radical that has considerable resonance stabilization. RRC is favored over RAC if only coulombic factors are taken into account, however; this leaves the initial question open to argument.

The yield of **35** from dianion 3 was not very impressive for any of the oxidizing agents used; however, the side products obtained from the reactions of 3 with CdI_2 and $ZnBr_2$ were indeed remarkable. Obviously, these products must result from involvement of the solvent, THF. Cleavage of THF under basic conditions to produce enolate and ethylene as shown below is known to occur [80].

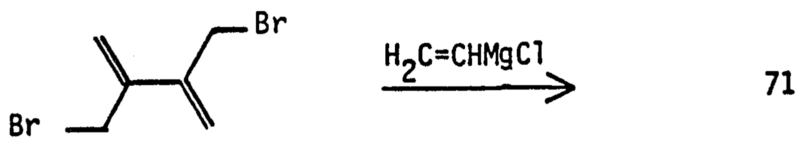


Compound 69 has already been observed as a side product in reactions of dianion 3 and shows incorporation of ethylene produced from THF [9,10]. Products 70-73 are apparently formed from enolate anion coordinated to a zinc or cadmium ion as shown below. Presumably the nucleophile (anion) attacks the double bond at the carbon bearing the oxygen, forming a four-membered metallocycle. This species may expel cadmium or zinc oxide to yield olefins or be protonated to yield alcohols upon workup. The metal ions are, of course, also coordinated to an undetermined number of THF molecules.



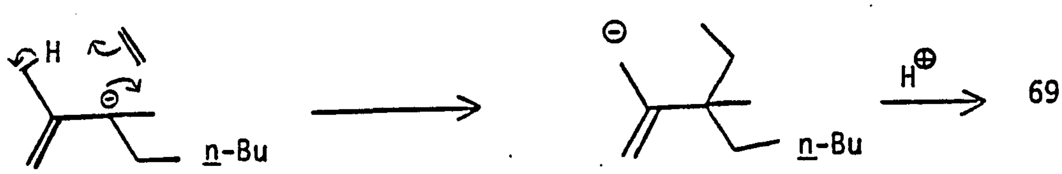
The zinc or cadmium enolates are acting as vinyl cation equivalents. Unfortunately, the yields of vinylated products so far are low; this reaction shows promise and warrants further investigation.

71 has been generated in 40% yield from the reaction of vinylmagnesium chloride with 2,3-bis(bromomethyl)-1,3-butadiene 98 [81]. 70 is known from the reaction of 3 with 1,1-dichloroethane [9,10]. Oxidative products 31,n=4 and 68 have been characterized as side products from the reaction of 100 with zinc [81]. 68 has also been generated in low yield from the palladium catalyzed pyrolysis of allene [82].



98

Compound 69 was shown to be formed quantitatively from the reaction of 4 with ethylene, confirming the previously proposed pathway [9,10]. This reaction was shown to be specific for ethylene, as propylene and isobutylene failed to give an analogous product. Reaction exclusively at the tertiary carbon of a primary-tertiary allyl anion has been shown by the reaction of the anion derived from vinylcyclohexane with acetone [83]. This anionic "ene" reaction has synthetic promise and its generality should be further investigated. The proposed concerted mechanism is drawn below [9,10]:



All three symmetrical dimethylenebiphenyl dianions (5-7) were easily prepared from Lochmann's base at room temperature. 5-7 reacted smoothly with dimethyl sulfate and 7 also reacted well with diethyl sulfate. These reactions most likely take place via the S_N2 mechanism. SET would be expected to be favored in the series I > Br >> Cl >> RSO_4. Alkyl sulfate is an excellent leaving group and is strongly disfavored for SET.

The reaction of 7 with allyl chloride can go by either S_N2 or S_N2' mechanisms (or both).

The reaction of 7 with isopropyl bromide gave a high yield of disubstitution product 81, but the same reaction with 5 gave a lower yield of disubstitution product 80 and a significant amount of 54,n=2 which must result from SET. Obviously, steric factors are becoming important as the alkyl group becomes larger.

t-Butylations of allylic and benzylic anions, although uncommon, have been reported in the literature [10,84,85,86]. The reaction of 7 with t-butyl iodide gave the highest yield for a di-t-butylated product from a dianion yet found. A reasonably high yield of mixed oxidation/alkylation product 83 was also found. The $S_{RN}1'$ mechanism is probably operating as HME (followed by S_N2) would appear to be thermodynamically very disfavored here. The same reaction with 5 produced only the oxidation product 54,n=2, and no alkylation products. In this case steric factors prevent t-butylation and only intramolecular coupling occurs.

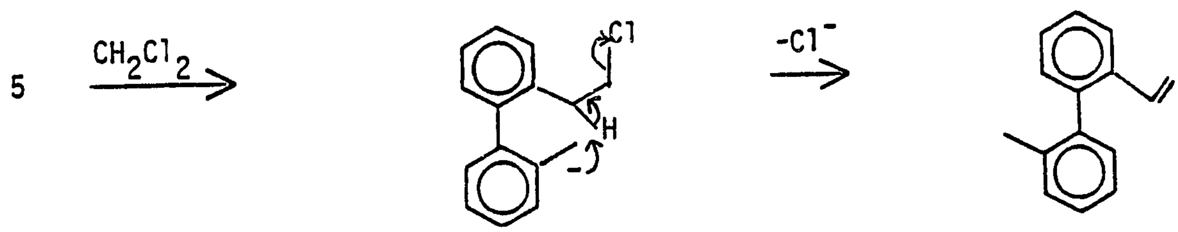
With the exception of the reaction of dianion 5 with t-butyl iodide, all of the just mentioned alkylations of 5-7 with alkyl bromides, iodides and sulfates are the easiest and most productive methods to prepare the compounds.

Dianions 5-7 were reacted with trimethylsilyl chloride to give the expected trimethylsilylated products. Trimethylgermyl bromide reacted "normally" with 5 and 7. These reactions take place by $S_N2\text{-}_{Si}$ mechanisms which involve the formation of a pentavalent intermediate analogous to the transition state in S_N2 reactions [87]. Trimethylstannyl chloride reacted sluggishly upon direct addition to dianion 7 and generated products in which an aromatic ring appears to be trimethylstannylated. Inverse addition of dianion **7** to a dilute THF solution of Me_3SnCl gave no reaction in three days; after workup starting materials were recovered. The reaction of Me_3SiCl with **5** was competitive with the same reaction with **5** generated from n-BuLi/TMEDA [28,29]. The reaction of **7** with Me_3SiCl provided a superior route to **53**. Dimeric **85** was formed, presumably from slow air oxidation of **53**.

The reaction of **5** with Me_2SiCl_2 yielded **52** in lower yield than that obtained from the di-Grignard [29]. However, the fact that the dichloride must be generated first may make the more straightforward reaction competitive.

Orthocyclophanes **54,n=5-7** were generated in good yields from the reaction of **5** with 1,3-dibromopropane, 1,4-dibromobutane and 1,5-dibromopentane. This preparation was far superior to the literature method for **54,n=5,6** [60]. **54,n=4** was generated in 5% yield from the reaction of **5** with 1,2-dichloroethane; literature methods are better in this case [58,59].

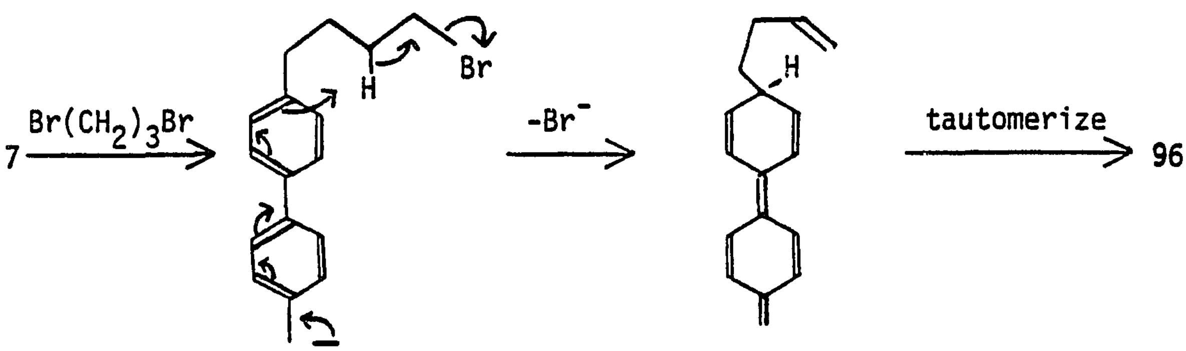
The reaction of **5** with dichloromethane gave **91** in good yield as well as **54,n=3**, presumably via intramolecular elimination as shown below.



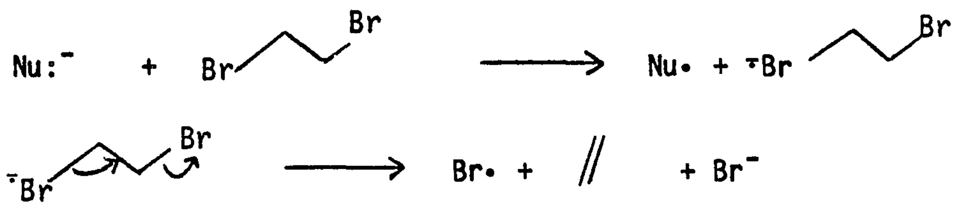
91

When **7** was reacted with dichloromethane, two of the primary products were **92** and **93** which result from elimination of chloride. Some disubstitution product **94** was obtained, but no [3.0.3.0]paracyclophane, **62,n=3**, was found. **92** has been prepared in superior yields from the dimerization of p-vinylphenylmagnesium chloride [88].

When **7** was reacted with 1,3-dibromopropane, a number of interesting products were obtained in addition to the desired [5.0.5.0]paracyclophane **62,n=5**. [2.0.5.0]Paracyclophane **97** was obtained in low yield, presumably from oxidative coupling at one end and substitution at the other end. A relatively high yield of **96** probably results from intramolecular elimination of bromide as shown below:



When **7** was reacted with 1,3-dichloropropane, little substitution occurred, and the reaction was very sluggish. The differences in reactivity between analogous chlorides and bromides point to an SET mechanism in the substitution reactions of even primary alkyl bromides, which undergo SET more easily than chlorides. This is exemplified by the reactivities of 1,2-dichloroethane and 1,2-dibromoethane with **5**. The dichloride gives a mixture of products resulting from substitution and/or elimination and gives very little oxidation. The dibromide gives exclusively oxidation product **54,n=2**. 1,2-Dibromoethane is a well-known oxidant probably reacting by the SET mechanism shown below to generate ethylene.

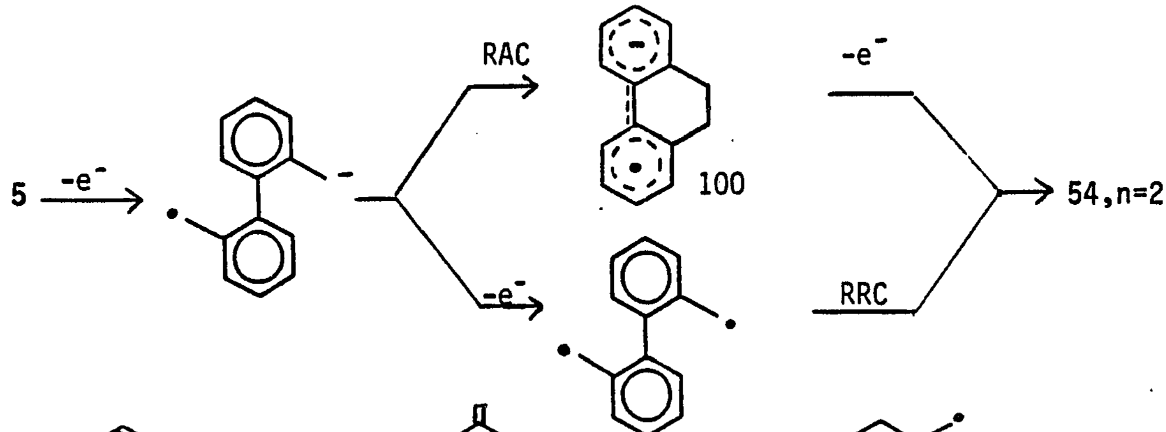


The preparation of **56,n=10** from **6** and 1,8-dibromooctane was clearly superior to the multistep literature preparation [64]. The yield of **56,n=9** prepared analogously dropped to 7%, presumably due to some increase in ring strain.

The preparation of **60,n=14** from **7** and 1,12-dibromododecane was clearly more efficient than the multistep literature preparation [65,66]. Only barely perceptible amounts of **60,n=12** were obtained, identified by an absorption at δ = -0.2 ppm [66]; this is upfield from TMS. Again, the low yield may be attributed to increased ring strain. **60,n=16** was very difficult to separate from side products but was obtained about 80% pure in small amounts. This is still probably superior to the literature method [65,66,89]. Numerous side products that were noted but not completely characterized were obtained in these reactions. These side products contained terminal bromides from half-reacted dibromides, terminal vinyl groups resulting from elimination, benzylic methyls, biphenyl and paraffin moieties in various combinations.

Dimeric products 65 and 62 were also isolated from the reactions of 6 and 7 with α,ω-dibromoalkanes, all in between 20 and 33% yield. These compounds or more complex derivatives may have potential for forming host-guest complexes somewhat analogous to dibenzene chromium. Compounds in these series such as 62,n=5 and even 65,n=2 which have no corresponding monomers would also be of interest for this reason.

Oxidation of 7 with either iodine or 1,2-dibromoethane failed to generate 62,n=2, not unexpectedly, as 62,n=2 is geometrically strained. Preparation of 65,n=2 by oxidizing dianion 6 with 1,2-dibromoethane is superior to other methods. Dianion 5 oxidizes very readily to monomeric 54,n=2, being generated in 68 and 67% yields using 1,2-dibromoethane and t-butyl iodide and as side product in varying amounts in every reaction of dianion 5 except that with dimethyl sulfate, which reacts purely in an S_N2 manner. The oxidation of dianion 5 to 54,n=2 is certainly a SET process. Intramolecular RAC of radical anion 99 to give ring-closed radical anion, 100, is the most likely pathway. However, RRC via diradical 101 cannot be rigorously excluded, as its resonance form 102 should contribute greatly to its stability despite some steric strain. Nevertheless, this requires the transfer of the second electron before ring closure. 7 may react via intermediate 103 which is the less sterically strained analog of 102. Conjugation across the aryl-aryl bond is not possible in the intermediate derived from 6; this species, 104, must exist solely as a diradical.



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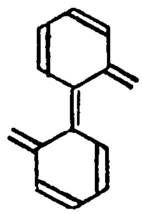

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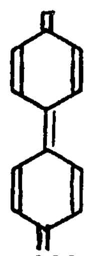

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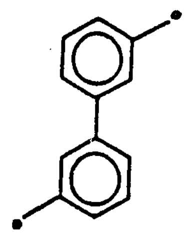

104

The reactions of 5 with α-α′-dibromo-m-xylene and 6 with α,α′-dichloro-p-xylene may well involve HME as the benzylic anions and possibly dianions thus formed would be of comparable stability to 5-7. HME is probably taking place by SET and other SET processes not leading to HME are probably occurring as well to complicate matters with these reactive species. The high yield of [2.2]metacyclophane, 45, relative to disubstitution product 66 strongly suggests that HME is involved. Coupling of benzylic halides is known in reactions of 3 with benzyl bromide and chloride [9,10]. Other alkyl and allyl halides do not exhibit this behavior, but HME would not be expected to be involved in their reactions. Although 66 and 67 were formed in lesser amounts than literature preparations, this method may retain some synthetic utility due to its shortness and availability of starting materials.

Before leaving the subject of reactivity of these dianions it should be pointed out that when one equivalent of base was used instead of two to deprotonate 10, dianion 7 was still formed in greater amounts based on quenching with Me_2SO_4 than monoanion 28 which might be expected to predominate based on simple consideration of REPA's. The dianion salts precipitate from the hydrocarbon solvent while the monoanions are considerably more soluble. Thus dianion may be formed preferentially to monoanion despite the latter's low thermodynamic acidity.

Another point to make is that even under relatively dilute conditions, the concentration of these dianions in THF during reactions may be quite high and the actual reacting species may be a dimeric, tetrameric, hexameric or higher aggregate rather than a monomeric species which would be expected in dilute solution. These higher aggregates may or may not react similarly to their corresponding monomers. This factor was neglected in the discussion of reactions of these dianions due to a lack of evidence as to aggregation states. These dianions exist as contact ion pairs as potassium salts in THF and not as solvent separated ion pairs [90]. The intimate proximity of the potassium to the anionic center may cause differences in reactivity relative to a free ion or solvent-separated ion pairs. These considerations were also neglected for simplicity.

Interest in biphenyls has largely been centered around the electronic and steric interactions between the two aromatic rings and their substituents. The key indicator giving us insight into these interactions is the central phenyl-phenyl bond and twisting, bending, and rotating of planes of the rings about this bond. The measure of the amount of rotaion of one ring away from the plane of the other is the dihedral angle θ of the intersecting planes. θ provides a simple yet powerful measure as to the magnitude of these interactions.

What is the best means with which to probe angle θ in these highly symmetrical molecules? Electronic interactions are maximized when the rings are coplanar and $\theta=0°$ or $180°$. When $\theta=90°$ electronic interactions are minimized. The obvious technique is UV/visible spectrophotometry and indeed most of the previous determinations of θ in symmetrically disubstituted biphenyls have been done using this technique. However, we wished to investigate high resolution ^1H NMR as a technique to probe the conformations of these molecules. Also UV/visible spectroscopy can be very sensitive to lingering impurities with high extinction coefficients. This a nagging problem with some of these compounds.

X-ray crystallography, of course, gives the most definitive information as to a molecule's conformation and configurations. However, crystals may be difficult to grow and the technique is time consuming and accordingly expensive. The molecule may also have differing conformations in the crystal, in solution and in the gas phase. Biphenyl itself is coplanar in the solid state [91], yet has $\theta \approx 45°$ in the gas phase and in solution [92]. Predictions of $\theta=20\text{-}30°$ from UV/visible data are now thought to be in error [94]. When $\theta \approx 45°$ there is still some stabilizing electronic interaction between the two rings but steric strain involving the hydrogens at the 2-positions has been relieved. Interestingly, coulombic repulsion as exhibited by the benzylic methylenes of dianion 5 opens θ to 73.7° [29].

One interesting anomaly that yields useful ^1H NMR information is the ring-current effect in which protons lying above or below an aromatic ring are highly shielded and are shifted upfield as a function of proximity to the center of the ring and to its plane. The change in chemical shift may be calculated if these parameters are known [95,96]. This effect can be quite dramatic in the 2,2′-disubstituted-biphenyls 77 as well as in the various cyclophanes for both methylene protons and aromatic protons in the position ortho to the second ring.

Disubstitution at the 3,3′ and 4,4′ positions alters the barriers of rotation for the central σ-bond very little and the ortho protons differ very little from one compound to the next. The barrier remains the same as in the parent biphenyl. Moderately bulky groups on the side chain may restrict rotation about the bond between the ring and the benzylic carbon. ESR studies of cation radicals of 53 [97,98] and 50 [99] show restricted rotation about this bond. However, the ^1H NMR spectra of **53**, **84**, **50** or other disubstituted biphenyls show no differences which could be attributed to this phenomenon.

Disubstitution at 2,2′ positions of biphenyl raises the barrier of rotation about the central σ-bond; when bulky groups are attached the molecules are held increasingly in conformations close to $\theta=90°$. When $\theta=90°$ the ortho protons are held in a position where they are feeling the maximum ring-current effect from the adjoining ring and their absorptions in ^1H NMR are shifted upfield enough to be resolved from the other aromatic protons which do not shift appreciably from their corresponding positions in the more freely rotating 3,3′-and

4,4′-disubstituted analogs. The ortho protons of 77 were consistently between δ7.07 and δ7.10 while those for 78 varied from δ7.21 to δ7.42 and those for 79 varied from δ7.44 to δ7.50. The inconsistency in the chemical shifts of the ortho protons of the 3,3′-disubstituted derivatives is largely due to enhanced sensitivity to inductive effects from the substituent, being ortho and para to the substituent in this case, but meta to the substituent in the other two cases. In all three cases the presence of trimethylsilyl groups on the benzylic carbons caused the largest perturbation in the chemical shifts of all the aromatic protons. The benzylic protons of 77 were shifted upfield 0.17 to 0.34 ppm from those of 78 and 79. In addition to this display of the ring current effect, these methylene protons show non-equivalence, having different chemical shifts and exhibiting geminal couplings of about 14 Hz. When rotation about the central σ-bond is hindered, rotation about the bond linking the benzylic carbon and the ring becomes increasingly hindered as well, leading to non-equivalence of the benzylic methylene protons and even those further away. As mentioned previously, the rotation barriers for the bond linking the benzylic carbon and the ring are present although very much smaller in 78 and 79.

The lower members of the orthocyclophanes 54 provide us with a series of compounds in which the two aromatic rings are more or less "locked" into rigid conformations and θ becomes relatively constant. θ increases incrementally as the number of methylenes (n) in the bridge is raised. θ=0° for fluorene, 54,n=1, in which the aromatic rings are locked rigidly in place. Various values for θ have been assigned for

54,n=2, all in the range of 15° to 24°, on the basis of theoretical calculations [100,101], UV-visible [102], ^{13}C NMR [94], and photoelectron spectroscopy [92] as well as Raleigh scattering experiments [103]. Unfortunately, no X-ray crystal structure has been obtained. As the ^{13}C NMR work of Paquette [94] will be parallelled to a certain extent by 'H NMR in this work, their value of 16° will be used for 54,n=2. Calculations have given a value of θ=49° for 54,n=3 [94,101,104] and a value of θ=59° for 54,n=4 [94,101]. Examination of models in conjunction with careful examination of 'H NMR parameters has led us to assign approximate values θ=65° for 54,n=5 and θ=105° for 54,n=6 for the most stable conformations in solution. In the case of 54,n=7, the use of models and 'H NMR leads to no obvious dominating conformation as the methylene chain has become long enough to allow several favorable conformations with θ varying between θ=65° and θ=115°.

As mentioned previously fluorene 54,n=1 is virtually rigid. 54,n=2 exhibits rapid interconversion on the NMR time scale between its two energy minimas where θ=±16° through its energy maximum where θ=0°, the benzylic protons being equivalent and appearing as a sharp singlet. 54,n=3 also interconverts rapidly on the NMR time scale and the benzylic protons are equivalent showing a broadened triplet and the homobenzylic protons exhibit a quintet. However, 54,n=4-7 as well as 77 display benzylic protons with different chemical shifts and typically large (14 Hz) geminal coupling constants. Other protons on the remaining methylenes become non-equivalent as well, also exhibiting different chemical shifts and geminal coupling constants. In these cases interconversion through the θ=0° energy maximum has become slower than the time frame for 'H NMR data acquisition. Space-filling models confirm this trend. Interestingly, for 54,n=3,5,7 the hydrogens of the single methylene farthest away from the aromatic rings are equivalent, while the hydrogens on the methylenes farthest away in 54,n=4,6 display different chemical shifts and geminal couplings. This spreading out of signals for individual protons allowed definitive assignment of chemical shifts and coupling constants for all aliphatic protons in 54,n=5,6,7. This allowed us to attempt to define the preferred conformations for these molecules by adjusting space-filling models to fit coupling magnitudes and ring current effects on chemical shift. Decoupling was done when necessary to confirm proton assignments and obtain coupling constants.

