PART I

STUDIES DIRECTED TOWARD THE SYNTHESIS OF "SUPERTRIPTYCENE"

PART II

BICYCLO [2.2.2] ALKYNES; REACTIVITY AND THE MECHANISM OF THE TRIMERIZATION

By

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ABSTRACT

PART I

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Fusion of six 9,10-anthradiyl groups to the six a,c bonds of triptycene would give a hydrocarbon trivially called "supertriptycene" 24. In the first part of this thesis a methodological approach to the synthesis of 24 and related a,c-fused iptycenes in general was explored. The yield of 3-chloro-1,4;1′,4′-di-o-benzeno-1,4,1′,4′-tetrahydro-2,2′-binaphthyl 32, a suitable starting material for such iptycenes, was optimized. Treatment of 32 with two equivalents of n-butyllithium, followed by aqueous quench, gave the parent hydrocarbon 1,4;1′4′-di-o-benzeno-1,4,1′,4′-tetrahydro-2,2′-binaphthyl 56. A Diels-Alder reaction of 56 with 1,2-dichloroethylene, followed by the dehydrochlorination of the cycloadduct, afforded the [1.1.1^a.1.1] pentiptycene 2. A similar reaction of 56 with 1,4-epoxynaphthalene gave the expected cycloadduct. Dehydration and the subsequent dehydrogenation of this cycloadduct

provided an a,c-9,10-anthradiyl bis-fused anthracene, which was converted by reaction with benzyne to the known [1.1.1^{ac}.1.1.1.1] heptiptycene **4**. Finally a formal bis-adduct of **56** with p-benzoquinone was elaborated to a novel a,c,a′,c′-9,10-anthradiyl tetrakis-fused anthracene, a potential precursor of **24**.

In the second part of this thesis, the reactivity and the trimerization mechanism of several bicyclo [2.2.2] alkyne derivatives, generated by the dehydrohalogenation, were studied. Generation of 1,4-dihydro-1,4-ethynonaphthalene **110** in the presence or absence of 1,3-diphenylisobenzofuran (trapping reagent) resulted only in the formation of a 1,3-butadiene coupling product which underwent a novel retro-Diels-Alder reaction. 1,2,3,4-Tetrahydro-1,4-ethynonaphthalene **115**, on the other hand, in the presence or absence of a trapping reagent, gave oligomeric products from which an all cis-trimer was isolated. 9-Methyl-9,10-ethynoanthracene **122** and 9,10-dimethyl-9,10-ethynoanthracene **133** underwent a Diels-Alder reaction with 1,3-diphenylisobenzofuran to give the expected cycloadducts. In the absence of the trapping reagent **122** afforded two trimeric products and two 1,3-butadiene coupling products. Attempted trimerization of the bicycloalkyne **133** resulted in the formation of only two coupling products. Based on the experimental results a stepwise mechanism for the trimerization of bicyclo [2.2.2] alkynes, under the mentioned reaction conditions, is proposed.

Dedicated to the memory of my father, Ebrahim Shahlai.

ACKNOWLEDGEMENTS

I wish to express my sincerest appreciation and gratitude to Professor Harold Hart for his guidance, encouragement, as well as his endless patience throughout the course of this study.

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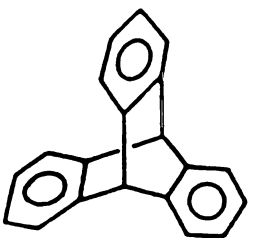
PART I

STUDIES DIRECTED TOWARD THE SYNTHESIS OF "SUPERTRIPTYCENE"

INTRODUCTION

Triptycene 1, which was first synthesized in 1942,[1] is the first member of a large series of compounds now designated as iptycenes, a general term coined by Hart.[2]



1

Despite the substantial number of studies regarding triptycene and its derivatives,[3] the potential for extending the rigid framework of this compound to other theoretically interesting and useful iptycenes has only recently been realized.[4,5]

By fusing one to six 9,10-anthradiyl moieties to the aromatic rings of triptycene, one can derive the first generation of iptycenes. Depending on the number and the site of fusions, twenty four structural variations are possible (Table 1). Only a few of the iptycenes listed in Table 1 are known. A low yield synthesis of 25, a derivative of 2 with two methyl substituents on the central ring, has been reported.[2]

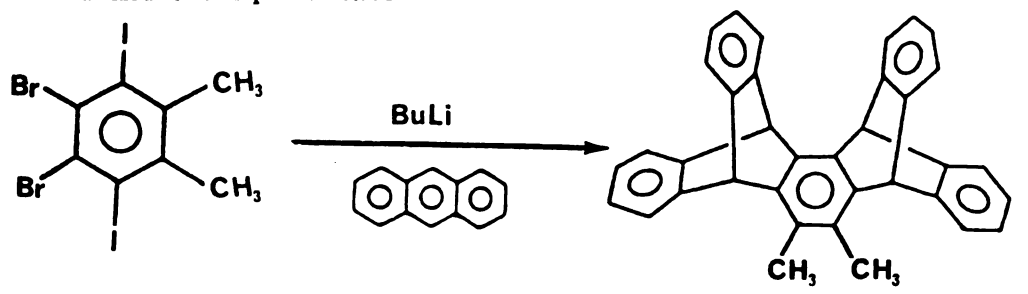
The synthesis is based on the previously known orthobenzyne bisannelation technique and involves the reaction of the orthodibenzyne

Table 1. Iptycenes derived from 1 by 9,10-anthradiyl fusions

Number of fusions	Number of isomers	Fusion bonds	Compound number	Point group	Iptycene prefix
0	1	—	1[a]	D_{3h}	tr(i)
1	2	a	2[b]	C_{2v}	pent
		b	3[a]	D_{2h}	
2	5	ac	4[a]	D_{3h}	hept
		aa′	5	C_s	
		ab′	6	C_1[c]	
		ac′	7	C_2[c]	
		bb′	8[a]	C_{2v}	
3	8	aca′	9	C_1[c]	non
		acb′	10	C_s	
		aa′a″	11	C_{3v}	
		aa′b″	12	C_s	
		aa′c″	13	C_s	
		ab′b″	14	C_s	
		ab′c″	15	C_2[c]	
		bb′b″	16[b]	D_{3h}	
4	5	aca′c′	17	C_{2v}	undeca
		aca′a″	18	C_s	
		aca′b″	19	C_1[c]	
		aca′c″	20	C_2[c]	
		acb′b″	21	C_{2v}	
5	2	aca′c′a″	22	C_s	trideca
		aca′c′b″	23	C_{2v}	
6	1	aca′c′a″c″	24	D_{3h}	pentadeca

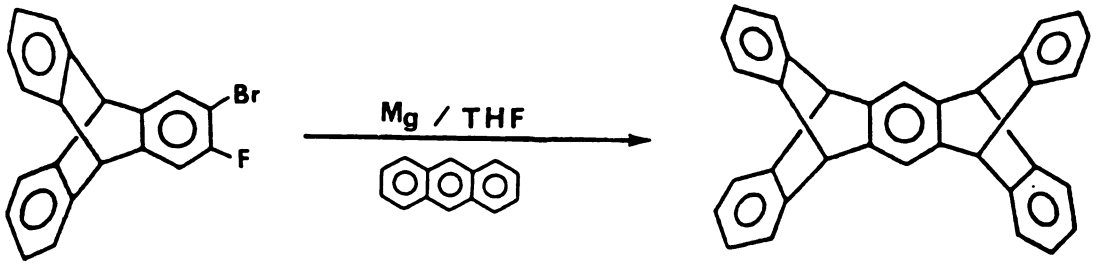
[a] The parent hydrocarbon is known.
[b] The ring system is known.
[c] Can exist as a pair of enantiomers.

equivalent 1,2-dibromo-3,6-diiodo-4,5-dimethylbenzene, with butyllithium and two equivalents of anthracene.



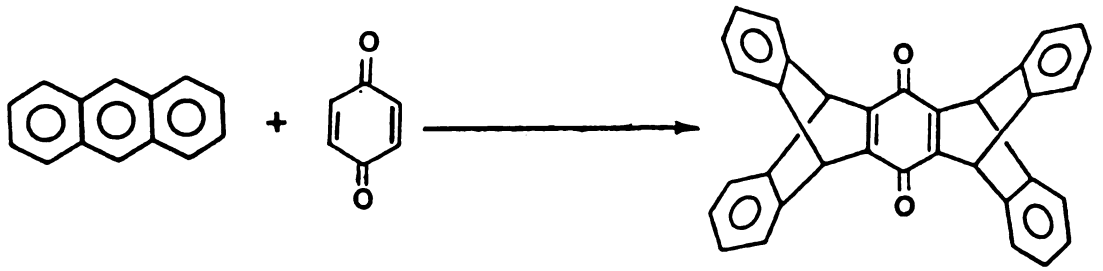
25

Pentiptycene 3 was first prepared through the addition of 2,3-triptycyne to anthracene.[7] The overall yield was only 3.7% (crude), since the required starting material 2- bromo-3-fluorotriptycene 26 had to be synthesized from anthracene in four steps (via nitro-, amino-, and 2-bromo-3-aminotriptycene).



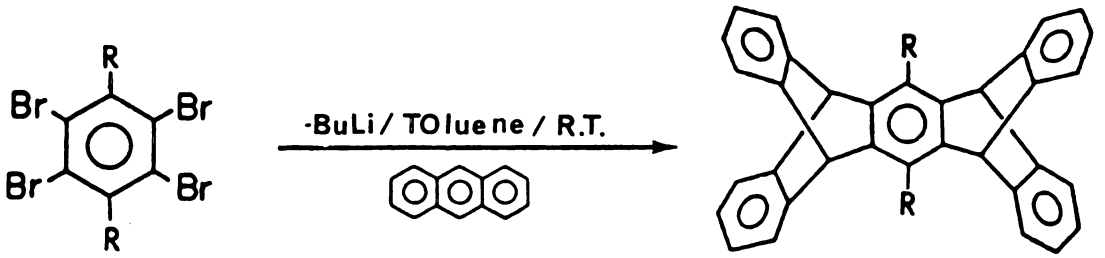
26 3

Although not fully aromatic, the pentiptycene quinone 27, which properly belongs to this class of compounds, has been known for a long time and can be readily prepared in high yield from inexpensive precursors, p-benzoquinone and anthracene.[8]



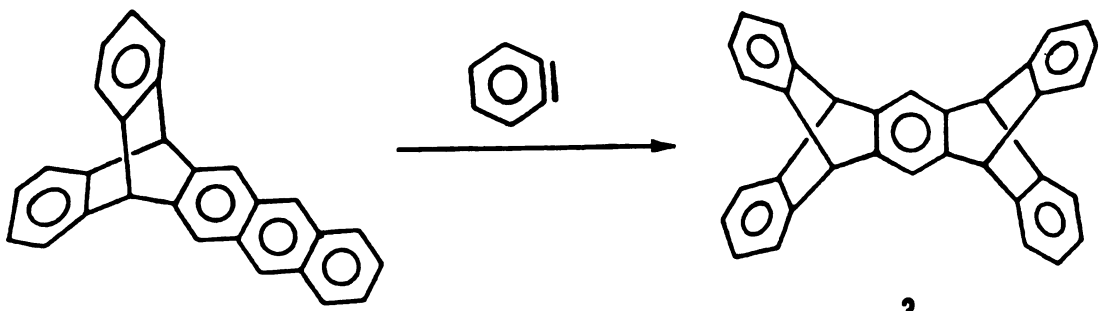
27

A much shorter, high yield route to 3 from 1,2,4,5-tetrabromobenzene, anthracene and butyllithium was achieved by Hart and co-workers and was extended to various substituted analogues.[9]



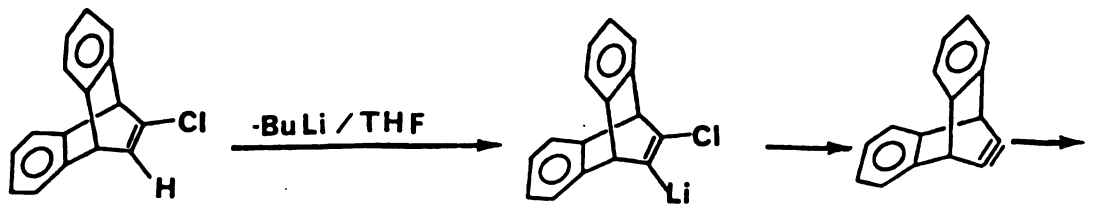
R = H , CH_3, OCH_3

A somewhat longer but more useful approach to 3 has recently been developed.[2] It involves the addition of benzyne generated from benzenediazonium carboxylate to the triptycene 28.

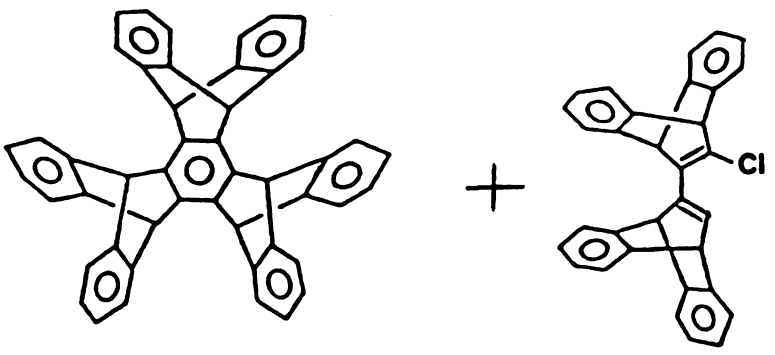


28 3

Huebner, et. al.,[10] showed that at -70°C in THF 29 was metalated by n-butyllithium to give the α-lithio derivative 30. Heptiptycene 4 was then reported to be formed as a minor product by heating a solution of 30, presumably via the trimerization of the cycloalkyne 31; the coupling product 32 was also formed.



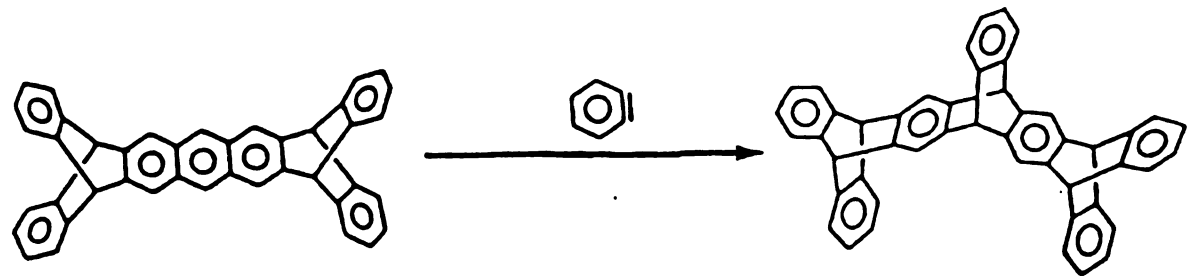
29 30 31



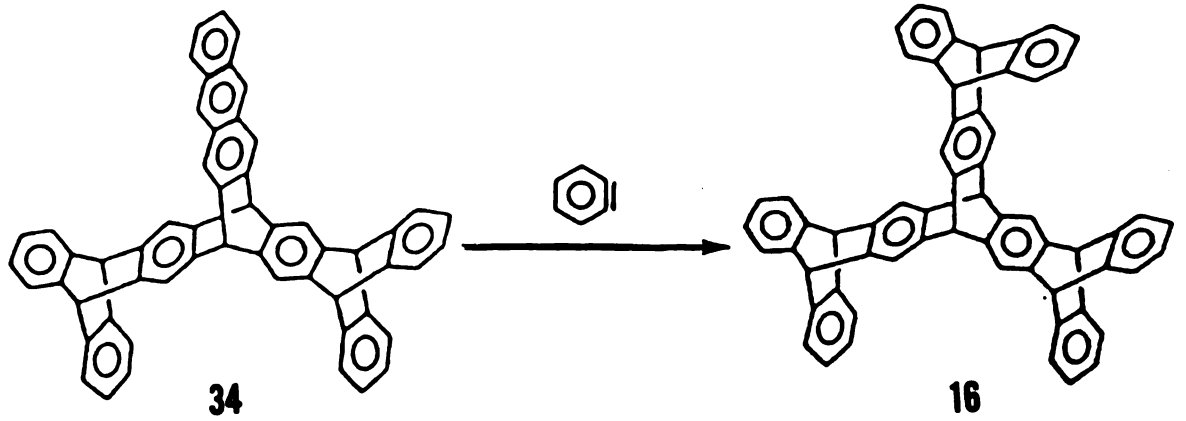
4 32

Hart and co-workers were able to increase the yield of 4 to 20% by modifying the reaction conditions.[2]

The synthesis of heptiptycene 8 and noniptycene 16 was successfully accomplished only recently, through the addition of benzyne to the iptycenes 33 and 34 respectively.[10,11]



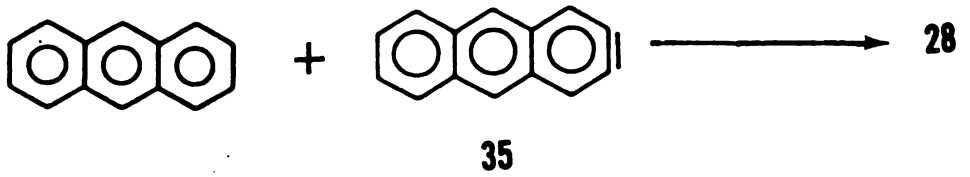
33 8

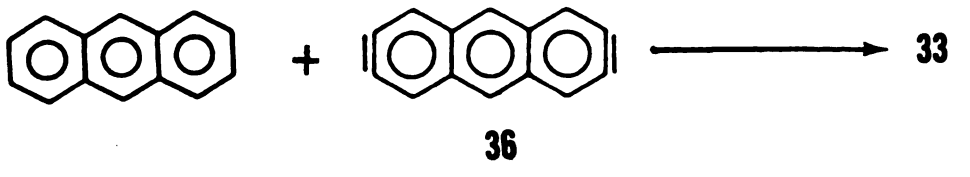


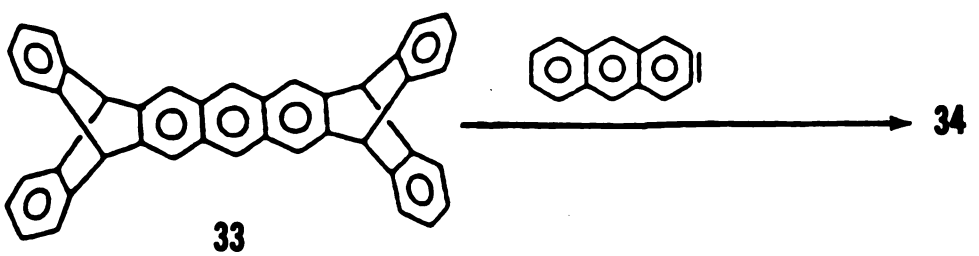
34 16

All of the iptycenes presented in Table 1 contain only benzenoid rings. Numerous iptycenes with polycyclic aromatic rings such as naphthalene, anthracene, phenanthrene, etc. are known.[12-16] Among these the iptycenes with fused anthracenes appear to be viable intermediates in the synthesis of the other iptycenes. Their utility has already been demonstrated in the construction of **3**, **8**, and **16**.

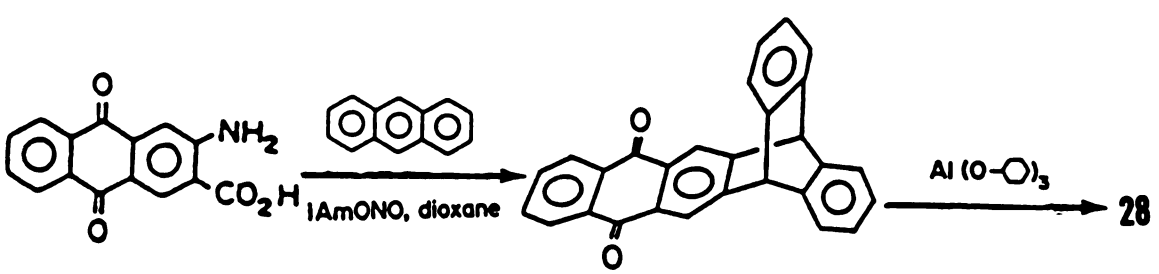
Compound **34** can be regarded as the product that would result from the cycloaddition of 2,3-anthryne **35** to **33**. Similarly **28** and **33** can be regarded as the cycloadducts of **35** and 2,3:6,7-anthradiyne **36**, with one or two equivalents of anthracene respectively.





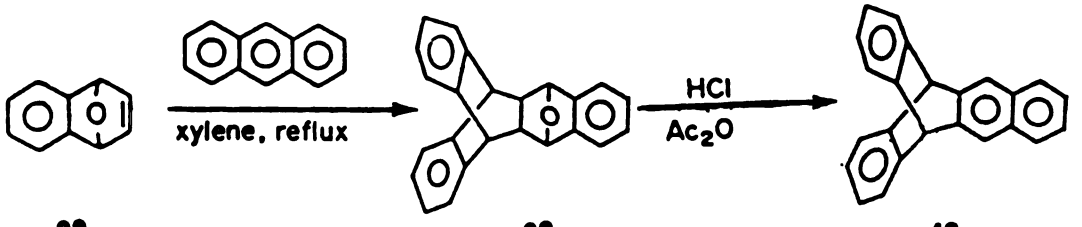


The first reported synthesis of **28** was therefore based on this concept.[14,15] It was originally prepared in 8.4% yield from **37**; unfortunately this precursor **37** required five steps for synthesis from toluene.



Other approaches to **37** from phthalic anhydride did not represent any advantage over the previous one.[17,18]

The potential usefulness of anthracene-fused iptycenes as building blocks for the synthesis of higher analogues therefore demanded shorter synthetic routes with reasonable yields. 2,3-Anthryne and 2,3:6,7-anthradiyne are not easily accessible. However in 1960, Wittig showed that 1,4-epoxynaphthalene **38** was a very effective dienophile.[12] It underwent cycloaddition to anthracene to give the corresponding adduct **39**, which upon dehydration gave the triptycene **40**.

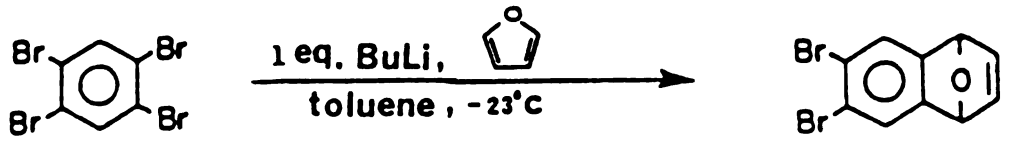


38 **39** **40**

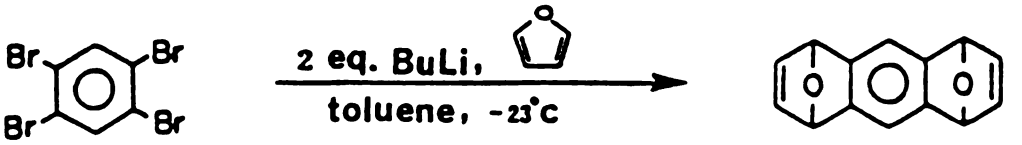
Thus, 1,4-epoxynaphthalene **38** can be considered as a useful 2,3-naphthyne equivalent. Similarly, 1,4-epoxyanthracene **41** and 1,4:5,8-diepoxyanthracene **42** can be regarded as 2,3-anthryne and 2,3:6,7-anthradiyne equivalents, respectively.

41 **42**

Both **41** and **42** can be conveniently prepared from 1,2,4,5-tetrabromobenzene.[19-22] Treatment with either one or two equivalents of butyllithium in the presence of furan gives 4,5-dibromo-1,4-epoxynaphthalene **43** and **42**.[23]

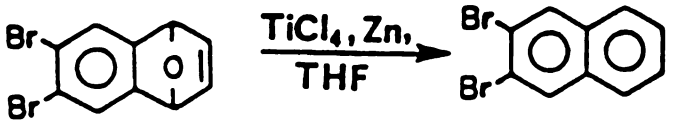


43



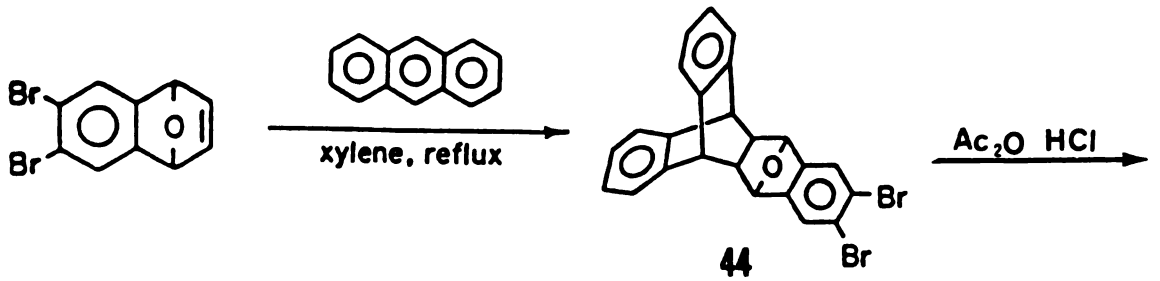
42

Adduct 43, although a useful synthon by itself, can be converted to 2,3-dibromonaphthalene, a precursor to 2,3-naphthyne and consequently to 41.