Having assigned values for angle θ to each member of 54, we can see which 'H NMR parameters are most sensitive to this change. The methylene protons are sensitive to θ but their chemical shifts are more dependent on the complex changes in the side chain as its size varies. Referring to the labeling scheme and data in Table A.1, we can see that H_b, which is para to the central σ bond, is almost totally insensitive to changes in θ. The changes in chemical shift for H_a do not correlate to changes in θ. However, H_d and to a lesser extent H_c display an upfield shift as a function of θ. We decided to explore this relationship to a further extent.

Paquette and coworkers showed that ^{13}C NMR chemical shifts of the charge bearing carbon in cations 105 were related linearly to $\cos^2\theta$

[94]. We wished to see if a similar relationship existed between δH_c or δH_d of **54** and $\cos^2\theta$. The stabilization energy available from interaction of the phenyl rings across the central bond is known to be directly proportional to $\cos^2\theta$ [105].

δH_d of **54** correlated quite well with $\cos^2\theta$ when only specifically known values of δH_d are used (Fig. 2); the values of δH_d for **54**,n=3,4 were not included as the chemical shifts are known to be in a certain range, but no specific values were assigned. Using the values for **54**,n=1,2,5,6,7, the equation δH_d=0.902 $\cos^2\theta$ + 6.93 ppm is obtained using the linear regression program on a Texas Instruments TI-59 hand calculator. The correlation coefficient was an excellent 0.9999 for this relationship. The resulting line lies in the middle of range of possible values for δH_d of **54**,n=4; however, the corresponding range of possible values for **54**,n=3 lie above the line. 4,4′-Dimethylbiphenyl **10** and 3,3′-dimethylbiphenyl **9** should, like biphenyl, have average conformations where θ=45° and $\cos^2\theta$=0.5 and should be good tests for the correlation. The value for **10** lies about 0.08 ppm above the line and the values for **9** lie 0.01 to 0.03 ppm below the line, which are not large deviations.

δH_c of **54** displayed a weaker correlation to $\cos^2\theta$ than did δH_d. Again only specifically known values for δH_c of **54**,n=1,5,6,7 were used and not δH_c ranges known for **54**,n=2,3,4. The correlation coefficient was found to be 0.9874, which is not very good. The equation obtained was δH_c=0.2507 $\cos^2\theta$ + 7.13 ppm. The resulting line goes through the range of values for **54**,n=3, but lies below those of **54**,n=4 and above

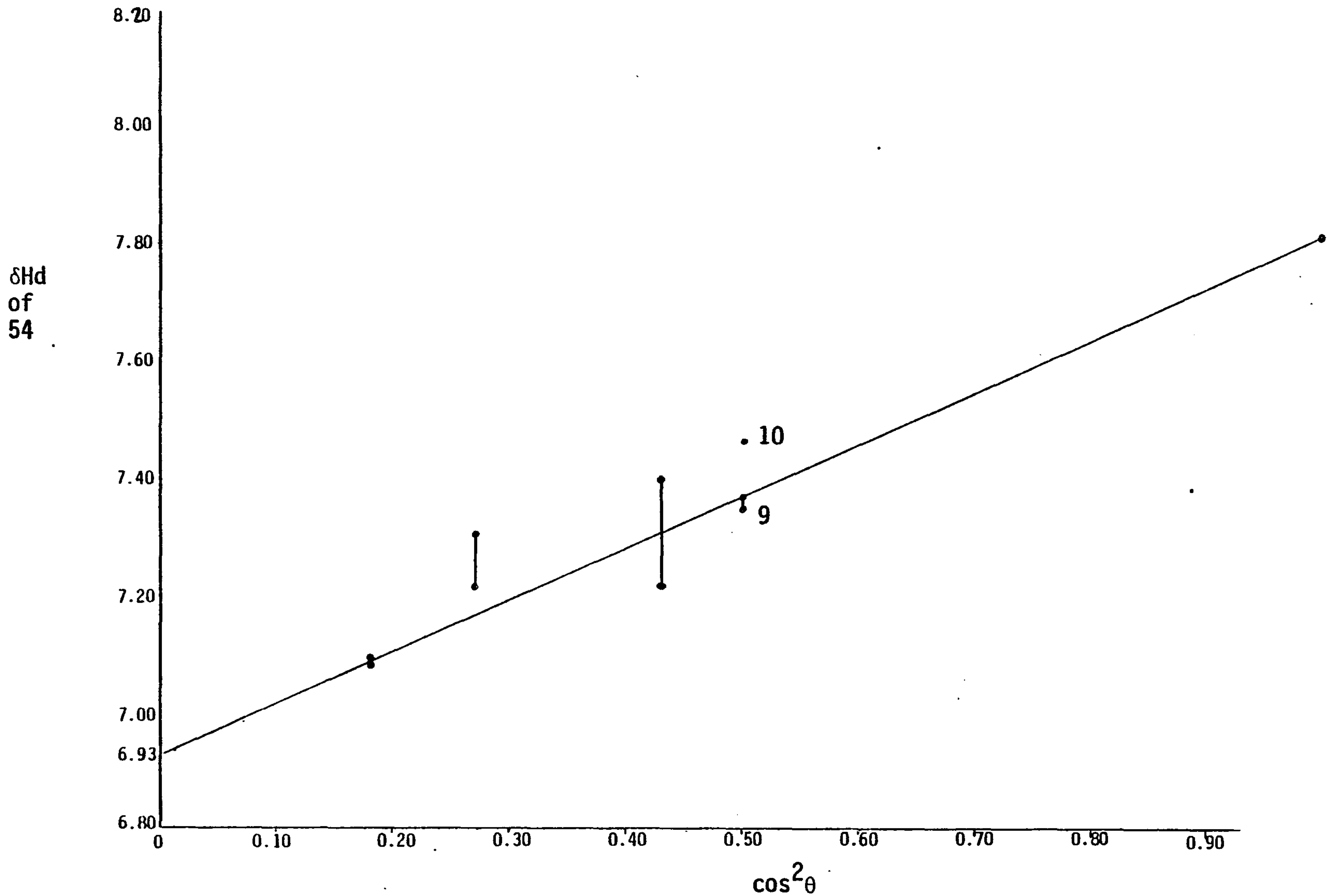

Fig. 2. Correlation of δH_d of 54 and $\cos^2\theta$

those for 54,n=3. The values of δH_c for 9 and 10 lie above and below the line but are reasonably close. δH_c would be expected to correlate with $\cos^2\theta$ to a lesser extent than δH_d as it lies too far away from the second ring to be influenced significantly by the ring current effect and it is less sensitive to resonance and inductive effects as well, yet a weak correlation between δH_c of 54 and $\cos^2\theta$ does exist.

52 represents a ring size slightly larger than 54,n=3. Interconversion of conformations through $\theta=0°$ is slow on the NMR time scale and the benzylic protons differ 0.04 ppm in chemical shift and a geminal coupling constant of 13.3 is observed. Chemical shift values of the aromatic protons of 52 do not correlate particularly well with those of 54. This is due to inductive effects of the silyl substitutent, as seen with the other silyl derivatives of 5-7.

[n.0]Paracyclophanes, 60, with the methylene chain lying directly over the aromatic rings, exhibit dramatic ring current effects on these methylene protons in the NMR. As the chain becomes smaller, the methylene protons are increasingly shielded and shifted upfield, the extreme being $\delta H = -0.2$ for 60,n=12 [65]. Reducing the length of the chain also strains the aromatic framework. There are several ways in which these molecules can relieve this strain. When θ is reduced, steric interaction between the methylene protons and aromatic protons is minimized. Angle abc can decrease from 180° or the aromatic rings can become distorted from planarity. The distance between the rings across the central σ bond can also be reduced. This distance is intimately related to θ as the bond takes on more double bond character as θ is decreased and more conjugation is allowed.

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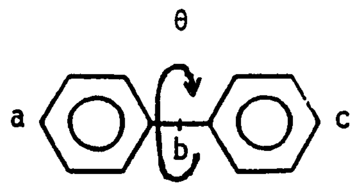


As **60,n=14** was the most easily obtained of this series and large single crystals could be grown, an X-ray diffraction study was carried out. We wished to compare the conformation observed in the crystal to that calculated to be most stable by MM2 [106], and to that indicated by ¹H NMR to predominate in solution. The tables of Johnson and Bovey [95,96] estimate the magnitude of the ring current effect on chemical shifts as a function of distance away from the plane of an aromatic ring and distance away from the center of that ring. The ring current effects from both rings were assumed to be additive and the values for the two protons on each methylene were averaged. These tables were used to estimate the chemical shifts of the methylene protons as calculated for the X-ray structure and MM2 structure. ORTEP [107] drawings of the X-ray (Fig. 3) and MM2 (Fig. 4) conformations show them to be considerably different, particularly for the methylene chain. Chemical

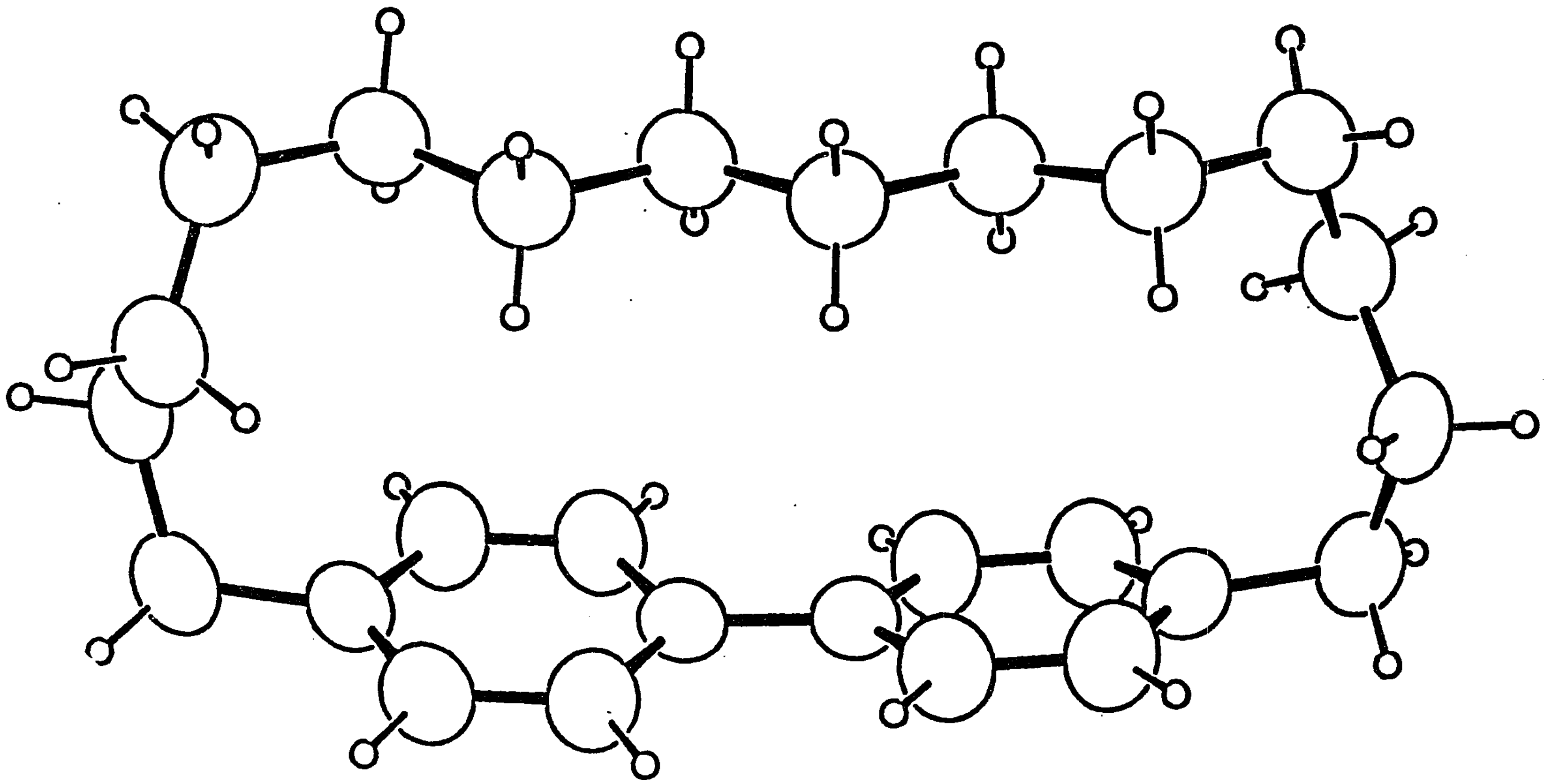


Fig. 3. ORTEP drawing of X-ray structure.

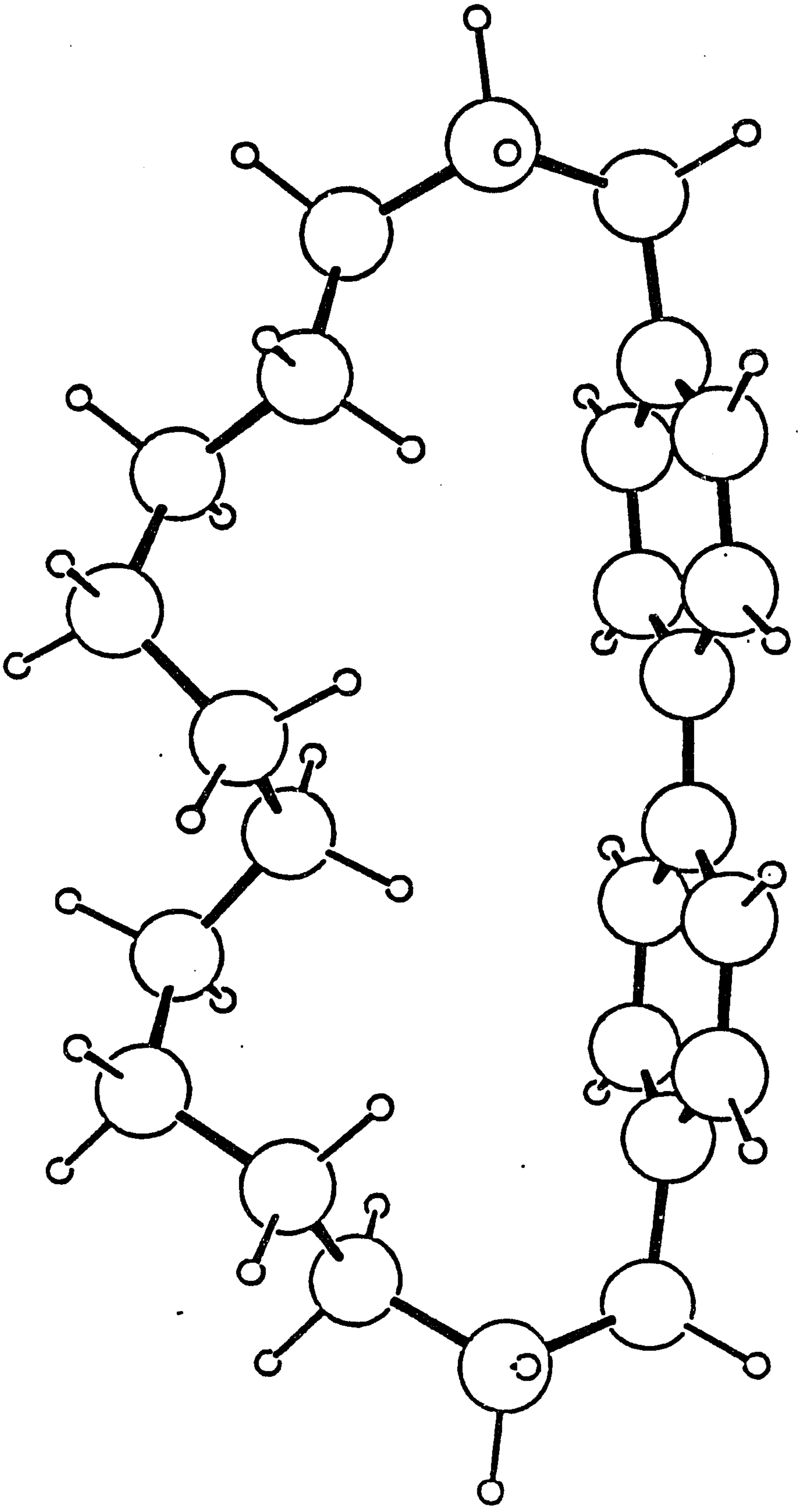


Fig. 4. ORTEP drawing of MM2 structure.

shifts estimated for both of these conformations do not fit well with the experimental data. However, averaging the X-ray and MM2 values gives estimated shifts similar to those determined experimentally (Table 7). If these two conformations are close in energy, are more stable than other conformations, and have a low interconversion barrier, then they would be expected to have similar populations in solution and the NMR spectrum would display an average of the two.

In order to be certain of chemical shift assignments for the protons on **60,n=14**, decoupling and the two dimensional ^{1}H NMR chemical shift correlation experiment, COSY [108] (Fig. A.10), were performed.

An examination of θ for **60,n=14** reveals that MM2 predicts 0° and the X-ray shows a value of 14.5°. The chemical shift of the aromatic protons ortho to the adjacent ring is shifted ~0.1 ppm downfield from the corresponding protons in the analogous aliphatic compounds. This is indicative of a reduction in θ; however, the relatively small change infers that θ is still significantly more than 0° for **60,n=14** in solution.

Angle abc, which is 180° in acyclic biphenyls, is 4° in **60,n=14** according to the X-ray structure. This angle was estimated to be smaller in the smaller analogs **60,n=11-13** based on ESR studies of the anion radicals in this series [89]. The X-ray structure of **60,n=14** revealed only a slight distortion in the planarity of each ring.

The bond distance between the two rings in **60,n=14** is 1.487 ± 0.0033Å which approaches that of fluorene (1.48Å) and is somewhat less

Table 7. Calculated and Experimental Values of the Chemical Shifts of Methylene Protons in 60,n=14 in ppm[ab]

	MM2	X-ray	Average	Observed
δH_a[c]	1.80	1.90	1.85	2.68
H_b	1.40	1.40	1.40	1.64
H_c	1.10	1.00	1.05	1.15
H_d	0.20	1.02	0.61	0.70
H_e	0.80	0.72	0.76	0.84
H_f	0.70	0.14	0.42	0.54
H_g	0.00	0.46	0.23	0.59

[a]labeling conforms to that shown in Table A.4.

[b]an unperturbed methylene proton is assumed to have a value of $\delta H=1.20$.

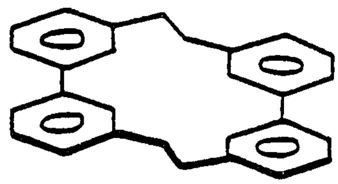
[c]Calculated δ values for benzylic protons H_c are included for completeness but probably have little meaning.

than that for biphenyl (1.52Å) [94,109]. This is quite consistent with θ being small in **60,n=14**.

Although hindered, the methylenes in **60,n=14** are probably able to move 360° around the aromatic rings in a "jumprope" fashion at room temperature (this is the same as the rings rotating 360° while the methylenes remain motionless). Hindered rotation in paracyclophanes had been previously demonstrated [110,111,112]. We wished to see if we could "freeze out" conformations by lowering the temperature. However, after lowering the temperature to -90° in THF-d_8 and CD_2Cl_2 only some broadening of methylene proton absorptions had occurred.

In **56** the rings are held coplanar (θ=0°) when the number of methylenes (n) in the chain is small. With an increase in n, there should be a corresponding increase in θ. ENDOR studies have indicated that the aromatic rings are near planarity in **56,n=8,10** [113]. Ortho protons, δH_a and δH_d (Table A.3) in **56,n=10**, which were shown to be linearly related to $\cos^2\theta$ in **54**, are shifted downfield relative to those of **9, 47** and dimeric **65,n=9,10** indicating that θ is lower than in these less constrained analogs. Although δH_b in **56,n=10** is the same as in the other 3,3′-disubstituted biphenyls, δH_c is shifted slightly downfield being less affected by θ than δH_a and δH_d. Benzylic and homobenzylic protons δH_e and δH_f of **56,n=10** are shifted downfield relative to those in the less constrained dimeric compounds **65,n=9,10**. δH_h and δH_i are more deshielded than δH_g and are shifted downfield. This effect is more pronounced in **56,n=8** [64]. However, **56,n=9** displays an ^{1}H NMR spectrum which is more similar to acyclics 9 and 47 and large ring dimeric compounds 65,n=9,10. Although the benzylic and homobenzylic protons in 56,n=9 are very similar to those in 56,n=10, the rest of the spectrum resembles those of 9,47 and 65,n=9,10. There are not enough data on this series of compounds (56) to explain this anomaly.

[2.0.2.0]Metacyclophane, 65,n=2, has been the subject of several studies [69,70,114]. The upfield shift of δH_a in 65,n=2 to 5.96 has been noted and two different conformations have been suggested to explain this shift. The anti conformation shown below was first proposed [70].



Twisted conformations having D_2 symmetry and $\theta \approx 30°$ between adjacent aromatic rings were later used to explain the 'H NMR spectrum [114]. An X-ray study of the corresponding compound with methoxyl groups in the 2-positions and methyl groups in the 5-positions showed D_2 symmetry with $\theta = 89.9°$ in the biphenyl moiety [115]. Our X-ray analysis of 65,n=2 exhibited a structure with approximate D_2 symmetry. θ was found to have different values: 52.1° between rings a and b and 46.8° between rings c and d. Angles of twist between the methylenes and aromatic carbons do not conform precisely with D_2 symmetry. The ORTEP view of 65,n=2 in Fig. 5 shows that protons on carbons 2a-2d are magnetically shielded by an aromatic ring across the larger ring. Using the tables of Johnson and Bovey [95,96], we calculated the upfield shift expected for the conformation observed in the crystal to be just what is observed in solution by 'H NMR. This conformation and its enantiomer probably represent the lowest energy minimum for the molecule as it predominates both in solid and in solution. Fig. 6 provides an orthogonal view to the one in Fig. 5.

'H NMR assignments were confirmed using the 2D COSY (Fig. A.13) experiment and NOE (nuclear Overhauser effect). ^{13}C NMR assignments were made based on the 2D $'H/^{13}C$ heteronuclear chemical shift correlation spectrum (Fig. A.14).

The ortho protons Ha of 67 (Table A.9) are shifted upfield by the third isolated ring, but not to the extent of those in 65,n=2.

An array of ring current effects from the three aromatic rings in 66 spreads out the absorptions of the aromatic protons and allows assignment for each chemical shift and coupling constant (Table A.10, Fig. A.16). The most stable conformations for this molecule conform with those of 54,n=7.

Lastly, [2.0.5.0]paracyclophane 95 is like 62,n=2 at one end and aromatic protons at that end are shielded and shifted upfield. The other end is like 62,n=5 and the aromatic protons at this end are the least shielded by the opposing ring. The shifts for this compound are listed in Table A.8. There is a gradient of shielding from the two methylene end of the molecule to the five methylene end, exemplifying the sensitivity of 'H NMR to structural factors in these compounds.