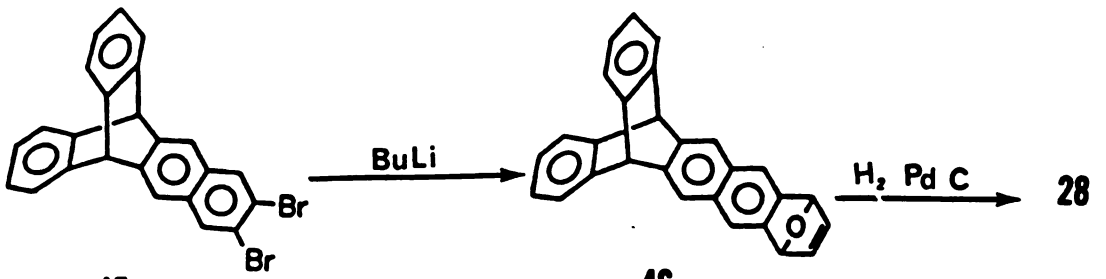


41

Availability of valuable synthons such as 41, 42 and 43 has supplemented the synthesis of b-fused type iptycenes. Thus the addition of 43 to anthracene in refluxing xylene gave a single adduct 44 in 96% yield. Dehydration of 44, followed by cycloaddition of the corresponding aryne from 45 to furan and subsequent deoxygenation of the resulting adduct 46 with low valent titanium, provided the iptycene 28 in four steps and 35% overall yield.[4]

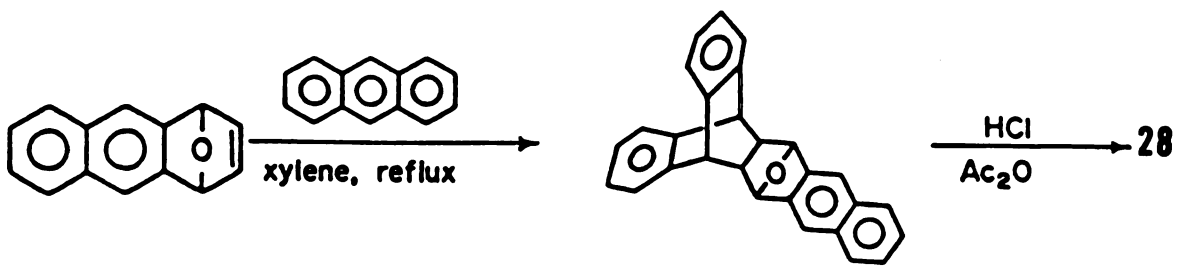


44



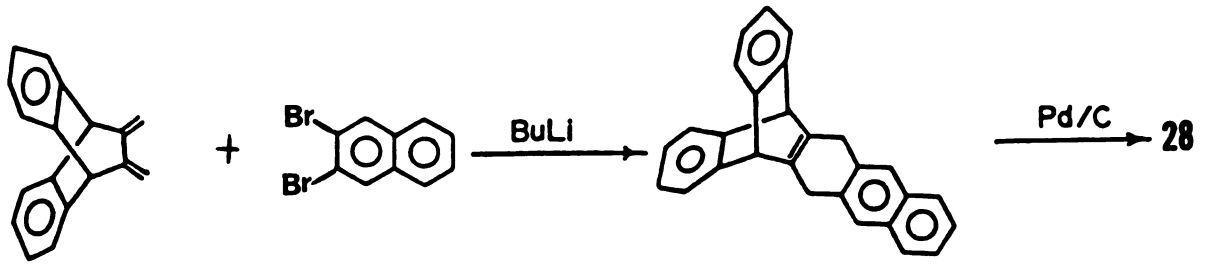
45 46

By starting with the three ring precursor 41, the synthesis has been shortened to two steps and an overall yield of 62%. Cycloaddition of 41 to anthracene gave adduct 47 in 93% yield and acid catalyzed dehydration gave 28.[4]



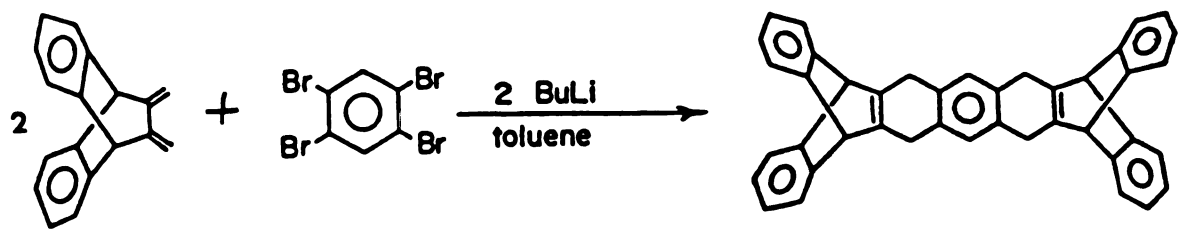
41 47

Complementary to the above routes, 28 has also been synthesized in two steps by the addition of 2,3-naphthyne to diene 48,[24] followed by dehydrogenation of the cycloadduct 49. The two steps gave 28 in 73% overall yield.[4]

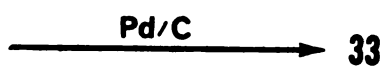


48 49

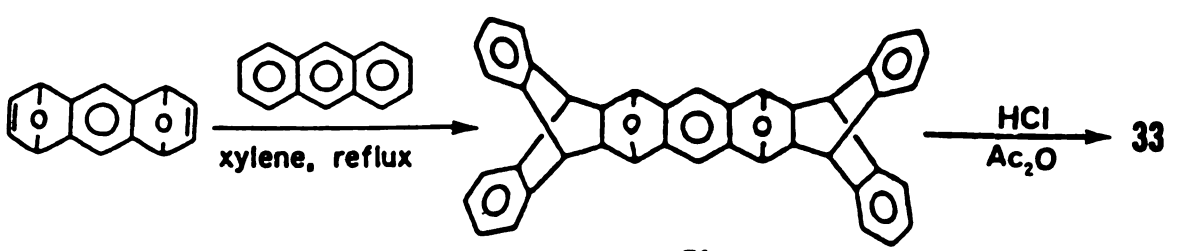
The diene **48** was found to undergo cycloaddition reactions with a 1,4-dibenzyne equivalent in a similar fashion, to give the cycloadduct **50** which, upon dehydrogenation, provided the iptycene **33** in >80% yield.[11]



48 50

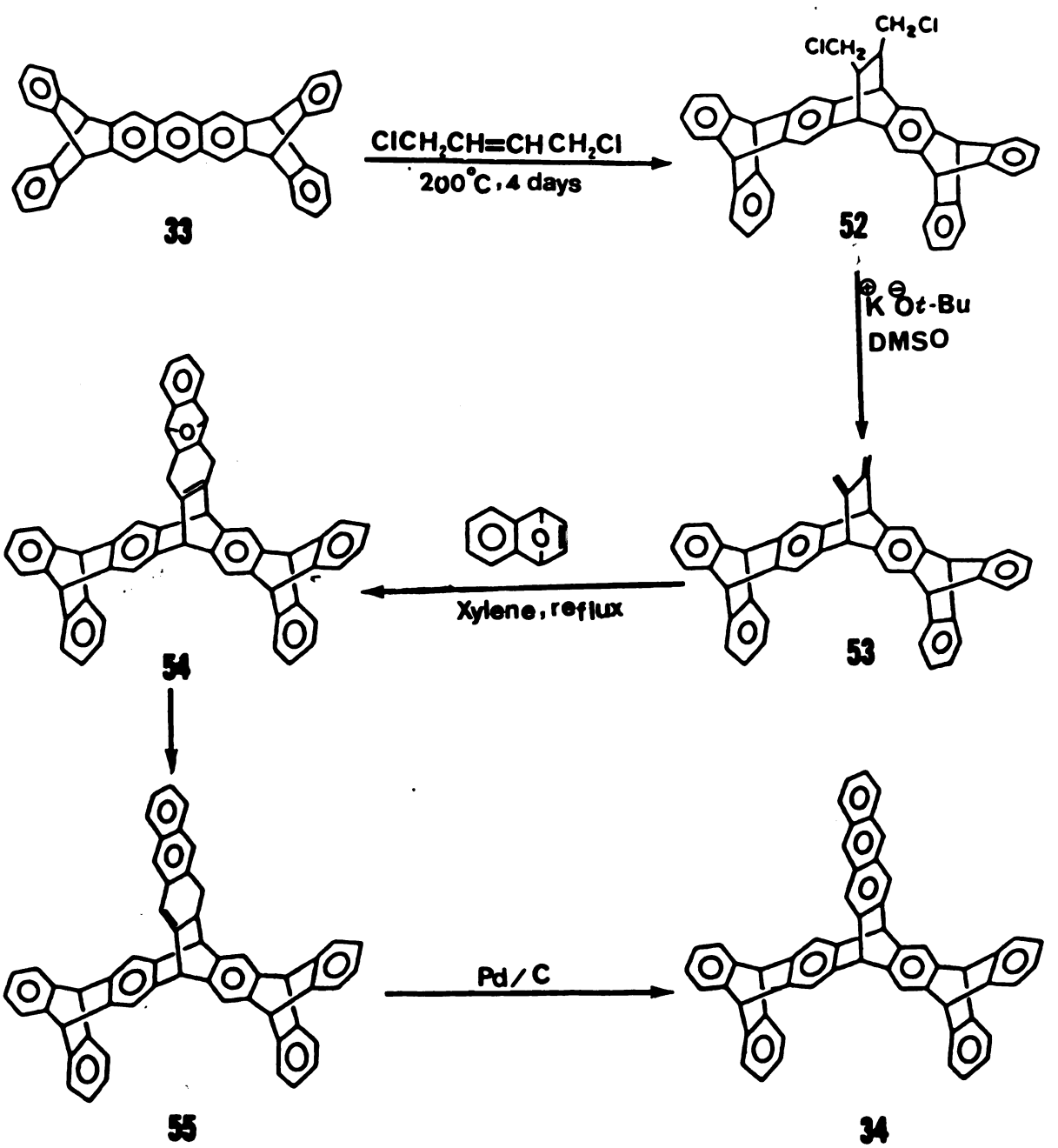


This procedure proved to be superior to a previous one in which the iptycene **33** had been prepared from the dehydration of bisadduct **51**, obtained by adding 1,4:5,8-diepoxyanthracene **42** to two equivalents of anthracene.[9]



42 51

Diene 53, an analog of 48, was synthesized by adding 1,4-dichloro-2-butene to iptycene 33, followed by dehydrochlorination of the corresponding adduct 52.[11] It has been used as the starting material for the construction of 34. As anticipated, diene 53 reacted with 1,4-epoxynaphthalene 38 to give 54. Dehydration of 54 gave 55, which upon dehydrogenation provided 34.



Except for compound **4**, all of the iptycenes synthesized have been the b-fused type. The remaining iptycenes in Table 1 have not been reported. Aside from the synthetic challenge, these compounds, along with their derivatives, are likely to possess a number of interesting properties. One of those properties is a high melting point and high thermal stability. For example, the melting points of triphenylmethane, triptycene, pentiptycene **3** and heptiptycene **8** increases from 94°C to 256°C to 483°C to >525°C and the melting point of heptiptycene **4** is reported to be 580°C! The nature of the intermolecular interactions that lead to such high melting points is not obvious. Structural determination by x-ray might provide valuable data regarding the packing patterns of these compounds. By the nature of their rigid frameworks, as well as their high melting points, polyiptycenes could serve as useful shock and heat-resistant materials.[26] Molecular cavities which could be useful in forming host-guest compounds is another interesting feature of these compounds. Iptycene **4** has two equivalent cup-like cavities above and below the central arene ring. Viewed in another sense, it has three equivalent cavities disposed symmetrically above the axes that lie in the plane of the central ring and bisect its non-fused bonds. Heptiptycene **8** has two types of cavities as shown in an end-on view (Figure 1). The larger and more enclosed cavity is U-shaped with two parallel arene rings, whereas the more open cavities are similar to those in **3**.

Figure 1. End on view b,b′,b′′-noniptycene **16.**

Compound **16** has three analogous U-shaped cavities. Pentadecaiptycene **24** (Figure 2), with the same symmetry as triptycene, has three large cavities symmetrically located around the three C_2 axes.

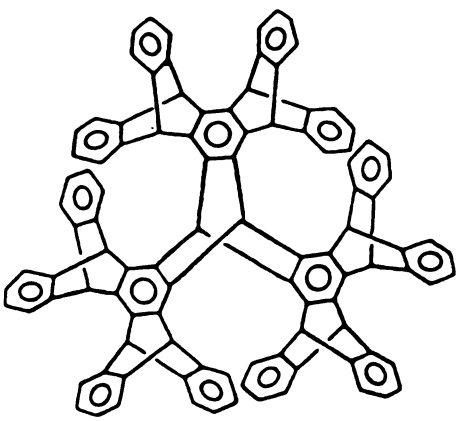


Figure 2. Structural representation of "Supertryptycene" **24.**

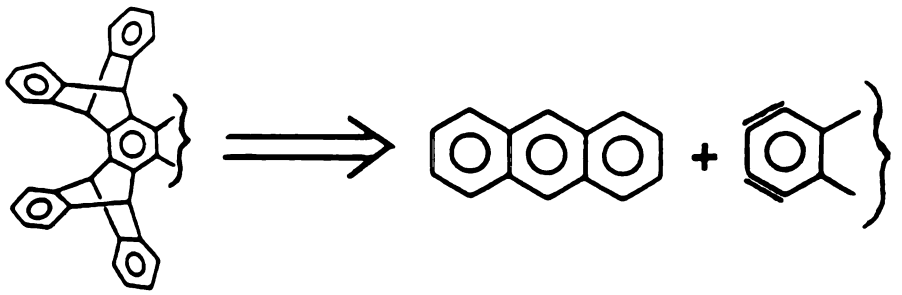
There are six chiral iptycenes listed in Table 1. Three have C_2 axes. Of special interest is iptycene **15**, in which a helical array of 9,10-anthradiyl moieties are attached to the central triptycene framework, resulting in three helically disposed cavities. Besides the

above structural features, iptycenes could also be the subject for other studies such as: organometallic complexes,[27] charge transfer complexes,[28] novel photochemistry,[29] unusual semi-conductor designs and interesting spectral properties related to the ring-ring interactions.[30]

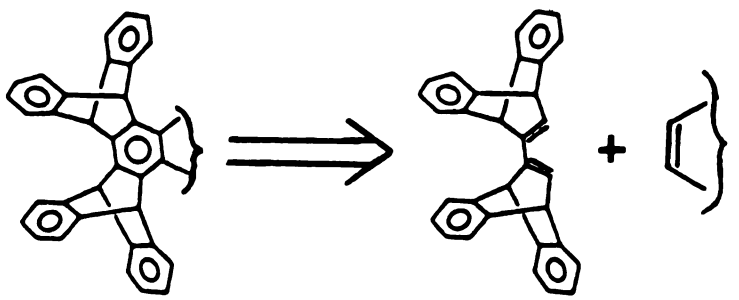
This work has been aimed at exploring useful routes to a,c-fused iptycenes in general and at synthesizing 24 in particular. The butadiene derivative 32, an undesirable side product in the synthesis of heptiptycene 4, seemed properly suited for the construction of such iptycenes. In the present research, its yield was optimized so that it could be used as a starting material for a,c-fused triptycenes. Although the synthesis of 24 was not achieved, the methodology was successfully applied to the synthesis of iptycenes 2 and 4 and to a promising precursor of 24.

RESULTS AND DISCUSSION

From the retrosynthetic point of view, a,c-fused iptycenes can be synthesized by either of the two general routes already developed for their b-fused counterparts.[4] (a) By addition of an ortho-bisaryne to two equivalents of anthracene.



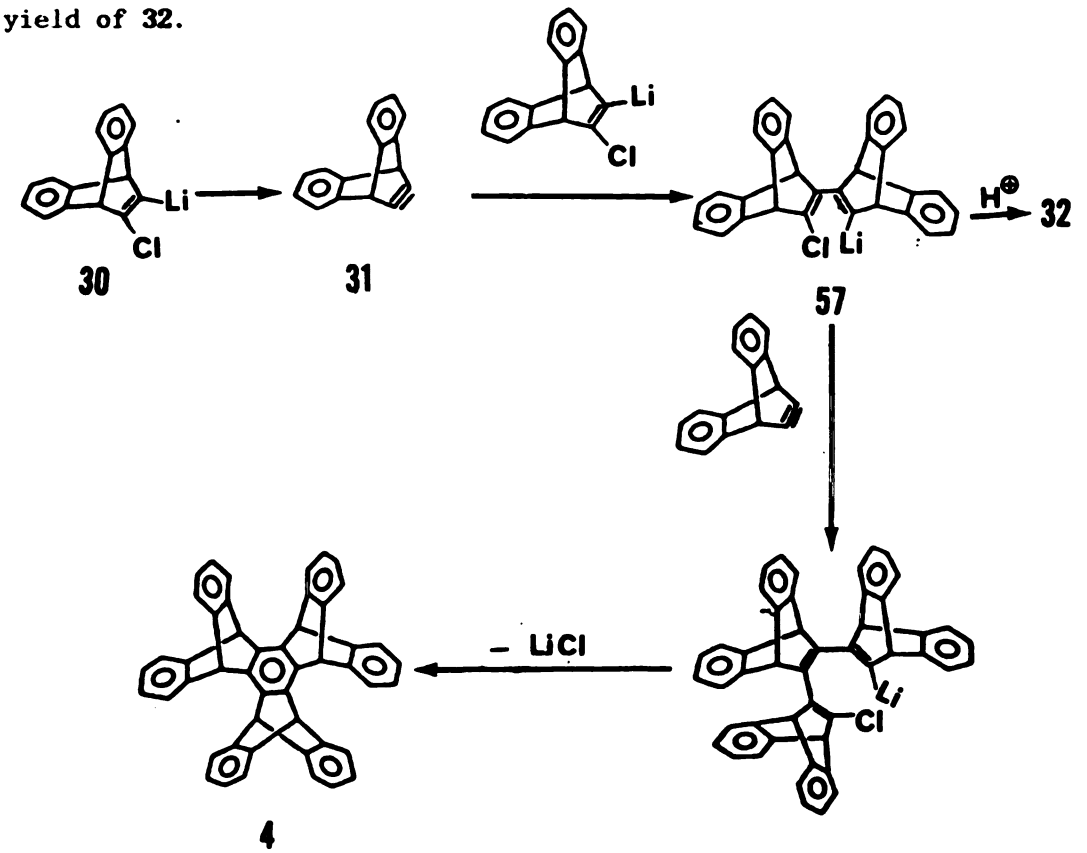
(b) Through the cycloaddition reaction between an appropriate dienophile and the butadiene derivative **56**, followed by the conversion of the cycloadduct to the final product.



56

Owing to the difficult access to suitable ortho-bisaryne equivalents, and inefficiencies associated with the addition of such bisarynes to anthracene, the first route, though plausible, has limited practical value. It was decided to employ the second route. The butadiene **32** (page 4), a 1-chloro-substituted derivative of **56**, was reported to form in 39% yield as the by-product in the synthesis of the heptiptycene **4**.[2] The demand for large quantities of **32** as the starting material and the

presumption that 4 was formed by a stepwise pathway in which the 4-lithio-butadiene derivative 57 is an intermediate which, upon quenching with a proton source, leads to 32, prompted us to explore the possibility of retarding the formation of 4 and therefore optimizing the yield of 32.

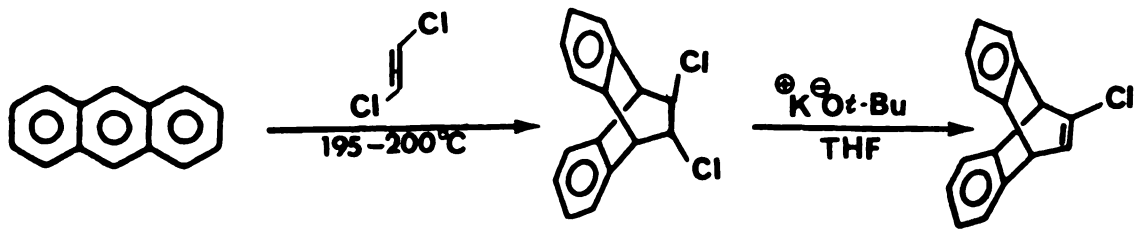


Compound 32 has a very low solubility in hexanes. Thus it might be assumed that 57, by the virtue of the presence of lithium, would be even less soluble in this solvent and consequently, less available for the reaction with the cycloalkyne 31.

1. Improved Synthesis of 3-chloro-1,4; 1′,4′-di-o-benzeno-1,1′,4,4′-tetrahydro-2,2′-binaphthyl 32.

The starting material, 11-chloro-9,10-dihydro-9,10-ethenoanthracene 29, was synthesized according to the literature.[31] A

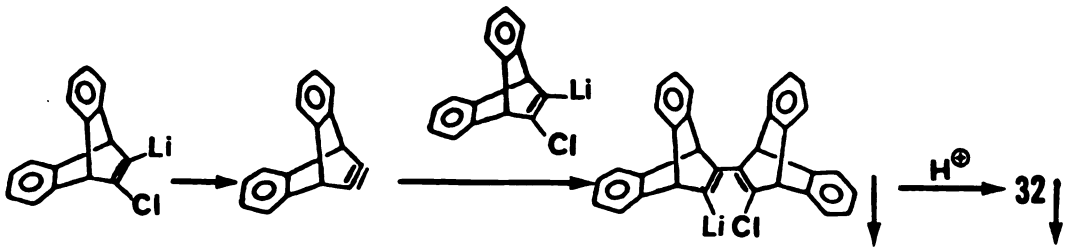
suspension of anthracene in trans-1,2-dichloroethylene in a sealed tube was heated at 195-200°C for 48 hours followed by dehydrochlorination of the resulting adduct with potassium t-butoxide in refluxing THF.



29

In a typical reaction, 29 was then dissolved in the least amount of a 5:1 mixture of anhydrous hexanes and THF (this usually corresponded to approximately 25 mL of hexanes and 5 mL of THF for 10 mmol of the substrate) at room temperature. The temperature was lowered to -78°C and 1.1 equivalent of n-butyllithium was added to the resulting suspension. The reaction mixture was stirred for another hour and then gently refluxed for 30 minutes.

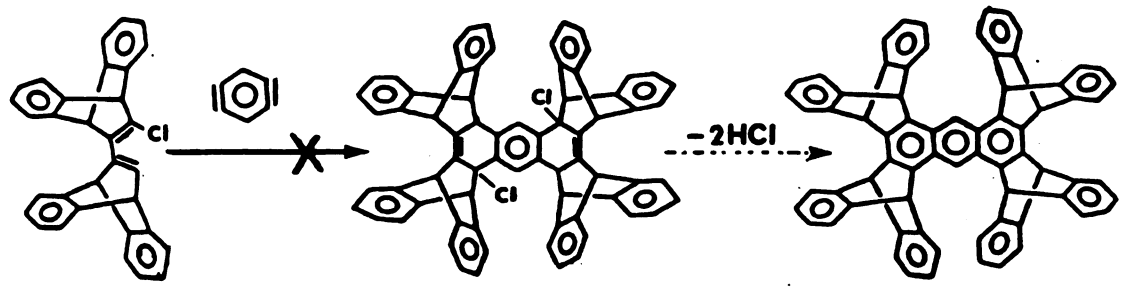
During the course of the reaction a gummy black precipitate formed which, upon quenching with methanol, decolorized. The melting point and the ^{1}H NMR spectrum of a purified sample of this precipitate were identical to those reported for 32.[9] Purification of the combined precipitate and the remaining residue after evaporation of the solvent gave 32 in 75-83% yield. In each reaction, only traces of the heptiptycene 4 were formed.



30 31

2. Attempted reaction of 32 with 1,4-bisbenzyne.

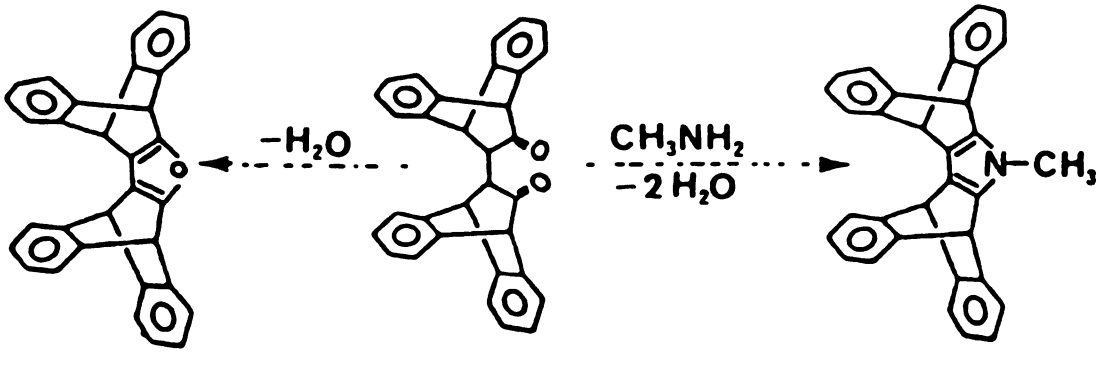
Arynes and bisarynes have been reported to undergo [4+2] cycloaddition reactions with 1,3-butadienes to form six-membered ring cycloadducts.[32] In the case of acyclic 1,3-butadienes, where rotation around the sp^3–sp^3 bond is allowed, these reactions usually proceed only in low yields. Such low yields can be attributed to the tendency of these dienes to adopt the thermodynamically more stable s-trans conformation. In spite of this, it was thought that the addition of a 1,4-bisbenzyne equivalent to 32, followed by dehydrochlorination of the expected bisadducts, might provide a short route to the anthracene derivative 58, a potential synthon for the pentadecaiptycene 24.



32 58

In this regard, two equivalents of n-butyllithium were added to a solution of a 1:2 mixture of 1,2,4,5-tetrabromobenzene and 32 in THF at -78°C. The reaction mixture was allowed to warm to room temperature and stirred for two hours. The ^1H NMR spectrum of the reaction mixture after work up did not show the presence of an adduct. Similar reactions with 1,2-dibromobenzene also failed.

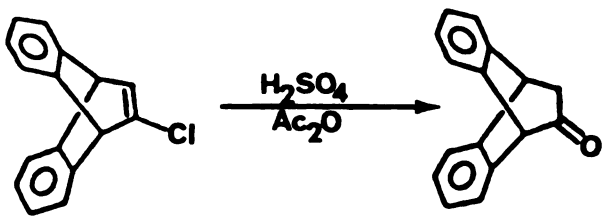
The failure of 32 to undergo any [4+2] cycloaddition reaction with benzynes urged us to seek other alternatives for the construction of 58. Furans and N-alkylpyrroles, in which the 1,3-diene is constrained to a s-cis conformation might provide such an alternative. Both furans and N-alkylpyrroles undergo cycloaddition reactions with benzynes to give the corresponding cycloadducts in excellent yields.[33] Furthermore, the resulting cycloadducts can effectively be converted into aromatic compounds. We therefore undertook the synthesis of the 1,4-diketone derivative 60, anticipating that dehydration of this diketone would provide the desired furan derivative 61 or the N-methylpyrrole derivative 62.



61 60 62

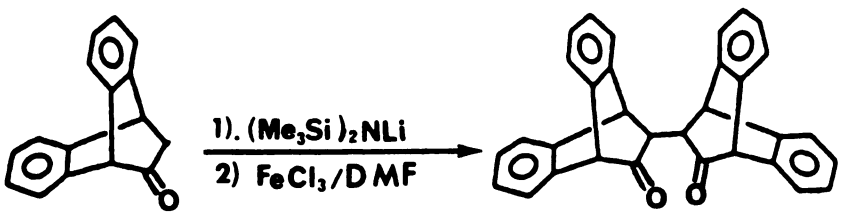
3. Synthesis of 1,4; 1′,4′-di-o-benzeno-1,1′,3,3′,4,4′-hexahydro-3,3′-binaphthyl-2,2′-dione 60

The starting material, 1,4-[1′,2′]-benzeno-1,3,4-trihydronaphthalene-2-one (59), was prepared in quantitative yield by the solvolysis of 29 in a mixture of glacial acetic acid and concentrated sulfuric acid.[34]



29 59

Using the lithium salt of hexamethyldisilazine as the base, 59 was converted to its enolate.[35] Oxidative coupling of the enolate was achieved by adding one equivalent of anhydrous ferric chloride in DMF[36] to a solution of the enolate in THF, to give 60 in 63% yield.



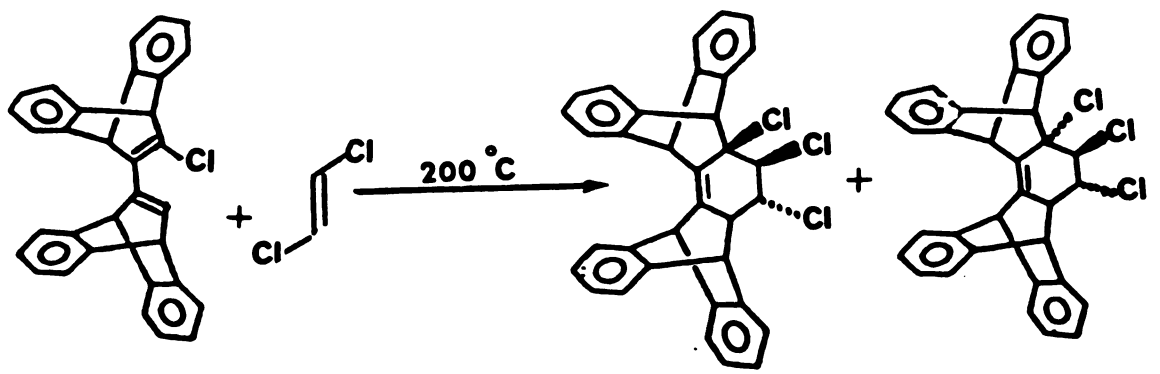
59 60

Other known methods for the coupling of enolates did not give satisfactory results.[37] The diketone 60 was characterized by its mass, ^1H NMR and ^{13}C NMR spectra. The mass spectrum of 60 showed a molecular

ion peak at m/e 438. The ^{1}H NMR spectrum showed a two-proton singlet at δ 1.73 for the methyne protons α-to the carbonyl groups, two two-proton singlets at δ 4.77 and 5.02 corresponding to the bridgehead protons and four sets of multiplets at δ 7.12-7.46 for the aromatic protons. ^{13}C NMR showed two peaks at δ 47.25 and 47.55 for the bridgehead carbon atoms, a peak at δ 63.70 for the carbon atoms α-to the carbonyl group, and a peak at δ 205.28 corresponding to the carbonyl carbon atom. Unfortunately, attempts to dehydrate 60 using several known methods did not give satisfactory results.[38,39] In every case the starting material 60 was recovered. Also, heating a solution of 60 in methylamine at 150°C in a sealed tube failed to give 62,[38] but instead gave several products which could not be characterized. With the failure of these routes, therefore cycloadditions of 32 with long-lived dienophiles was tried next.

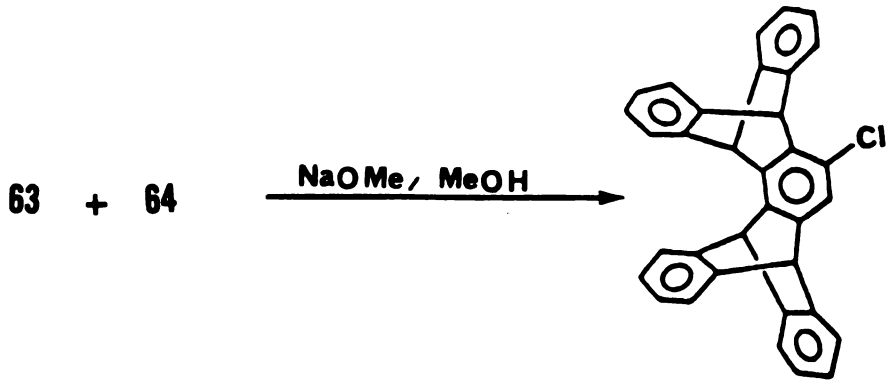
4. Reaction of 32 with 1,2-dichloroethylene

A suspension of 32 in trans-1,2-dichloroethylene was heated at 195-200°C in a sealed tube for 36 hours. Analysis of the tube contents after evaporation of the solvent indicated the absence of the starting material and the presence of two major products, possibly the two isomers 63 and 64 anticipated for the reaction.



32 63 64

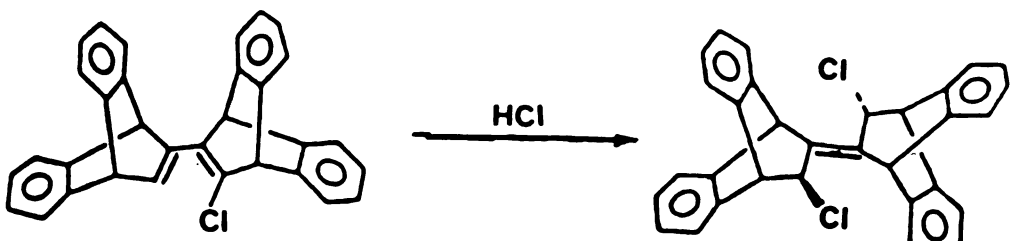
Dehydrochlorination of the crude mixture, without further purification, using sodium methoxide in refluxing methanol, afforded a single product 65 in 68% yield.



65

The structure of 65 was confirmed by its mass, ^{1}H NMR and ^{13}C NMR spectra. The mass spectrum showed a molecular ion peak at m/e 467. The ^{1}H NMR spectrum showed four one-proton singlets at δ 5.28, 5,83, 5.91 and 5.96 for the bridgehead protons, a one-proton singlet at δ 7.03 for the proton next to the chlorine atom on the central ring and four sets of multiplets corresponding to the remaining 16 aromatic protons. The ^{13}C NMR spectrum, which showed four distinct peaks with equal intensities for the sp^3 hybridized bridgehead carbon atoms, was also consistent with structure 65. When high concentrations of 32 were used in the Diels- Alder reaction with trans-1,2-dichloroethylene, a crystalline compound separated from the reaction mixture. This compound melted at 321°C with gradual decomposition, and was practically insoluble in all organic and inorganic solvents. X-ray crystallography (Figure 3) showed the compound to be 66. Reactions of chlorinated

ethylenes at high temperatures are usually accompanied by the formation of considerable amounts of hydrogen chloride. Compound 66 most likely originates from the 1,4-addition of hydrogen chloride to 32.



32 66

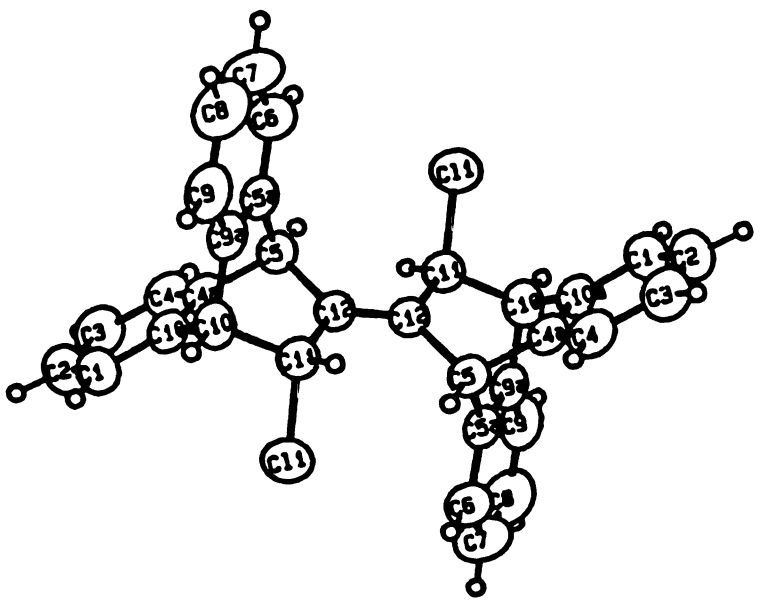
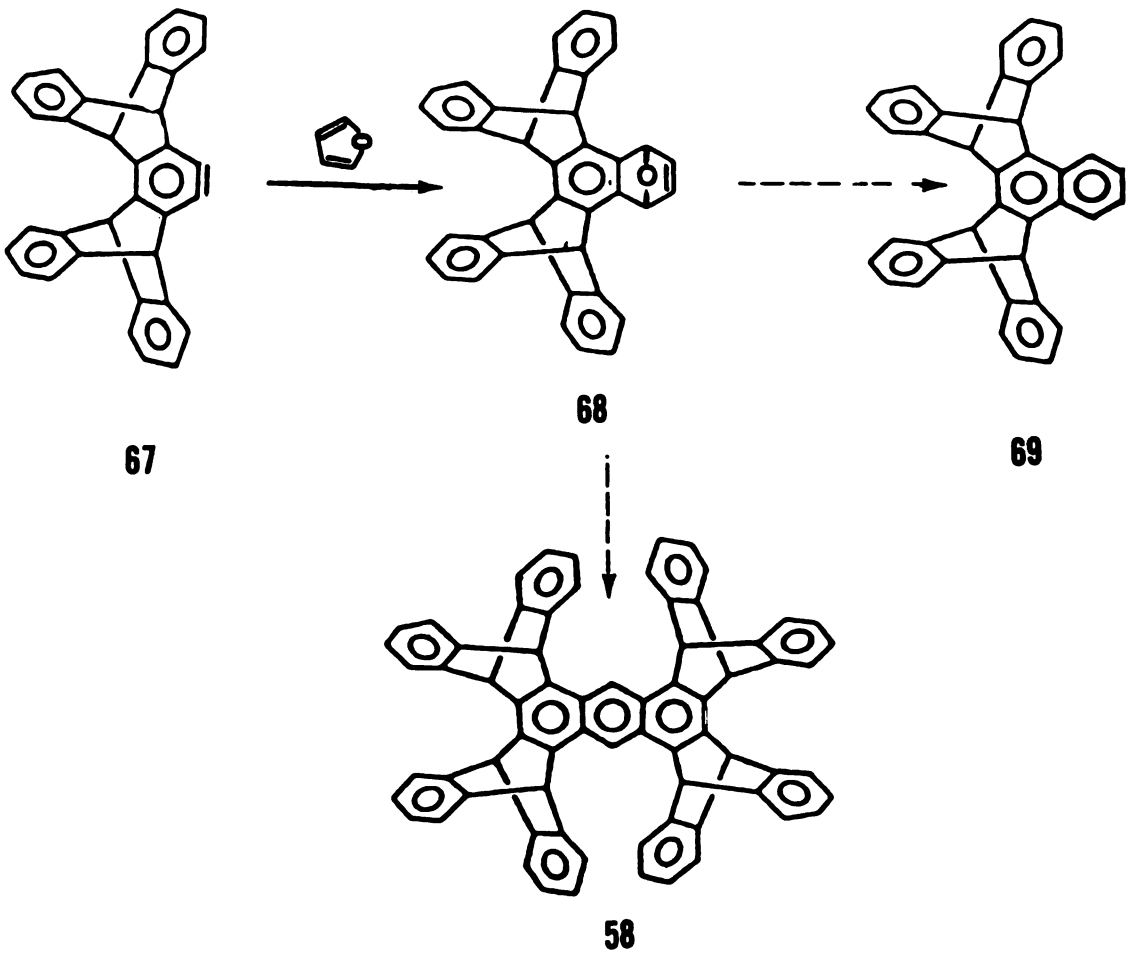


Figure 3. Crystal structure of compound 66.

5. Attempted generation of pentiptycyne 67 from 65

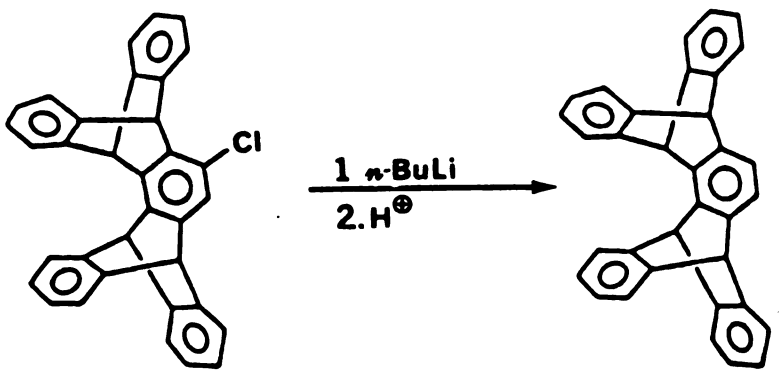
The cycloaddition reactions of arynes and furan have routinely been used to construct polycyclic aromatic compounds. It was anticipated that the reaction of the pentiptycyne 67, generated from 65, could react with furan to provide the cycloadduct 68, a valuable synthon

for the synthesis of the anthracene derivative **58**, and also a potential precursor of the a,c-fused naphthalenoid iptycene **69**.



67 **68** **69** **58**

Thus a solution of **65** in THF in the presence of excess furan was treated with n-butyllithium at -78°C. Analysis of the reaction mixture after stirring at room temperature for two hours showed only the starting material **65**. Other attempts using harsher conditions, such as refluxing the reaction mixture or treatment with n-butyllithium and potassium t-butoxide as the base, resulted mainly in halogen-metal exchange, and consequently in the formation of pentiptycene **2**.

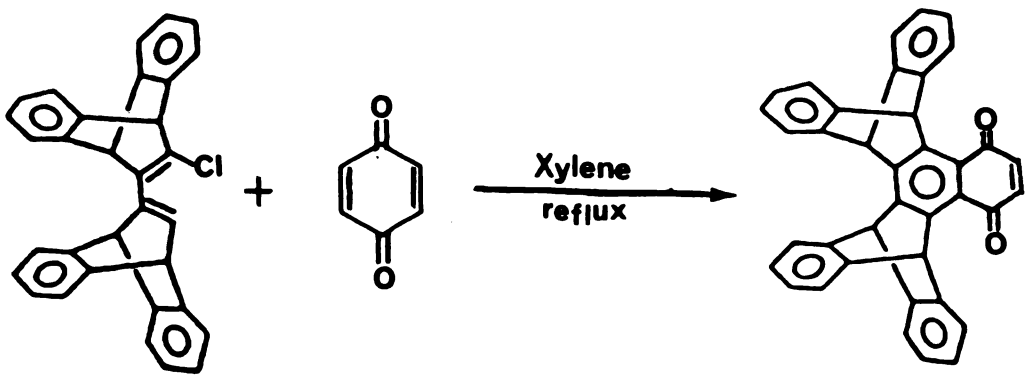


65 2

The structure of 2 was confirmed by its ^{1}H NMR and ^{13}C NMR spectra. The ^{1}H NMR spectrum of 2 showed only two two- proton sharp singlets at δ 5.31 and 5.94 for the two sets of bridgehead hydrogens (C_2h symmetry) and three sets of multiplets in the aromatic region for the total of 18 protons. The ^{13}C NMR spectrum showed two peaks at δ 50.51 and 54.59 corresponding to the sp^3 bridgehead carbon atoms, as expected by the symmetry of 2, and a total of seven peaks for the sp^2 carbon atoms.

6. Synthesis of 1′,4′; 7,12-di-o-benzeno-1′,4′,7,12-tetrahydro-5,6-naphthotetraphene-1,4-dione 70

p-Benzoquinone adds to one or two equivalents of a 1,3-diene to form either mono- or bis-adducts.[41] These adducts can readily be converted to the corresponding hydrocarbons. Thus one equivalent of p-benzoquinone in xylenes was heated at reflux with two equivalents of diene 32 for 24 hours. The two major components obtained from the reaction were found to be unreacted 32 and the naphthoquinone derivative 70.

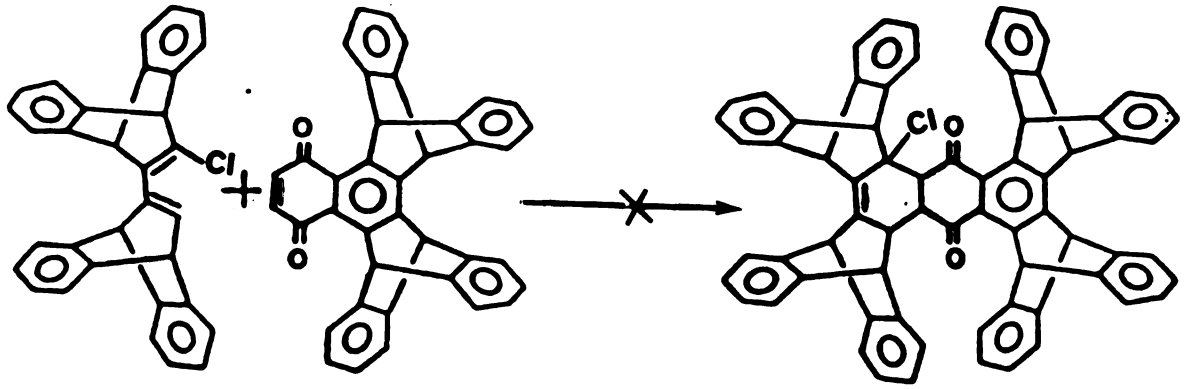


32 70

The structure of 70 was established by its mass, ^{1}H NMR and ^{13}C NMR spectra. The mass spectrum showed a molecular ion aeak at m/e 510. The ^{1}H NMR spectrum of 70 consisted of a singlet at δ 6.13 for the "outer" bridgehead hydrogens, a two-proton singlet at δ 6.77 for the "inner" bridgehead hydrogens, a two-proton singlet at δ 7.41 for the quinoid ring hydrogens and three sets of multiplets in the aromatic region for the total of 16 hydrogens. The ^{13}C NMR spectrum of 70, which showed two peaks at δ 48.69 and 50.27 for the sp^3 bridgehead carbon atoms, as required by symmetry, eight peaks for the sp^2 carbon atoms and a single peak at δ 188.55 for the carbonyl carbon atoms, also supported this structure.

Several factors may be responsible for the low yield (<30-35%) of 70 and the absence of the bisadduct. The low yield may result because some of the p-benzoquinone is consumed by the dehydrogenation. The absence of the bisadduct can be accounted for by assuming that the rate of the second cycloaddition reaction is slower than the rate of the dehydrogenation-dehydrochlorination of the monoadduct. The yield of 70

increased to >80% when up to ten equivalents of p-benzoquinone were used in this reaction. A follow-up reaction in which a 1:1 mixture of 32 and 70 in xylenes was heated at reflux for 24 hours did not give the expected bisadduct 71.



32 70 71

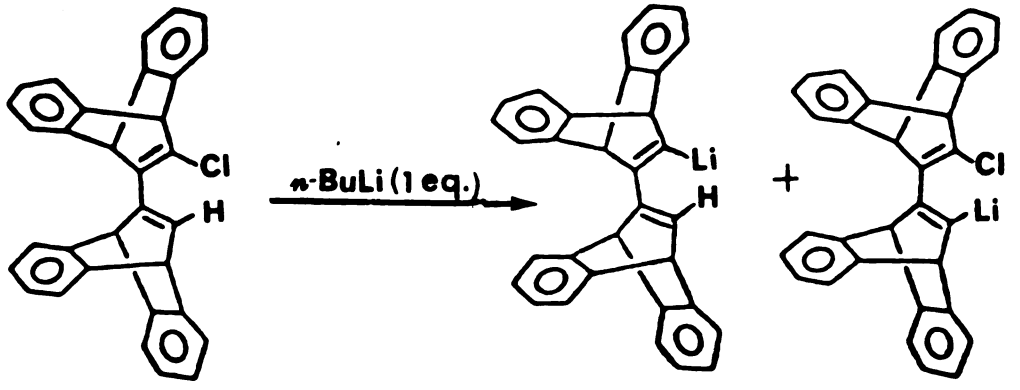
When a mixture of 32 and 70 in xylenes was heated at 210-220°C in a sealed tube, an inseparable mixture of products was obtained from which the desired 71 could not be isolated.

7. Synthesis of 1,4; 1′,4′-di-o-benzeno-1,1,′4,4′-tetrahydro-2,2′-binaphthyl 56

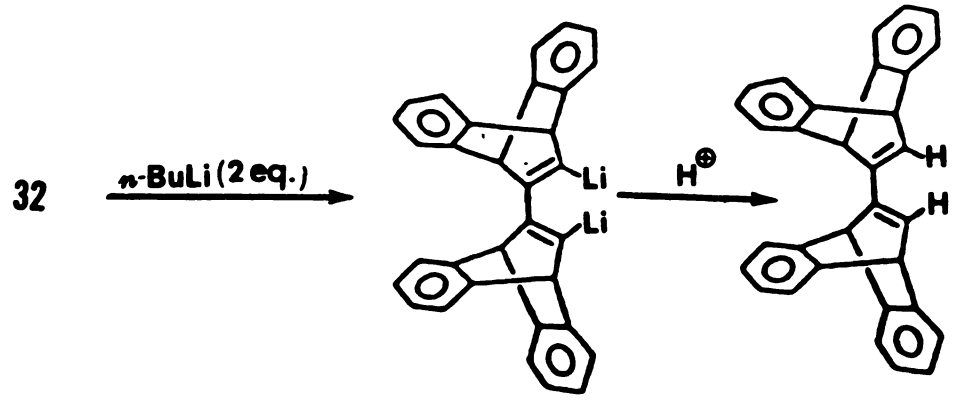
The complexity of the reaction of 32 with naphthoquinone 70 and the formation of hydrogen chloride in the reactions of 32 at high temperatures, which might be responsible for the unprecedented outcomes of some of these reactions, called for the synthesis of the parent hydrocarbon, the butadiene derivative 56. The dechlorination of 32 was achieved by treating a solution of this compound in THF with 2.2 equivalents of n-butyllithium for four hours at -78°C, followed by 30 minutes at reflux. The solution was then cooled and quenched with methanol, to give 63% of the desired 56. The structure of 56 was confirmed by mass, ^{1}H NMR and ^{13}C NMR spectra. The mass spectrum showed

a molecular ion peak at m/e 406. The ^{1}H NMR spectrum showed a singlet at 5.12 for the "inner" bridgehead protons, and a peak at 7.10 for the vinyl protons, as well as appropriate peaks for the aromatic protons. The ^{13}C NMR spectrum, as required by the symmetry, showed only two peaks for the sp^3 hybridized bridgehead carbon atoms, at 51.31 and 52.60, and a total of seven peaks for the sp^2 carbon atoms.

Since treatment of 32 with 1.1 equivalent of n-butyllithium under the same conditions, followed by quenching with methanol, resulted in the partial dechlorination of 32 and recovery of some of the starting material, it seems likely that the intermediate in this reaction is the dilithiated 1,3-butadiene derivative 72, which upon quenching with a proton source gives 56. The existence of 1,4-dilithiated-1,3-butadiene species similar to 56 is experimentally well established.[40] (Z)-1,4-dilithio-1,3-butadiene is predicted to be a very stable compound.[40]



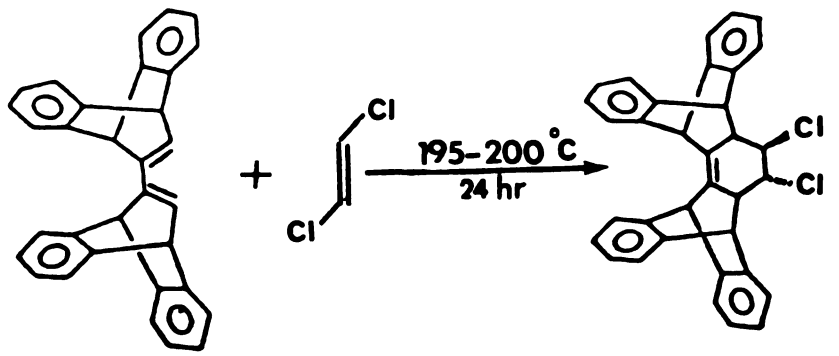
32



72 56

8. Reaction of 56 with trans-1,2-dichloroethylene.

Heating a suspension of 56 in trans-1,2-dichlorethylene at 195-200°C in a sealed tube for 24 hours gave the expected cycloadduct 73 in 91% yield.

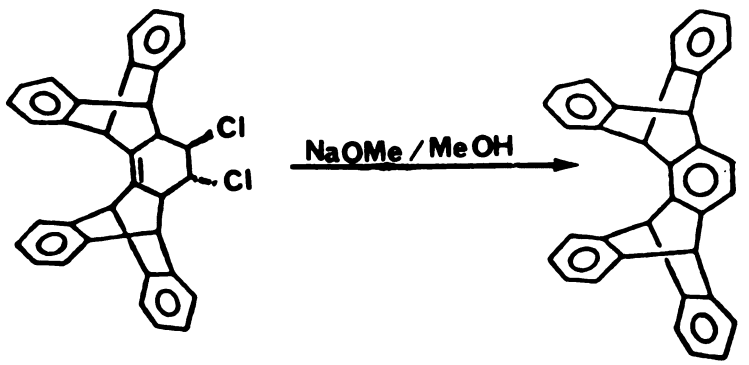


56 73

The structure of 73 was confirmed by its ^{1}H NMR and ^{13}C NMR spectra. The ^{1}H NMR spectrum of 73 showed four sets of multiplets, each for one proton on the central ring, doublets at δ 4.51 and 4.60, each for one proton for the "inner" bridgeheads and two singlets at δ 5.31 and 5.35 for the "outer" bridgeheads, and two sets of multiplets for the aromatic protons. The ^{13}C NMR spectrum was also consistent with this structure, with eight peaks corresponding to the 8 sp^3 hybridized carbon atoms and 20 peaks corresponding to the sp^2 hybridized carbon atoms.

9. Synthesis of [1.1.1^a .1.1] pentiptycene 2.

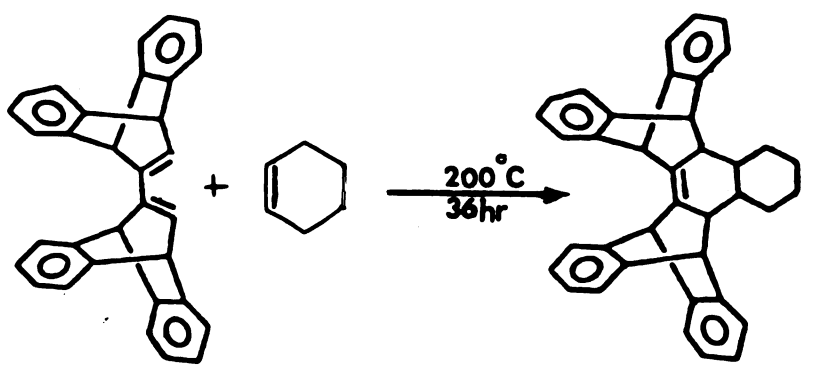
Dehydrochlorination of the cycloadduct 73, with excess sodium methoxide in refluxing methanol, afforded the a,c- fused pentiptycene 2 in 87% yield. The ^{1}H NMR and ^{13}C NMR spectra of 2 have been previously described (p.27).