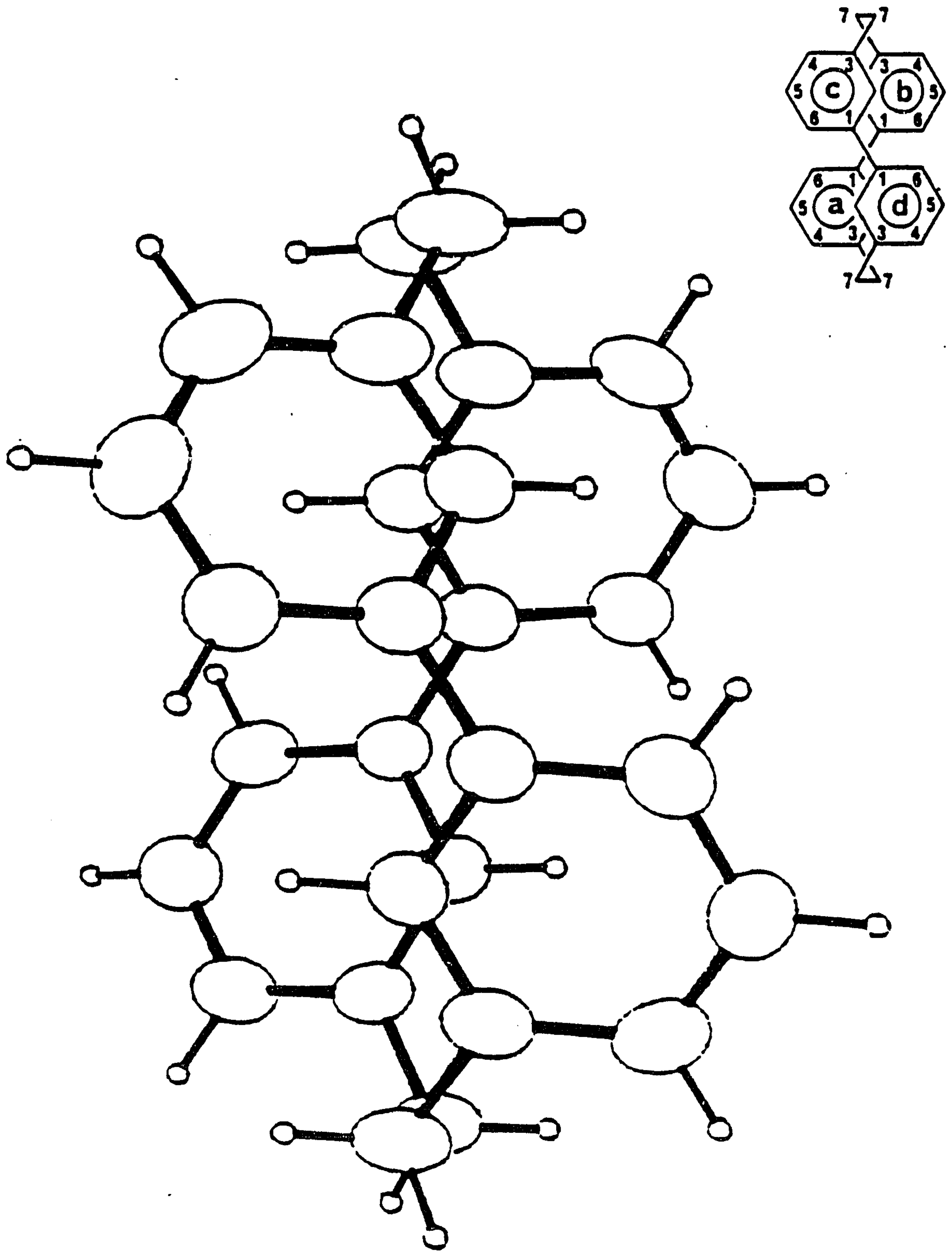


Fig. 5. ORTEP view of 65,n=2.

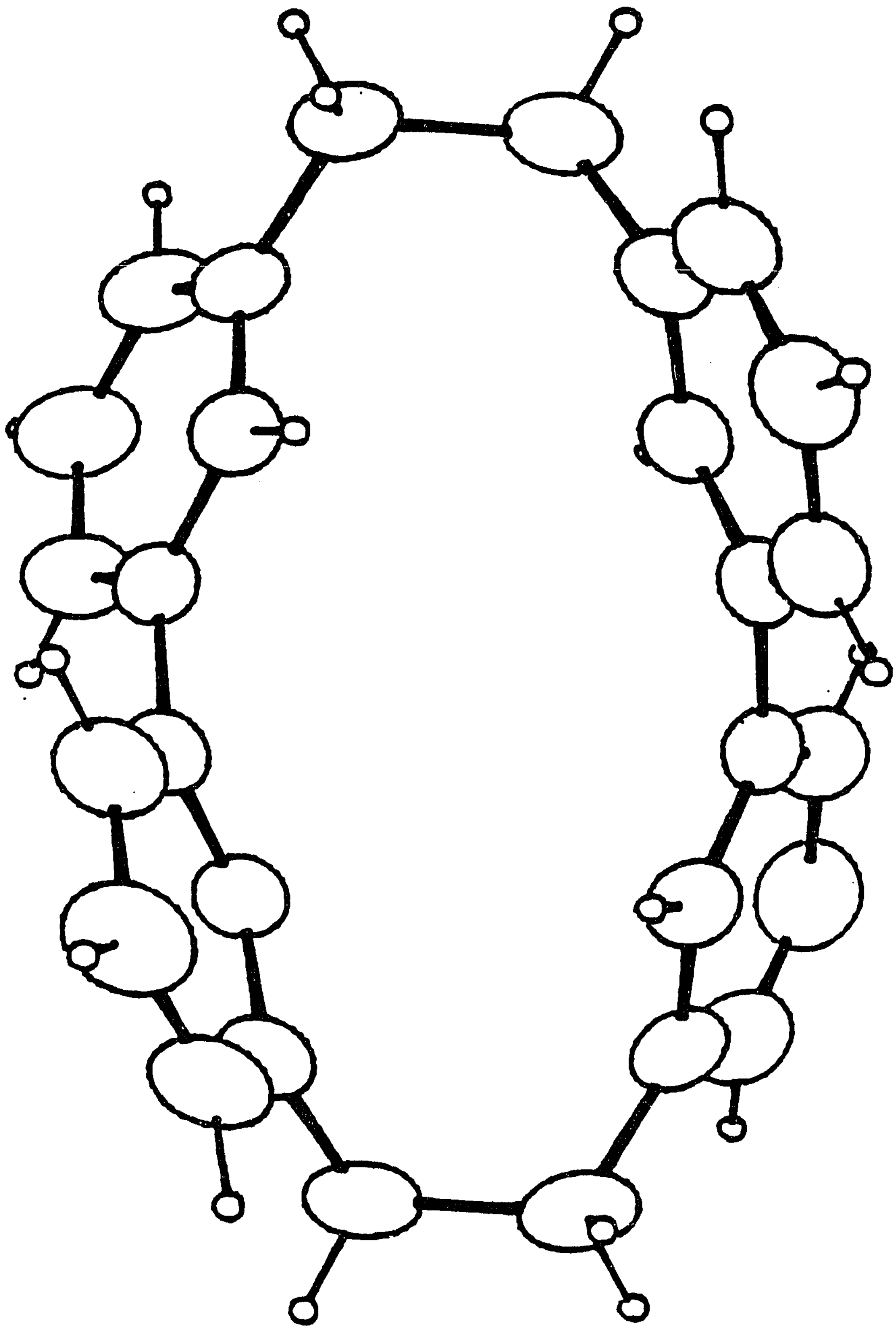


Fig. 6. ORTEP view of 65,n=2, rotated 90° from that in Fig. 5.

EXPERIMENTAL

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker WM-250 spectrometer at the University of Arizona, on 300, 400, or 500 MHz spectrometers at the University of Chicago, or on a 600 MHz spectrometer at Carnegie-Mellon University. All samples were run with $CDCl_3$ as the solvent unless otherwise noted. Chemical shifts are reported in parts per million downfield from tetramethylsilane (TMS). Elemental analyses were performed at the University Analytical Center, Tucson, Arizona or MicAnal, Tucson, Arizona. Melting points were uncorrected.

Products were isolated using simple liquid chromatography with a 70-230 mesh silica gel packing. Various solvents were used.

Tetrahydrofuran was freshly distilled from sodium/benzophenone. Pentane and hexane were washed with sulfuric acid, fractionally distilled from NaOH and stored over KOH. 4,4´-Dimethylbiphenyl (10) and 3,3´-dimethylbiphenyl **9** were prepared and purified using the method of McKillop et al. [48]. 2,2´-Dimethylbiphenyl was prepared and purified by the method of Hall, Leslie and Turner [51]. Other reagents were used as received or purified by standard methods. Drying of organic solutions was done using anhydrous magnesium sulfate. All glassware used in anion preparations and reactions was dried for several hours at 120° before use. All preparations and reactions of anions were done under positive argon pressure. All transfers of anions were done via syringe or cannula. Solvents were removed using a rotary evaporator where appropriate.

^{1}H NMR, ^{13}C NMR, 2D NMR and X-ray crystallographic data are compiled in tables and figures at the end of the Experimental Section. Reported yields are based on the parent hydrocarbon. Yields were determined by adding known amounts of benzene, dichloromethane or p-dioxane to the sample and measuring the areas of the pertinent signals. Monosubstituted products from monoanions **26-27** were not isolated in general; their yields were estimated from the areas of benzylic methyl groups and comparison with those of the corresponding starting materials **8-10**. All products were liquids at room temperature except those for which melting points are listed, or otherwise noted. All derivatives of **7** are solids.

Reaction of Dianions with Electrophiles

Three methods of addition were used in the reactions of dianions with electrophiles. Direct addition involved the addition of two equivalents of electrophile directly to the stirring THF suspension of the dianion. Inverse addition required the addition of the dianion suspension to two equivalents of electrophile in 200 mL THF with stirring. Simultaneous addition was done by adding the dianion suspension dropwise to stirring THF (200 mL) while one equivalent of dihalide in 50 mL THF was added dropwise simultaneously from an addition funnel over about 40 min. The receiver for simultaneous and inverse addition was generally a 500 mL three-neck round-bottom flask kept at 0° in an ice bath. After the additions were completed the reaction mixtures were stirred while warming to room temperature. Reactions of dianions with monofunctional electrophiles were done by inverse addition and reactions of dianions with dihalides were done using simultaneous addition unless otherwise noted.

Dianion 3

2,3-Dimethylenebutadiene dianion **3** was prepared by adding 2.0 mL (17.7 mmol) of 2,3-dimethyl-1,3-butadiene in 25 mL of pentane dropwise to a stirred mixture of 4.0 g (35.6 mmol) potassium t-butoxide, 75 mL pentane and 2.47 mL (3.56 mmol) 1.44 M n-butyllithium (in hexane) in a 250 mL round bottom flask. After 30 min. continued stirring, the orange dianion salt was filtered using a Schlenk filter and washed with 100 mL pentane to remove lithium t-butoxide and any excess n-butyllithium. The resulting solid was blown dry with argon. The dianion salt was suspended with stirring in precooled THF (60 mL) at 0° for reactions. The yield of **3** is known to be 73% based on D_2O quench [22,24].

Reaction of Dianion 3 with Cadmium Iodide in THF

Dianion **3** was reacted with 7.0 g (17.9 mmol) cadmium iodide in THF using inverse addition. Pentane (200 mL) and water (200 mL) were added. A massive flocculent precipitate formed in the aqueous phase. Just enough 2M aqueous HCl was added to dissolve the precipitate. The two phases were filtered through Celite. The organic phase was washed twice with conc. NaI solutions (200 mL) and twice with water (150 mL). The crude product was obtained following drying, filtering and removing the pentane. Following bulb to bulb distillation, the products were separated by preparative gas chromatography (GC) using a Varian

Aerograph, Model 700 equipped with 10% SE-30 on Chromosorb W-HP. The products were characterized by ^{1}H NMR.

1,2,5,6-Tetramethylenecyclooctane (**31**,n=4) [9,10,41,43] (Table A.22) was produced in 11% yield. 2,3,6,7-Tetramethyleneoctane (**68**) [81,82] (Table A.23) was made in 2% yield. 3-Ethyl-2,3-dimethyl-1-octene (**69**) [9,10] (Table A.24) was found in 12% yield.

5-Ethyl-5-methyl-4-methylene-1-decene (**74**) (Table A.25) was detected in 2% yield. 2-Methyl-3-methylene-1,5-hexadiene (**70**) [9,10,81] (Table A.26) was formed in 9% yield. A 4% yield of 4,5-dimethylene-1,7-octadiene (**71**) [81] (Table A.27) was obtained. 4,5-Dimethylene-2-hexanol (**72**) (Table A.28) was generated in 5% yield and a 15% yield of 4,5-dimethylene-1-octen-7-ol (**73**) (Table A.29) was also found.

Reaction of Dianion 3 with Other Oxidizing Agents

Dianion **3** was reacted similarly with other oxidizing agents. Generally only the yield of **31,n=4** [9,10,41,43] (Table A.22) was determined; these yields are given in Table 2. The reaction of **3** with $ZnBr_2$ in THF gave the same products in the same proportions as in the CdI_2 reaction above except oxidative coupling products **31,n=4** and **68** were not formed.

Monoanion 4

Monoanion **4** was prepared by adding 2.0 mL (17.7 mmol) of 2,3-dimethyl-1,3-butadiene in 25 mL of hexane to a sixfold excess of n-butyllithium to warm to room temperature and react for two days before quenching.

Reaction of Monoanion 4 with H_2O

The reaction mixture from above was quenched with ice and 200 mL hexane was added. The organic phase was washed 7 x 300 mL precooled 2M HCl and then 2 x 200 mL water. After drying and filtering, the hexane was removed and ^{1}H NMR showed a 4:1 mixture of 2,3-dimethyl-2-octene (**75**) (Table A.30) and 2,3-dimethyl-1-octene (**76**) (Table A.31) in a combined yield of 50%.

Reaction of Monoanion 4 with Ethylene

Ethylene was allowed to bubble through the reaction mixture containing **4** for half an hour. The resulting solution was quenched as above. **69** was obtained in 50% yield by ^{1}H NMR (Table A.24). Therefore the reaction of **4** with ethylene is quantitative.

Dianion 5

2,2′-Dimethylenebiphenyl dianion **5** was prepared by adding 8.0 mL 1.55 M n-butyllithium (12.4 mmol) in hexane via syringe to a stirred mixture of 1.0 mL (5.5 mmol) 2,2′-dimethylbiphenyl, 1.4g (12.5 mmol) potassium t-butoxide and 125 mL pentane in a 250 mL round bottom flask. After two hours continued stirring, the dark orange-red dianion salt was filtered using a Schlenk filter and washed with 100 mL pentane. The resulting solid was blown dry with argon. The dianion salt was suspended with stirring in precooled THF (60 mL) at 0° for reactions.

Dianion 6

3,3′-Dimethylenebiphenyl dianion **6** was prepared as was dianion **5** above, except that only 45 min. are required for reaction. The dianion salt is dark reddish purple in color.

Dianion 7

4,4′-Dimethylbiphenyl dianion **7** was prepared exactly as was dianion **6** above. The dianion salt is the color of liver, similar to but darker than dianion **6**.

Reaction of Dianion 5 with Dimethyl Sulfate

Dimethyl sulfate was reacted with **5** using direct addition. 6M NaOH was added to the reaction mixture to quench excess methyl sulfates. THF was removed and the products were taken up in dichloromethane (200 mL) and water (150 mL). Both phases were filtered through Celite which was washed with CH_2Cl_2 (50 mL). The organic phases were combined and washed 5 x 200 mL with water. The resulting organic solution was dried and filtered. After removal of CH_2Cl_2, the crude product was purified using LC with 1:1 CCl_4/cyclohexane as the solvent, giving an 86% yield of 2,2′-diethylbiphenyl (**48**) [51], identified by ^{1}H NMR (Table A.5). Examination of the crude product by ^{1}H NMR showed the presence of 8% 2-ethyl-2′-methylbiphenyl and 5% starting material (Table A.5).

Reaction of Dianion 5 with 2-Bromopropane

2-Bromopropane was reacted with **5** using inverse addition. After removal of THF, the reaction mixture was taken up in CH_2Cl_2 (200 mL) and water (150 mL). Both phases were filtered through Celite which was washed with CH_2Cl_2 (50 mL). The organic phases were combined and washed 5 x 200 mL with water. The resulting organic solution was dried and filtered. After removal of CH_2Cl_2, the crude products were separated using LC with 1:1 CCl_4/cyclohexane as the solvent. A 50% yield of 2,2′-disobutylbiphenyl (**80**) was identified by 'H NMR (Table A.5). 9,10-Dihydrophenanthrene (**54**,n=2) (Tables A.1, A.2), 20%, 2-isobutyl-2′-methylbiphenyl, 8%, and starting material, **8** (Table A.5), 6%, were also found.

Reaction of Dianion 5 with t-Butyl Iodide

Reaction of t-butyl iodide with **5** as above gave **54**,n=2 as the only identified product in 67% yield by 'H NMR (Tables A.1, A.2).

Reaction of Dianion 5 with Trimethylsilyl Chloride

Dianion **5** was reacted with trimethylsilyl chloride using direct addition. The product was purified using LC with 1:1 CCl_4/cyclohexane. 2,2′-Bis(trimethylsilylmethyl)-biphenyl (**51**) [28,29] was found in 44% yield and identified by 'H NMR (Table A.5).

Reaction of Dianion 5 and Trimethylgermyl Bromide

Trimethylgermyl bromide was reacted similarly with **5**. 2,2′-Bis(trimethylsilylmethyl)-biphenyl (**86**) had virtually the same retention time as **51** above and was generated in 39% yield and identified by 'H NMR (Table A.5).

Reaction of Dianion 5 with Dichloromethane

Dichloromethane was reacted with **5** by simultaneous addition. [3.0]Orthocyclophane (**54**,n=3) [55,56,57] was formed in 29% yield and identified by ^{1}H NMR (Tables A.1, A.2). Also found and characterized by ^{1}H NMR were 2-methyl-2′-vinylbiphenyl (**91**, Table A.16), 29%, **54**,n=2 (Tables A.1, A.2), 2%, and starting material, **8** (Table A-5), 18%.

Reaction of Dianion 5 with 1,2-Dichloroethane

1,2-Dichloroethane was reacted similarly with **5**. A 4% yield of [4.0]orthocyclophane (**54**,n=4) [58,59] was obtained following recrystallization from absolute ethanol and identified by m.p. 149-152° (lit. [58] m.p. 151-152°) and ^{1}H NMR (Tables A.1, A.2).

Reaction of Dianion 5 with 1,3-Dibromopropane

Dianion **5** was reacted in a similar manner with 1,3-dibromopropane. [5.0]Orthocyclophane (**54**,n=5) [60] was generated in 31% yield and was characterized by ^{1}H NMR (Tables A.1, A.2).

Reaction of Dianion 5 with 1,4-Dibromobutane

1,4-Dibromobutane was similarly reacted with **5**. The crude product was bulb to bulb distilled (200°, 10 mm Hg) and chromatographed. [6.0]Orthocyclophane (**54**,n=6) [60], m.p. 88-89°, was found in 41% yield, recrystallized from absolute ethanol and identified by ^{1}H NMR (Tables A.1, A.2) (Fig. A.1).

The presence of **54**,n=2 (Tables A.1, A.2), 1%, and starting material, **8** (Table A.5), 8%, was also detected.

Reaction of Dianion 5 with 1,5-Dibromopentane

1,5-Dibromopentane and **5** were reacted in similar fashion. [7.0]Orthocyclophane (**54**,n=7) was generated in 26% yield and characterized by 'H NMR (Tables A.1, A.2). A 2% yield of **54**,n=2 (Tables A.1, A.2) was also noted.

Reaction of 5 with Dichlorodimethylsilane

Dianion **5** was reacted with dichlorodimethylsilane in a similar manner (no distillation, however). 1,2,3,4-Dibenzo-6,6-dimethyl-6-silacycloheptadiene (52) [29] was generated in 55% yield and characterized by 'H NMR (Table A.11). A 2% yield of **54**,n=2 (Tables A.1, A.2) and a 19% yield of starting material, **8** (Table A.5), were also detected.

Reaction of 5 with α,α′-Dibromo-m-xylene

α,α′-Dibromo-m-xylene was reacted similarly with **5**. Cyclophane **66** [71] was found in 8% yield and characterized by m.p. 82-88° (lit. [71] m.p. 83-88°), 'H NMR (Table A.10) (Fig. A-16) and ^{13}C NMR (Table A.34). Also formed in the reaction were **54**,n=2 (Tables A.1, A.2) in 32% yield, and [2.2]metacyclophane (45) (Table A.32) in 4% yield.

Reaction of Dianion 5 with 1,2-Dibromoethane

Dianion **5** was reacted with 1,2-dibromoethane by inverse addition. Workup was done as described in the previous reactions. 'H NMR showed that **54**,n=2 (Tables A.1, A.2) was generated in 68% yield.

Reaction of Dianion 6 with Dimethyl Sulfate

Dimethyl sulfate was reacted with **5** using direct addition. Workup was done as described in the previous reactions. 3,3'-Diethylbiphenyl (**47**) [48] was identified by ^{1}H NMR (Table A.6) in 84% yield. The remaining 16% was 3-ethyl-3'-methylbiphenyl, resulting from monoanion.

Reaction of Dianion 6 with Trimethylsilyl Chloride

Trimethylsilyl chloride was reacted similarly with **6**. 3,3'-Bis(trimethylsilylmethyl)biphenyl (**84**) was characterized by ^{1}H NMR (Table A.6) in 69% yield. A 20% yield of 3-methyl-3'-trimethylsilylmethylbiphenyl was also found.

Reaction of Dianion 6 with 1,7-Dibromoheptane

1,7-Dibromoheptane was reacted with **6** using simultaneous addition. Workup was done as described in previous reactions. LC was done with hexane as the solvent. [9.0]Metacyclophane (**56,n=9**) was characterized by ^{1}H NMR (Table A.3) in 7% yield. [9.0.9.0]Metacyclophane (**65,n=9**) was obtained in 33% yield and identified by ^{1}H NMR (Table A.3).

Reaction of Dianion 6 with 1,8-Dibromooctane

Dianion **6** was reacted similarly with 1,8-dibromooctane; [10.0]-metacyclophane (**56,n=10**) [64], obtained in 38% yield, was recrystallized from absolute ethanol and characterized by m.p. 59-60° (lit. [64] m.p. 58-59°), ^{1}H NMR (Table A.3) (Figs. A.2, A.3, A.5), ^{1}H COSY NMR (Figs.

A.4, A.6) and ^{13}C NMR (Fig. A.7). Dimeric [10.0.10.0]metacyclophane (**65,n=10**) was found in 20% yield and identified by ^1H NMR (Table A.3).

Reaction of Dianion 6 with α,α′-Dichloro-p-xylene

Dianion **6** was reacted in a similar manner with α,α′-dichloro-*p*-xylene. CCl_4 was the chromatography solvent. Cyclophane **67** [72], identified by ^1H NMR (Table A.9), was obtained in 4% yield and dimeric **97** was found in 6% yield and identified by ^1H NMR (Table A.9).

Reaction of Dianion 6 with Iodine

Dianion **6** was reacted with iodine using inverse addition. After chromatography with CCl_4, [2.0.2.0]metacyclophane (**65,n=2**) [69,70] was recrystallized from pentane and identified by m.p. 184-185° (lit. [69,70] m.p. 184-185°), ^1H NMR (Table A.3) (Fig. A.11, A.12) and ^{13}C NMR (Table A.33) (Fig. A.15). Two-dimensional experiments (COSY, Fig. A.13, and $^1H/^{13}C$ heteronuclear chemical shift correlation, Fig. A.14) were also performed on this compound. Dimeric **89** and trimeric **90** were found in 40 and 17% yields respectively and identified by ^1H NMR (Tables A.17, A.18).