73 2

10. Reaction of 56 with cyclohexene.

Cycloadduct 74 was prepared in 91% yield by heating a suspension of 56 in cyclohexene at 195-200°C in a sealed tube for 36 hours.



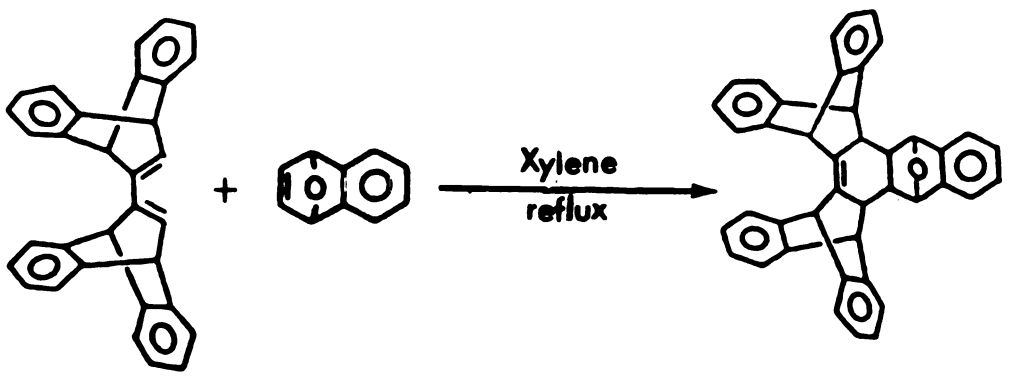
56 74

Compound 74 was characterized by its mass, ^{1}H NMR and ^{13}C NMR spectra. The mass spectrum had a peak at m/e 488 corresponding to the molecular ion. The ^{1}H NMR spectrum showed a broad singlet, a broad doublet, and a broad singlet at δ 0.47, 1,32 and 1.53 for 2,2 and 6 protons respectively, corresponding to the aliphatic protons. It also showed a

broad doublet at δ 1.88 for the allylic protons, a doublet at δ 4.18 for the "inner" bridgehead and a sharp singlet at δ 5.35 for the "outer" bridgehead protons. The 16 aromatic protons appeared at δ 6.93-7.38 as a multiplet. The ^{13}C NMR spectrum of 74 showed six peaks for the sp^3 hybridized carbon atoms, as expected by symmetry, and a total of 10 peaks for the sp^2 carbon atoms. Attempted dehydrogenation of 74 with 10% palladium on charcoal in refluxing mesitylene for four days gave a complex mixture of products, which were not separated.

11. Reaction of 56 with 1,4-epoxynaphthalene 38

Heating a solution of 56 and 1,4-epoxynaphthalene in xylenes at reflux for eight hours gave the expected cycloadduct 75 in 95% yield.



56 75

The mass spectrum of 75 showed a molecular ion peak at m/e 550. The ^1H NMR spectrum showed a doublet of doublets at δ 0.97, a broad doublet at 2.33, and a doublet at δ 4.40 corresponding to the a,b and c protons respectively (Figure 4).

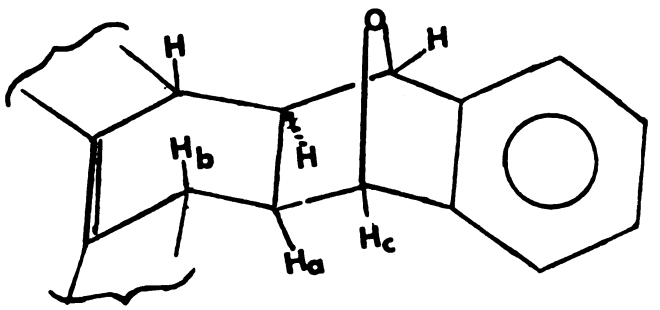
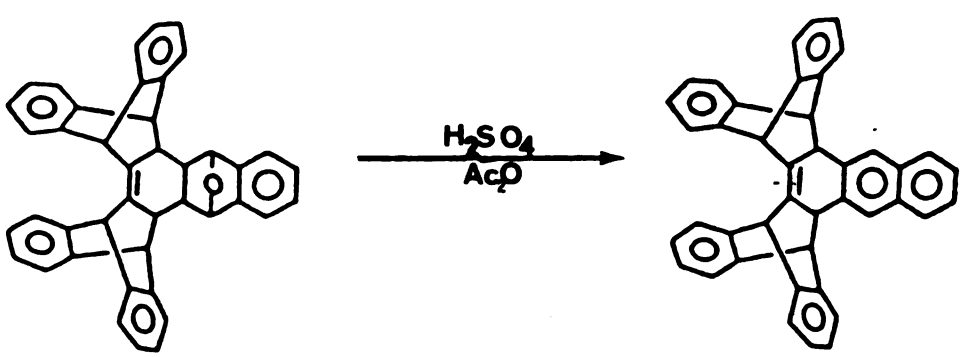


Figure 4. Stereo drawing of the central ring of the cycloadduct 75.

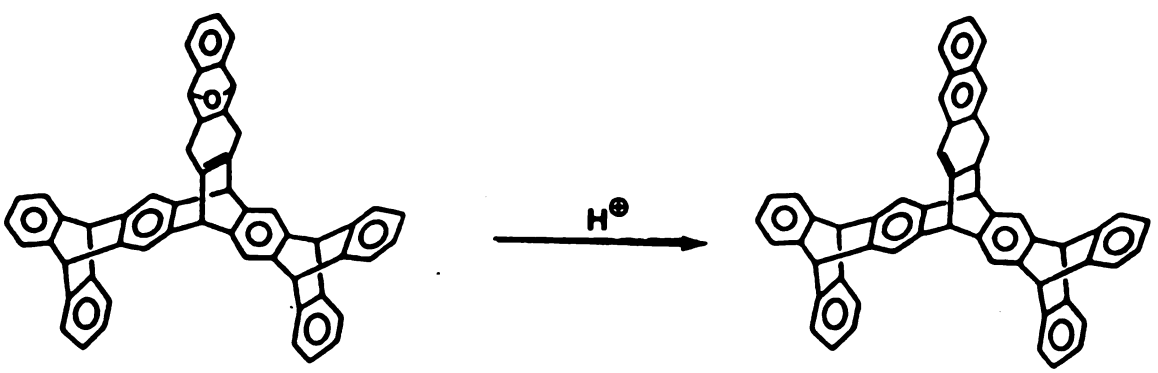
The bridgehead protons appeared at δ 5.28 and 5.30 as sharp singlets, and the 20 aromatic protons at δ 6.95-7.31 as a multiplet. The stereo-chemistry of 75 was not established unequivocally. However, the dramatic upfield shift of the a protons and the small coupling with the c protons ($J_{ac} \approx 0$) suggests an exo addition in which the a protons are sandwiched between the aromatic rings. The ^{13}C NMR spectrum of 75 showed five peaks for the sp^3 carbon atoms (plane of symmetry) and a total of 14 peaks for the sp^2 carbon atoms. Cycloadducts such as 75 can readily be dehydrated with acid. Thus 75 was dehydrated by addition of concentrated sulfuric acid to a solution of 75 in acetic anhydride and stirring for 10 minutes to give 76 in 73% yield.



75 76

The structure of 76 was established based on its ^1H NMR and ^{13}C NMR spectra. The ^1H NMR showed a broad singlet at δ 3.16 for the methyne protons on the non-aromatic ring, a broad singlet at δ 5.14 for the "inner" bridgehead protons, a sharp singlet at δ 5.46 for the "outer" bridgehead protons and four sets of multiplets at δ 6.85-7.48 corresponding to the 22 aromatic protons. The ^{13}C NMR spectrum showed three peaks at δ 46.30, 46.68 and 48.88 for the sp^3 carbon atoms (plane of symmetry) and a total of 13 peaks for the sp^2 carbon atoms.

In the acid catalyzed dehydration of 54, a 1,3 hydrogen shift was observed.

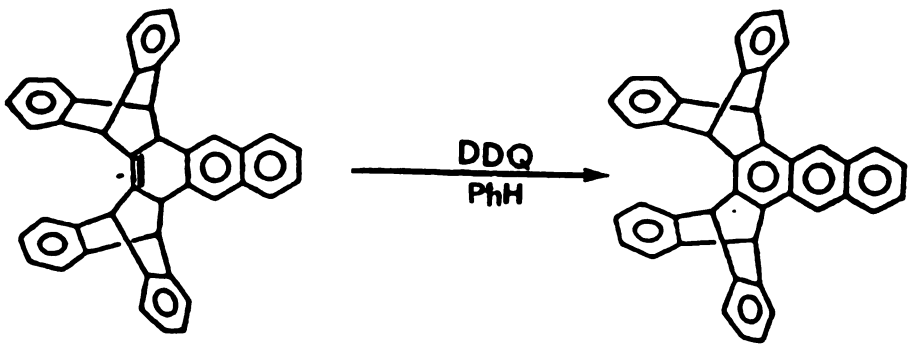


54 55

The orbital symmetry rules require that such 1,3 shifts be antarafacial. This process introduces a small amount of additional strain which can be compensated for by the energy gained through conjugation. The symmetry of 76, deduced from its ^1H NMR and ^{13}C NMR spectra, indicate the lack of any rearrangement. A 1,3 hydrogen migration in 76 would imply a trans fusion of one of the 9,10-anthradiyl moieties, thus imposing considerable strain on the molecule. Therefore, in contrast with 54, hydrogen migration in 76 is a very unfavorable process.

12. Dehydrogenation of 76

Dehydrogenation of 76 in the presence of DDQ in refluxing benzene gave 77 in 92% yield.

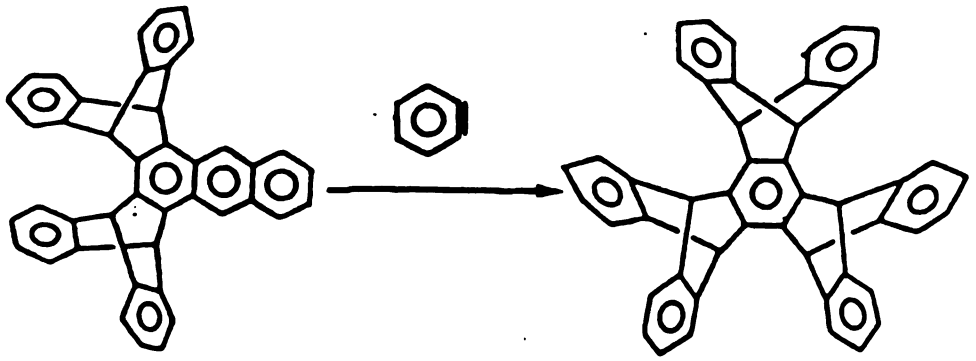


76 77

Solutions of 77 were greenish yellow, and under UV light showed a very strong fluorescence, consistent with the presence of an anthracene moiety. The structure of 77 was confirmed by its ^{1}H NMR spectrum, which showed two singlets at δ 6.25 and 6.36 for the "inner" and "outer" bridgehead protons respectively. A singlet at δ 8.84 corresponded to the protons on the middle anthracene ring. The rest of the aromatic protons appeared at δ 6.94-8.03 as five sets of multiplets. The ^{13}C NMR spectrum, which showed two peaks at δ 50.64 and 51.57 for the sp^3 bridgehead carbon atoms and a total of 13 peaks for the aromatic carbon atoms (C_2h symmetry), also supported this structure.

13. Synthesis of the Heptiptycene 4

Refluxing a solution of 77, excess benzenediazoniumcarboxylate hydrochloride and propylene oxide in 1,2-dichloroethane for 12 hours afforded the known heptiptycene 4 in 26% yield.

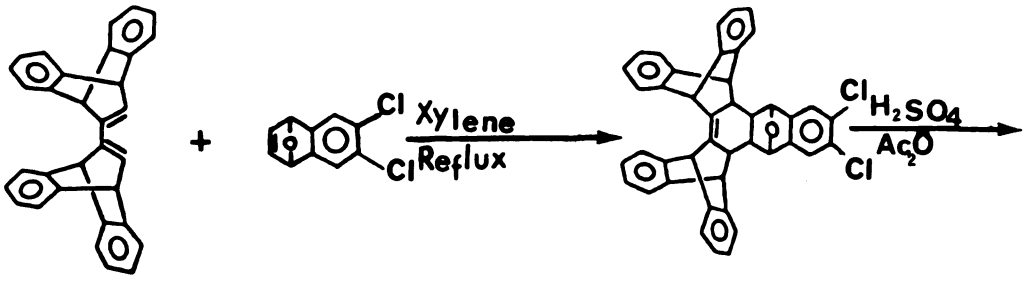


77 4

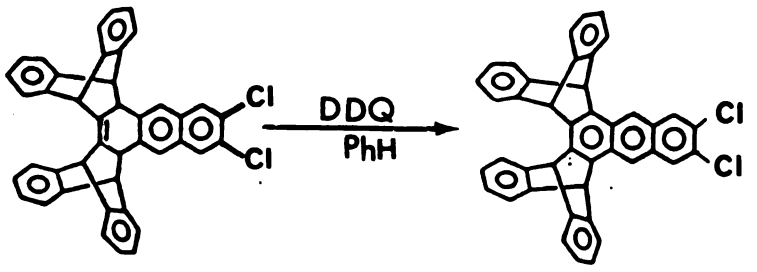
Considering the yield and the number of steps involved, this method is obviously not comparable with the previously known one step synthesis of 4 via the trimerization of the cycloalkyne 31 in 20% yield (p. 4). This synthesis of 4, however, demonstrates the potential utility of this method in the construction of other iptycenes bearing a,c-fused 9,10-anthradiyl moieties.

14. Synthesis of 5,14; 8,13-di-o-benzeno-6′,7′-dichloro-5,8,13,14-tetrahydro-6,7-naphthopentaphene 81.

It was mentioned earlier that the addition of iptycynes to anthracene is not a preferred method for the construction of the other iptycenes. The method, nevertheless, can be regarded as an alternative. Taking this into consideration, compound 81, a dichloro derivative of 77 and a potential iptycyne precursor, was synthesized using the same sequence of reactions as for 77 itself. Thus, 6,7-dichloro-1,4-epoxynaphthalene 78 was added to 56 to give 79 in quantitative yield. Dehydration of 79 in acetic anhydride by concentrated sulfuric acid gave 80 in 76% yield. Dehydrogenation by DDQ in refluxing benzene afforded 81 in 95% yield.



56 78 79

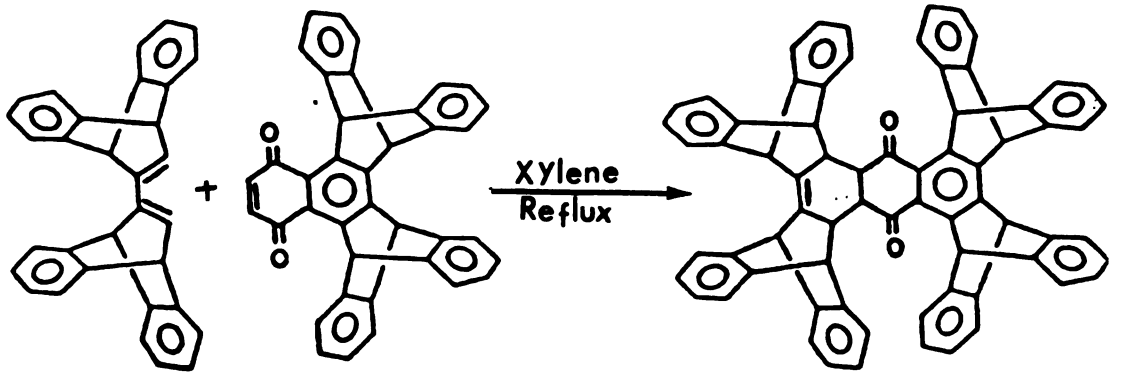


80 81

The structures of 79, 80 and 81 were confirmed by their mass, ^1H NMR and ^{13}C NMR spectra. Tables 2 and 3 lists the spectral data for these three compounds.

15. Reaction of 56 with 70

A solution of 56 and 70 in xylenes at reflux for 12 hours gave the cycloadduct 82 in 94% yield.



56 70 82

Table 2. ^{1}H NMR Chemical Shifts (ppm) of Compounds 79, 80 and 81.

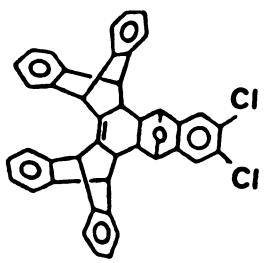
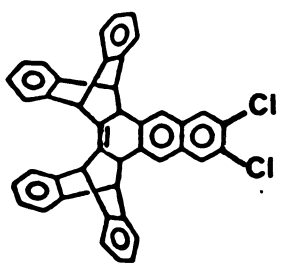
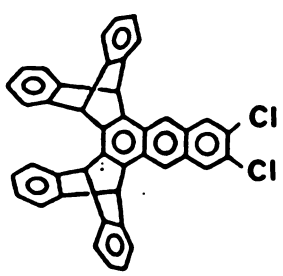
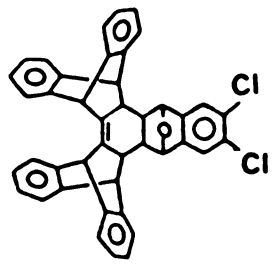
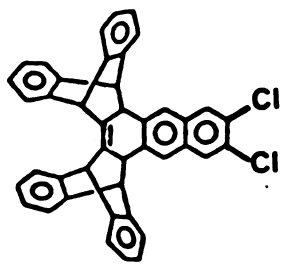
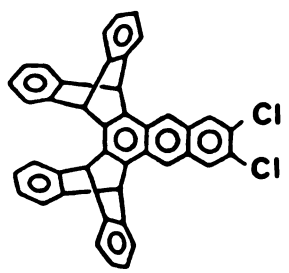
Compound	Chemical Shift (ppm)
 79	0.97 (dd,2H), 2.31 (broad d, 2H), 4.40 (d,2H), 5.29 (s,2H), 5.49 (s,2H), 6.90 (s,2H), 6.98 (m, 4H), 7.09 (m,4H), 7.21 (m,4H), 7.32 (m,4H).
 80	3.21 (s,2H), 5.20 (s,2H), 5.47 (s,2H), 6.89 (m,4H), 7.15 (m,8H), 7.36 (s,2H), 7.45 (m,4H), 8.27 (s,2H).
 81	6.29 (s,2H), 6.40 (s,2H) 6.97 (m,8H), 7.39 (s,2H), 7.51 (m,4H), 7.53 (m,4H), 9.26 (s,2H)

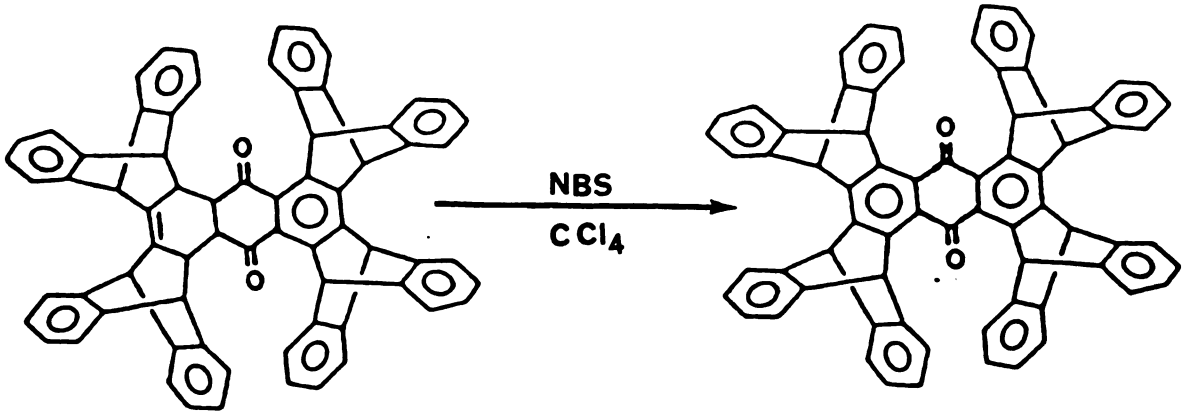
Table 3. ^{13}C NMR Chemical Shifts (ppm) of Compounds **79**, **80** and **81**.

Compound	Chemical Shift (ppm)
 **79**	45.61, 48.55, 49.29, 83.06 123.15, 124.11, 124.46, 126.14 126.19, 126.57, 126.95, 129.00, 131.13, 141.04, 142.39, 143.95, 145.49
 **80**	46.61 (overlap), 49.04, 120.53, 123.36, 124.11, 124.70, 126.07, 126.12, 126.44, 126.90, 127.03, 130.40, 131.35, 140.91, 141.41, 142.62, 142.80, 144.33, 146.03.
 **81**	50.72, 51.64, 120.00, 124.06, 124.32 125.03, 125.72, 127.05, 129.20, 131.66, 140.63, 141.49, 145.95, 146.33.

The structure of 82 was confirmed by its mass, ^{1}H NMR and ^{13}C NMR spectra. The mass spectrum showed a molecular ion peak at m/e 918. The ^{1}H NMR spectrum showed a four proton multiplet at δ 1.85 for the protons on the cyclohexene ring, two singlets, each for two protons, at δ 4.57 and 5.31 for the bridgehead protons of the 9,10-anthradiyl moieties fused to the non-aromatic site, two singlets, each for two protons, at δ 6.04 and 6.63 for the bridgehead protons of the 9,10-anthradiyl moieties fused to the aromatic site, as required by symmetry, and six sets of multiplets for the 32 aromatic protons at δ 6.98-7.67. The ^{13}C NMR spectrum of 82, in which six peaks appeared for the six pairs of the sp^3 carbon atoms and a peak at δ 199.25 for the pair of carbonyl carbon atoms, supported this structure. This compound was found to oxidize gradually when exposed to air.

16. Oxidation of 82 to the anthraquinone derivative 83.

There are several methods for oxidizing a saturated 1,4-cyclic dione to the corresponding quinone.[42] Among these, halogenation-dehydrogenation by NBS and NCS is frequently used. Heating a solution of 82 and NBS in carbon tetrachloride at reflux afforded 83 in quantitative yield.



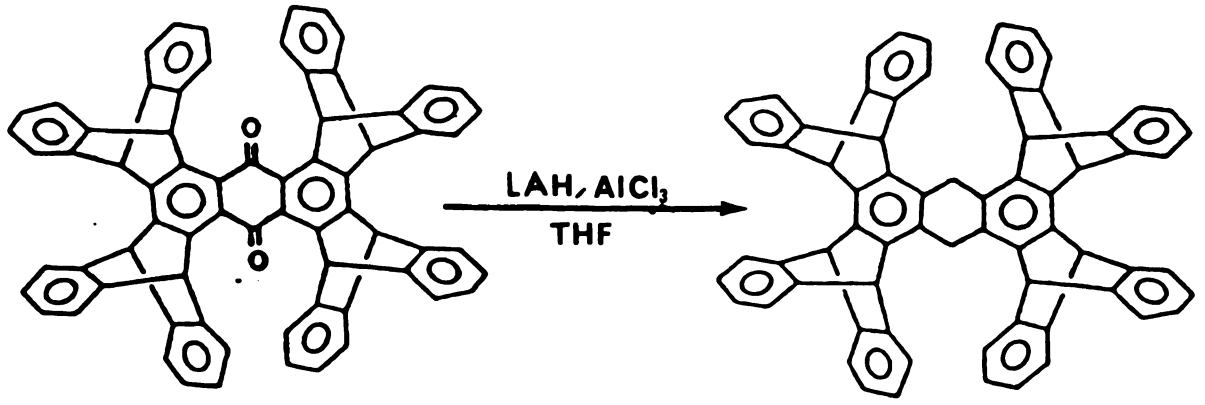
82 83

The melting point of this compound is >500°C. It was characterized by its ^{1}H NMR and ^{13}C NMR spectra. Both spectra showed very simple patterns due to the high symmetry of the compound ($D_{2}d$). The ^{1}H NMR spectrum showed two four-proton singlets at δ 6.08 and 7.10 for the "outer" and "inner" bridgehead protons respectively. The 32 aromatic protons appeared as three sets of triplets. The ^{13}C NMR spectrum showed two peaks at δ 50.01 and 50.70 for the sp^{3} bridgehead carbon atoms, 9 peaks for the sp^{2} carbon atoms, and a single peak at δ 188.63 for the carbonyl carbon atoms.

17. Reduction of 83.

Reduction of anthraquinones to the corresponding anthracenes has been carried out under various conditions and by a variety of reducing agents. These reactions are sensitive to the nature of the substituents and substitution pattern and often give a mixture of products. We investigated the reduction of 83 using several methods such as catalytic hydrogenation, lithium trialkoxyaluminum hydride, sodium borohydride/ trifluoroacetic acid, zinc sodium hydroxide, lithium aluminum hydride/aluminum chloride, zinc acetic acid/pyridine, to name a few.[44]

Except for the last two methods, the others lead to a mixture of products which, during the work up and purification, oxidized mostly to the starting material 83. Zinc/acetic acid/pyridine always lead to a mixture of 58 and its dihydro derivative 84.



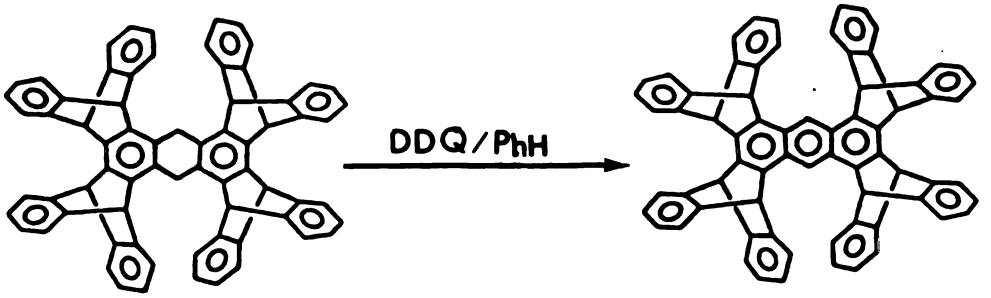
83 84

The lithium aluminum hydride/aluminum chloride method gave predominantly 84 in 91% yield along with a trace of 58. The two compounds were separated by addition of an excess TCNE to a solution of 84 and 58 in methylene chloride, followed by chromatography of the residue after evaporation of the solvent. The structure of 84 was determined by its ^{1}H NMR and ^{13}C NMR spectra. The ^{1}H NMR spectrum showed a four proton singlet at δ 4.24 for the benzylic protons on the middle ring, two four proton singlets at δ 5.90 and 5.94 for the "inner" and "outer" bridgehead protons respectively, and three sets of doublets of doublets for the 32 aromatic protons, as required by symmetry (D_2d). The ^{13}C NMR spectrum showed three peaks for the sp^3 hybridized carbon atoms and 8 peaks for the sp^2 aromatic carbon atoms. The melting point of 84 is above 500°C.