An X-ray study was performed on a single crystal of **65,n=2** as follows. Colorless crystals grown by slow evaporation from pentane at -10°C. Crystal dimensions 0.5 x 0.5 x 0.5 mm. Syntex $P2_1$ diffractometer. Cell constants from 25 reflections with $13 < 2\theta < 27°$. M_r = 360.5, orthorhombic, Pbca, a = 8.968(4), b = 12.337(3), c = 36.75(1)Å,

$V = 4066(3)Å^3$, $Z = 8$, $D_x = 1.18\ cm^{-3}$, MoKα, $\lambda = 0.71073$ Å, $\mu = 0.62\ cm^{-1}$, F(000) = 1536, T = 295 K, $2\theta_{max} = 50°$. Range of hkl: 0-10, 0-14, 0-43. Two check reflections every 98 data points showed 3.6% average decay, so linear decay correction applied. No absorption correction. 2175 of 3583 reflections with $I>3\sigma(I)$ used in F^2 full-matrix refinement, R_{int} = 0.036. Structure solved by MULTAN80 using 288 highest E values; all non-H atoms found in first E map. Refinement of non-H atoms with isotropic temperature factors gave R = 0.13; final refinement (253 parameters) of non-H atoms with anisotropic temperature factors after adding H atoms in calculated positions with isotropic temperature factors of 5.0 $Å^2$; R = 0.044, wR = 0.049. Two views of a molecule of **65,n=2** are given in Figs. 5 and 6, and tables of coordinates, temperature factors, and bond lengths and angles, and a packing diagram are given in Appendix B.

Reaction of Dianion 6 with Dibromoethane

Dianion **6** was reacted with dibromoethane similarly to yield **65,n=2** in 39%; characterization was the same as in the previous reaction. The yields of **89** and **90** were not determined.

Reaction of Dianion 7 with Dimethyl Sulfate

Dianion **7** was reacted with dimethyl sulfate using direct addition. A 79% yield of 4,4′-diethylbiphenyl (49) was obtained. It was recrystallized from absolute ethanol and was identified by m.p. 82-83°

(lit. [51] m.p. 83°) and 'H NMR (Table A.7). A 21% yield of 4-ethyl-4′-methylbiphenyl was also detected, resulting from monoanion.

Reaction of Dianion 7 with Diethyl Sulfate

Dianion **7** was reacted similarly with diethyl sulfate 4,4′-Dipropylbiphenyl (50) [53] was obtained in 86% yield by recrystallization from absolute ethanol, and identified by 'H NMR (Table A.7). A 14% yield of 4-methyl-4′-propylbiphenyl was also detected.

Reaction of Dianion 7 with 2-Bromopropane

Dianion **7** was reacted with 2-bromopropane using inverse addition. 4,4′-Diisobutylbiphenyl (81) was generated in 78% yield, having a m.p. 47-48° when recrystallized from absolute ethanol, and was characterized by 'H NMR (Table A.7). A 22% yield of 4-isobutyl-4′-methylbiphenyl was also produced. A satisfactory elemental analysis was obtained for **81**.

Reaction of Dianion 7 with t-Butyl Iodide

t-Butyl iodide was reacted similarly with **7**. The chromatography solvent was 2:1 hexane /CCl_4. 4,4′-Dineopentylbiphenyl **82**, formed in 44% yield, was recrystallized from absolute ethanol, had m.p. 131-133°, and was identified by 'H NMR (Table A.7). Dimeric **83**, m.p. 189-192° was produced in 20% yield and characterized by 'H NMR (Table A.20). A 12% yield of 4-methyl-4′-neopentylbiphenyl was also found, resulting from monoanion. Satisfactory elemental analyses were obtained for **82** and **83**.

Reaction of Dianion 7 with Trimethylsilyl Chloride

7 was reacted with trimethylsilyl chloride in a similar manner. 4,4′-Bis(trimethylsilylmethyl)biphenyl (53) [54] was generated in 71% yield and recrystallized in absolute ethanol to give needles and identified by m.p. 80-82° (lit. [54] m.p. 80-82°) and ^{1}H NMR (Table A.7). A 25% yield of 4-methyl-4′-trimethylsilylmethylbiphenyl was also detected. The crude product upon standing six months gave about 5% of dimeric **85** as identified by ^{1}H NMR (Table A.19) following chromatography with hexane; a satisfactory elemental analysis was also obtained.

Reaction of Dianion 7 with Trimethylgermyl Bromide

Trimethylgermyl bromide was reacted similarly with **7**. A 77% yield of 4,4′-bis(trimethylgermylmethyl)biphenyl (87) was found; recrystallization from absolute ethanol gave m.p. 76-78°, a consistent ^{1}H NMR spectrum (Table A.7) and a satisfactory elemental analysis. A 17% yield of 4-methyl-4′-trimethylgermylmethylbiphenyl was also detected, resulting from monoanion.

Reaction of Dianion 7 with Allyl Chloride

Dianion 7 was reacted in a similar manner with allyl chloride. 4,4′-Bis(1-butenyl)biphenyl (88) was generated in 79% yield and identified by ^{1}H NMR (Table A.12). 4-(1-Butenyl)-4′-methylbiphenyl (96) was also obtained in 19% yield and identified by ^{1}H NMR (Table A.13).

Reaction of Dianion 7 with Dichloromethane

Simultaneous addition was used in the reaction 7 with dichloromethane. A mixture of products was generated and identified by 'H NMR. 4,4'-Divinylbiphenyl (92) [88] (Table A.14) was found in 13% yield, 4-methyl-4'-vinylbiphenyl (93) (Table A.15) was produced in 31% yield and 94 (Table A.21) was formed in 13% yield. 92 and 93 polymerize fairly rapidly to give an intractable mixture.

Reaction of Dianion 7 with 1,3-Dibromopropane

1,3-Dibromopropane was reacted similarly with dianion 7 to give a mixture of products separated using 4:1 hexane/dichloromethane as a chromatography solvent. Identification was done by 'H NMR. [5.0.5.0]Paracyclophane (62,n=5) (Table A.4) was found in 6% yield, [2.0.5.0]paracyclophane (95) (Table A.8) was detected in 2% yield and 96 (Table A.13) was formed in 24% yield.

Reaction of Dianion 7 with 1,10-Dibromodecane

Similar reaction of dianion 7 with 1,10-dibromodecane gave only a trace of [12.0]paracyclophane (60,n=12), but yielded dimeric [12.0.12.0]paracyclophane (62,n=12) in 27% yield. 62,n=12, when recrystallized from absolute ethanol, had m.p. 132-135°, gave a consistent 'H NMR spectrum (Table A.4) and had a satisfactory elemental analysis.

Reaction of Dianion 7 with 1,12-Dibromododecane

Dianion **7** was reacted similarly with 1,12-dibromododecane. Chromatography was done using 2:1 hexane/CCl_4 as the solvent. [14.0]Paracyclophane (**60,n=14**) [65], formed in 14% yield and coeluted with 12-bromo-1-dodecene, was twice recrystallized from absolute ethanol, and identified by m.p. 113-115° (lit. [65] m.p. 112.5-114.5°), ^{1}H NMR (Table A.4) (Figs. A.8, A.9) ^{1}H COSY NMR (Fig. A.10) and ^{13}C NMR (Table A.35). Dimeric **62,n=14** was generated in 20% yield; recrystallization from abolute ethanol gave m.p. 132-135°, consistent ^{1}H NMR (Table A.4), and a satisfactory elemental analysis.

An X-ray study was carried out on a single crystal of **60,n=14** as follows. Colorless crystals grown by slow evaporation from pentane at -10°C. Crystal dimensions 0.4 x 0.4 x 0.4 mm. Syntex $P2_1$ diffractometer. Cell constants from 25 reflections with $13 < 2\theta < 24°$. M_r = 348.6, monoclinic, C2/c, a = 23.986(9), b = 7.844(3), c = 11.415(4)Å, β = 92.29(3)°, U = 2146(1)Å^3, Z = 4, D_x = 1.08 g cm^{-3}, MoK_α, λ = 0.7173 Å, μ = 0.56 cm^{-1}, F(000) = 768, T = 297 K, $2\theta_{max}$ = 60°. Range of hkl: 0-28, 0-9, -13-13. Two check reflections every 98 data points showed 0.4% average decay; no absorption correction. 1362 of 3147 reflections with $I>2.5\sigma(I)$ used in F^2 refinement, R_{int} = 0.012. Structure solved by MULTAN80 using 224 highest E values; all non-H atoms found in first E map. Refinement of non-H atoms with isotropic temperature factors gave R = 0.10; final refinement (118 parameters) of non-H atoms with anisotropic temperature factors after adding H atoms in calculated positions with isotropic temperature factors of 5.0 Å^2; R = 0.054, wR = 0.061. The resulting structure is shown in Fig. 3, and tables of coordinates, temperature factors, and bond lengths and angles are given in Appendix C.

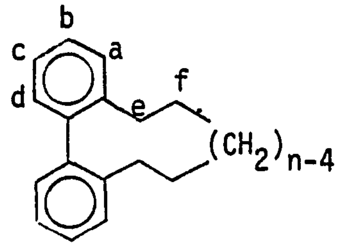
Reaction of Dianion 7 with 1,14-Dibromotetradecane

1,14-Dibromotetradecane was reacted with dianion 7 in a similar manner. [16.0]Paracyclophane (**60,n=16**) [65] was found in 5% yield and identified by ^{1}H NMR (Table A.4) and m.p. 105-109° (lit. [65,] m.p. 110-111°). Dimeric [16.0.16.0]paracyclophane (**62,n=16**) was made in 22% yield and recrystallization from absolute ethanol gave m.p. 131-135° and a consistent ^{1}H NMR (Table A.4).

APPENDIX A

NMR DATA AND SPECTRA

Table A.1 'H NMR chemical shift assignments (ppm) for **54**



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<tr><td>a</td><td>7.55</td><td rowspan="3">7.22-
7.34</td><td rowspan="4">7.21-
7.41</td><td rowspan="4">7.23-
7.31</td><td>7.21</td><td>7.27</td><td>7.26</td></tr>
<tr><td>b</td><td>7.28</td><td>7.28</td><td>7.26</td><td>7.26</td></tr>
<tr><td>c</td><td>7.38</td><td>7.20</td><td>7.14</td><td>7.16</td></tr>
<tr><td>d</td><td>7.84</td><td>7.76</td><td>7.10</td><td>7.00</td><td>7.09</td></tr>
<tr><td>e</td><td rowspan="2">3.87</td><td rowspan="2">2.88</td><td rowspan="2">2.50</td><td>2.72</td><td>2.63</td><td>2.53</td><td>2.78</td></tr>
<tr><td>e´</td><td rowspan="2">2.05-
2.27</td><td>2.09</td><td>2.52</td><td>2.53</td></tr>
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<tr><td>f´</td><td>-</td><td>-</td><td>1.52</td><td>1.53</td><td>1.43</td><td>1.49</td></tr>
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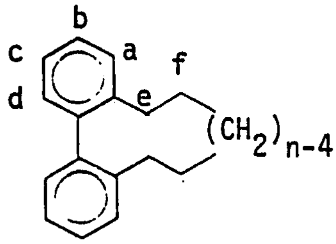
</table>

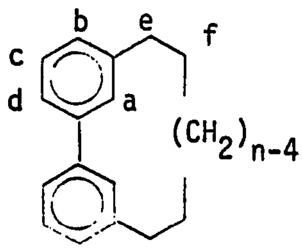
Table A.2 'H NMR coupling constant assignments (Hz) for 54

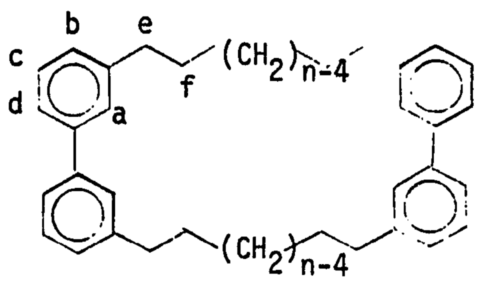


J	n=1	n=2	n=3	n=4	n=5	n=6	n=7
ab	7.2	i	i	i	7.6	7.5	i
ac	1.6	i	i	i	1.7	2.5	i
bc	6.5	i	i	i	6.8	6.5	i
bd	1.6	i	i	i	2.0	1.0	i
cd	7.5	7.6	i	i	7.4	7.3	7.4
ee'	-	-		13.3	14.0	i	14.6
ef	-	-	7.0	8.6	6.9	~0	8.5
ef'	-	-		~0	3.8	3.5	4.6
e'f	-	-	-	i	3.4	7.4	4.7
e'f'				i	10.6	~0	7.8
ff'	-	-	-	i	14.1	13.4	14.1
fg	-	-	-	-	7.2	~0	6.6
fg'	-	-	-	-	7.2	2.5	6.6
f'g	-	-	-	-	5.0	0.9	6.6
f'g'	-	-	-	-	5.0	12.0	6.6
gg'	-	-	-	-	-	14.0	14.0
gh	-	-	-	-	-	-	6.6

i = indeterminate

Table. A.3 'H NMR assignments for 56 and 65

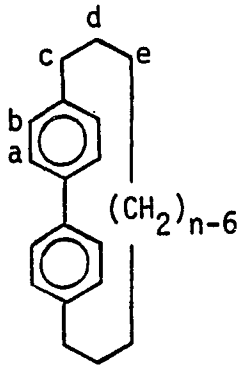


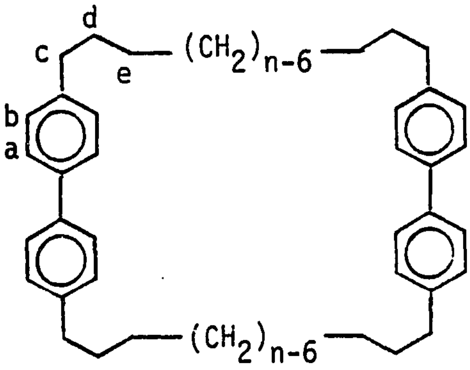


	56,n=9	56,n=10	65,n=2	65,n=9	65,n=10
δH_a	7.36	7.53	5.96	7.35	7.37
δH_b	7.11	7.12	7.16	7.11	7.11
δH_c	7.30	7.34	7.24	7.29	7.30
δH_d	7.37	7.47	6.98	7.36	7.35
δH_e	2.80	2.79	2.86	2.64	2.65
δH_f	1.78	1.76	-	1.66	1.67
δH_g		1.34	-		
δH_h	} 1.34	1.44	-	} 1.34	} 1.35
δH_i		1.40	-		
J_{ab}	1.8	1.7	1.3	1.8	1.8
J_{ac}	i	i	0.9	i	i
J_{ad}	1.8	1.7	1.3	1.8	1.8
J_{bc}	7.5	7.6	7.4	7.5	7.5
J_{bd}	1.0	1.3	7.4	1.0	1.1
J_{cd}	7.5	7.6	-	7.5	7.3
J_{ef}	5.8	6.1	-	7.5	7.2
J_{fg}	6.6	6.7	-	6.7	6.6

i = indeterminate

Table A.4 'H NMR assignments for 60 and 62

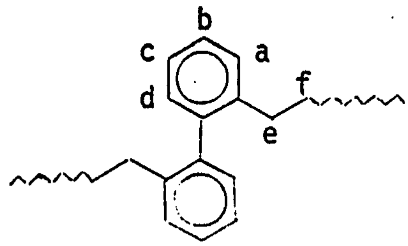




	60,n=14	60,n=16	62,n=5	62,n=12	62,n=14	62,n=16
δH_a	7.56	7.53	7.49	7.47	7.48	7.48
δH_b	7.23	7.23	7.23	7.21	7.22	7.23
δH_c	2.68	2.67	2.65	2.63	2.63	2.63
δH_d	1.64	1.65	1.70	1.63	1.63	1.63
δH_e	1.15	1.22-1.40	1.44	1.24	1.31	1.34
δH_f	0.70		-		1.29	1.32
δH_g	0.84	1.06-1.12	-		1.24	1.25
δH_h	0.54		-			
δH_i	0.59	0.76-0.84	-	-		
δH_j	-		-	-	-	
J_{ab}	8.2	8.2	8.2	8.1	8.2	8.1
J_{cd}	6.0	6.7	7.6	7.3	7.3	7.6
J_{de}	6.2	i	6.9	i	i	i
J_{ef}	7.0	i	-	i	i	i
J_{fg}	6.6	i	-	i	i	i
J_{gh}	4.4	i	-	-	i	i
J_{hi}	5.7	i	-	-	i	i

i = indeterminate

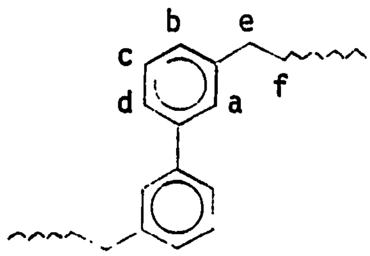
Table A.5 'H NMR assignments for **77** with saturated side chains



	8	48	80	51	86
δH_a		7.30	7.25	7.10	7.11
δH_b	7.17 7.26	7.30	7.28	7.18	7.24
δH_c		7.21	7.19	7.11	7.14
δH_d	7.09	7.10	7.09	7.07	7.09
δH_e	2.05	2.38	2.25	1.99	2.16
$\delta H_{e'}$	-	2.35	2.17	1.97	2.15
δH_f	-	1.04	1.69	Si	Ge
δH_g	-	-	0.78	-0.16	-0.01
$\delta H_{g'}$	-	-	0.66	-	-
J_{ab}	i	i	6.2	7.0	7.2
J_{ac}	i	i	2.7	1.7	1.6
J_{bc}	i	i	6.5	7.0	7.3
J_{bd}	2.0	2.0	0.8	2.1	1.8
J_{cd}	7.8	7.4	7.2	7.0	7.4
$J_{ee'}$	-	15.0	13.6	13.1	12.3
J_{ef}	-	7.5	7.2	-	-
J_{fg}	-	-	6.6	-	-

i = indeterminate

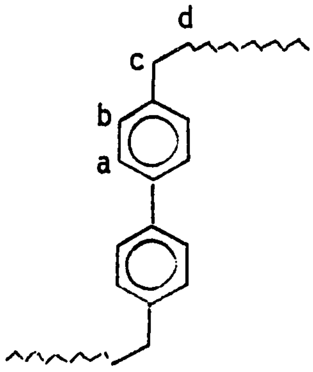
Table A.6 'H NMR assignments for 78 with saturated side chains



	9	47	84
δH_a	7.38	7.42	7.21
δH_b	7.14	7.17	6.97
δH_c	7.29	7.33	7.28
δH_d	7.36	7.39	7.29
δH_e	2.39	2.70	2.15
δH_f	-	1.27	Si
δH_g	-	-	0.03
J_{ab}	i	i	i
J_{ad}	i	i	i
J_{bc}	7.5	7.4	i
J_{bd}	i	i	i
J_{cd}	7.5	7.2	i
J_{ef}	-	7.6	-

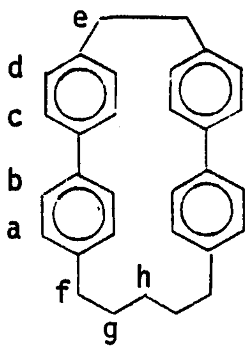
i = indeterminate

Table A.7 'H NMR assignments for 79 with saturated side chains



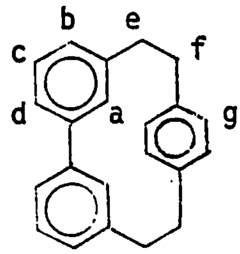
	10	49	50	81	82	53	87
δH_a	7.47	7.46	7.47	7.50	7.50	7.44	7.47
δH_b	7.22	7.19	7.18	7.20	7.18	7.03	7.06
δH_c	2.38	2.62	2.56	2.50	2.52	2.10	2.25
δH_d	-	1.22	1.64	1.89	C	Si	Ge
δH_e	-	-	0.94	0.93	0.93	0.00	0.15
J_{ab}	8.2	8.2	8.2	8.1	8.2	8.2	8.2
J_{cd}	-	7.6	7.7	7.2	-	-	-
J_{de}	-	-	7.3	6.6	-	-	-

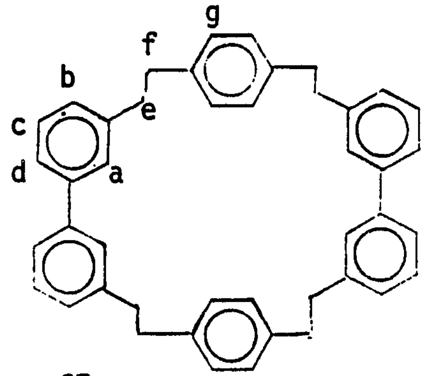
Table A.8 'H NMR assignments for 95



Chemical Shift (ppm)	Coupling Constants (Hz)
δH_a = 7.07	J_{ab} = 8.2
δH_b = 6.89	J_{cd} = 8.2
δH_c = 6.94	J_{fg} = 6.2
δH_d = 6.69	J_{gh} = 7.0
δH_e = 3.02	
δH_f = 2.56	
δH_g = 1.70	
δH_h = 1.45	

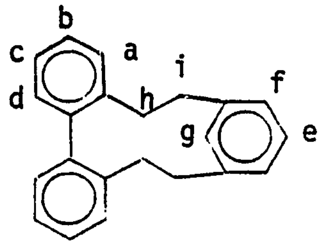
Table A.9 'H NMR assignments for 67 and 97





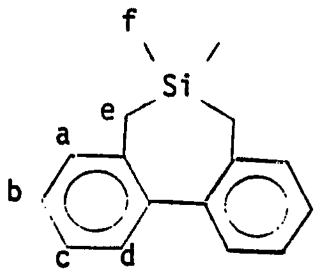
	67	97
δH_a	6.21	6.85
δH_b	7.02	7.14
δH_c	7.22	7.31
δH_d	7.41	7.36
δH_e	~2.92	2.83-2.97
δH_f		
δH_g	6.84	7.10
J_{ab}	1.5	1.8
J_{ad}	1.8	1.7
J_{bc}	7.8	7.5
J_{bd}	1.6	1.7
J_{cd}	7.6	7.5

Table A.10 ^{1}H NMR assignments for **66**



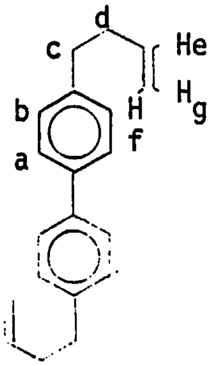
Chemical Shift (ppm)	Coupling Constants (Hz)
δH_a = 7.35	J_{ab} = 7.7
δH_b = 7.23	J_{ac} = 1.4
δH_c = 7.09	J_{bc} = 7.2
δH_d = 6.98	J_{bd} = 1.4
δH_e = 6.87	J_{cd} = 7.6
δH_f = 6.64	J_{ef} = 7.5
δH_g = 6.73	J_{fg} = 1.7
δH_h = 2.97	
$\delta H_{h'}$ = 2.86	
δH_i = 2.96	

Table A.11 'H NMR assignments for 52



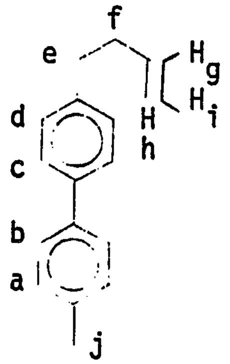
Chemical Shift (ppm)	Coupling Constants (Hz)
δH_a = 7.09	$J_{ee'}$ = 13.3
δH_{bcd} = 7.19-7.22	
δH_e = 1.85	
$\delta H_{e'}$ = 1.81	
δH_f = 0.08	