18. Dehydrogenation of 84.

Catalytic dehydrogenation of 84 by palladium/charcoal in refluxing mesitylene failed to give the expected product 58. Reaction of 84 with DDQ in refluxing benzene,[45] however, resulted in its conversion to 58. This transformation could be verified by the ^{1}H NMR spectrum of the

crude product, in which the signals for the benzylic protons of **84**, at 4.24 disappeared. Compound **58** complexes with either excess DDQ present in the solution or with its reduced form DDHQ. Separation is achieved quantitatively by absorbing the reaction mixture on silica gel and heating at 250-300°C under vacuum for 10 minutes, followed by chromatography.

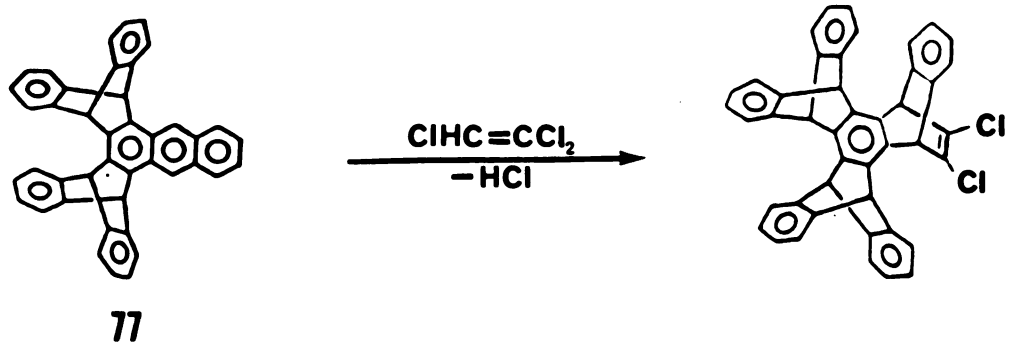


84 **58**

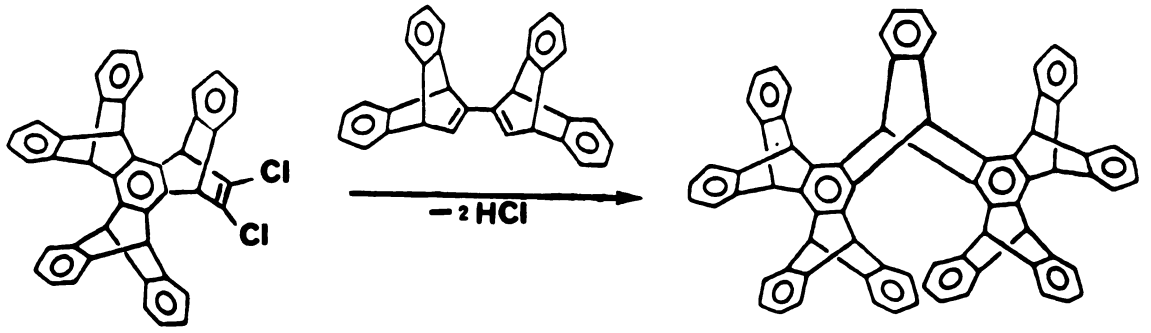
The melting point of **58** is >500°C. It was characterized by its mass and ^{1}H NMR spectra. The mass spectrum of **58** showed a molecular ion peak at m/e 882. The ^{1}H NMR spectrum showed two four proton singlets at δ 6.31 and 6.42 for the "inner" and "outer" bridgehead protons, three sets of multiplets for 32 protons on the benzene rings of the 9,10-anthradiyl moieties and a singlet at δ 9.28 for the two protons of the anthracene moiety.

The utility of the 9,10-anthradiyl fused anthracenes as easy entries into higher iptycenes need not be emphasized. The synthesis of **58** and **77** undoubtedly constitutes an important step toward the construction of the other a,c-fused members of this class of compounds. For example, the Diels-Alder reactions of **58** and **77**, with suitable

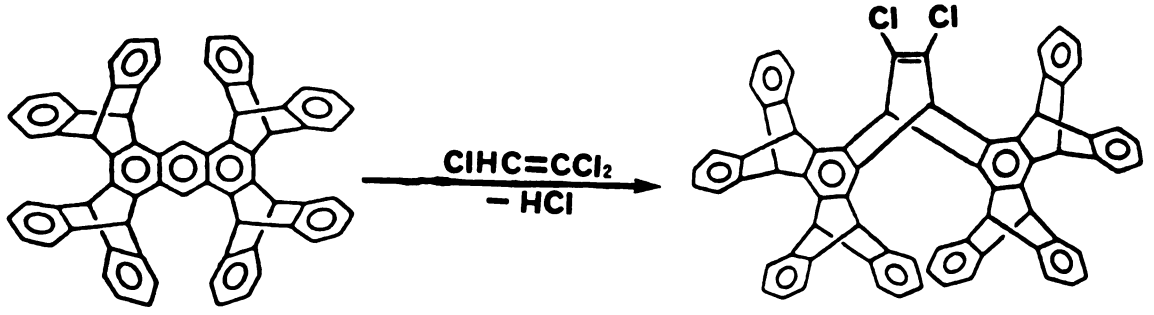
dienophiles such as trichloroethylene and 1,4-epoxyanthracene **41**, could provide entries into iptycenes **24**, **17**, **23**, and **10** (Table 1) by elaboration of the resulting cycloadducts, as illustrated in Figures 5 and 6.



77



17



58

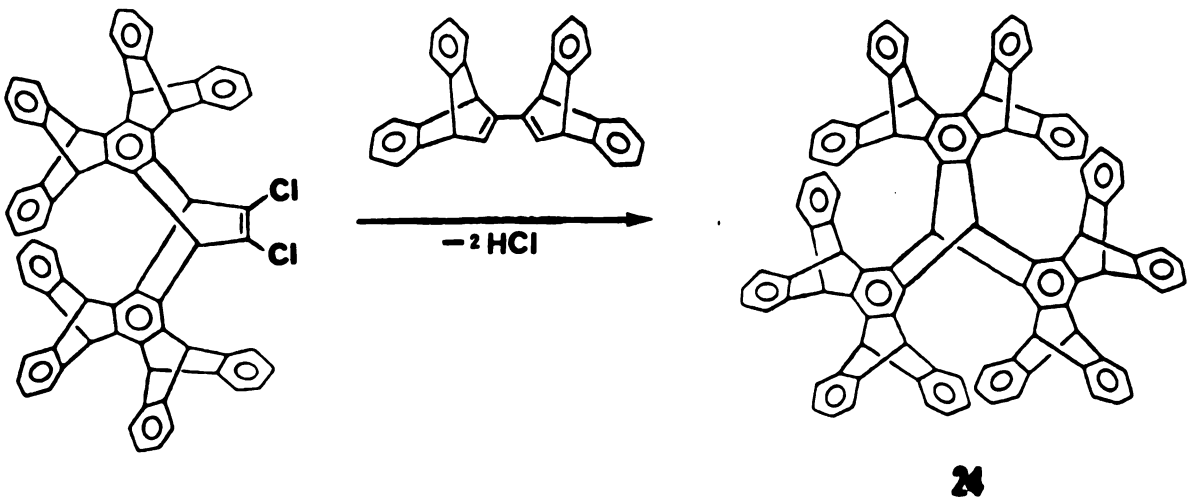
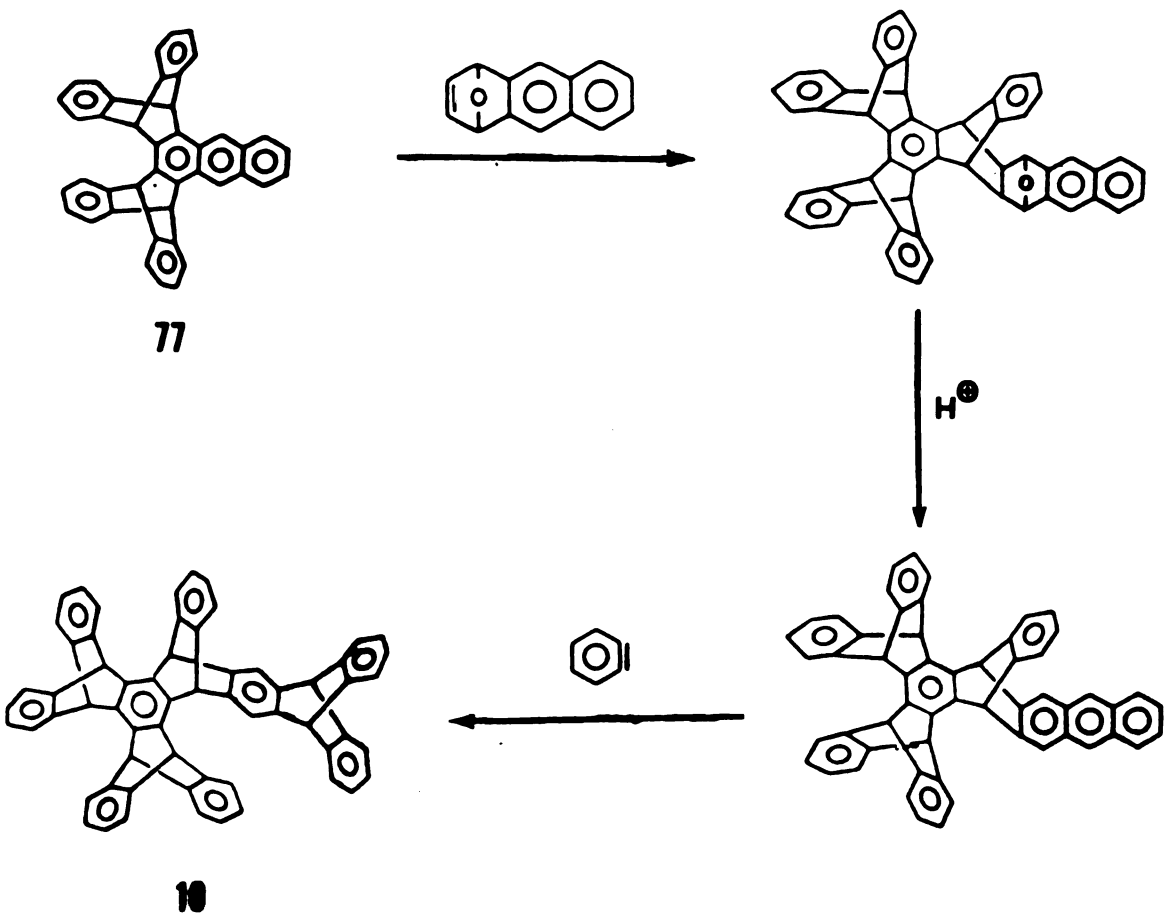


Figure 5. Schematic representation of the possible syntheses of iptycenes 17 and 24 from the reaction of anthracene derivatives 77 and 58 with 1,2-dichloroethylene.



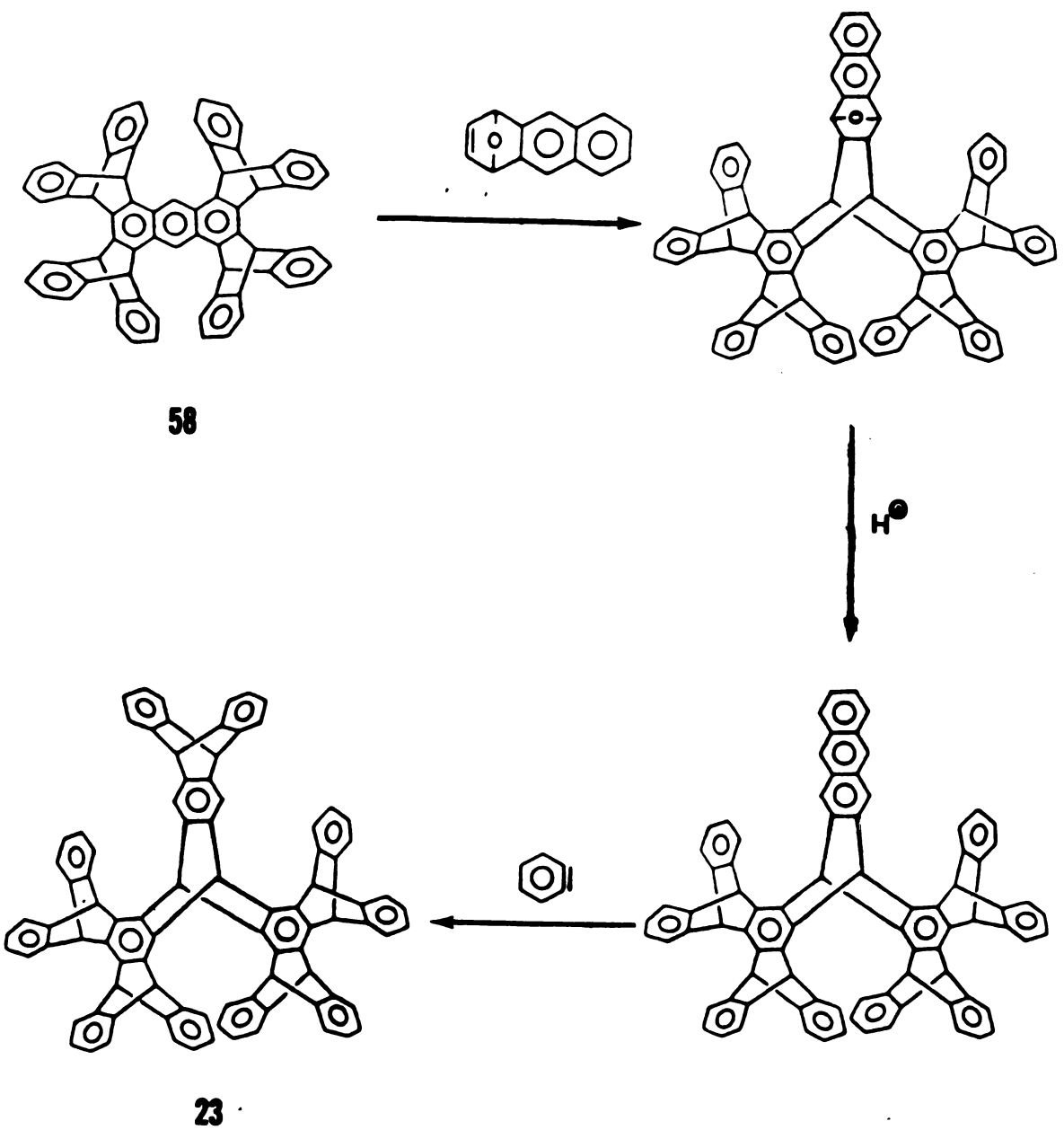


Figure 6. Schematic representation of the possible syntheses of iptycenes 10 and 23 from the reaction of anthracene derivative 17 and 58 with 1,4-epoxyanthracene.

EXPERIMENTAL

1. General Procedure

NMR spectra were recorded on a Brucker WM 250 MHz spectrometer using $CDCl_3$ as solvent (except 58, for which CD_2Cl_2 was used) and $(CH_3)_4Si$ as the internal reference. IR spectra were determined on a Perkin Elmer 167 spectrometer. Mass spectra were measured at 70 eV using a Finnigan 4000 spectrometer with the INCOS data system, operated by Mr. Ernest Oliver or Mr. Richard Olson. High resolution mass spectra were obtained with a JEOL HX110 HF spectrometer at Michigan State University Mass Spectrometry Facility. Melting points were determined with an electrothermal melting point apparatus (Fisher Scientific), or with a Thomas Hoover melting point apparatus and are uncorrected. Microanalyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, Michigan.

2. 3-Chloro-1,4,1′4′-tetrahydro-1,4;1′,4′-di-o-benzeno-2,2′--binaphthyl 32

To a suspension of 9.55 g (40 mmol) of 11-chloro-9,10-dihydro-9,10-ethenoanthracene in 100 mL of anhydrous hexanes and 25 mL of anhydrous THF under argon at -78°C was added dropwise 18 mL (45 mmol) of 2.5M n-butyllithium in hexanes. The reaction mixture was brought to room temperature, vigorously stirred (mechanical stirrer) for two hours, refluxed for 30 minutes, and then allowed to cool to room temperature. Water was slowly added (50 mL) followed by 200 mL of methylene chloride. The aqueous layer was discarded. The organic layer was washed with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The solvent was removed. Chromatography of the residue on a

silica gel column using a 1:5 mixture of methylene chloride/hexanes as eluent gave 6.5 g (73%) of the desired product as a white solid; m.p. 268°C (Lit. 268°C).[10]

3. 6-Chloro-5,8,13,14-tetrahydro-5,14;8,13-di-o-benzeno-pentaphene 65

A suspension of 1.77 g (4.0 mmol) of 31 in 30 mL of trans-1,2-dichloroethylene in a sealed tube was heated at 190-195°C for 36 hours. After cooling to 0°C the tube was opened and the excess solvent was removed. The residue was added to 125 mL solution of 4:1 THF/methanol containing 0.4 g (10 mmol) of sodium hydroxide. The mixture was heated at reflux for 48 hours. The solvent was removed and the residue was taken up in methylene chloride. The methylene chloride solution was washed with water, saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Evaporation of the solvent and chromatography of the residue on a silica gel column using a 1:4 mixture of methylene chloride/hexane as eluent gave 1.27 g (68%) of the desired product as a white solid; m.p. 358-359°C, ^{1}H NMR ($CDCl_3$) δ 5.28 (s,1H), 5.83 (s,1H), 5.91 (s,1H), 5.96 (s,1H), 6.94 (m,8H), 7.03 (s,1H), 7.29 (m,2H), 7.36 (m,2H), 7.42 (m,4H); ^{13}C NMR ($CDCl_3$) δ 50.02, 50.63, 50.83, 53.94, 121.11, 123.96, 124.08, 124.45, 125.84, 138.13, 139.31, 141.54, 144.13, 144.78, 144.89, 145.13; mass spectrum m/e (relative intensity) 467(6), 466(43), 464(67), 429(49), 138(78), 111(100), 82(96), 77(70). Anal. Calcd. for $C_{34}H_{21}Cl$: C, 87.82; H, 4.56. Found: C, 87.91; H, 4.53.

4. 1,4,1′,4′-Tetrahydro-1,4;1′,4′-di-o-benzeno-2:2′-binaphthyl 56

To a suspension of 8.82 g (20 mmol) of 32 in 250 mL of anhydrous THF under argon at -78°C was added dropwise 18 mL (45 mmol) of 2.5 M n-butyllithium in hexanes. The reaction mixture was brought to room temperature and stirred for four hours, heated at reflux for 30 minutes and then cooled to 0°C. The dark brown solution was slowly and carefully quenched with 5 mL of methanol. The solvent was removed and the residue was taken up in methylene chloride. The methylene chloride solution was washed with water, saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Evaporation of the solvent and chromatography of the solid material on a silica gel column using 1:4 methylene chloride/hexanes as eluent gave 5.1 g (63%) of 56 as a white solid, m.p. 323-324°C; ^{1}H NMR ($CDCl_3$) δ 5.13 (d,3H), 5.16 (s,1H), 6.88 (m,8H), 7.10 (dd,2H), 7.21 (m,8H); ^{13}C NMR ($CDCl_3$) δ 51.31, 52.60, 123.12, 123.78, 124.90, 125.10, 131.04, 145.80; mass spectrum m/e (relative intensity), 407(6), 406(24), 228(34), 203(26), 202(1(), 191(12), 178(100). Anal. Calcd. for $C_{32}H_{22}$: C, 94.54; H, 5.45. Found: C, 94.41; H, 5.48.

5. 6,7-Dichloro-5,6,7,8,13,14-hexahydro-5,14;8,13-di-o-benzenopentaphene 73

A suspension of 1.63 g (4 mmol) of 56 in 30 mL of trans-1,2-dichloroethylene in a sealed tube was heated at 190-195°C for 24 hours. After cooling to 0°C the tube was opened and excess solvent was evaporated. Chromatography of the remaining residue on a silica gel column using 5:1 hexanes/methylene chloride as eluent gave 1.84 g (91%) of the desired product as an off-white solid; m.p. 267-268°C, ^{1}H NMR ($CDCl_3$) δ 2.23 (d,1H), 2.67 (dd,1H), 2.73 (d,1H), 4.41 (t,1H), 4.51

(d,1H), 4.60 (d,1H), 5.31 (s,1H), 5.35 (s,1H), 7.03 (m,8H), 7.29 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 45.62, 47.59, 48.56, 48.86, 49.11, 49.32, 66.63, 69.89, 122.80, 123.14, 123.57, 124.27, 124.50, 126.10, 125.19, 126.64, 126.86, 127.36, 128.15, 130.34, 131.16, 139.25, 141.54, 142.03, 142.34, 142.96, 143.16, 144.68; mass spectrum m/e (relative intensity), 502(5), 467(4), 431(19), 289(8), 253(13), 178(100). Anal. Calcd. for $C_{34}H_{24}Cl_2$: C, 81.11; H, 4.80. Found: C, 80.94; H, 4.77.

6. 5,8,13,14-Tetrahydro-5,14;8,13-di-o-benzenopentaphene 2

To a solution of 0.40 g (excess) sodium hydroxide in 250 mL of 4:1 tetrahydrofuran/methanol was added 1.52 g (3 mmol) of 73. The solution was heated at reflux for 36 hours. The solvent was then removed and the residue was taken up in methylene chloride. The methylene chloride solution was washed with water, saturated sodium chloride solution and dried over anhydrous magnesium sulfate. After evaporation of the solvent, chromatography of the residue on a silica gel column using a 1:3 methylene chloride/hexanes as eluent gave 1.15 g (87%) of the product, m.p. 315-316°C, ^1H NMR ($CDCl_3$) δ 5.31 (s,2H), 5.94 (s,2H), 6.94 (m, 10H), 7.30 (m,4H), 7.42 (m,4H); ^{13}C NMR ($CDCl_3$) δ 50.51, 54.59, 120.43, 124.05, 125.71, 139.62, 142.57, 145.43, 146.01; mass spectrum m/e (relative intensity), 431(22), 430(100), 252(49), 178(20). Anal. Calcd. for $C_{34}H_{22}$: C, 94.85; H, 5.15. Found: C, 94.89; H, 5.12.

7. 5,6,7,8,13,14,1′,2′,3′,4′-Decahydro-5,14;8,13-di-o-benzeno-6,7-benzopentaphene 74

A suspension of 1.63 g (4.0 mmol) of 56 in 30 mL of cyclohexene in a sealed tube was heated at 195-200°C for 36 hours. After cooling to 0°C the tube was opened and the excess cyclohexene was removed.

Chromatography of the residue on a silica gel column using a mixture of 4:1 hexanes/methylene chloride as eluent afforded 1.78 g (91%) of **74** as a white solid, m.p. 295-296°C, ^{1}H NMR ($CDCl_3$) δ 0.49 (broad s,2H), 1.32 (broad d,2H), 1.53 (broad s,6H), 1.88 (broad d,2H), 4.18 (d,2H), 5.35 (s,2H). 6.93-7.38 (m,16H); ^{13}C NMR ($CDCl_3$) δ 23.75, 28.12, 40.41, 47.02, 49.05, 49.58, 123.33, 123.96, 124.83, 125.75, 126.58, 132.30, 141.25, 142.50, 142.83, 145.41; mass spectrum m/e (relative intensity), 4.88(1), 310(8), 178(100). Anal. Calcd. for $C_{38}H_{32}$: C, 93.40; H, 6.60. Found: C, 93.49; H, 6.69.

8. 1',4',7,12-Tetrahydro-1',4';7,12-di-o-benzeno-5,6-naphthotetraphene-1,4-dione **70**

A solution of 4.41 g (10 mmol) of **32** and 10.80 g (excess of p-benzoquinone in 250 mL of xylenes was heated at reflux for 36 hours. The solvent, along with most of the excess p-benzoquinone, was removed by vacuum distillation. Chromatography of the remaining dark brown solid on a silica gel column using a mixture of 3:2 methylene chloride/hexanes as eluent afforded 4.4 g (86%) of **70** as a bright yellow solid, m.p. 393°C, ^{1}H NMR ($CDCl_3$) δ 6.13 (s,2H), 6.77 (s,2H), 7.01 (m,8H), 7.41 (s,2H), 7.48 (dd,8H); ^{13}C NMR ($CDCl_3$) δ 48.69, 50.27, 118.53, 123.69, 125.11, 126.22, 139.00, 143.84, 144.32, 146.06, 188.55; mass spectrum m/e (relative intensity), 512(8), 511(44), 410(100), 427(23), 178(28). Anal. Calcd. for $C_{38}H_{22}O_2$: C, 89.39; H, 4.34. Found: C, 89.23; H, 4.24.

9. 1,1′,1″,1‴,1⁗,4,4′,4″,4‴,4⁗-Decahydro-1′,4′;1″,4″;1‴,4‴,1⁗,4⁗-tetra-o-benzeno-1,2;3,4;5,6;7,8-tetranaphthoanthra-9,10-dione 82

A solution of 2.05 g (5 mmol) of 56 and 2.51 g (5 mmol) of 70 in 250 mL of xylenes was heated at reflux for 12 hours. The solvent was removed. Chromatography of the remaining solid using 2:1 methylene chloride/hexanes as eluent gave 4.3 g (94%) of 82 as a white solid, m.p. 380- 382°C, ^{1}H NMR ($CDCl_3$) δ 1.85 (m,4H), 4.57 (s,2H), 5.31 (s,2H), 6.04 (s,2H), 6.63 (s,2H), 6.98 (m,8H), 7.10 (m,4H), 7.27 (m,8H), 7.44 (m,6H), 7.56-7.67 (m,6H); ^{13}C NMR, δ 45.33, 47.88, 48.63, 49.86, 50.63, 52.90, 123.12, 123.94, 124.13, 124.22, 124.33, 124.67, 125.36, 126.21, 126.36, 126.66, 127.13, 127.24, 128.75, 128.94, 130.72, 140.20, 142.07, 143.58, 144.04, 144.64, 144.95, 145.19, 199.25. Mass spectrum m/e (relative intensity), 918(0.7), 917(2), 916(2), 738(19), 485(22), 427(14), 426(12), 178(100). Anal. Calcd. for $C_{70}H_{44}O_2$: C, 91.67; H, 4.83. Found: C, 91.63; H, 4.82.