Table A.12 'H NMR assignments for 88



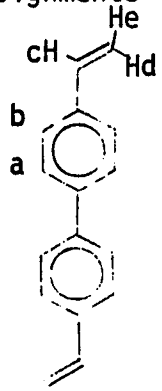
Chemical Shift (ppm)	Coupling Constants (Hz)
δH_a = 7.51	J_{ab} = 8.1
δH_b = 7.26	J_{cd} = 7.8
δH_c = 2.75	J_{de} = 6.6
δH_d = 2.40	J_{df} = 1.2
δH_e = 5.89	J_{ef} = 17.0
δH_f = 5.07	J_{eg} = 10.4
δH_g = 5.00	J_{fg} = 2.0

Table A.13 'H NMR assignments for **96**



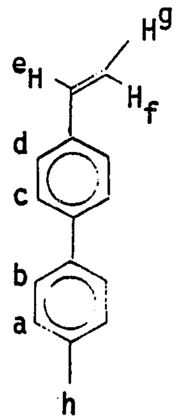
Chemical Shift (ppm)	Coupling Constants (Hz)
δH_a = 7.48	J_{ab} = 7.9
δH_b = 7.23	J_{cd} = 8.1
δH_c = 7.25	J_{ef} = 7.9
δH_d = 7.50	J_{fg} = 6.6
δH_e = 2.75	J_{fh} = 1.3
δH_f = 2.40	J_{gh} = 17.1
δH_g = 5.89	J_{gi} = 10.2
δH_h = 5.07	J_{hi} = 1.9
δH_i = 5.00	
δH_j = 2.39	

Table A.14 'H NMR assignments for 92



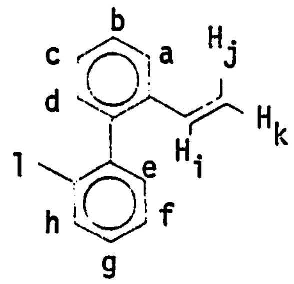
Chemical Shift (ppm)	Coupling Constants
δH_a = 7.56	J_{ab} = 8.4
δH_b = 7.26	J_{cd} = 17.6
δH_c = 6.75	J_{ce} = 10.8
δH_d = 5.78	J_{de} = 0.9
δH_e = 5.27	

Table A.15 'H NMR assignments for 93



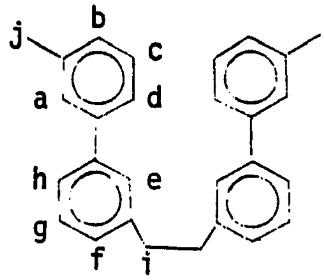
Chemical Shift (ppm)	Coupling Constants (Hz)
δH_a = 7.49	J_{ab} = 8.4
δH_b = 7.24	J_{cd} = 8.4
δH_c = 7.25	J_{ef} = 17.6
δH_d = 7.54	J_{eg} = 10.8
δH_e = 6.75	J_{fg} = 0.8
δH_f = 5.77	
δH_g = 5.25	
δH_h = 2.37	

Table A.16 ^1H NMR assignments for 91



Chemical Shift (ppm)	Coupling Constants (Hz)
δH_a = 7.66	J_{ab} = 7.3
$\delta H_{bcdefgh}$ = 7.08 - 7.40	J_{ac} = 2.0
δH_i = 6.40	J_{ij} = 17.5
δH_j = 5.66	J_{ik} = 11.0
δH_k = 5.08	J_{jk} = 1.2
δH_l = 2.05	

Table A.17 'H NMR assignments for 89



Chemical Shift (ppm)

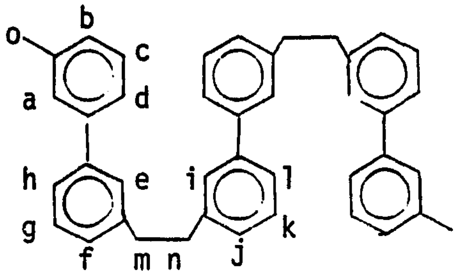
δH_{acdegh} = 7.29 - 7.43

δH_{bf} = 7.12 - 7.18

δH_{i} = 3.03

δH_{j} = 2.40

Table A.18 'H NMR assignments for 90



Chemical Shift (ppm)

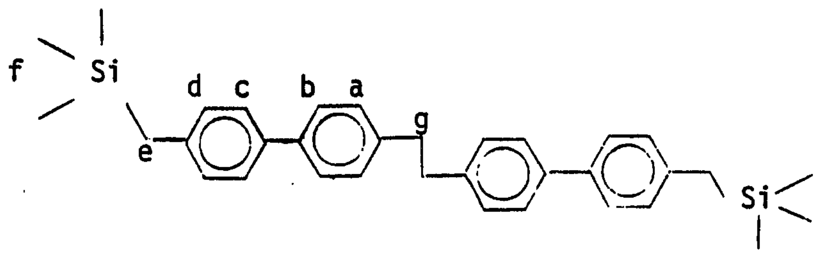
$\delta H_{acdeghikl}$ = 7.30 - 7.44

δH_{bfj} = 7.13 - 7.19

δH_{mn} = 3.01

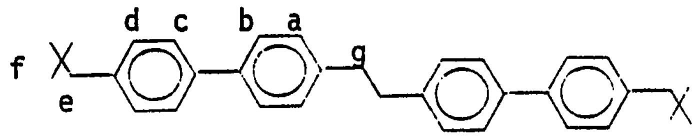
δH_{o} = 2.39

Table A.19 'H NMR assignments of 85



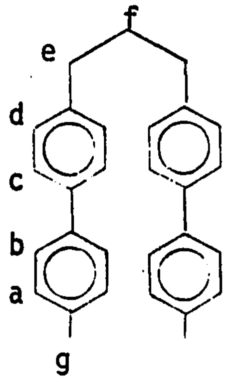
Chemical Shift (ppm)	Coupling Constants (Hz)
$\delta H_a = 7.24$	$J_{ab} = 8.1$
$\delta H_b = 7.49$	$J_{cd} = 8.3$
$\delta H_c = 7.43$	
$\delta H_d = 7.03$	
$\delta H_e = 2.09$	
$\delta H_f = 0.00$	
$\delta H_g = 2.96$	

Table A.20 'H NMR assignments for 83



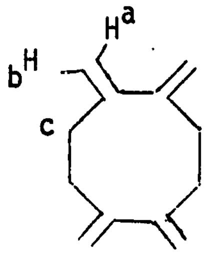
Chemical Shift (ppm)	Coupling Constants (Hz)
$\delta H_a = 7.27$	$J_{ab} = 8.1$
$\delta H_b = 7.53$	$J_{cd} = 8.1$
$\delta H_c = 7.50$	
$\delta H_d = 7.19$	
$\delta H_e = 2.53$	
$\delta H_f = 0.94$	
$\delta H_g = 2.99$	

Table A.21 'H NMR assignments for **94**



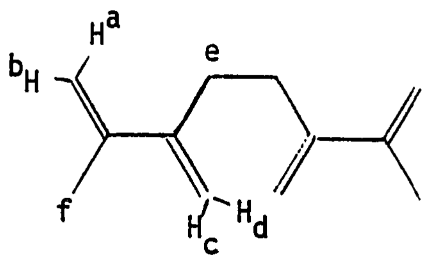
Chemical Shift (ppm)	Coupling Constants (Hz)
$\delta H_a = 7.22$	$J_{ab} = 8.4$
$\delta H_b = 7.49$	$J_{cd} = 8.4$
$\delta H_c = 7.46$	$J_{ef} = 6.4$
$\delta H_d = 7.24$	
$\delta H_e = 2.71$	
$\delta H_f = 2.01$	
$\delta H_g = 2.38$	

Table A.22 'H NMR assignments for **31**,n=4



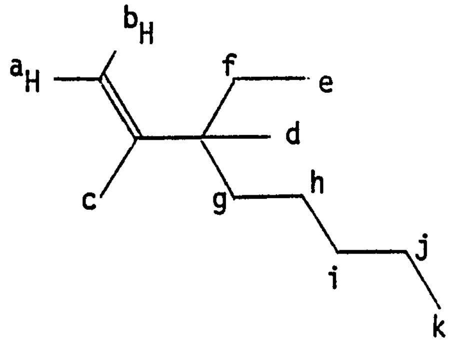
Chemical Shift (ppm)	Coupling Constants (Hz)
δH_a = 4.89	J_{ab} = 2.2
δH_b = 4.81	
δH_c = 2.39	

Table A.23 'H NMR assignments for **68**



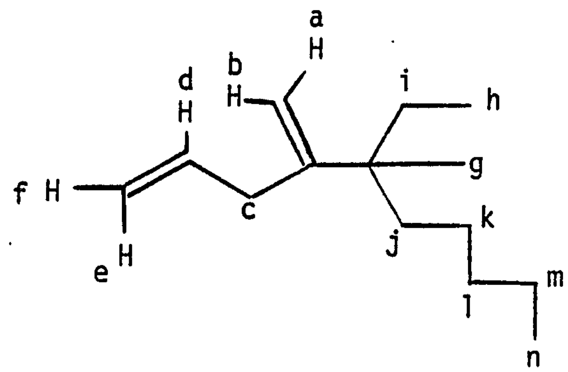
Chemical Shift (ppm)	Coupling Constants (Hz)
δH_a = 5.10	J_{ab} = 0.8
δH_b = 4.99	J_{cd} = 0.9
δH_c = 5.10	J_{bf} = 1.1
δH_d = 4.97	
δH_e = 2.45	
δH_f = 1.92	

Table A.24 'H NMR assignments for 69



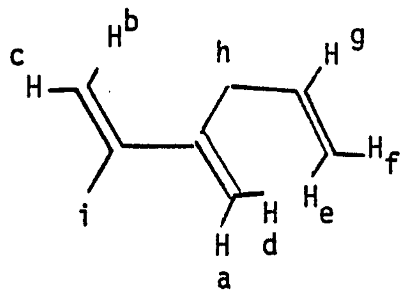
Chemical Shift (ppm)	Coupling Constants (Hz)
δH_a = 4.81	J_{ab} = 1.6
δH_b = 4.63	J_{ac} = 0.9
δH_c = 1.63	J_{ef} = 6.9
δH_d = 0.95	J_{jk} = 7.5
δH_e = 0.71	
δH_{fghij} = 1.18-1.31	
δH_k = 0.87	

Table A.25 'H NMR assignments for 74



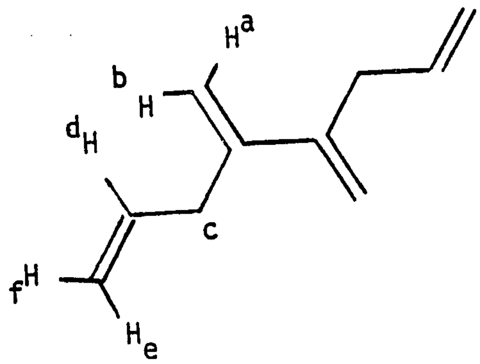
Chemical Shift (ppm)	Coupling Constants (Hz)
δH_a = 4.81	J_{cd} = 7.4
δH_b = 4.87	J_{de} = 17.5
δH_c = 2.66	J_{df} = 10.5
δH_d = 5.81	J_{hi} = 7.5
δH_e = 5.02	J_{mn} = 6.9
δH_f = 5.04	
δH_g = 0.97	
δH_h = 0.71	
δH_{ijklm} = 1.10-1.50	
δH_n = 0.87	

Table A.26 'H NMR assignments for **70**



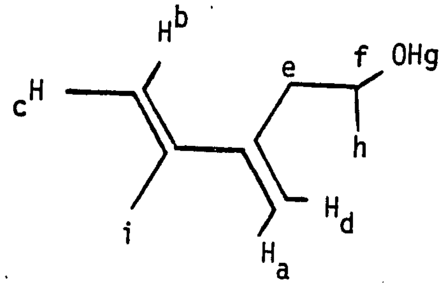
Chemical Shift (ppm)	Coupling Constants (Hz)
δH_a = 5.15	J_{ad} = 0.5
δH_b = 5.10	J_{ah} = 1.3
δH_c = 5.00	J_{eg} = 17.3
δH_d = 5.00	J_{fg} = 10.4
δH_e = 5.07	J_{gh} = 6.6
δH_f = 5.05	
δH_g = 5.90	
δH_h = 3.03	
δH_i = 1.92	

Table A.27 'H NMR assignments for **71**



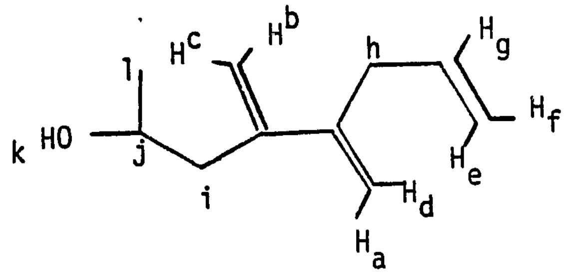
Chemical Shift (ppm)	Coupling Constants (Hz)
δH_a = 5.15	J_{ab} = 0.7
δH_b = 5.02	J_{cd} = 6.8
δH_c = 3.02	J_{de} = 17.4
δH_d = 5.91	J_{df} = 10.5
δH_e = 5.07	
δH_f = 5.06	

Table A.28 'H NMR assignments for 72



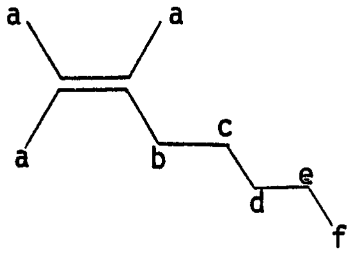
Chemical Shift (ppm)	Coupling Constants (Hz)
δH_a = 5.23	$J_{ee'}$ = 13.9
δH_b = 5.12	J_{ef} = 4.1
δH_c = 5.02	$J_{e'f}$ = 9.0
δH_d = 5.05	J_{fh} = 6.3
δH_e = 2.57	
$\delta H_{e'}$ = 2.30	
δH_f = 3.91	
δH_g = 1.57	
δH_h = 1.22	
δH_i = 1.93	

Table A.29 'H NMR assignments for 73



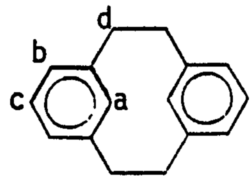
Chemical Shift (ppm)	Coupling Constants (Hz)
$\delta H_a = 5.17$	$J_{ef} = 1.7$
$\delta H_b = 5.25$	$J_{eg} = 17.3$
$\delta H_c = 5.07$	$J_{eh} = 1.1$
$\delta H_d = 5.04$	$J_{fg} = 10.4$
$\delta H_e = 5.07$	$J_{gh} = 6.7$
$\delta H_f = 5.05$	$J_{ii'} = 14.0$
$\delta H_g = 5.86$	$J_{ij} = 4.1$
$\delta H_h = 3.02$	$J_{i'j} = 8.8$
$\delta H_i = 2.54$	$J_{jl} = 6.1$
$\delta H_{i'} = 2.29$	
$\delta H_j = 3.90$	
$\delta H_k = 1.58$	
$\delta H_l = 1.22$	

Table A.30 'H NMR assignments for 75



Chemical Shift (ppm)	Coupling Constants (Hz)
δH_a = 1.64	J_{bc} = 7
δH_b = 2.00	J_{ef} = 6.8
δH_{c-e} = 1.30	
δH_f = 0.89	

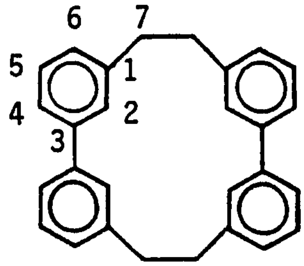
Table A.31 'H NMR assignments for 45



Chemical Shift (ppm)	Coupling Constants (Hz)
δH_a = 4.27	J_{ab} = 2
δH_b = 7.05	J_{ac} = ~0
δH_c = 7.20	J_{bc} = ~8
δH_d = 2.08	$J_{dd'}$ = 9*
$\delta H_{d'}$ = 3.11	

*Apparent coupling constant

Table A.32 ^{13}C NMR assignments for 65,n=2



<u>Chemical Shift (ppm)</u>

δC_1 = 140.37

δC_2 = 131.22

δC_3 = 141.35

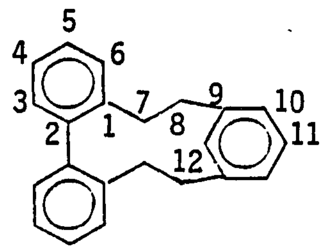
δC_4 = 124.56

δC_5 = 128.53

δC_6 = 127.04

δC_7 = 38.60

Table A.33 ^{13}C assignments for 66



<u>Chemical Shift (ppm)</u>

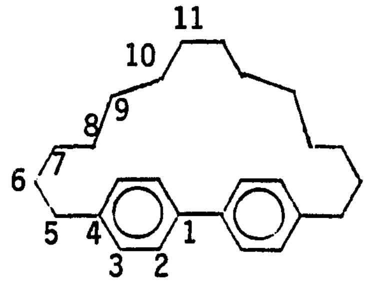
δC_1, C_2, C_9 = 141.88, 140.74, 140.68

δC_3, C_4, C_5, C_6, C_{10} = 131.44, 130.63, 127.24, 125.58, 124.68

δC_7, C_8 = 36.54, 31.69

δC_{11}, C_{12} = 127.93, 127.69

Table A.34 ^{13}C NMR assignments for **60**,n=14



Chemical Shift (ppm)

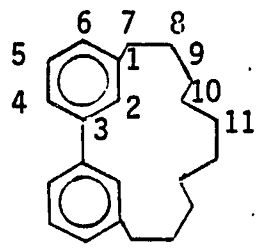
δC_1, C_4 = 142.0, 138.4

δC_2, C_3 = 129.8, 126.1

δC_5 = 35.5

δC_6, C_7, C_8, C_9, C_{10}, C_{11}, = 30.8, 29.5, 28.9, 28.8, 28.4, 26.5

Table A.35 ^{13}C NMR assignments for 56,n=10



Chemical Shift (ppm)

δC_1, C_3 = 143.42, 141.77

δC_2, C_4, C_5, C_6 = 129.92, 129.29, 128.14, 124.97

δC_7 = 34.20

δC_8, C_9, C_{10}, C_{11} = 29.68, 29.10, 28.94, 27.27

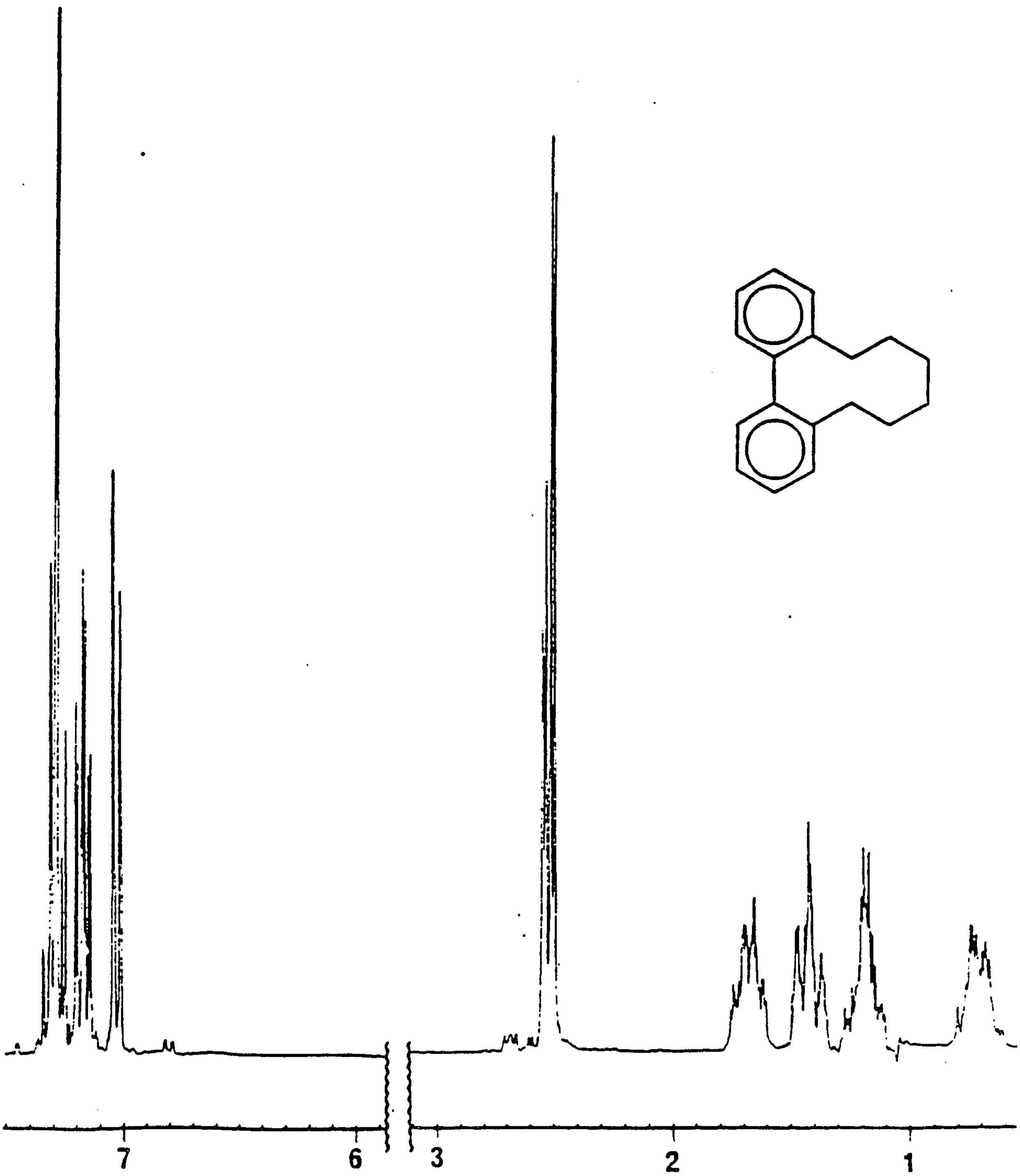


Fig. A.1. 250 MHz 'H NMR spectrum of 54,n=6.