10. 1,1′,1″,1‴,1⁗,4,4′,4″,4‴,4⁗-Decahydro-1′,4′;1″,4″;1‴,4‴,1⁗,4⁗-tetra-o-benzeno-1,2;3,4;5,6;7,8-tetranaphthoanthra-9,10-dione 83

A solution of 1.84 g (2 mmol) of 82 and 2.5 g (excess) of N-bromosuccinimide in 300 mL of carbon tetrachloride was heated at reflux for 12 hours. The solvent was removed. Chromatography of the resulting solid on a silica gel column using 1:1 methylene chloride/hexanes as eluent gave 1.78 g (97%) of 83 as a pale yellow solid; m.p. >450°C; ^{1}H NMR ($CDCl_3$) δ 6.08 (s,4H), 7.00 (t,16H), 7.10 (s,4H), 7.45 (t,8H), 7.56 (t,8H); ^{13}C NMR ($CDCl_3$) δ 50.01, 50.70, 124.14, 125.18, 126.27, 126.37, 127.85, 143.90, 144.48, 144.93, 145.09, 188.63; the mass spectrum could

not be obtained. Anal. Calcd. for $C_{70}H_{40}O_2$: C, 92.08; H, 4.41. Found: C, 91.96; H, 4.39.

11. 5,5a,6,7,7a,8,13,14,1′,4′-Decahydro-5,14;8,13-di-o-benzeno-1′,4′,-oxo-6,7 naphthopentaphene 75

A solution of 1.02 g (2.5 mmol) of 56 and 0.36 g (2.5 mmol) of 1,4-epoxynaphthalene in 125 mL of xylenes was heated at reflux for eight hours, after which the solvent was removed. Chromatography of the residue on a silica gel column using 2:1 hexanes/methylene chloride afforded 1.3 g (95%) of 75 as a white solid; m.p. 369-370°C, ^{1}H NMR ($CDCl_3$) δ 0.97 (dd,2H), 2.33 (broad d,2H), 4.40 (d,2H), 5.28 (s,2H), 5.30 (s,2H), 6.95 (m,4H), 7.08 (m,6H), 7.17 (m,6H), 7.31 (m,4H); ^{13}C NMR ($CDCl_3$) δ 46.10, 48.63, 49.54, 83.43, 119.14, 123.17, 124.01, 124.10, 125.80, 126.48, 126.87, 127.08, 131.05, 141.27, 142.29, 142.54, 144.23, 145.98; mass spectrum m/e (relative intensity), 550(5), 445(1), 431(2), 253(5), 178(100), 118(46). Anal. Calcd. for $C_{42}H_{30}O$: C, 91.60; H, 5.49. Found: C, 91.31; H, 5.63.

12. 5,14;8,13-Di-o-benzeno-5,5a,7a,8,13,14-hexahydro-6,7-naphthopentaphene 76

To a solution of 0.56 g (1.0 mmol) of 75 in 15 mL of acetic anhydride was added slowly 2 mL of concentrated sulfuric acid. The solution was stirred for 3-5 minutes and then poured onto ice water. The organic material was extracted in ether. The ether solution was washed three times with 10% sodium hydroxide solution, water, saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Evaporation of the solvent and chromatography of the residue on a silica gel column using 4:1 hexanes/methylene chloride as eluent gave 0.39 g

(73%) of **76** as a white solid, m.p. >400°C (dec.), ^{1}H NMR ($CDCl_3$) δ 3.15 (s,2H), 5.14 (s,2H), 5.46 (s,2H), 6.85 (m,4H), 7.12 (m,6H), 7.39 (m,8H), 7.48 (m,4H); ^{13}C NMR ($CDCl_3$) δ 46.30, 46.68, 48.88, 122.63, 123.02, 124.23, 125.71, 125.99, 125.58, 127.92, 131.08, 132.00, 138.97, 140.85, 142.44, 144.47; mass spectrum m/e (relative intensity) 533(8), 532(29), 355(24), 354(100), 353(50), 179(8), 178(15), 86(24), 84(44). High resolution mass spectrum calcd. for $C^{42}H^{28}$ = 532.6914; Found: 532.6882.

13. 5,14;8,13-Di-o-benzeno-5,8,13,14-tetrahydro-6,7-naphthopentaphene **77**

A solution of 0.54 g (1 mmol) of **76** and 0.23 g (1 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzenoquinone in 50 mL of benzene was heated at reflux under argon for 12 hours. Evaporation of the solvent and chromatography of the resulting solid on a silica gel column using 3:1 hexanes/methylene chloride as eluent gave 0.50 g (92%) of **77** as a yellow solid, m.p. 470-72°C (dec.), ^{1}H NMR ($CDCl_3$) δ 6.25 (s,2H), 6.36 (s,2H), 6.94 (m,8H), 7.39 (dd,2H), 7.48 (m,8H), 8.03 (dd,2H), 8.84 (s,2H); ^{13}C NMR ($CDCl_3$) δ 50.64, 51.57, 121.70, 123.95, 124.12, 126.58, 127.69, 128.81, 129.20, 131.69, 146.26, 146.70; mass spectrum m/e (relative intensity) 531(30), 530(100), 352(36), 256(7). High resolution mass spectrum calcd. for $C^{42}H^{26}$ = 530.6755; Found: 530.6735.

14. 5,5a,6,7,7a,8,13,14,1′,4′-Decahydro-5,14;8,13-di-o-benzeno-6′,7′-dichloro-1′,4′-oxo-6,7-naphthopentaphene **79**

A solution of 1.02 g (2.5 mmol) of **56** and 0.54 g (2.5 mmol) of 6,7-dichloro-1,4-epoxynaphthalene in 125 mL xylenes was heated at reflux for eight hours, after which the solvent was removed. Chromatography of the residue on a silica gel column using 2:1 hexanes/methylene chloride

as the eluent gave 1.42 g (91%) of 79 as a white solid, m.p. 360-361°C, ^{1}H NMR ($CDCl_3$) δ 0.97 (dd,2H), 2.31 (broad d,2H), 4.40 (d,2H), 5.29 (s,2H), 5.49 (s,2H), 6.90 (s,2H), 6.98 (m,4H), 7.089 (m,4H), 7.21 (m,4H), 7.32 (m,4H); ^{13}C NMR ($CDCl_3$) δ 45.61, 48.55, 49.29, 83.06, 123.15, 124.11, 124.46, 126.14, 126.19, 126.57, 126.95, 129.00, 131.13, 141.04, 142.39, 143.95, 145.49; mass spectrum m/e (relative intensity), 620(0.3), 618(0.9), 431(3), 186(10), 178(100), 86(16), 84(26). Anal. Calcd. for $C_{42}H_{28}Cl_2O$: C, 81.42; H,4.55. Found: C, 81.44; H, 4.53.

15. 5,14;8,13-Di-o-benzeno-5,5a,7a,8,13,14-hexahydro-6′,7′-dichloro-6,7-naphthopentaphene 80

To a solution of 0.62 g (1.0 mmol) of 79 in 15 mL of acetic anhydride was slowly added 2 mL of concentrated sulfuric acid. The reaction mixture was stirred for 3-5 minutes and then poured onto ice. The organic compounds were extracted with ether. The ether solution was washed with water, 10% sodium hydroxide solution, water, saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Evaporation of the solvent and chromatography of the residue on a silica gel column using 3:1 hexanes/methylene chloride as eluent gave 0.46 g (76%) of 80 as a faint yellow solid, m.p. 340-342°C; ^{1}H NMR spectrum ($CDCl_3$) δ 3.21 (S,2H), 5.20 (S,2H), 5.47 (S,2H), 6.89 (m,4H), 7.15 (m,8H), 7.36 (s,2H), 7.45 (m,4H), 8.27 (s,2H); ^{13}C NMR spectrum ($CDCl_3$) δ 46.6 (overlap), 49.0, 120.5, 123.3, 124.1, 124.7, 126.0, 126.1, 126.4, 126.9, 127.0, 130.4, 131.3, 140.9, 141.4, 142.6, 142.8, 144.3, 146.0; mass spectrum m/e (relative intensity) 603(2), 602(6), 601(6), 600(18), 598(15), 422(20), 179(27), 178(100). High resolution mass spectrum calcd. for $C^{42}H^{26}Cl_2$: 601.5817; Found: 601.5695.

16. 5,14;8,13-Di-o-benzeno-6′,7′-dichloro-5,8,13,14-tetrahydro-6,7-naphthopentaphene 81

A solution of 0.60 g (1 mmol) of **80** and 0.23 g (1 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 75 mL of benzene was heated at reflux under argon for 12 hours. Evaporation of the solvent and chromatography of the resulting solid on a silica gel column using 3:1 hexanes/methylene chloride as eluent gave .57 g (95%) of **81** as a bluish yellow solid, m.p. 380-382°C; ^{1}H NMR ($CDCl_3$) δ 6.29 (s,2H), 6.40 (s,2H), 6.97 (m,8H), 7.39 (s,2H), 7.51 (m,4H), 7.53 (m,4H), 9.26 (s,2H); ^{13}C NMR ($CDCl_3$) δ 50.72, 51.64, 120.00, 124.06, 124.32, 125.03, 125.72, 127.05, 129.20, 131.66, 140.63, 141.49, 145.95, 146.33; mass spectrum m/e (relative intensity) 602(3), 601(10), 600(40), 598(48), 422(16), 420(26), 264(18), 262(14), 178(46), 44(100). Anal. Calcd. for $C_{42}H_{24}Cl_2$: C, 84.14; H, 4.03. Found: C, 84.22; H, 4.11.

17. 1,1′,3,3′,4,4′-Hexahydro-1,4;1′,4′-di-o-benzeno-3:3′-binaphthyl-2,2′-dione 60

To a solution of 3.6 g (22 mmol) of 1,1,1,3,3,3-hexamethyl-disilazine in 20 mL of anhydrous ether was added dropwise 9.0 mL (22 mmol) of 2.5 M n-butyllithium in hexanes. The exothermic reaction was accompanied by formation of a crystalline product. After the addition was complete, the solvents were removed by flushing argon gas through the flask, and were replaced by 50 mL of dry THF. The solution was cooled to -78°C and a solution of 4.4 g (20 mmol) of 1,3,4-trihydro-1,4-o-benzeno-naphthalene-2-one in 40 mL of anhydrous THF was added dropwise. The reaction mixture was stirred for two hours at -78°C and then a solution of 3.3 g (20 mmol) of ferric chloride in 25 mL of dry N,N-dimethylformamide was added. The reaction mixture was warmed to

room temperature and stirred over night. The solution was diluted with 150 mL of methylene chloride, washed with water, 10% hydrochloric acid solution, water, saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Evaporation of the solvent and chromatography of the residue on a silica gel column using 2:1 hexanes/methylene chloride provided 2.8 g (59%) of 60 a white solid, m.p. 321-322°C. ^{1}H NMR ($CDCl_3$) δ 1.73 (s,2H), 4.77 (s,2H), 5.02 (s,2H), 7.12 (m,8H), 7.23 (m,2H), 7.31 (m,2H), 7.46 (m,2H); ^{13}C NMR ($CDCl_3$) δ 47.25, 47.55, 63.70, 125.01, 125.60, 127.18, 127.87, 205.28;. Anal. Calcd. for $C_{32}H_{22}O_2$: C, 87.46; H, 5.05. Found: C, 87.50; H, 5.11.

18. 9,10-Dihydroanthracene Derivative 84

To a suspension of 0.38 g (10 mmol) of $LiAlH_4$ in 100 mL of anhydrous THF under argon was added 0.92 g (1 mmol) of 83. The reaction mixture was heated at reflux for four hours, cooled to 0°C and 0.66 g (5 mmol) of aluminum chloride was added in small portions. The solution was then heated at reflux for two hours and the excess $LiAlH_4$ was hydrolyzed with 3 mL of water. The organic layer was decanted, the solvent was removed and the remaining residue was dissolved in methylene chloride. The methylene chloride solution was washed with water and sodium chloride solution and dried over anhydrous magnesium sulfate. The solvent volume was reduced to 10mL, a small amount of tetracyanoethylene (TCNE) was added to the methylene chloride solution. Absorption of the mixture onto silica gel and chromatography using 1:2 methylene chloride/hexanes as the eluent gave 0.8 g (90%) of the desired product as a white solid; m.p. >500°C. ^{1}H NMR ($CDCl_3$) δ 4.24 (s,4H), 5.90 (s,4H), 5.94 (s,4H), 6.94 (m,16H), 7.35 (m,16H); ^{13}C NMR ($CDCl_3$) δ 28.71, 50.58, 50.84, 124.07, 125.63, 125.84, 128.11, 137.11, 137.25,

138.45, 145.57, 145.80. Anal. Calcd. for $C_{70}H_{44}$: C,94.99; H, 5.01. Found: C, 94.83; H, 5.17.

19. Anthracene Derivative 58

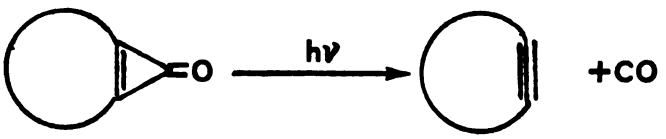
A solution of 0.89 g (1 mmol) of 84 and 0.3 g (1.3 mmol) of DDQ in 150 mL of benzene was heated at reflux under argon for 16 hours. The solvent was removed and the residue was absorbed onto 10 g of 30-60 mesh silica gel. Heating the silica gel containing the reaction mixture at 250-300°C under vacuum for 10 minutes and immediate chromatography using 2:1 hexanes/methylene chloride as the eluent gave 0.86 g (97%) of the desired product as a yellow solid; m.p. >500°C. ^{1}H NMR (CD_2Cl_2) δ 6.31 (s,4H), 6.42 (s,4H), 6.97 (t,16H), 7.24 (t,8H), 7.54 (t,8H); ^{13}C NMR (CD_2Cl_2) δ 50.61, 51.54, 119.98, 124.30, 125.04, 125.71, 127.57, 145.90, 146.30; mass spectrum m/e (relative intensity) 883 (M+1, 15), 882 (M+,18), 207(24), 178(16), 149(54), 44(100). Anal. Calcd. for $C_{70}H_{42}$: C, 94.20; H, 4.80. Found: C, 93.91; H, 4.72.

PART II

BICYCLO [2.2.2] ALKYNES; REACTIVITY AND THE MECHANISM OF THE TRIMERIZATION

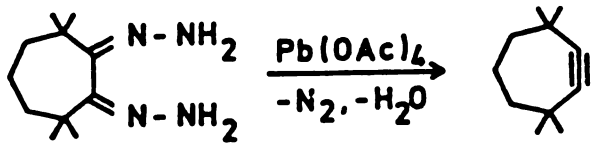
Cyclononyne and cyclooctyne were the first small ring cycloalkynes to be synthesized, by Blomquist and co-workers about 30 years ago.[46] Since then a considerable amount of information regarding the existence and stability of smaller ring cycloalkynes has been reported.[47] According to an arbitrary definition suggested by Krebs and Wilke, any cycloalkyne with an angle deformation larger than 10° is considered a strained cycloalkyne.[47] Based on this definition, cyclononyne and cycloalkynes with smaller ring sizes fulfill this criterion. Cyclononyne and cyclooctyne are isolable compounds. Those unsubstituted cycloalkynes with fewer carbon atoms in their rings have only a transitory existence. There is no evidence as to the existence of cyclopropyne.[48]

Cycloalkynes can be generated by several methods. Matrix photolysis, in which the cycloalkyne is generated by the photolytic decomposition of the cyclopropenones, is used for spectroscopic studies.[49]



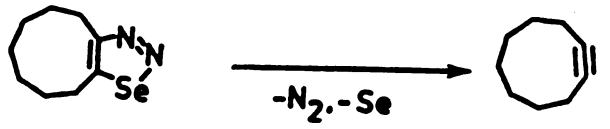
Oxidative decomposition of 1,2-hydrazones and 1-amino-1,2,3-triazoles is another method for generating cycloalkynes.[50,51] If a short-lived isolable cycloalkyne is to be prepared, lead tetraacetate is the preferred reagent for the oxidation, since the decomposition is fast

and takes place at low temperatures. Tetramethylcycloheptyne **85**, the most strained known isolable cycloalkyne has been prepared by this method.[52]



85

In some cases, cycloalkynes have been generated by the thermal decomposition of the corresponding selenadiazoles.[53] Pure cyclononyne **86** was prepared this way.[54]



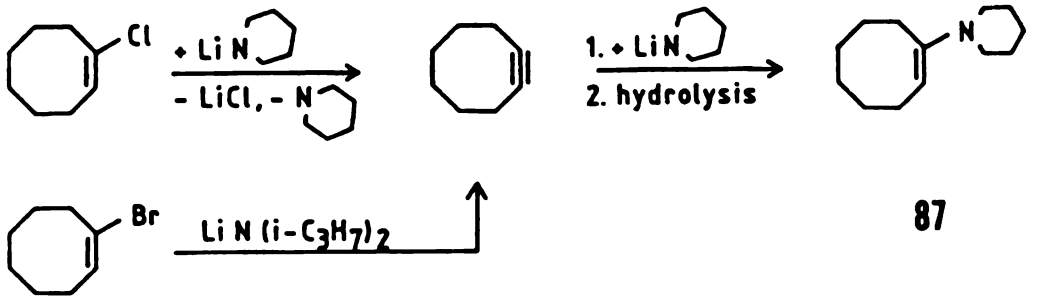
86

Dehydrohalogenation of 1-halocycloalkenes with strong bases, however, is the most frequently used method for generating these reactive intermediates.

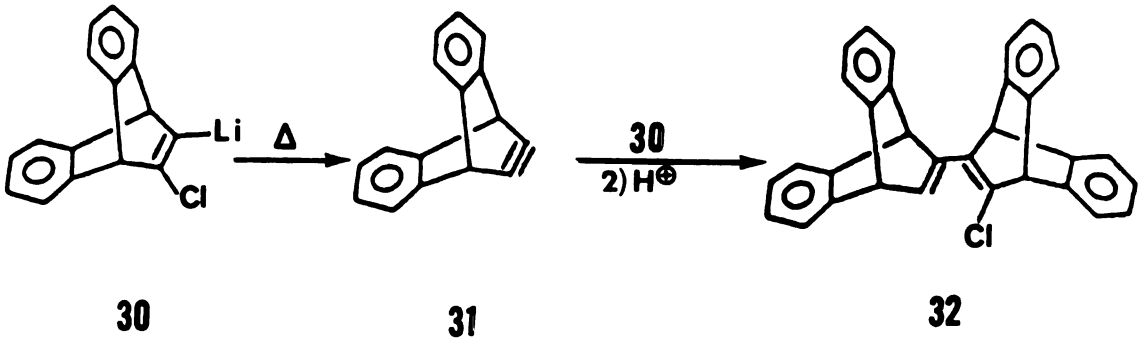
The following experimental observations usually provide the evidence for the existence of non-isolable cycloalkynes.

(a) Addition of Nucleophiles

Cycloalkynes are relatively strong electrophiles. Thus addition to the base is common in the preparation of these species by base-catalyzed elimination reactions.[55] For example, **87** is assumed to form by addition of cyclooctyne to lithium piperidide in the following reaction.[56]

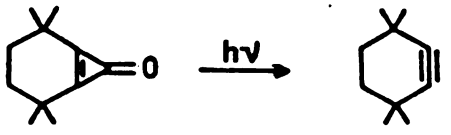


Coupling products such as 32 are presumably formed through this mechanism (see p. 5).



(b) Spectroscopy

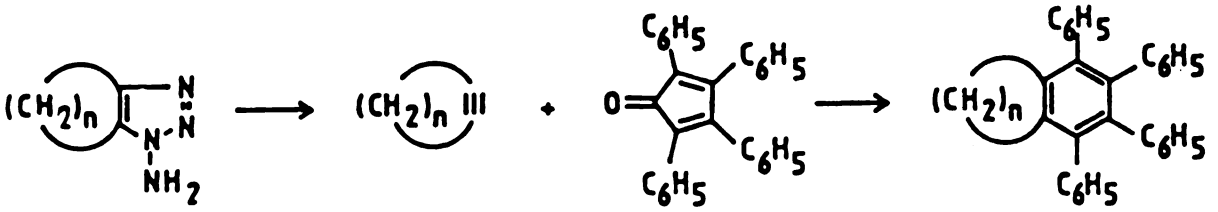
In these experiments, cycloalkynes are generated photolytically in a matrix at low temperatures and their spectra are recorded. For example, appearance of a new band at 2108 cm^{-1} in the IR spectrum obtained from the photolytic decomposition of 88 in a matrix at 20°K has been assigned to the C≡C stretching vibration in 89.[47]



88 89

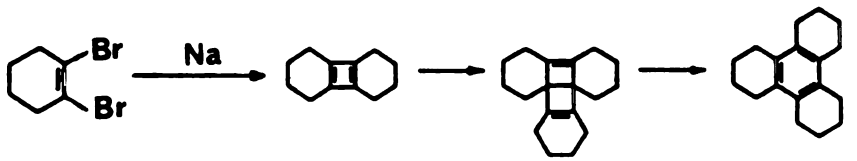
(c) Trapping Experiments

Due to their structural strain, small ring cycloalkynes undergo [4+2] cycloaddition reactions with active dienes to give the corresponding cycloadducts.[57,58]



(d) Oligomerization

In the absence of any reactive reagent, strained cycloalkynes react with each other to form oligomeric species such as **90**.[59] Kinetic investigations and isotope labeling experiments have also been used for probing the existence of strained cycloalkynes.[60]



90

Cycloalkynes possessing hydrogen atoms in the allylic positions, in the presence of strong bases, rearrange to the isomeric allenes, since an allene requires only three colinear carbon atoms.[61] It is believed that the equilibrium shifts toward the allene as the ring size decreases.[62] Labeling experiments have shown, for example that the addition products from the reaction of 1- halocyclohexene and 1-halocyclopentene with phenyllithium arise from the reaction of both allenic and acetylenic species with this reagent.[63]

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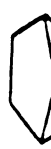

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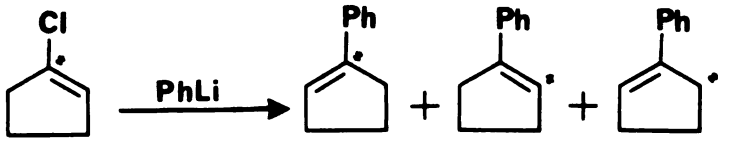
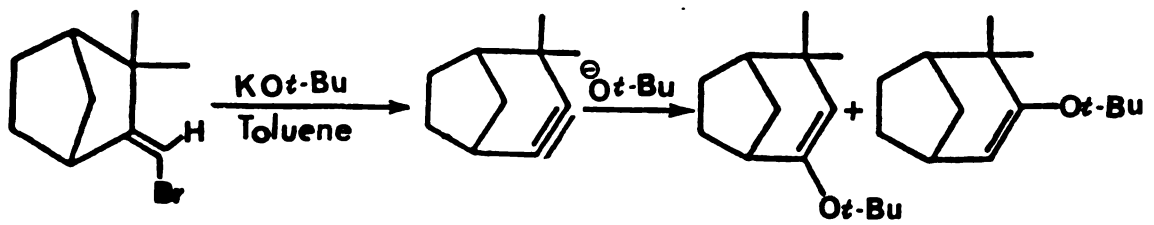


In this respect, bridged bicyclic systems have an advantage over simple cyclic systems. Due to the lack of any active allylic hydrogen atoms, the possibility of isomerization to an allene, as frequently encountered in the case of simple cycloalkynes, would be eliminated. Presence of the bridge should also impose considerable strain on the molecule and therefore a higher reactivity for the cycloalkynes would be expected.

Only a few bridged bicycloalkyne systems have been reported. Compound **91** is reported to react with potassium t-butoxide in refluxing toluene to give the isomeric products **93** and **94** in quantitative yield, presumably through the bicycloalkyne intermediate **92**.[64]



91 **92** **93** **94**

Vinyl halides **95** and **29**, upon treatment with n-butyllithium at low temperatures in THF, form the lithiated species **96** and **30**, respectively.[65,57]

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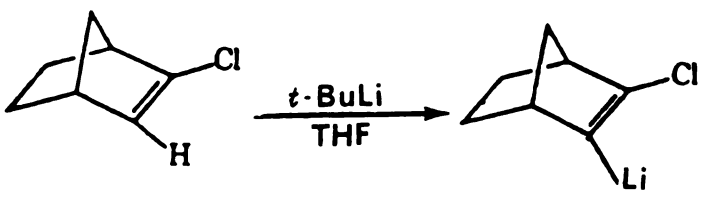
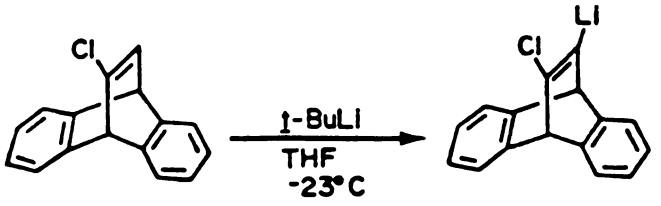
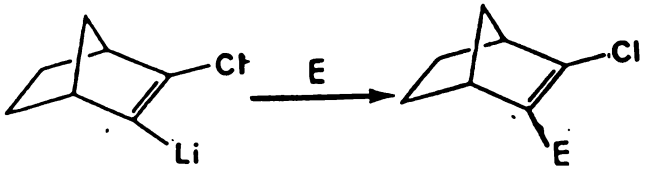


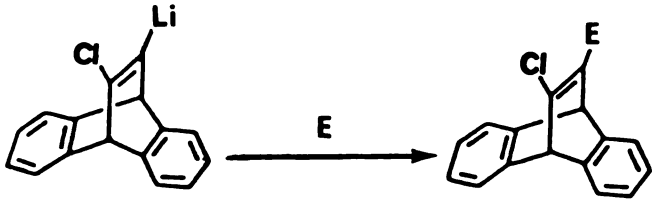
95 96



29 30

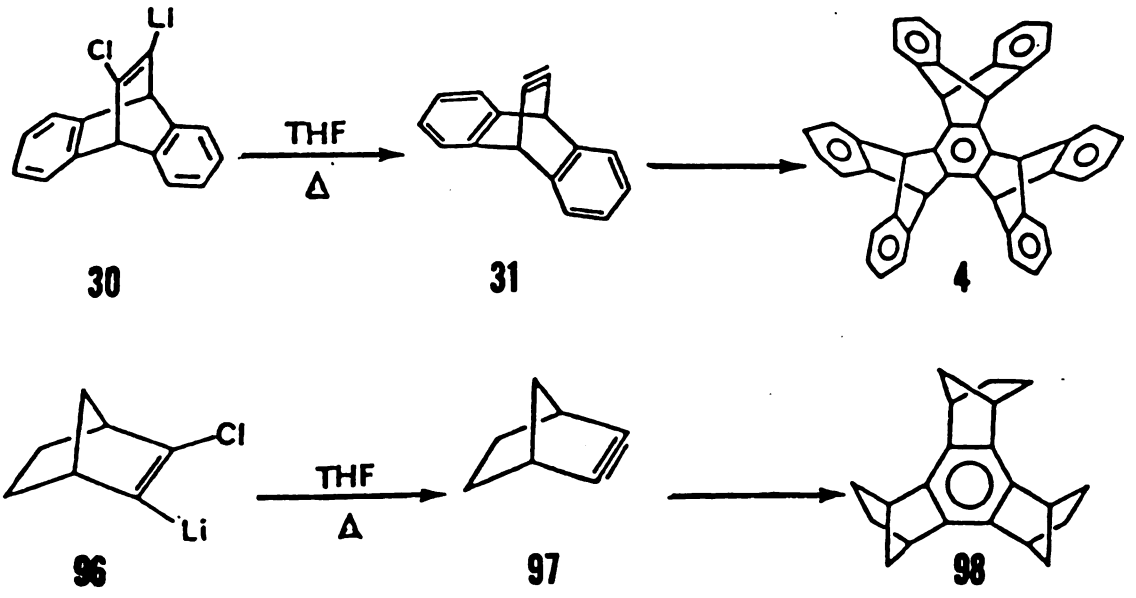
The formation of these lithiated species has been proved by trapping with electrophiles, through which a variety of substituted derivatives of 95 and 29 have been prepared.