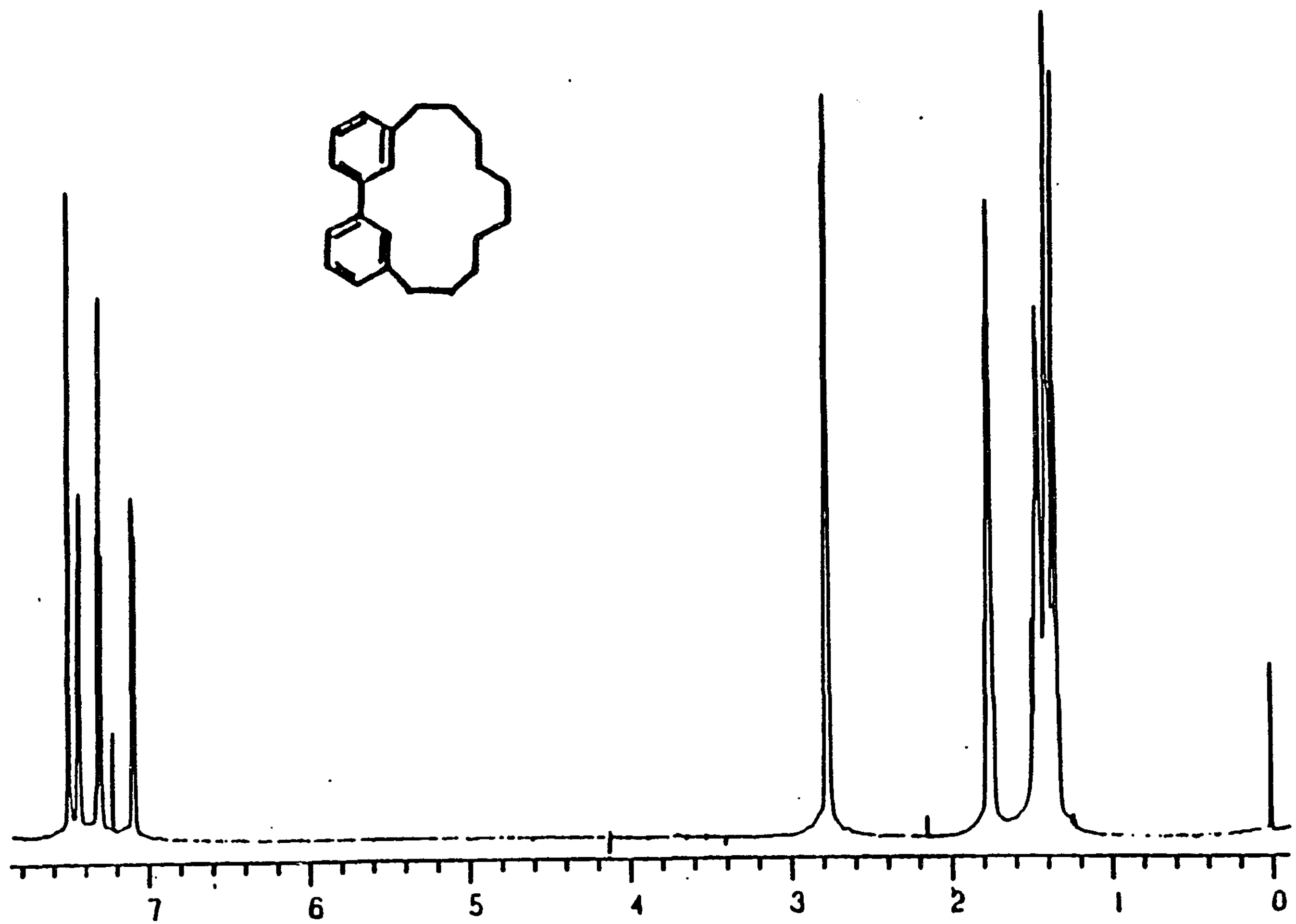


Fig. A.2. 500 MHz 'H NMR spectrum of 56,n=10.

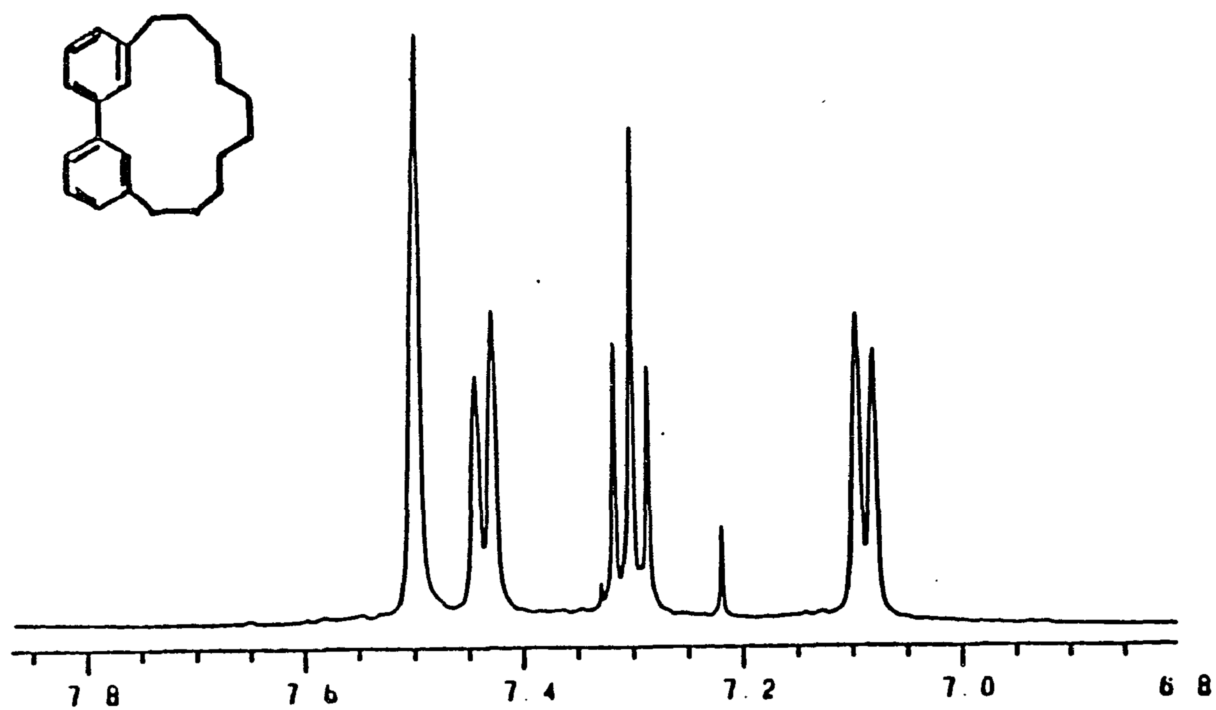


Fig. A.3. Aromatic region of 500 MHz ^{1}H NMR spectrum of 56,n=10.

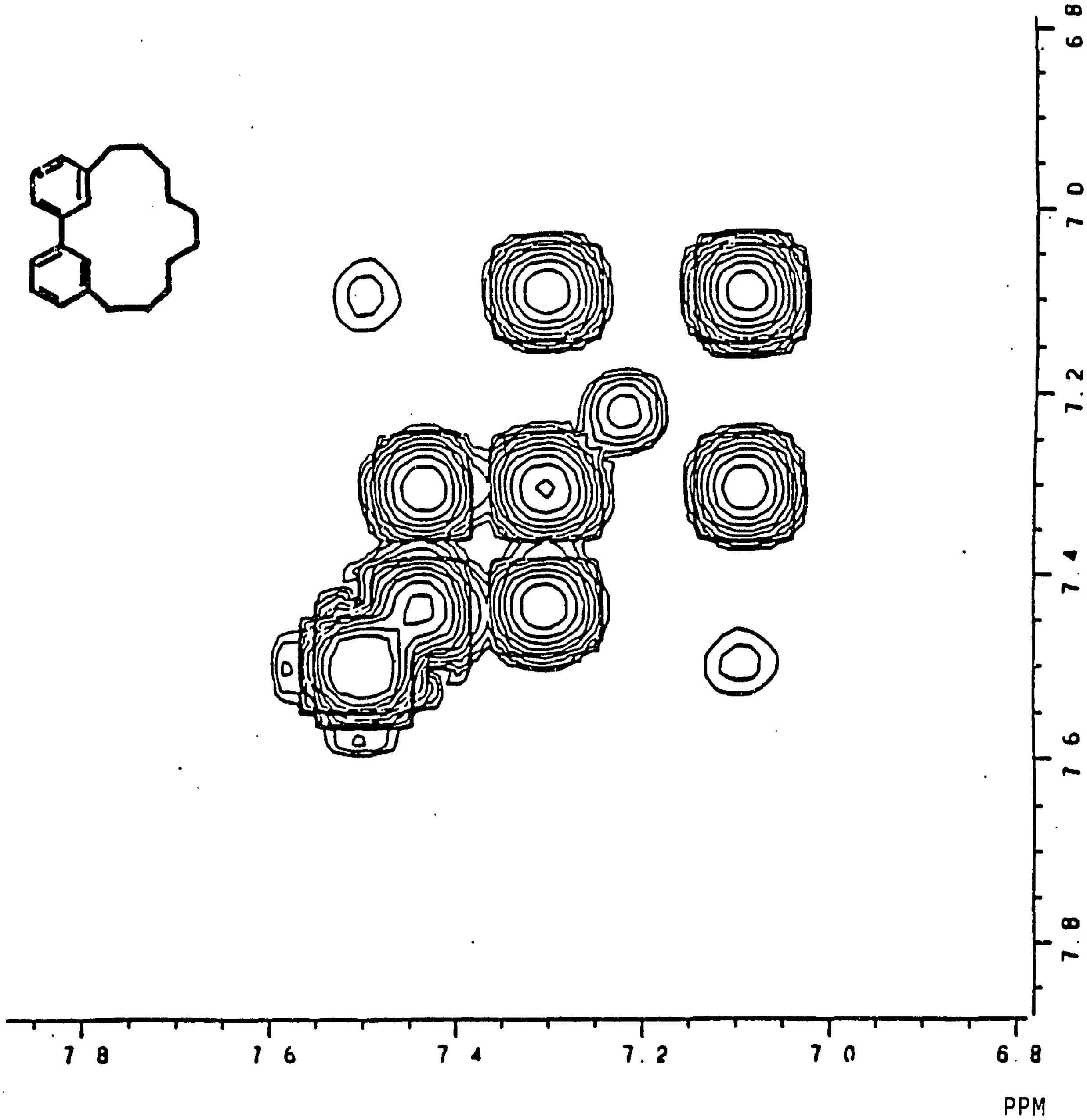


Fig. A.4. Aromatic region of 500 MHz 'H-'H COSY NMR spectrum of 56,n=10.

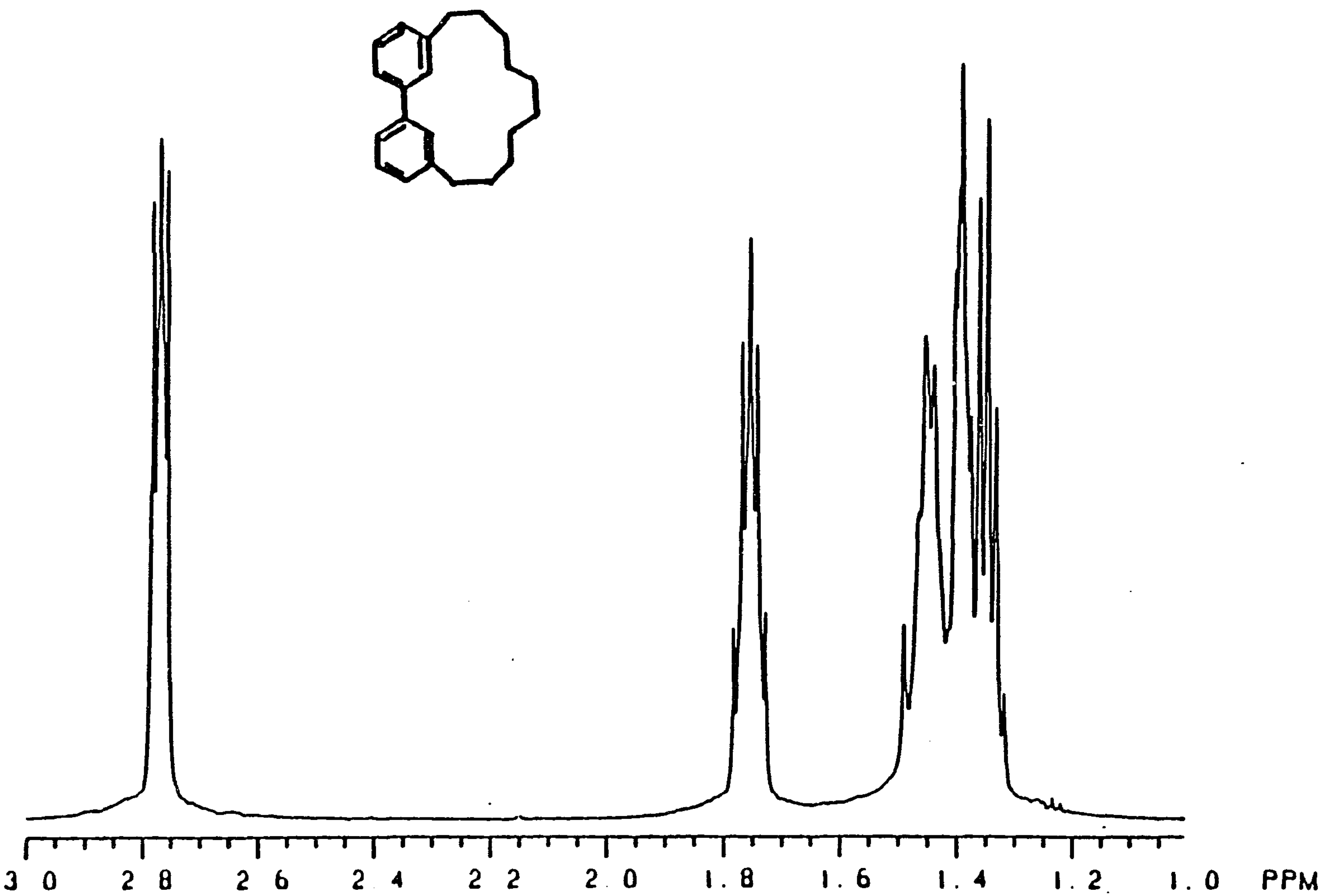


Fig. A.5. Aliphatic region of 500 MHz 'H NMR spectrum of 56,n=10.

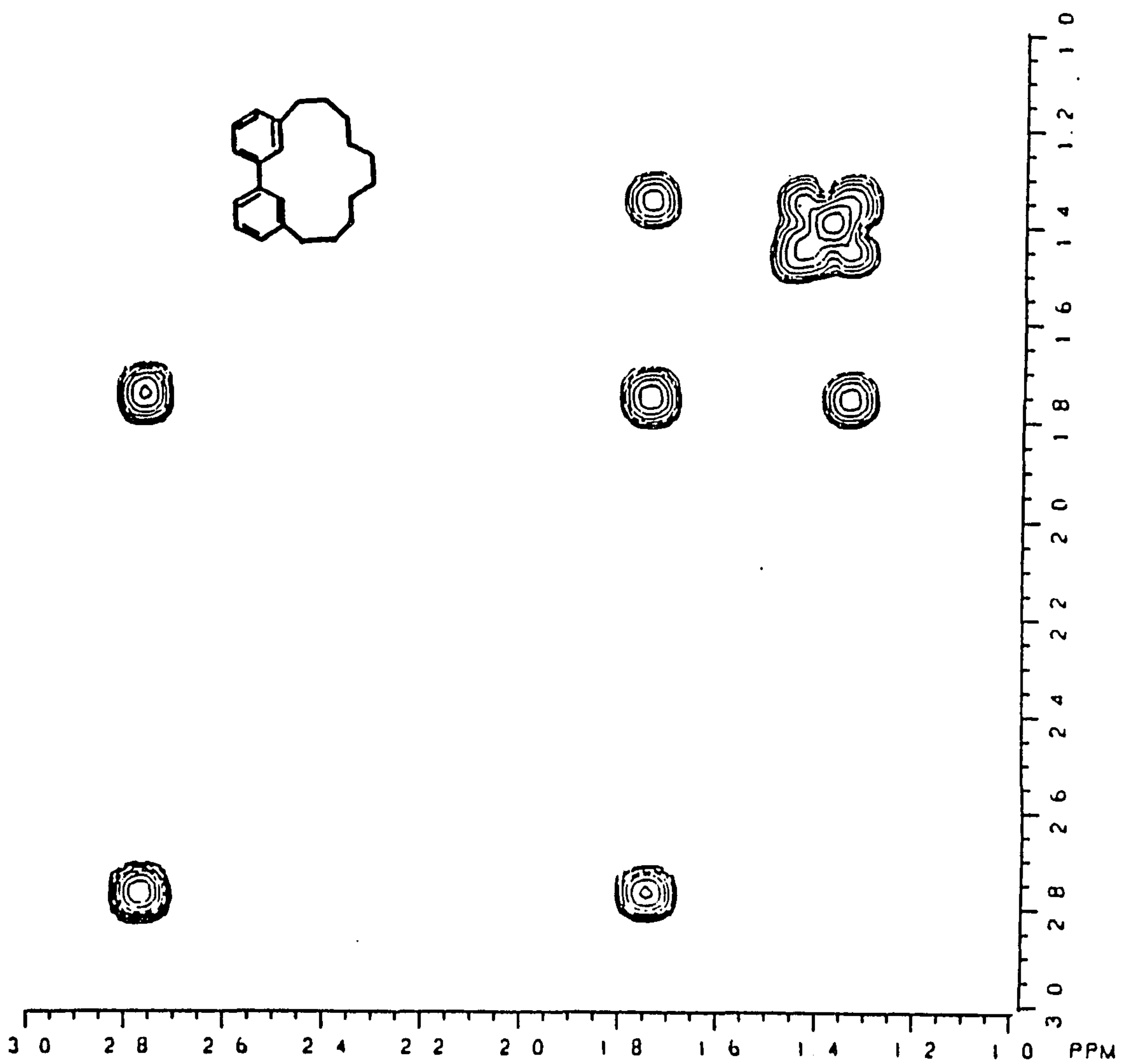


Fig. A.6. Aliphatic region of 500 MHz 'H-'H COSY NMR spectrum of 56,n=10.

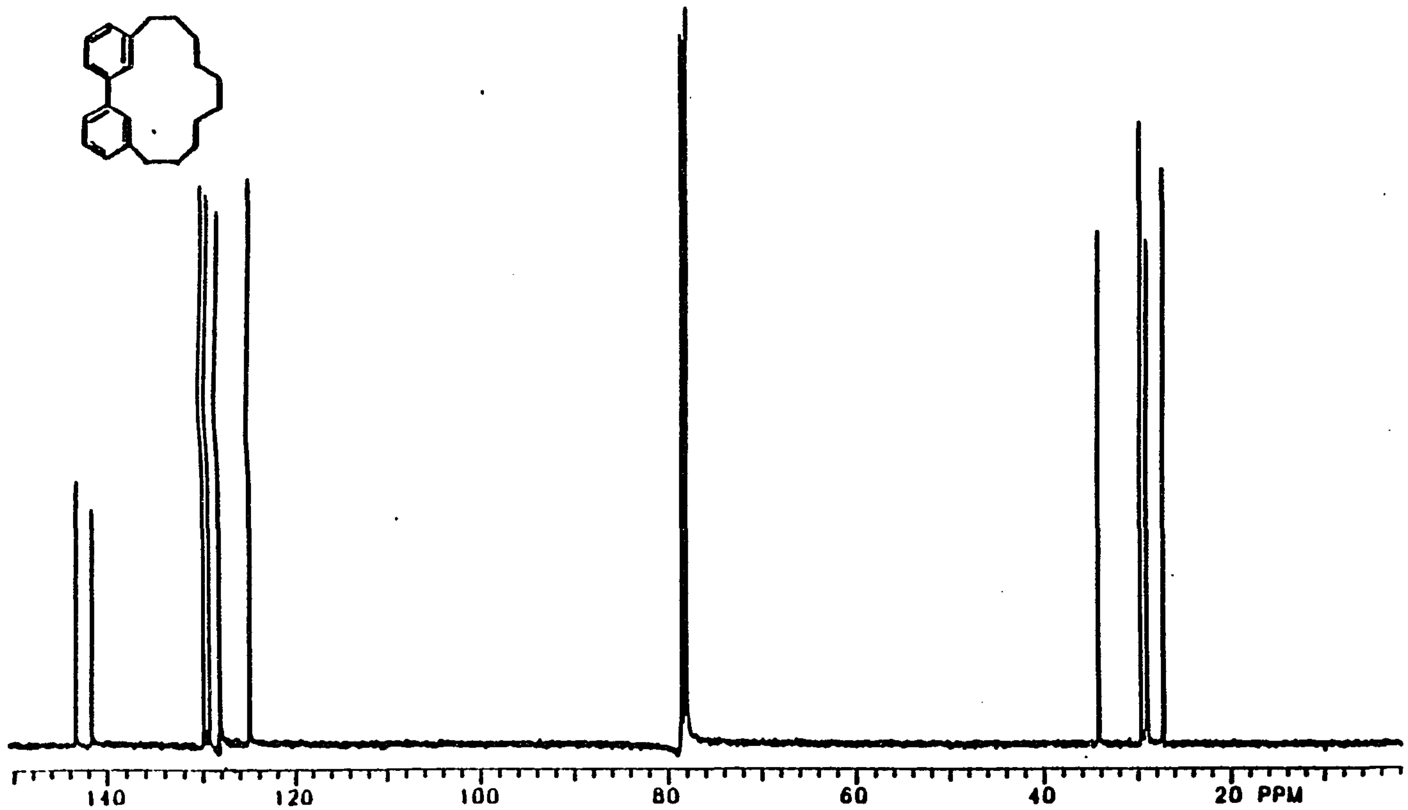


Fig. A.7. 100 MHz ^{13}C NMR spectrum of 56,n=10.

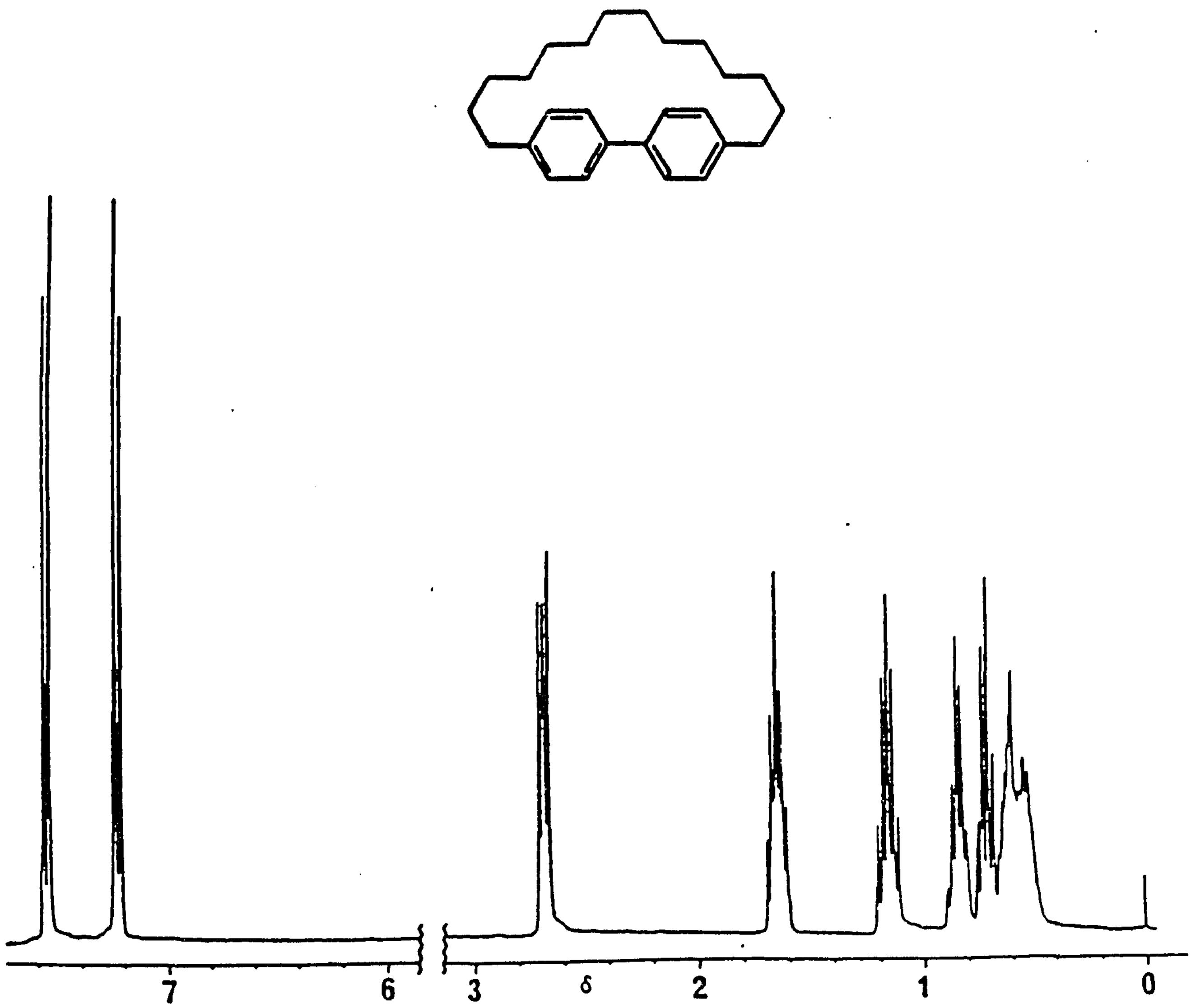


Fig. A.8. 300 MHz 'H NMR spectrum of 60,n=14.

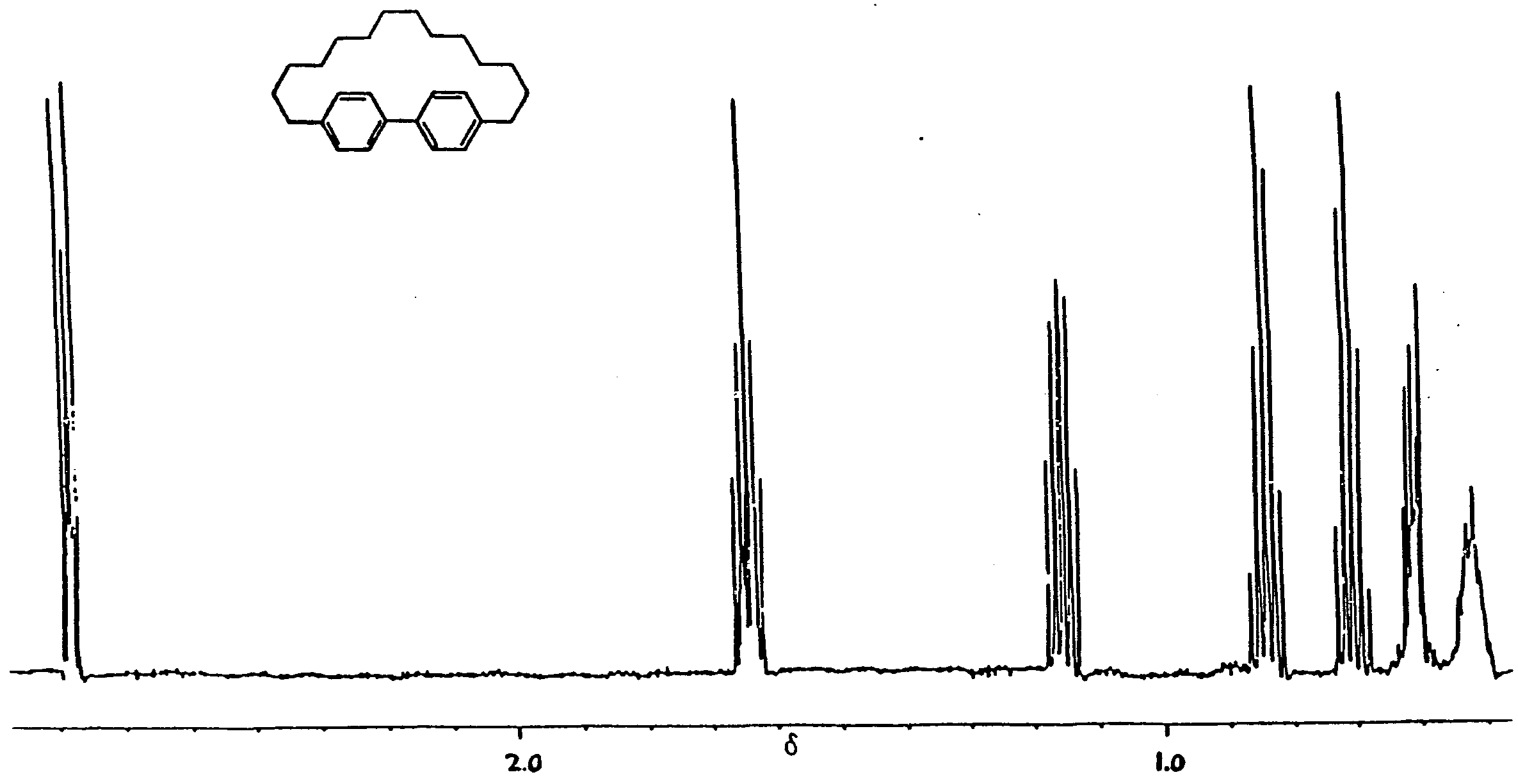


Fig. A.9. Aliphatic region of 600 MHz 'H NMR spectrum of 60,n=14.

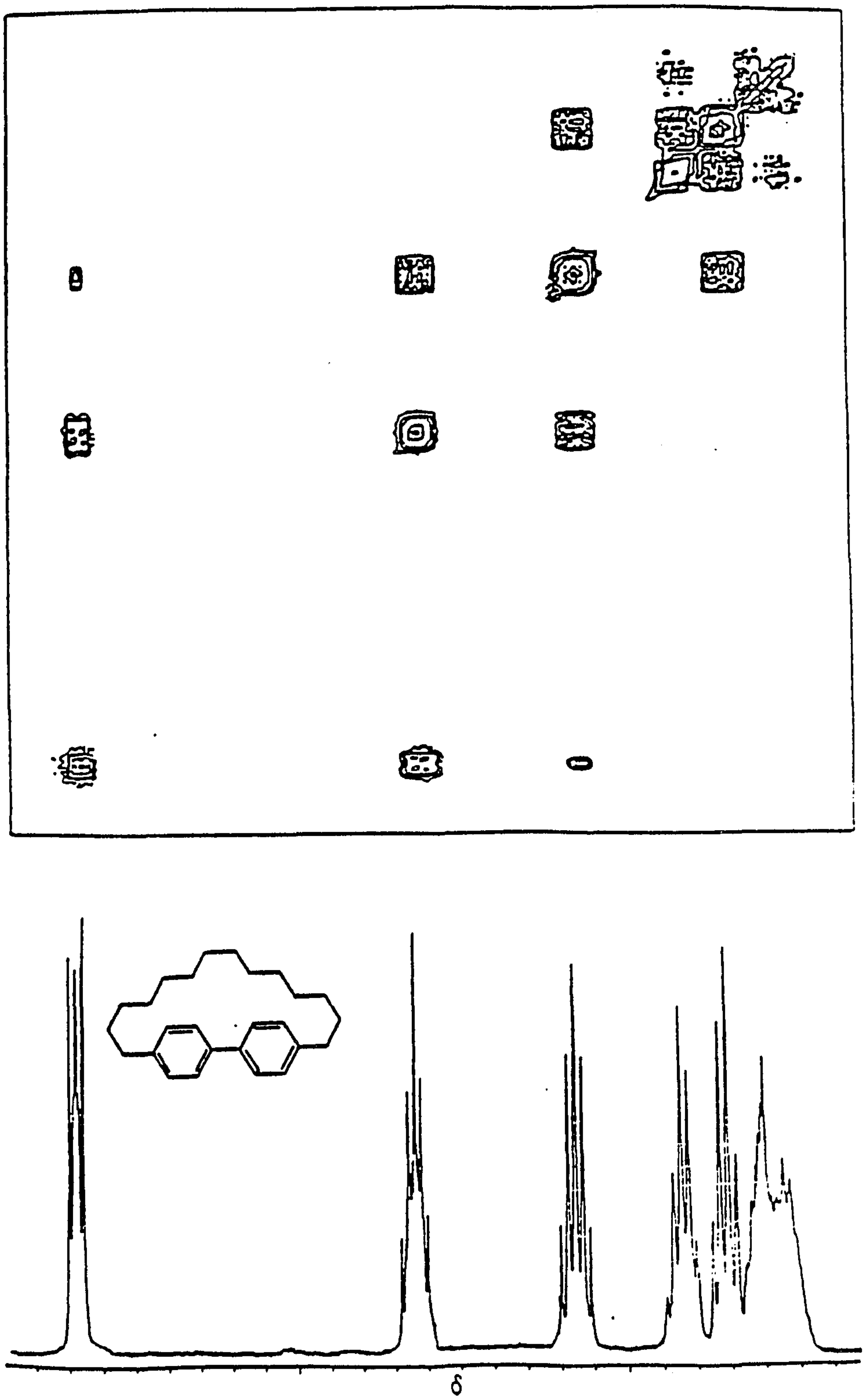


Figure A.10. Aliphatic region of 300 MHz 'H-'H COSY NMR spectrum of 60,n=14.

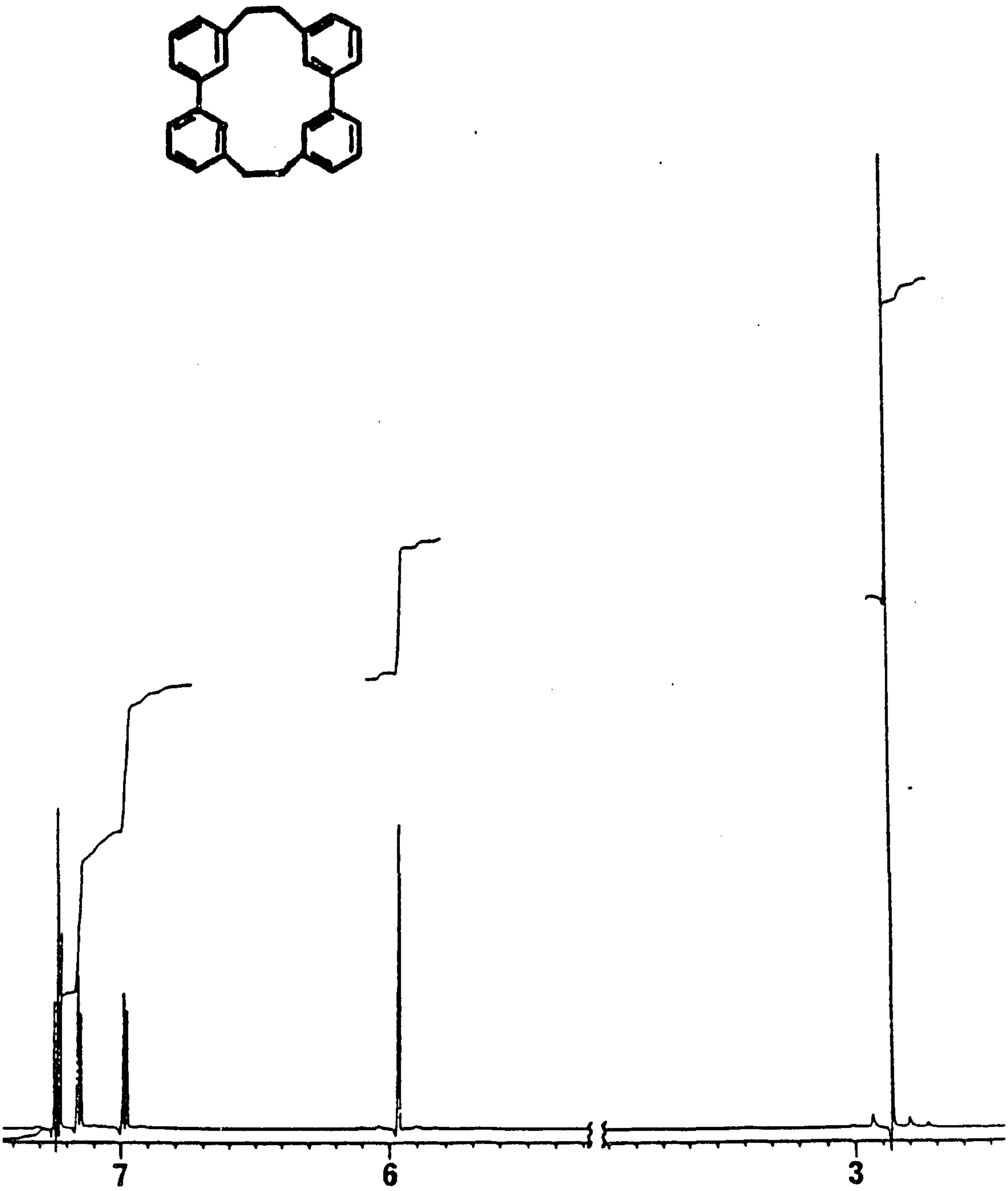


Fig. A.11. 500 MHz 'H NMR spectrum of 65,n=2.

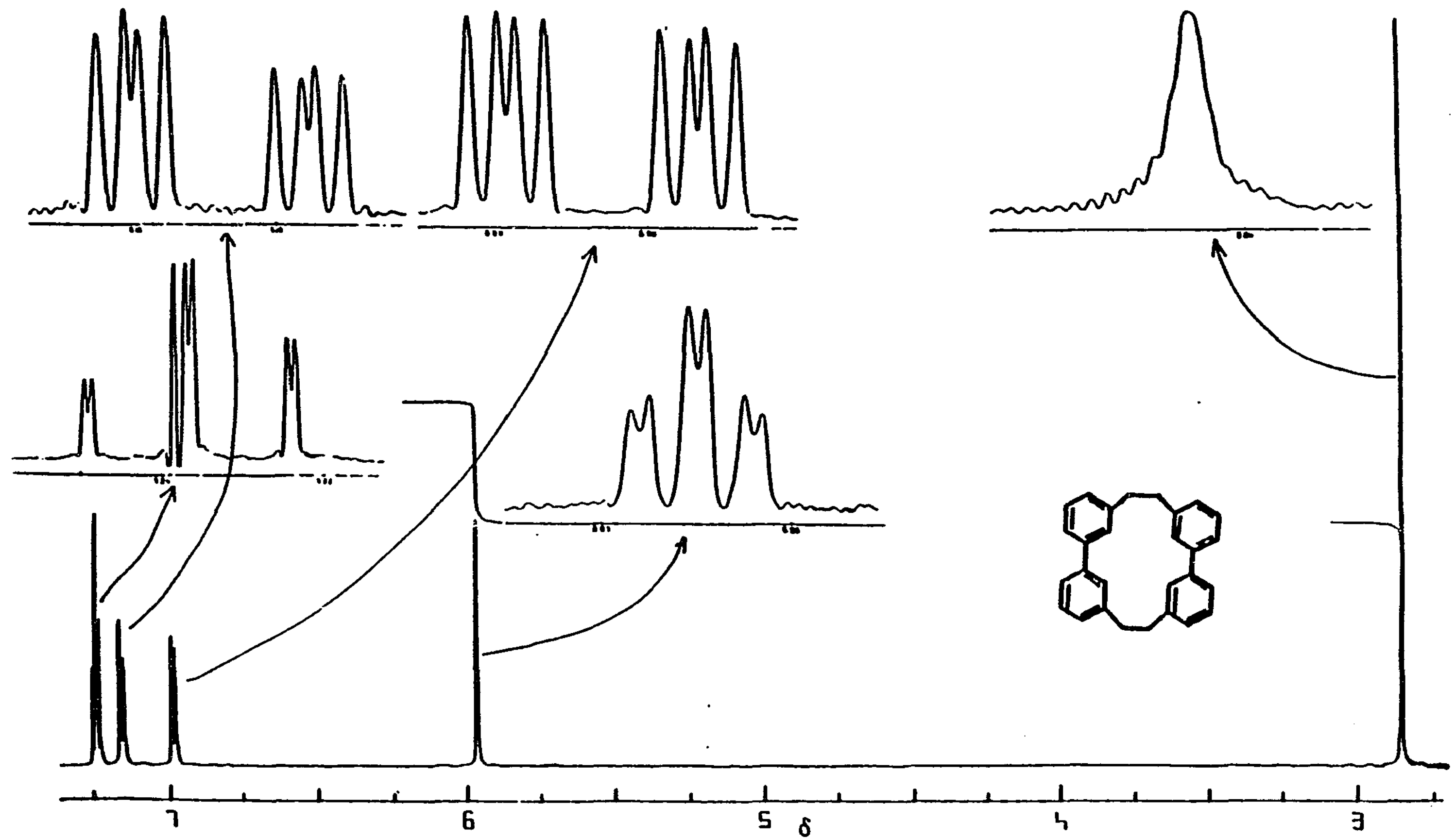


Fig. A.12. 500 MHz 'H NMR spectrum of 65,n=2

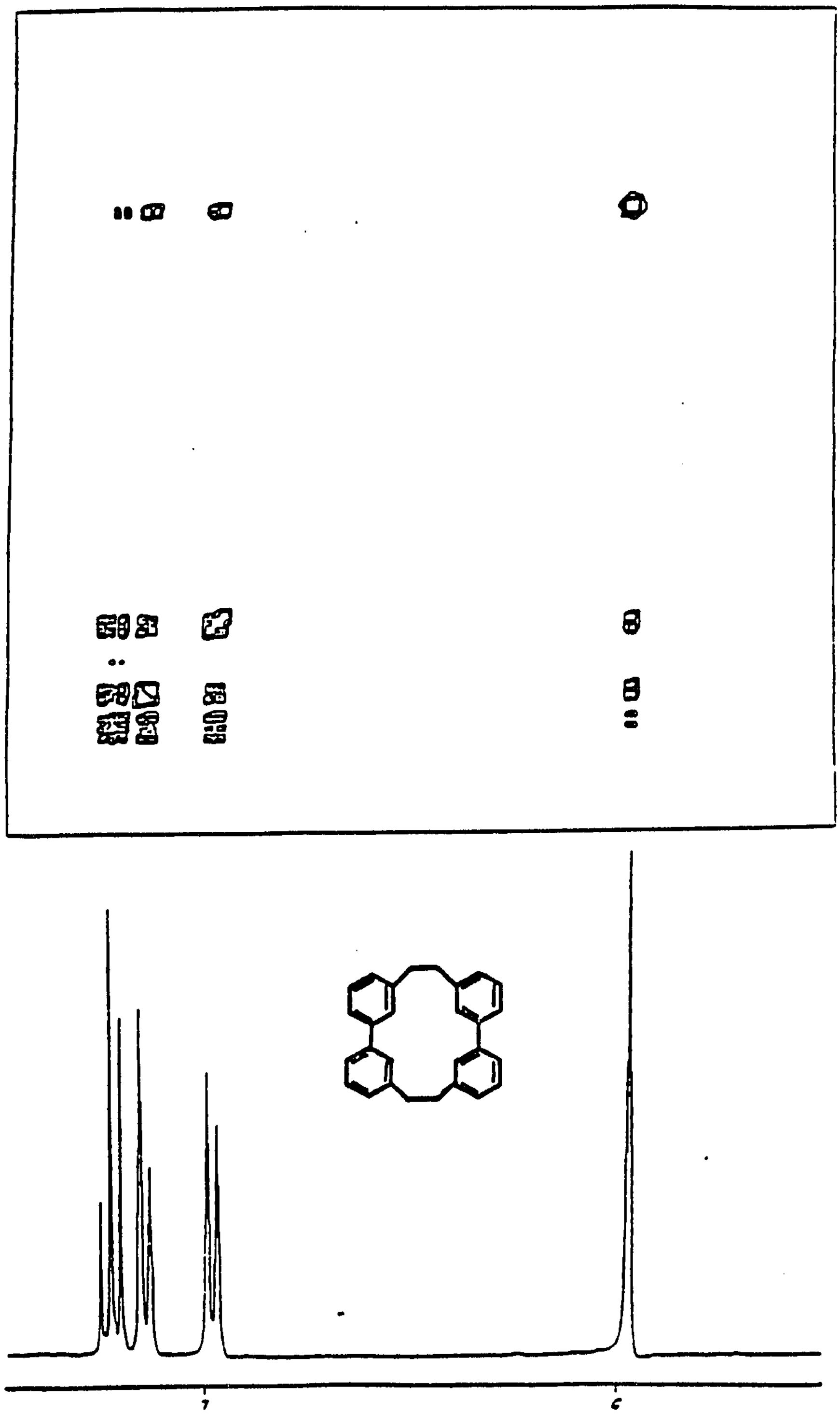


Fig. A.13. Aromatic region of 500 MHz 'H-'H COSY NMR spectrum of 65,n=2.

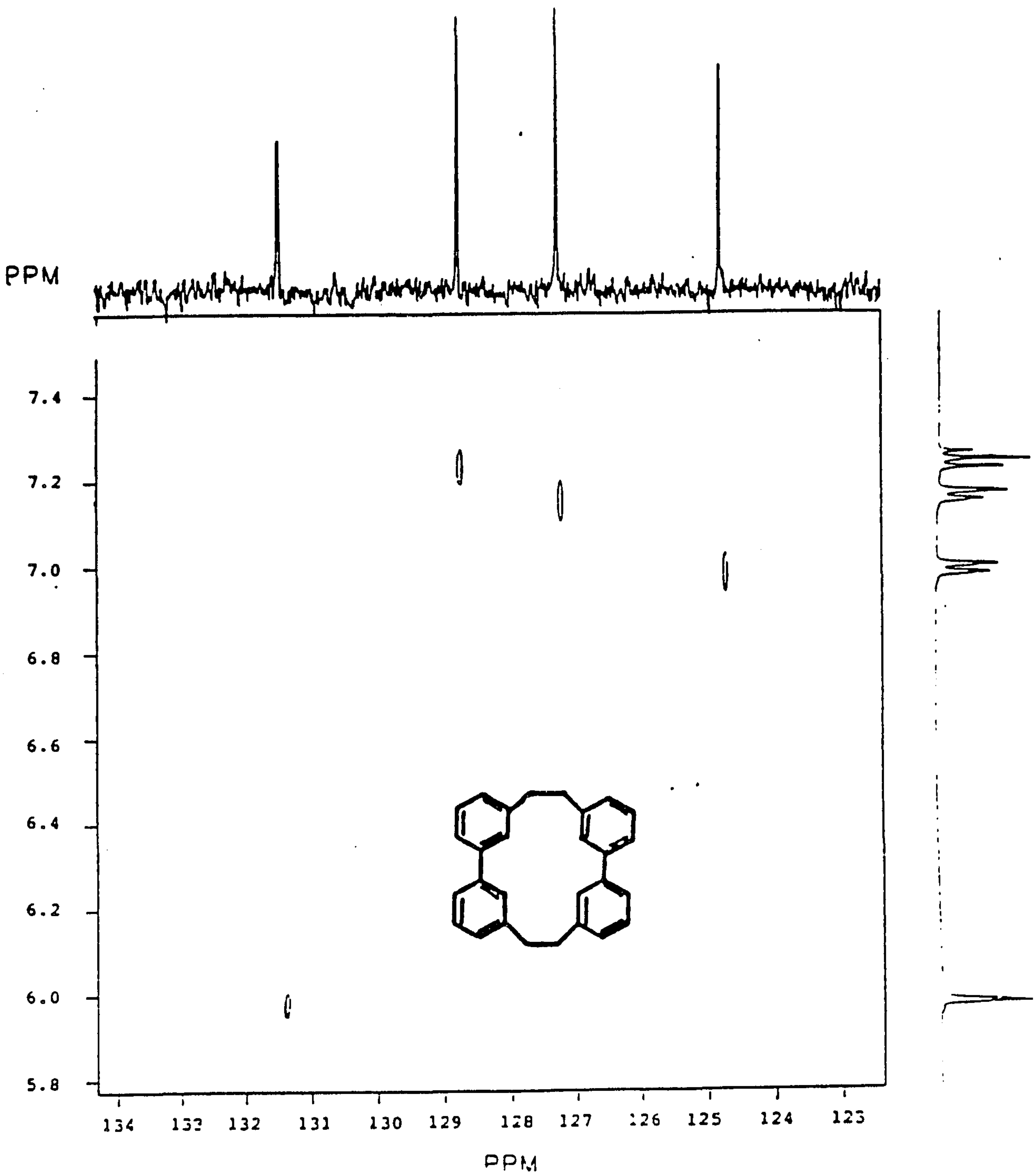


Fig. A.14. Aromatic region of ^{13}C-'H Hetcor NMR spectrum of 65,n=2.