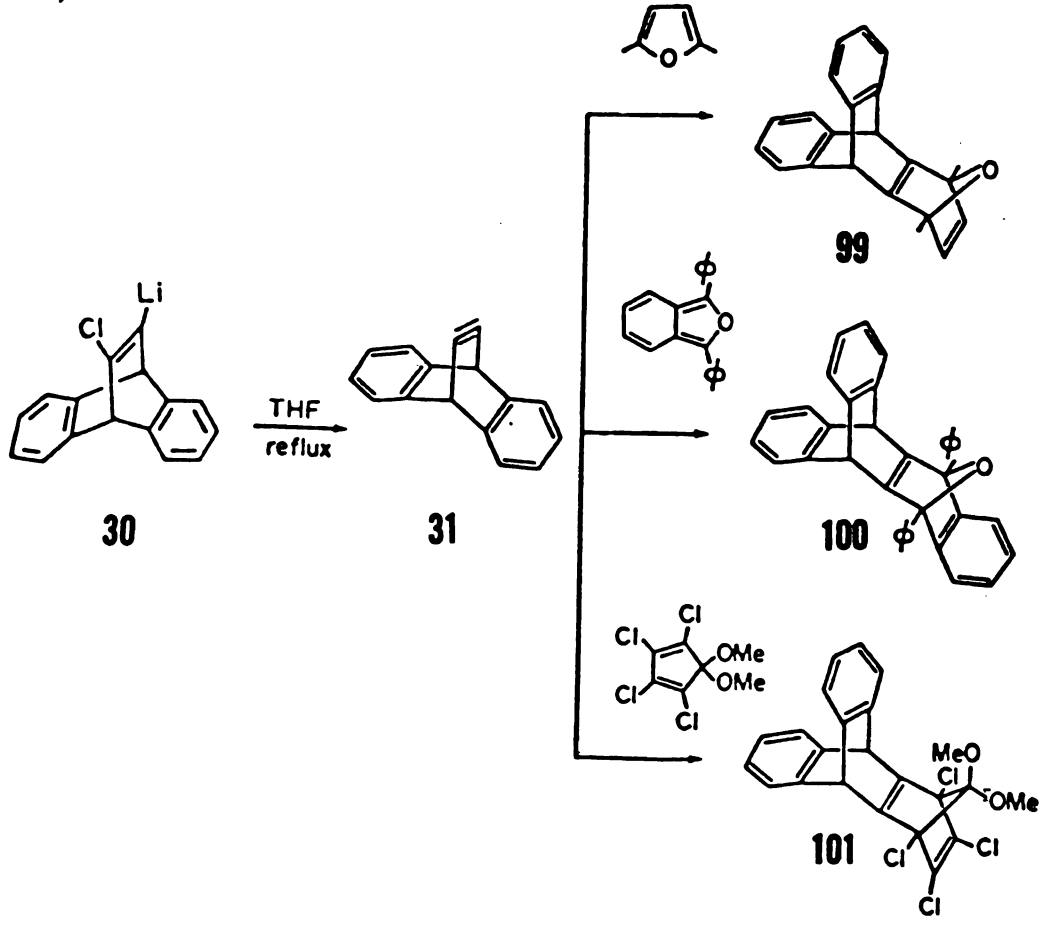


E = Br , D , CH_3 , $Si(CH_3)_3$

Heating THF solutions of 96 or 30 afforded the trimeric products 98 and 4, respectively, presumably via the cycloalkyne intermediates 97 and 31.[66,57]

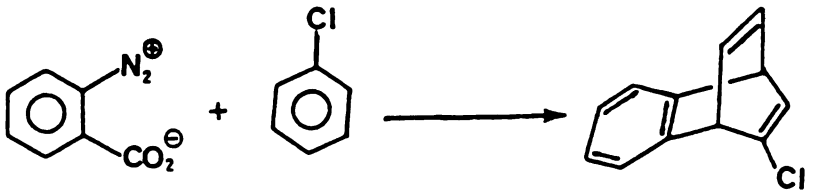


Bicycloalkyne **31** has also been trapped with several dienes, such as dimethylfuran, 1,3-diphenylisobenzofuran and 1,1-dimethoxytetrachlorocyclopentadiene to give the expected cycloadducts **99**, **100**, and **101**, respectively.[57] There is no evidence for **97** being trapped by any diene, however.



RESULTS AND DISCUSSION

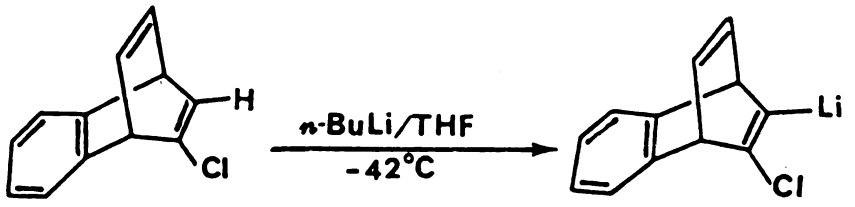
As part of a continuing study of bridged bicycloalkynes, regarding their occurrence, their dienophilic and electrophilic reactivity and the mechanism of the oligomerization of these species, 1-chloro-1,4-dihydro-1,4-ethenonaphthalene **102** was prepared in 30-40% yield and gram quantities, by heating a suspension of benzenediazonium carboxylate in chlorobenzene at 55°C for 12-16 hours.[67]



102

The lithiation of **102** was achieved by treating a THF solution of this compound at -42°C with n-butyllithium, to give **103**.

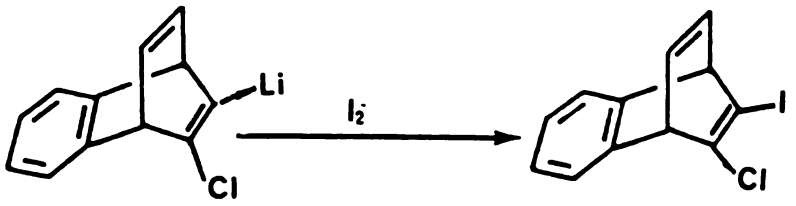
103 is relatively stable at room temperature. Its formation was demonstrated by addition of various electrophiles to THF solutions containing **103** at room temperature.



102 **103**

1. Reaction of 103 With Iodine

Addition of a solution of iodine in THF to a solution of **103** in THF resulted in the formation of **104**.

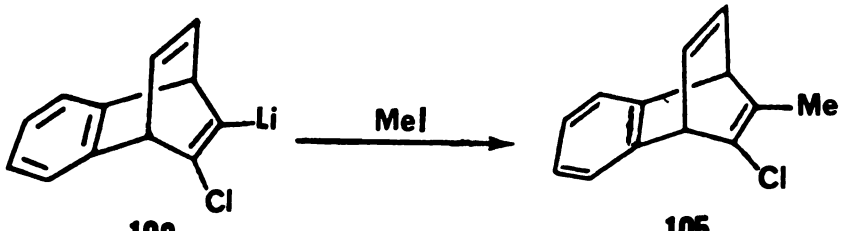


103 104

The structure of **104** was confirmed by its mass and ^1H NMR spectra. The mass spectrum of **104** showed a molecular ion peak at m/e 316. The ^1H NMR spectrum showed two one-proton doublet of doublets at δ 4.85 and 4.95 for the two bridgehead protons, a set of doublet of doublets at δ 6.78 for the two vinylic protons, and two sets of doublet of doublets for the aromatic protons.

2. Reaction of **103** with Methyl Iodide

Methyl iodide reacted with **103** at room temperature within one hour to give 2-chloro-3-methyl-1,4-dihydro-1,4-ethenonaphthalene **105** in 86% yield.

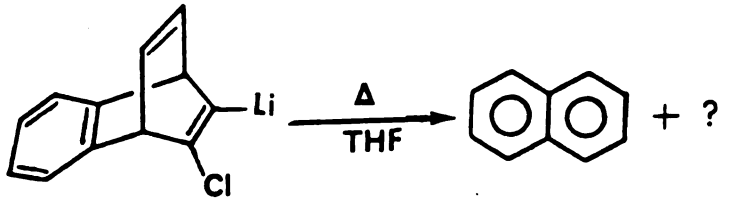


103 105

Mass spectrum of **105** gave a molecular ion peak at m/e 202. The ^1H NMR spectrum showed a singlet at δ 1.84 for the methyl protons, two sets of doublets of doublets at δ 4.56 and 4.67 for the bridgehead protons, and two sets of multiplets in the aromatic region for the vinylic and aromatic protons. The ^{13}C NMR spectrum, which showed a peak at δ 16.89 for the methyl carbon atom, two peaks at δ 55.09 and 56.44 for the bridgehead carbon atoms and appropriate peaks for the rest of the carbon atoms, supported this structure.

3. Attempted Generation of a Bicycloalkyne from 103

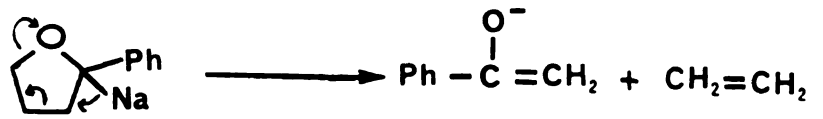
Heating a solution of 103 in THF at reflux for two hours resulted in the disappearance of the starting material. Work up and purification of the reaction mixture gave a white solid in 47% yield, whose melting point, mass and ^1H NMR spectra corresponded to those of naphthalene.

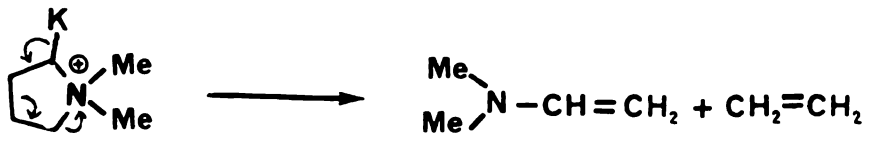


103

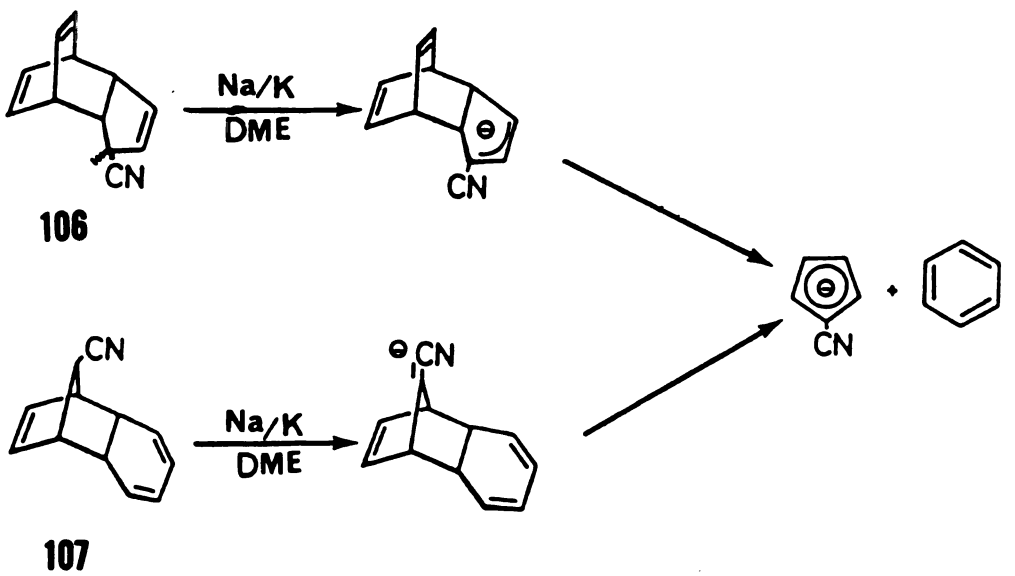
Naphthalene has been shown to be one of the primary products formed from the pyrolysis of indanetrione in chlorobenzene at 500°C, evidently through the thermal decomposition of 102.[68] We repeated this experiment by heating a neat sample of 102 at 350°C in a sealed tube. We found that naphthalene, 1-chloronaphthalene and 2-chloronaphthalene were formed in a 1:0.8:2 ratio respectively, a result that is fairly consistent with those reported.

Notice that both ethenyl bridges are lost in the pyrolysis of 102, whereas only the halogen-bearing bridge is eliminated from 103. Formation of naphthalene from 103 suggested an anion assisted cycloreversion reaction. Such reactions are well documented in the literature. The fragmentation of 2-phenyl tetrahydrofuran and N,N-dimethyl tetrahydropyrollidium iodide in the presence of strong bases are possibly the first examples of such reactions.[69,70]



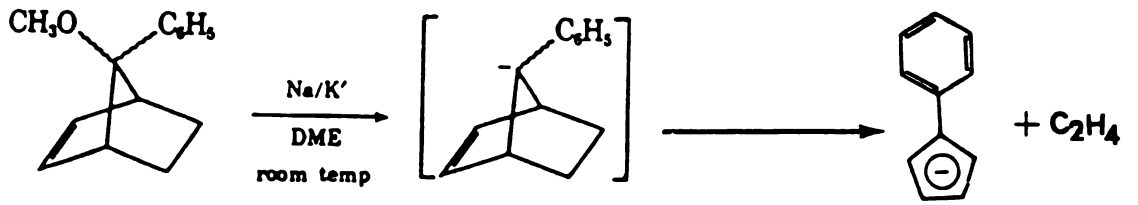


Oxyanion assisted [1,3]- and [3,3]-sigmatropic rearrangements and [4+2] retro-Diels-Alder reactions are other examples of cycloreversion reactions.[71] Grime and coworkers predicted that cycloreversions become exothermic if they combine the formation of aromatic systems with the release of ring strain.[73] Accordingly, they found that the pair of 5-cyanocyclopentadiene adducts to benzene **106** and **107**, upon treatment with LiTMP, cyclorevert within a minute to the cyanocyclopentadiene anion and benzene.



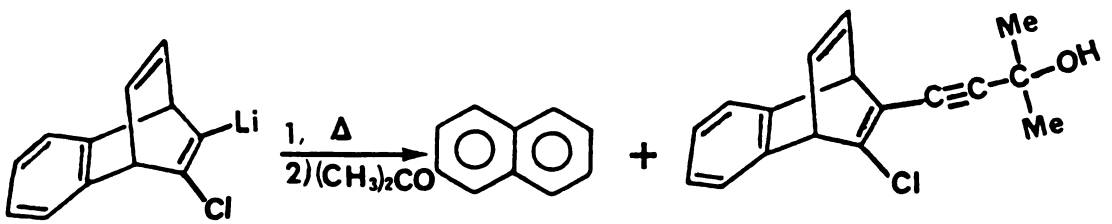
Similarly, Grutzner, et. al.[73] found that a mixture of syn- and anti-7-methoxy-7-phenylnorbornene in dimethoxyethane, when treated with sodium-

potassium alloy, underwent cycloreversion at room temperature in 30 minutes to give the phenylcyclopentadiene anion 108.



108

Whether naphthalene was a primary product resulting from the retro-Diels-Alder reaction of 103, or was formed via other pathways was resolved by trapping the missing fragment in this reaction by acetone. The ^{1}H NMR spectrum of the crude reaction mixture, after complete evaporation of the solvent, showed a 1:1 mixture of naphthalene and another compound. This compound was separated and characterized as 109 based on its mass, ^{1}H NMR and ^{13}C NMR spectra.

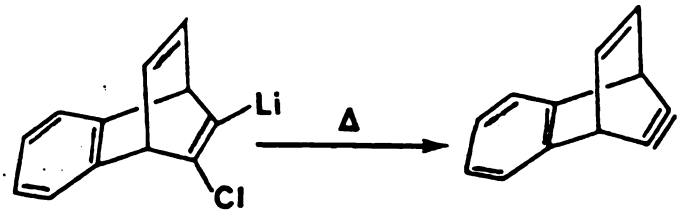


103 109

The mass spectrum of 109 showed a molecular ion peak at m/e 270. The ^{1}H NMR spectrum showed a six proton sharp singlet at δ 1.48 for the methyl groups, two one-proton triplets at δ 4.71 and 4.78 for the bridgehead protons and two sets of multiplets for the six vinylic and aromatic protons. The peak for the hydroxyl proton appeared at δ 2.16 as a broad singlet. The ^{13}C NMR spectrum of 109 showed a peak at δ 31.83 for the

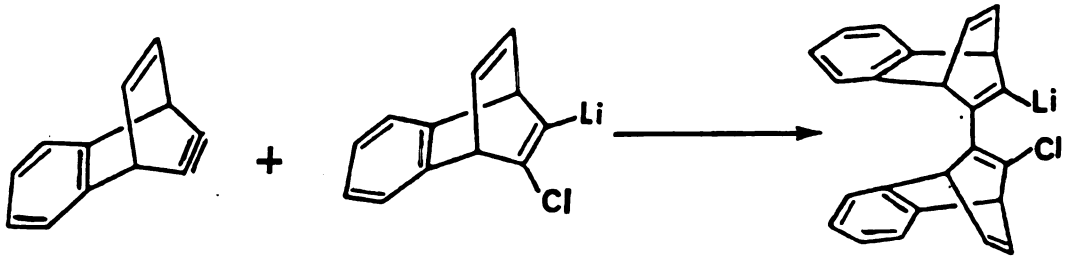
two methyl carbon atoms, two peaks at δ 54.34 and 56.63 for the bridgehead carbon atoms, a small peak at δ 66.27 for the carbon atom bearing the hydroxy group and the appropriate peaks for the rest of the carbon atoms.

Formation of 109 in a 1:1 ratio with naphthalene indicates that naphthalene is not a primary product in this reaction. More important, it suggests that the bridged bicycloalkyne 110 is first formed.



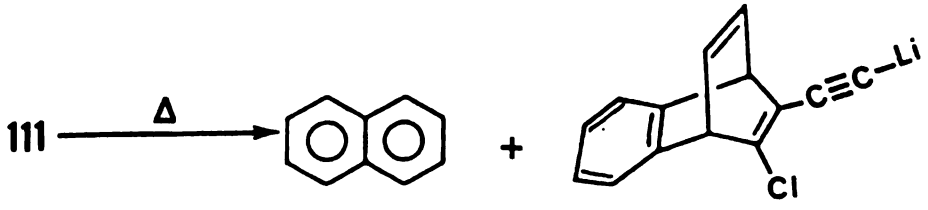
103 110

Upon formation, 110 reacts with one equivalent of 103 to give the coupling product, intermediate 111.



110 103 111

Subsequently, 111 undergoes a retro-Diels-Alder reaction to give naphthalene and the acetylene derivative 112.



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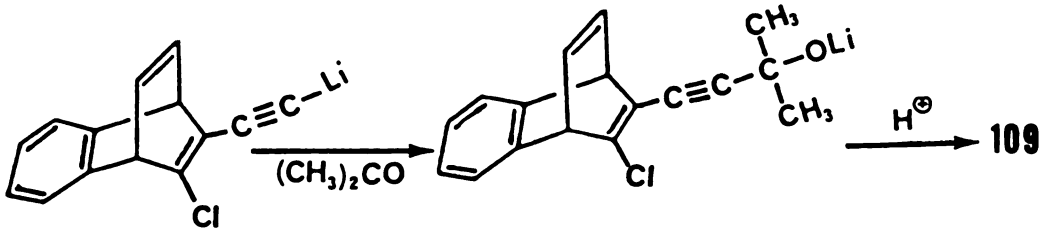
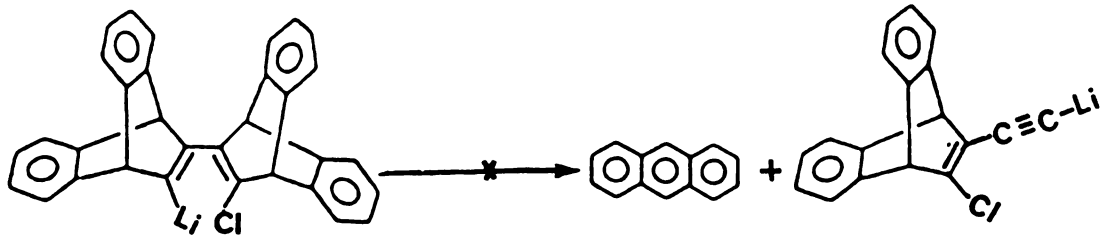
Reaction of **112** with acetone gives the lithium alkoxide derivative **113**. Protonation of **113** during the work up then affords the observed product **109**.



112 **113**

4. Attempted Trapping of 110 With 1,3-Diphenylisobenzofuran

An attempt to trap the bridged bicycloalkyne **110** with 1,3-diphenylisobenzofuran failed to give any cycloadduct. Instead naphthalene was formed via the same sequence of reactions described above. The facile retro-Diels-Alder reaction of **111** prompted us to investigate the possibility of a similar reaction in the dibenzobicyclic system **29**. Thus the coupling product **57** was synthesized *in situ* in toluene. The reaction mixture was heated at reflux for 12 hours. Since the T.L.C. analysis of the reaction mixture during the course of the reaction did not show any significant change, the reaction was stopped.



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The greater stability of **57** in comparison with **111** can be rationalized based on the resonance energy gained through the retro-Diels-Alder reaction. Assuming that breaking two bonds in both systems requires approximately the same amount of energy, then the energy gained through resonance by **111** amounts to:[74]

$$DRE_{naphthalene} + DRE_{benzene} = 33 - 21 = 12 \text{ Kcal/mole}$$

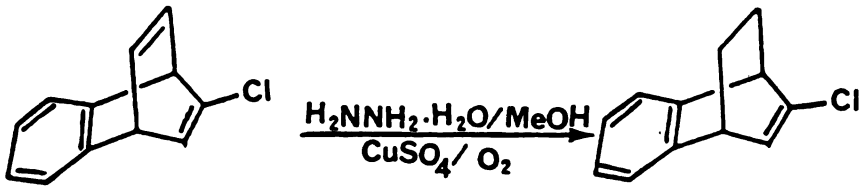
By the same token, for **57**:

$$DRE_{naphthalene} - 2DRE_{benzene} = 43 - 2 \times 21 = 1 \text{ Kcal/mole}$$

Thus, **111** is predicted to be about 11 Kcal/mole less stable than **57**. Since in the pyrolysis of **102**, via a retro-Diels-Alder reaction, naphthalene and 2-chloronaphthalene are the only products expected, the 1-chloro-isomer must be a secondary product. It is possibly formed through the isomerization of the 2-chloro-isomer. The isomerization of 1-chloronaphthalene to 2-chloronaphthalene and the reverse reaction, in the presence and absence of catalysts at elevated temperatures is well established.[75]

5. Reduction of 102

Based on the conclusion drawn from the above argument, we decided to block the retro-Diels-Alder reaction of **111** by reducing the unsubstituted vinylic double bond in **102**. The selective reduction of **102** was achieved using hydrazine as the reducing agent.[76] The reduction was carried out according to the literature, the course of the reduction being monitored by ^1H NMR spectroscopy in order to avoid over reduction.

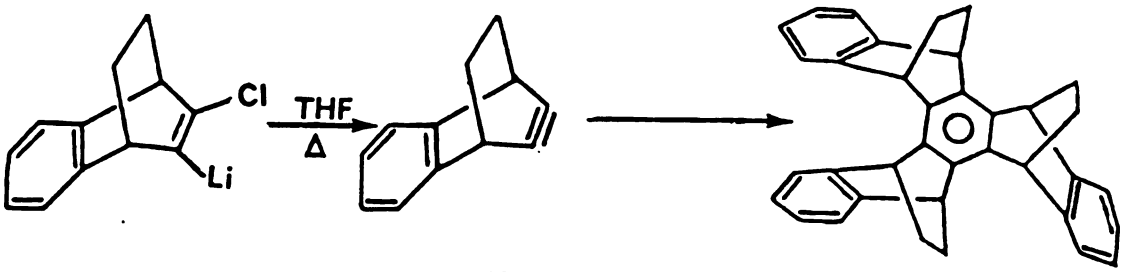


102 **114**

Compound 114 was obtained as a colorless liquid in 88% yield and was characterized by its mass, ^{1}H NMR and ^{13}C NMR spectra. The mass spectrum of 114 showed a molecular ion peak at m/e 190. The ^{1}H NMR spectrum showed three sets of multiplets at δ 1.39, 1.57 and 1.74 for 1,1 and 2 protons of the saturated bridge, a multiplet at δ 3.87 for the bridgehead protons, a doublet of doublets for the vinyl proton at δ 6.24 and a multiplet at δ 7.06 for the four aromatic protons. The ^{13}C NMR showed a peak at δ 26.49 for the saturated bridge carbon atoms, two peaks at δ 42.04 and 48.94 for the two bridgehead carbon atoms and the appropriate peaks for the remaining carbon atoms.