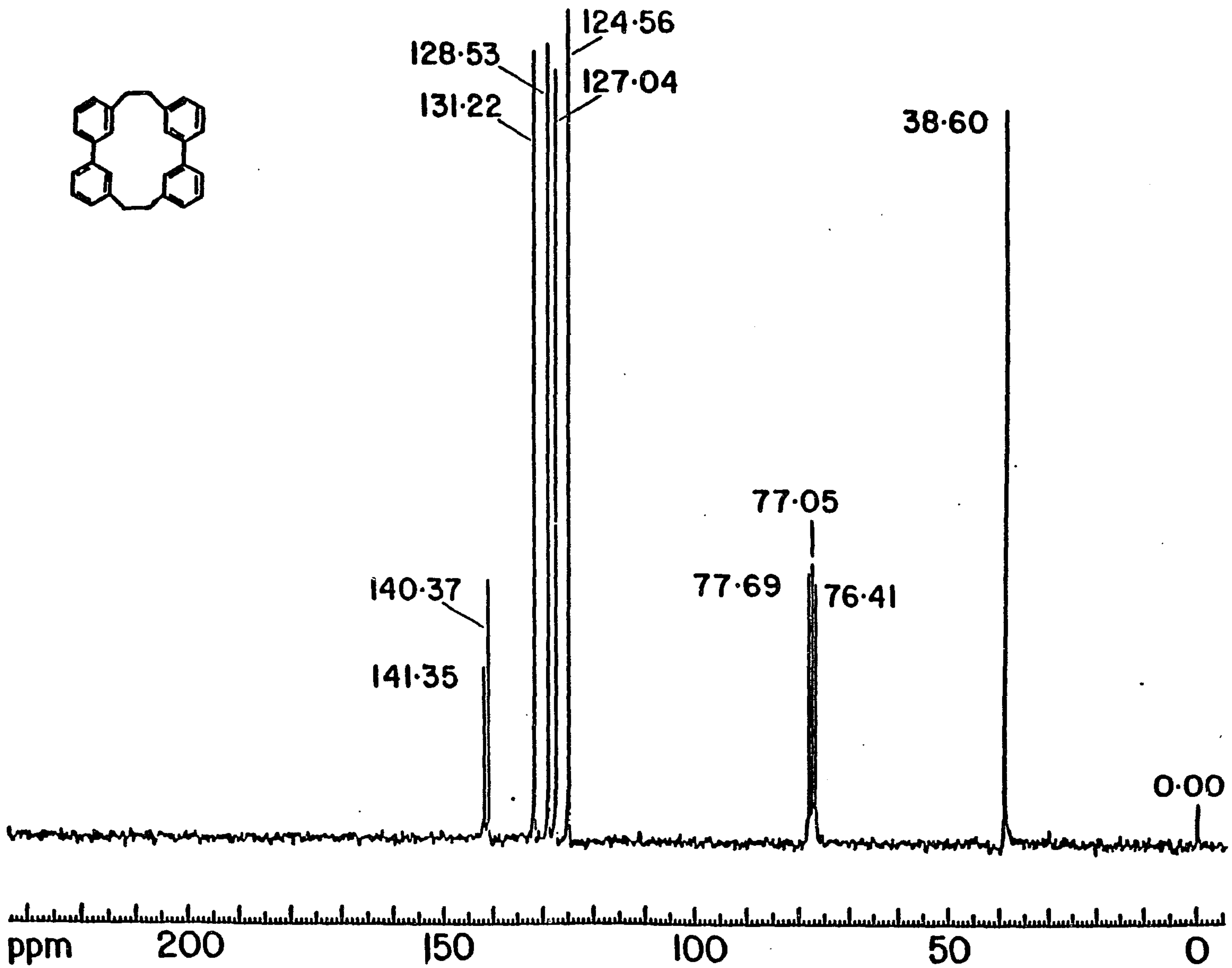


Fig. A.15. 50 MHz ^{13}C NMR spectrum of 65,n=2.

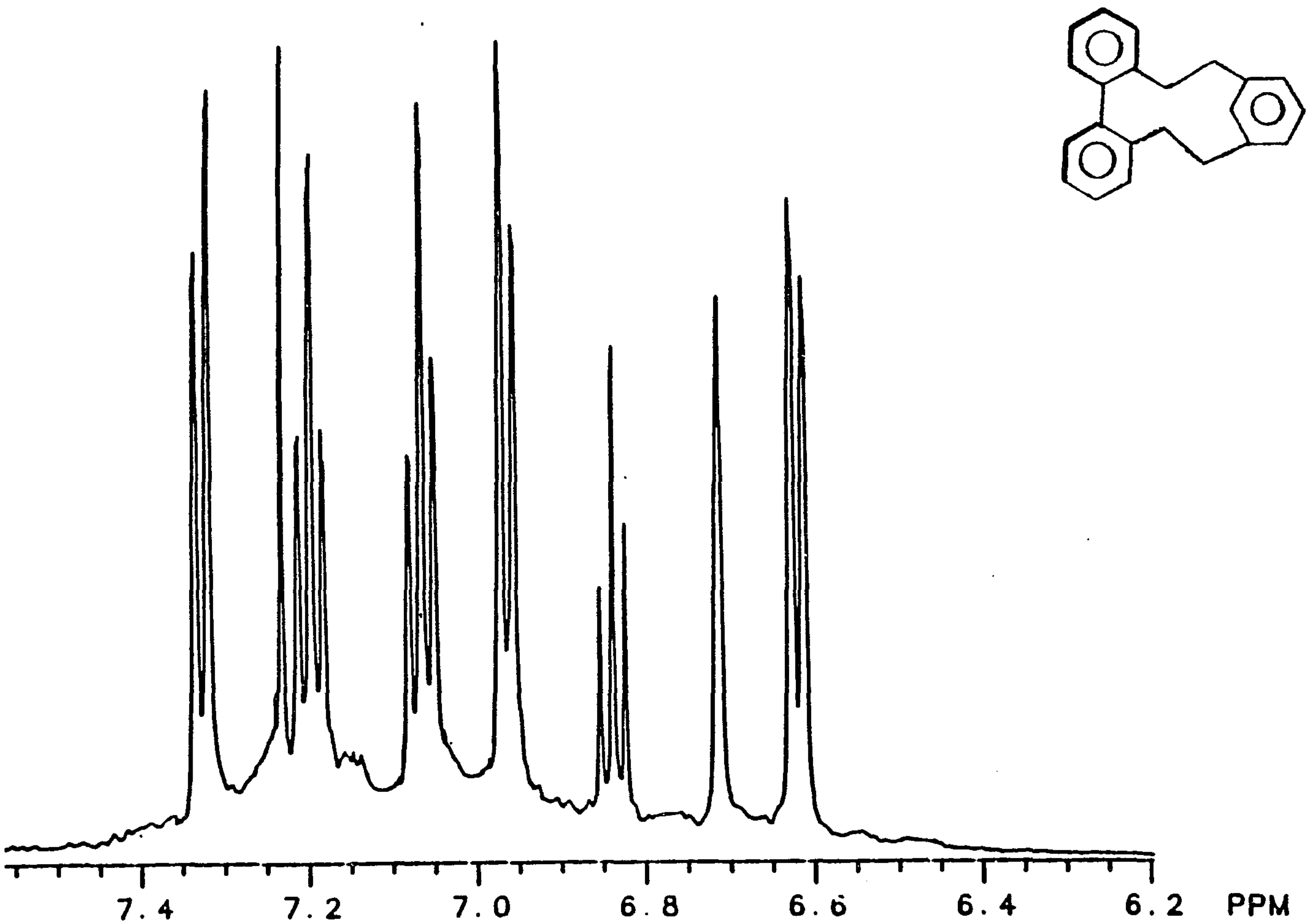


Fig. A.16. Aromatic region of 300 MHz ^{1}H NMR spectrum of 66.

APPENDIX B

X-RAY DATA ON [2.0.2.0]METACYCLOPHANE, 65,n=2

Positional parameters and their e.s.d.'s

	x	y	z	$B_{eq}(A^2)$
C(1a)	1.2440(3)	−0.0828(2)	0.17100(5)	3.30(4)
C(1b)	1.3315(2)	−0.0409(2)	0.13950(5)	3.42(4)
C(1c)	0.9309(2)	−0.0114(2)	0.07899(5)	3.45(4)
C(1d)	0.8912(2)	0.0598(2)	0.11005(6)	3.34(4)
C(2a)	1.1436(2)	−0.0152(2)	0.18884(5)	3.37(4)
C(2b)	1.3304(3)	−0.0956(2)	0.10623(6)	3.70(5)
C(2c)	1.0634(3)	0.0050(2)	0.05988(5)	3.76(5)
C(2d)	0.8477(2)	0.0146(2)	0.14299(6)	3.47(4)
C(3a)	1.0524(3)	−0.0530(2)	0.21679(5)	3.58(4)
C(3b)	1.4020(2)	−0.0545(2)	0.07585(6)	4.16(5)
C(3c)	1.1114(3)	−0.0670(2)	0.03321(5)	4.25(5)
C(3d)	0.8183(2)	0.0771(2)	0.17342(6)	3.72(5)
C(4a)	1.0685(3)	−0.1594(2)	0.22772(6)	4.53(5)
C(4b)	1.4783(3)	0.0425(2)	0.07924(6)	5.15(6)
C(4c)	1.0220(3)	−0.1544(2)	0.02503(6)	5.19(6)
C(4d)	0.8295(3)	0.1889(2)	0.17029(6)	4.27(5)
C(5a)	1.1716(3)	−0.2263(2)	0.21115(6)	5.17(6)
C(5b)	1.4835(3)	0.0966(2)	0.11177(7)	5.56(6)
C(5c)	0.8893(3)	−0.1708(2)	0.04277(7)	5.53(6)
C(5d)	0.8726(3)	0.2354(2)	0.13781(7)	4.41(5)
C(6a)	1.2570(3)	−0.1892(2)	0.18256(6)	4.45(5)
C(6b)	1.4082(3)	0.0559(2)	0.14170(6)	4.49(5)
C(6c)	0.8440(3)	−0.1007(2)	0.06995(6)	4.41(5)
C(6d)	0.9039(3)	0.1718(2)	0.10777(6)	4.04(5)
C(7a)	0.9343(3)	0.0187(2)	0.23315(6)	4.36(5)
C(7b)	1.3862(3)	−0.1071(2)	0.03916(6)	5.15(6)
C(7c)	1.2630(3)	−0.0540(2)	0.01621(6)	5.22(6)
C(7d)	0.7913(3)	0.0258(2)	0.21001(6)	4.52(5)

$$B_{eq} = 8\pi^2(U_{11}+U_{22}+U_{33})/3$$

Bond lengths (Å) and bond angles (°)

Numbers are average values for the bonds indicated and bonds which would be equivalent to these if the molecule possessed D_2 symmetry. Numbers in parentheses are e.s.d.'s in the least significant digits.

C(1a)	C(1b)	1.487(2)
C(1a)	C(2a)	1.393(2)
C(1a)	C(6a)	1.386(2)
C(2a)	C(3a)	1.388(2)
C(3a)	C(4a)	1.382(3)
C(3a)	C(7a)	1.505(3)
C(4a)	C(5a)	1.376(3)
C(5a)	C(6a)	1.382(3)
C(7a)	C(7d)	1.539(3)

C(1b)	C(1a)	C(2a)	120.2(2)
C(1b)	C(1a)	C(6a)	121.3(2)
C(2a)	C(1a)	C(6a)	118.3(2)
C(1a)	C(2a)	C(3a)	121.9(2)
C(2a)	C(3a)	C(4a)	118.2(2)
C(2a)	C(3a)	C(7a)	120.9(2)
C(4a)	C(3a)	C(7a)	120.6(2)
C(3a)	C(4a)	C(5a)	120.8(2)
C(4a)	C(5a)	C(6a)	120.4(2)
C(1a)	C(6a)	C(5a)	120.3(2)
C(3a)	C(7a)	C(7d)	112.6(2)

Calculated Hydrogen Positional Parameters

	x	y	z
H(2a)	1.1357	0.0591	0.1814
H(2b)	1.2777	−0.1640	0.1042
H(2c)	1.1236	0.0688	0.0652
H(2d)	0.8371	−0.0630	0.1446
H(4a)	1.0069	−0.1874	0.2474
H(4b)	1.5293	0.0718	0.0579
H(4c)	1.0529	−0.2057	0.0066
H(4d)	0.8068	0.2340	0.1910
H(5a)	1.1849	−0.3002	0.2200
H(5b)	1.5376	0.1652	0.1138
H(5c)	0.8254	−0.2321	0.0358
H(5d)	0.8792	0.3130	0.1359
H(6a)	1.3252	−0.2368	0.1699
H(6b)	1.4093	0.0947	0.1648
H(6c)	0.7512	−0.1131	0.0832
H(6d)	0.9337	0.2055	0.0851
H(7a)	0.9100	−0.0069	0.2571
H(7a')	0.9741	0.0913	0.2359
H(7b)	1.4789	−0.1045	0.0263
H(7b')	1.3602	−0.1829	0.0421
H(7c)	1.2850	0.0234	0.0142
H(7c')	1.2620	−0.0822	−0.0079
H(7d)	0.7160	0.0663	0.2226
H(7d')	0.7532	−0.0464	0.2063

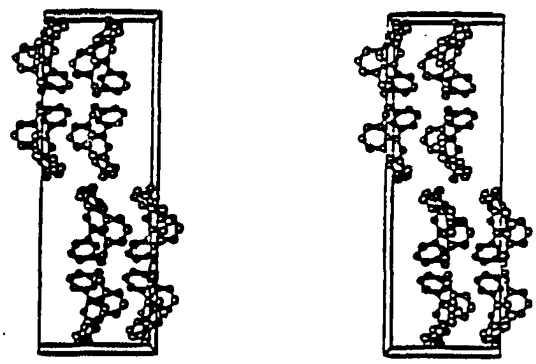
General Temperature Factor Expressions - U's

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1a)	0.042(1)	0.048(1)	0.0357(9)	0.003(1)	-0.003(1)	-0.0008(9)
C(1b)	0.035(1)	0.052(1)	0.043(1)	0.007(1)	0.001(1)	0.004(1)
C(1c)	0.043(1)	0.050(1)	0.039(1)	0.004(1)	-0.005(1)	0.005(1)
C(1d)	0.030(1)	0.051(1)	0.046(1)	0.002(1)	-0.003(1)	0.002(1)
C(2a)	0.045(1)	0.044(1)	0.039(1)	0.000(1)	-0.002(1)	-0.001(1)
C(2b)	0.046(1)	0.050(1)	0.045(1)	0.009(1)	0.005(1)	0.004(1)
C(2c)	0.051(1)	0.053(1)	0.040(1)	0.001(1)	-0.001(1)	0.006(1)
C(2d)	0.034(1)	0.048(1)	0.050(1)	-0.004(1)	0.001(1)	0.000(1)
C(3a)	0.051(1)	0.053(1)	0.032(1)	0.001(1)	0.001(1)	-0.006(1)
C(3b)	0.043(1)	0.065(1)	0.050(1)	0.016(1)	0.010(1)	0.005(1)
C(3c)	0.065(1)	0.065(1)	0.032(1)	0.011(1)	-0.001(1)	0.005(1)
C(3d)	0.031(1)	0.060(1)	0.050(1)	0.001(1)	0.005(1)	-0.001(1)
C(4a)	0.073(2)	0.061(1)	0.038(1)	-0.005(1)	0.010(1)	0.004(1)
C(4b)	0.046(1)	0.084(2)	0.065(1)	-0.002(1)	0.019(1)	0.011(1)
C(4c)	0.080(2)	0.070(1)	0.046(1)	0.010(1)	-0.005(1)	-0.011(1)
C(4d)	0.045(1)	0.061(1)	0.056(1)	0.007(1)	0.002(1)	-0.011(1)
C(5a)	0.094(2)	0.049(1)	0.054(1)	0.007(1)	0.013(1)	0.011(1)
C(5b)	0.052(1)	0.078(2)	0.081(2)	-0.020(1)	0.011(1)	0.002(1)
C(5c)	0.077(2)	0.066(1)	0.067(2)	-0.008(1)	-0.015(1)	-0.013(1)
C(5d)	0.052(1)	0.048(1)	0.068(1)	0.006(1)	-0.001(1)	-0.001(1)
C(6a)	0.069(1)	0.051(1)	0.050(1)	0.013(1)	0.009(1)	0.002(1)
C(6b)	0.045(1)	0.065(1)	0.061(1)	-0.007(1)	0.006(1)	-0.006(1)
C(6c)	0.055(1)	0.061(1)	0.052(1)	-0.005(1)	-0.003(1)	-0.000(1)
C(6d)	0.043(1)	0.053(1)	0.057(1)	0.002(1)	0.001(1)	0.007(1)
C(7a)	0.060(1)	0.069(1)	0.036(1)	0.004(1)	0.009(1)	-0.006(1)
C(7b)	0.064(1)	0.083(2)	0.048(1)	0.019(1)	0.022(1)	0.003(1)
C(7c)	0.075(2)	0.083(2)	0.040(1)	0.014(2)	0.016(1)	0.004(1)
C(7d)	0.050(1)	0.074(1)	0.051(1)	0.001(1)	0.016(1)	-0.004(1)

The form of the anisotropic thermal parameter is:

$\exp[-2PI^2\{(ha)^2U_{11}+(kb)^2U_{22}+(lc)^2U_{33}+2hkabU_{12}+2hlacU_{13}+2klbcU_{23}\}]$,

where a,b, and c are reciprocal lattice constants.



ORTEP stereo views of a unit cell, *c* horizontal, *b* vertical.

APPENDIX C

X-RAY DATA ON [14.0]PARACYCLOPHANE, 60,n=14

Positional parameters and their e.s.d.'s

	x	y	z	B_{eq} (Å^2)
C(1)	0.52921(9)	0.1839(3)	0.2305(2)	4.01(5)
C(2)	0.5744(1)	0.2033(4)	0.3098(2)	5.13(6)
C(3)	0.6281(1)	0.2148(4)	0.2736(2)	5.34(6)
C(4)	0.6405(1)	0.2086(3)	0.1563(2)	4.40(5)
C(5)	0.5961(1)	0.1825(4)	0.0779(2)	5.26(6)
C(6)	0.5421(1)	0.1708(4)	0.1141(2)	5.07(6)
C(7)	0.6987(1)	0.2410(3)	0.1170(2)	5.10(6)
C(8)	0.7164(1)	0.4247(4)	0.1397(2)	5.10(6)
C(9)	0.6840(1)	0.5529(4)	0.0629(2)	5.35(6)
C(10)	0.6743(1)	0.7235(4)	0.1207(2)	5.49(6)
C(11)	0.6324(1)	0.7196(3)	0.2170(2)	5.11(6)
C(12)	0.5719(1)	0.6943(3)	0.1754(2)	5.16(6)
C(13)	0.5305(1)	0.6963(3)	0.2711(2)	4.96(6)

$$B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3$$

Bond lengths (A) and bond angles(°)

Numbers in parentheses are e.s.d.'s in the least significant digits.
Symmetry operations for equivalent atoms (i) 1-X Y 1/2-Z.

C(1)	C(1)i	1.487(3)
C(1)	C(2)	1.393(2)
C(1)	C(6)	1.381(2)
C(2)	C(3)	1.372(2)
C(3)	C(4)	1.383(2)
C(4)	C(5)	1.378(2)
C(4)	C(7)	1.505(2)
C(5)	C(6)	1.378(2)
C(7)	C(8)	1.521(3)
C(8)	C(9)	1.526(2)
C(9)	C(10)	1.514(3)
C(10)	C(11)	1.519(3)
C(11)	C(12)	1.522(2)
C(12)	C(13)	1.505(2)
C(13)	C(13)i	1.521(3)

C(1)i	C(1)	C(2)	121.6(2)
C(1)i	C(1)	C(6)	122.6(2)
C(2)	C(1)	C(6)	115.8(2)
C(1)	C(2)	C(3)	121.8(2)
C(2)	C(3)	C(4)	122.0(2)
C(3)	C(4)	C(5)	116.3(2)
C(3)	C(4)	C(7)	121.4(2)
C(5)	C(4)	C(7)	122.2(2)
C(4)	C(5)	C(6)	121.7(2)
C(1)	C(6)	C(5)	122.2(2)
C(4)	C(7)	C(8)	111.4(1)
C(7)	C(8)	C(9)	113.2(1)
C(8)	C(9)	C(10)	114.5(2)
C(9)	C(10)	C(11)	114.5(2)
C(10)	C(11)	C(12)	115.4(1)
C(11)	C(12)	C(13)	114.9(1)
C(12)	C(13)	C(13)i	115.1(2)

Calculated Hydrogen Atom Positions

	x	y	z
H(2)	0.5677	0.2084	0.3910
H(3)	0.6576	0.2261	0.3306
H(5)	0.6030	0.1721	-0.0033
H(6)	0.5129	0.1520	0.0572
H(7-1)	0.7116	0.2086	0.0426
H(7-2)	0.7155	0.1717	0.1762
H(8-1)	0.7550	0.4344	0.1253
H(8-2)	0.7105	0.4504	0.2196
H(9-1)	0.6487	0.5042	0.0409
H(9-2)	0.7043	0.5717	-0.0060
H(10-1)	0.6608	0.8007	0.0619
H(10-2)	0.7089	0.7626	0.1531
H(11-1)	0.6352	0.8247	0.2587
H(11-2)	0.6425	0.6287	0.2693
H(12-1)	0.5691	0.5879	0.1365
H(12-2)	0.5624	0.7836	0.1221
H(13-1)	0.5368	0.7955	0.3177
H(13-2)	0.5366	0.5978	0.3188

General Temperature Factor Expressions - U's

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0.059(1)	0.045(1)	0.049(1)	0.002(1)	0.003(1)	-0.000(1)
C(2)	0.065(1)	0.086(2)	0.044(1)	0.002(1)	0.003(1)	0.003(1)
C(3)	0.058(1)	0.090(2)	0.055(1)	0.004(1)	-0.004(1)	0.001(1)
C(4)	0.055(1)	0.053(1)	0.059(1)	0.009(1)	0.005(1)	-0.004(1)
C(5)	0.067(2)	0.084(2)	0.049(1)	-0.001(1)	0.007(1)	-0.013(1)
C(6)	0.057(1)	0.085(2)	0.050(1)	-0.005(1)	-0.002(1)	-0.009(1)
C(7)	0.060(1)	0.075(2)	0.059(1)	0.012(1)	0.010(1)	-0.003(1)
C(8)	0.048(1)	0.083(2)	0.063(1)	0.006(1)	0.008(1)	-0.005(1)
C(9)	0.068(1)	0.079(2)	0.057(1)	0.002(2)	0.014(1)	0.004(1)
C(10)	0.064(1)	0.073(2)	0.071(2)	-0.004(1)	0.003(1)	0.008(1)
C(11)	0.067(2)	0.062(2)	0.065(1)	0.004(1)	0.004(1)	-0.003(1)
C(12)	0.070(2)	0.064(2)	0.062(1)	-0.001(1)	0.008(1)	-0.002(1)
C(13)	0.069(1)	0.062(1)	0.058(1)	0.006(1)	0.006(1)	0.004(1)

The form of the anisotropic thermal parameter is:
$\exp[-2PI^2\{(ha)^2U_{11}+(kb)^2U_{22}+(lc)^2U_{33}+2hkabU_{12}+2hlacU_{13}+2klbcU_{23}\}]$.
where a,b, and c are reciprocal lattice constants.

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