6. Synthesis of 1,2,3,4,5,6,7,8,9,10,11,12-dodecahydro-1,4:5,8:9,12-tri-o-benzenotriphenylene (116)

Treating a solution of 114 in THF with n-butyllithium at -42°C followed by refluxing the reaction mixture for one hour gave a single product in 9% yield. This product was characterized as 116 based on its mass, ^{1}H NMR and ^{13}C NMR spectra.



114 115 116

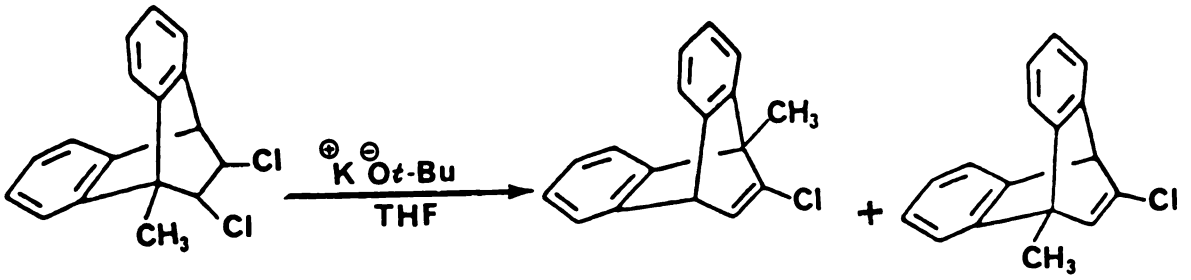
The mass spectrum of this compound showed a molecular ion peak at m/e 462. The ^{1}H NMR spectrum showed a 12 proton singlet at δ 1.76 for the ethano-bridge hydrogens, a 6 proton singlet at δ 4.71 for the bridgehead

hydrogens and two sets of doublet of doublets at δ 6.96 and 7.15 for the 12 aromatic protons. The ^{13}C NMR spectrum showed a peak at δ 27.21 for the six equivalent methylene carbon atoms, a peak at δ 39.91 for the six methyne bridgehead carbon atoms, three peaks for the carbon atoms on the peripheral aromatic rings and a single peak for the central benzene ring. The ^{1}H NMR and ^{13}C NMR spectra are consistent with those predicted for the syn-syn-syn (C_{3h}) isomer. The yield of **116** was calculated based on the pure sample used for elemental analysis, which was obtained from several consecutive recrystallizations. Isolation of **116** not only is a strong indication for the occurrence of bridged bicycloalkyne **115**, but also a proof that the resonance energy is a major contributor to the retro-Diels-Alder reaction of **111**.

In the previous chapters we have shown some evidence that the trimerization of bridged bicycloalkynes involves a stepwise pathway (optimizing the yield of **32**, trapping of **111**). The last step is the cyclization of the hexatriene moiety with the simultaneous loss of lithium chloride to give benzene. In order to examine this idea further, we thought the presence of bulky groups at the bridgehead positions might provide enough steric hinderance to obstruct this step. In this regard, we synthesized the mono-methyl substituted compounds **118** and **119**.

7. Synthesis of 11-chloro-9-methyl-9,10-ethenoanthracene (**118**) and its 12-chloro isomer (**119**).

The two isomeric compounds were obtained in a 1:1 ratio from the dehydrohalogenation of **117** in 94% yield.[77]



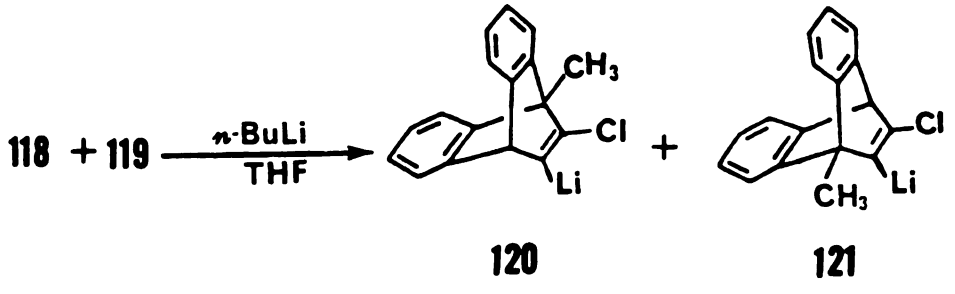
117 118 119

The isomers were separated by fractional recrystallization and their structures were confirmed by their mass, ^{1}H NMR and ^{13}C NMR spectra. The mass spectrum of both 118 and 119 showed a molecular ion peak at m/e 252. The ^{1}H NMR spectrum of 118 showed a three proton singlet at δ 2.15 for the methyl hydrogens, a doublet at δ 5.01 for the single bridgehead proton, a one-proton doublet at δ 6.93 for the vinyl hydrogen and two sets of multiplets for the eight aromatic protons. The ^{13}C NMR spectrum of 118 showed a peak at δ 15.30 for the methyl carbon atom, a peak at δ 50.90 for the methyl substituted bridgehead carbon atom, a peak at δ 58.57 for the other bridgehead carbon atom and the appropriate peaks for the remaining carbon atoms. The ^{1}H NMR spectrum of 119 showed a three-proton singlet at δ 2.20 for the methyl hydrogens, a one-proton singlet at δ 4.94 for the bridgehead hydrogen, a one-proton singlet at δ 6.41 for the vinyl hydrogen and two four-proton multiplets for the aromatic hydrogens. The ^{13}C NMR spectrum of 119 showed a peak at δ 13.75 for the methyl carbon atom, a peak at δ 51.25 for the tertiary bridgehead carbon atom, a peak at δ 53.45 for the methyl-substituted bridgehead carbon atom and appropriate peaks for the rest of the carbon atoms. The assignment of the two structures 118 and 119 to the isomers was mainly based on the chemical shifts of the vinyl protons. An upfield shift

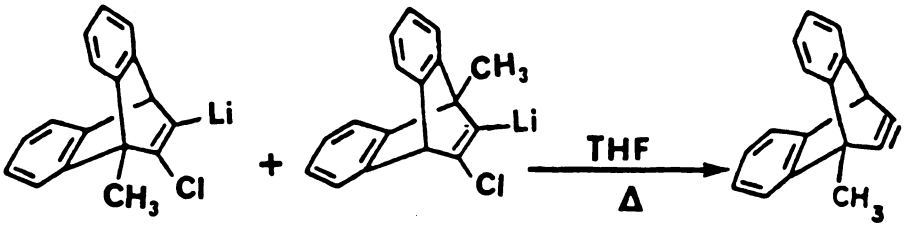
(0.52 ppm) of the vinyl proton in **119** was attributed to the shielding effect of the methyl group, due to their proximity.

8. Trapping the Cycloalkyne Generated from **118** and **119** by 1,3-diphenylisobenzofuran.

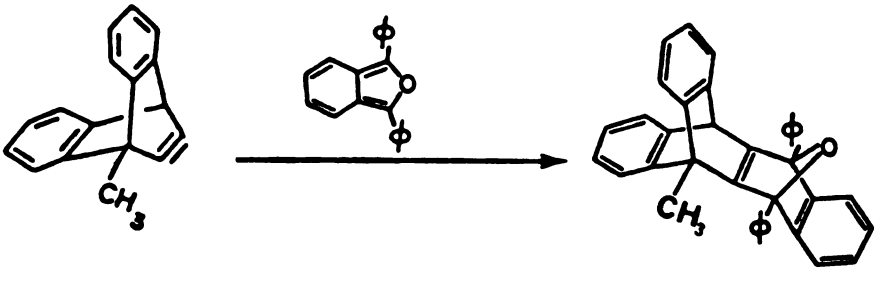
Heating at reflux a THF solution of **120** and **121** prepared by treating a 1:1 mixture of **118** and **119** with n-butyllithium at -78°C, in the presence of 1,3-diphenylisobenzofuran for two hours afforded a single product **123** in 34% yield.



120 **121**



122



122 **123**

The mass spectrum of the coupling product 124 showed a molecular ion peak at m/e 468. The ^1H NMR of 124 showed two three-proton singlets at δ 1.62 and 2.11 for the methyl groups, a one-proton doublet for the bridgehead hydrogen β-to the vinyl proton at δ 4.67, a one proton singlet for the bridgehead hydrogen β-to the chlorine atom at δ 4.96 and a one-proton doublet at δ 6.14 for the vinyl proton. The 16 aromatic protons appeared as two sets of multiplets. The ^{13}C NMR spectrum of 124 showed two peaks at δ 14.30 and 15.39 corresponding to the methyl carbon atoms, two peaks at δ 49.82 and 53.68 for the quaternary bridgehead carbon atoms, two peaks at δ 52.71 and 55.76 for the tertiary bridgehead carbon atoms, and the appropriate peaks for the remaining carbon atoms.

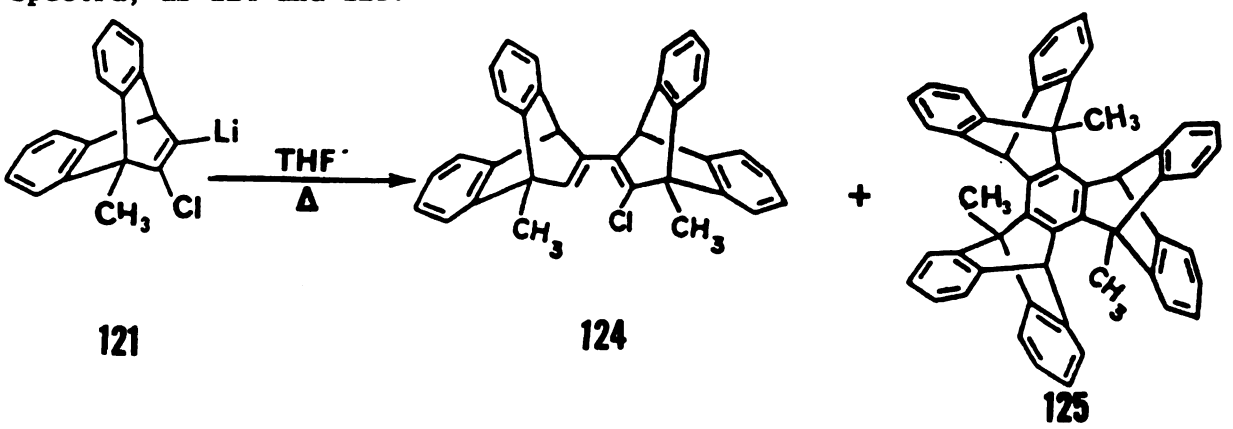
The mass spectrum of 125 showed a molecular ion peak at m/e 648. The ^1H NMR spectrum, as required by symmetry (C_3h) showed only four sets of peaks; a nine-proton singlet at δ 3.02 for the three methyl group hydrogens, a three-proton singlet at δ 6.73 for the bridgehead protons and two sets of 12 proton multiplets at δ 6.95 and 7.36 for the aromatic hydrogens. The ^{13}C NMR of 122 spectrum showed a peak at δ 20.19 for the three methyl group carbon atoms, a peak at δ 48.70 for the three tertiary bridgehead carbon atoms, a peak at δ 51.82 for the three quaternary bridgehead carbon atoms and a total of seven peaks for the aromatic carbon atoms.

A 3:1 mixture of 118 and 119 in THF, on the other hand, upon treatment with n-butyllithium at -78°C, followed by warming to room temperature and immediately refluxing for two hours, gave a mixture of three products 124, 126 and 127 in 72% overall yield.

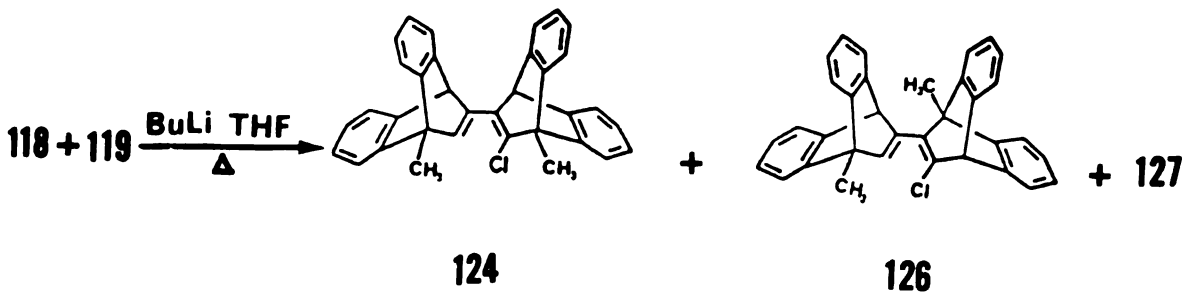
Compound 123 was characterized by its mass, ^{1}H NMR and ^{13}C NMR spectra. The mass spectrum showed a molecular ion peak at m/e 486. The ^{1}H NMR spectrum of 123 showed a three-proton singlet at δ 1.65 for the methyl hydrogens, a one-proton singlet at δ 5.24 for the bridgehead hydrogen and a 22-proton multiplet at δ 6.26-7.73 for the aromatic hydrogens. The ^{13}C NMR spectrum showed a peak at δ 18.70 for the methyl carbon atom, a peak at δ 50.60 for the methyl-substituted bridgehead carbon atom, a peak at δ 51.78 for the bridgehead carbon atom bearing a hydrogen and a peak at 65.52 for the two phenyl-substituted bridgehead carbon atoms. Due to the unsymmetric structure of 123, the peaks beyond 100 ppm do not provide any useful information. Isolation of 123 in this reaction strongly indicates the involvement of a single intermediate, namely the bridged bicycloalkyne 122.

9. Trimerization of Bridged Bicycloalkyne 122

Stirring a THF solution of pure 121 prepared by treating a solution of pur 117 in THF with n-butyllithium at -78°C, stirring for two hours at room temperature followed by heating at reflux for 30 minutes gave two products in 74% overall yield. The two products were separated and identified, based on their mass, ^{1}H NMR and ^{13}C NMR spectra, as 124 and 125.



121 124 125



124 126

The individual yields for **124**, **126** and **127** were 42%, 14% and 44% respectively. The ^{1}H NMR spectrum of **127** showed a six-proton doublet at δ 2.78, a six proton broad singlet at δ 3.02, four one-proton singlets at δ 6.02, 6.08, 6.71 and 6.73 and two sets of 16-proton multiplets at δ 6.96 and 6.37. The ^{1}H NMR spectrum pointed to a tetrameric species; however, the possibility of such a species was ruled out by the mass spectrum which showed a molecular ion peak at m/e 648 (trimer). Based on a comparison of the ^{1}H NMR spectrum of this product with that obtained for the symmetrical trimer, it was concluded that **127** was a 3:1 mixture of **128** and **125** (Figure 7). Unfortunately, attempts to separate these two isomers failed.

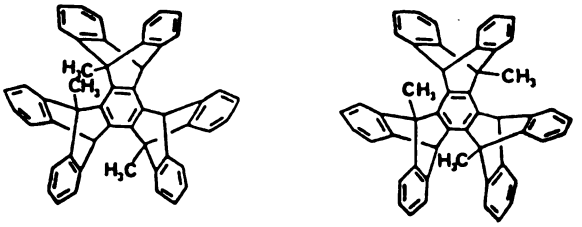
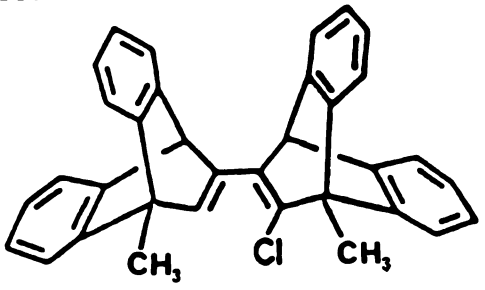


Figure 7. Structural representation of the isomeric trimers 128 and 125 obtained from the trimerization of the bicycloalkyne 122.

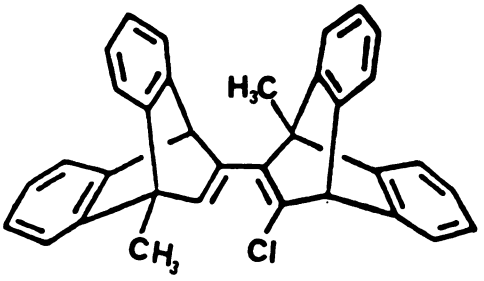
The structure of the coupling product **126** was confirmed by its mass, ^{1}H NMR and ^{13}C NMR spectra. The mass spectrum showed a molecular

ion peak at m/e 468. The ^1H NMR spectrum showed two three-proton singlets at δ 2.14 and 2.16 for the two methyl groups, a one-proton singlet at δ 4.99 for the bridgehead hydrogen adjacent to the chlorine atom, a one-proton doublet for the other bridgehead hydrogen at δ 5.66, a one-proton doublet at δ 6.68 for the vinyl hydrogen and two 8-proton multiplets for the aromatic hydrogens. The ^{13}C NMR spectrum showed six peaks for the sp^3 hybridized carbon atoms as expected and a total of 16 peaks for the sp^2 hybridized carbon atoms as required by symmetry (plane).

Based on the intermediacy of the cycloalkyne 122, four isomeric coupling products are expected for these reactions, 124, 126, 129, and 130.



124



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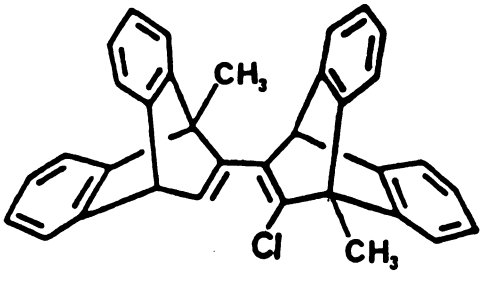
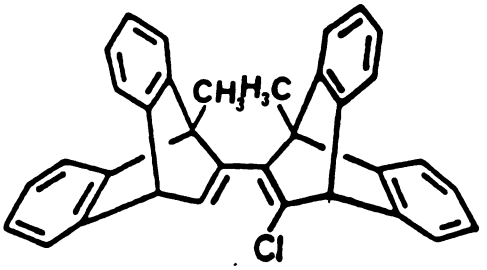


129



130

The absence of the coupling product 129 and the exclusive formation (>95%) of the trimer with C_3h symmetry in the trimerization reaction of pure 121 suggests that: (a) only 129 is involved in the

formation of 125 (since 124 leads to 128) possibly due to steric hindrance, and (b) the addition of the cycloalkyne 122 to 129 must take place regiospecifically, since an indiscriminate attack of 122 on 126 would lead to the formation of both trimeric species. Further support for the above argument is the absence of 127 and the formation of a 3:1 mixture of 128 and 125, when a 3:1 mixture of 118 and 119 is used for this reaction.

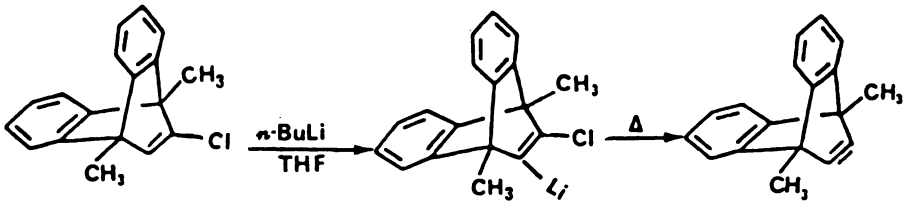
10. Synthesis of 11-chloro-9,10-dimethyl-9,10-ethenoanthracene (131)

Although the presence of a methyl group at the bridgehead position of the cycloalkyne 122 might have been responsible for part of the unexpected results in the trimerization reactions, apparently it is not bulky enough to obstruct the cyclization process. Thus we decided to synthesize a more sterically hindered bridged bicycloalkyne precursor. In this regard, compound 131 was prepared by a procedure similar to that used for 118. The structure of 131 was confirmed by its mass and ^{1}H NMR spectra. The mass spectrum of this compound showed a molecular ion peak at m/e 266. The ^{1}H NMR spectrum showed two three-proton singlets at δ 2.08 and 2.13 for the methyl groups, a one-proton singlet at δ 6.55 for the vinyl hydrogen and two four-proton multiplets for the aromatic hydrogens.

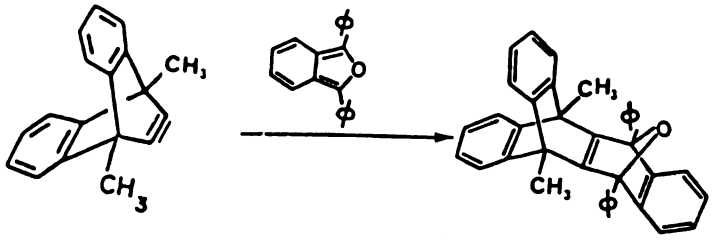
11. Synthesis of 6,11-dimethyl-5,12-diphenyl-5,12-oxo-6,11-o-benzenonaphthacene 134

Stirring a solution of 131 and 1.1 equivalent n-butyllithium in THF in the presence of 1,3-diphenyl isobenzofuran for two hours,

followed by heating the reaction mixture at reflux for another two hours afforded the expected cycloadduct 134 in 19% yield as a white solid.



131 132 133

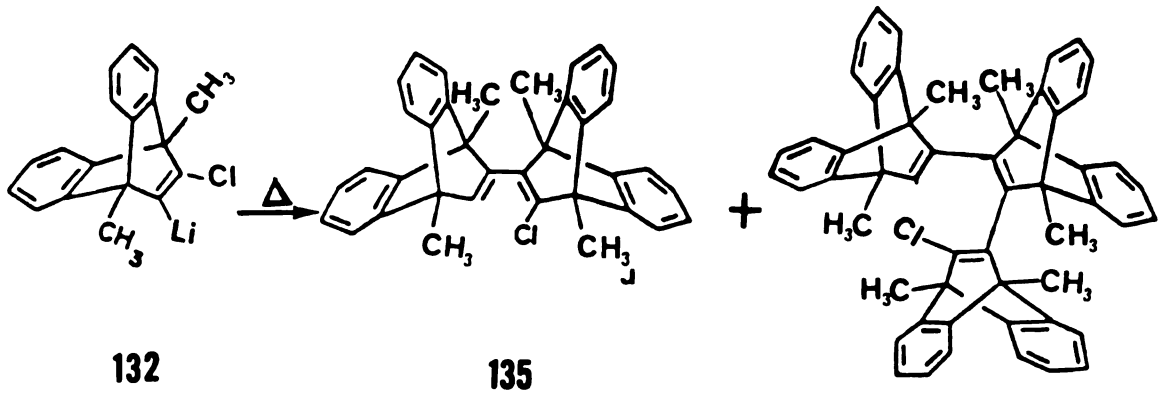


133 134

The structure of this compound was confirmed by its mass, ^{1}H NMR and ^{13}C NMR spectra. The mass spectrum of 134 showed a molecular ion peak at m/e 500. The ^{1}H NMR spectrum showed a six-proton singlet at δ 1.82 for the methyl groups and six sets of multiplets at δ 6.64-7.73 for the 22 aromatic protons. The ^{13}C NMR spectrum showed a peak at δ 15.53 for the two methyl carbon atoms, a peak at δ 51.49 for the two methyl substituted bridgeheads, a peak at δ 66.65 for the oxygen-bridged carbon atoms and a total of 12 peaks for the sp^2 hybridized carbon atoms, as required by symmetry.

12. Attempted Trimerization of 133

Heating a solution of 132 in THF at reflux for two hours gave two products, 135 and 136 in 37% overall yield, and in individual yields of 26% and 11% respectively.



132 135 136

Compound 135 was characterized by its mass, ^{1}H NMR and ^{13}C NMR spectra. The mass spectrum of 135 showed a molecular ion peak at m/e 496. The ^{1}H NMR spectrum showed four three proton singlets for the methyl group hydrogens, a one proton singlet for the vinyl hydrogen and four sets of multiplets for the 16 aromatic hydrogens. The ^{13}C NMR spectrum showed four peaks for the methyl group carbon atoms, three peaks (overlap) for the four bridgehead carbon atoms and the appropriate peaks for the sp^2 hybridized carbon atoms as required by symmetry (Cs).

Compound 136 was characterized from its ^{1}H NMR and ^{13}C NMR spectra. The ^{1}H NMR spectrum of 136 showed six three-proton singlets for the six methyl groups, a one-proton singlet at δ 5.96 for the vinyl hydrogen and a 24-proton multiplet at δ 6.37-7.36 for the aromatic hydrogens. The ^{13}C NMR spectrum showed six peaks for the six methyl group carbon atoms and 15 peaks for the sp^2 hybridized carbon atoms. The peaks corresponding to the bridgehead carbon atoms were not obvious. Moreover, the mass spectrum of this compound did not show a molecular ion peak.

In conclusion, the absence of any trimer in the attempted trimerization of **133** and the isolation of the hexatriene derivative **136** in this experiment, as well as the other results obtained in the course of this study, strongly suggests a stepwise mechanism (p. 17) for the trimerization of the [2.2.2]bicycloalkyne systems, by the dehydrohalogenation method.

EXPERIMENTAL

1. 2-Chloro-3-iodo-1,4-dihydro-1,4-ethenonaphthalene (104)

To a solution of 1.9 g (10 mmol) of 2-chloro-1,4-dihydro-1,4-ethenonaphthalene in 25 mL of anhydrous THF under argon at -78°C was added dropwise 4.4 mL (1.1 equivalent) of 2.5 M n-butyllithium in hexanes. The solution was stirred for two hours, brought to 0°C and stirred at this temperature for 30 minutes, then quenched with 1.40 g (11 mmol) of iodine in THF. The solvent was removed and the brown oily residue was taken up in ether. The ether solution was washed with saturated sodium bisulfate solution, water, and saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Evaporation of the solvent and chromatography of the residue on a silica gel column using hexanes as eluent gave 2.93 g (93%) of **104** as an off-white solid; m.p. 85-86°C, ^{1}H NMR ($CDCl_3$) δ 4.85 (dd,1H), 4.95 (dd, 1H), 6.78 (dd,2H), 6.9 (dd,2H), 7.16 (dd,2H); ^{13}C NMR ($CDCl_3$) δ 57.51, 61.66, 97.50, 122.91, 124.79, 137.92, 139.37, 144.58, 145.41, 147.91; mass spectrum m/e (relative intensity) 316 (10), 314 (24), 189 (17), 187 (52), 152 (100), 125 (8), 76 (15). Anal. Calcd. for $C_{12}H_8ClI$: C, 45.80; H, 2.56. Found: C, 45.68; H, 2.51.

2. 2-Chloro-3-methyl-1,4-dihydro-1,4-ethenonaphthalene 105

To a solution of 0.38 g (2 mmol) of 2-chloro-1,4-dihydro-1,4-ethenonaphthalene in 10 mL of anhydrous THF under argon at -78°C was added dropwise 1.0 mL (1.1 equivalent) of 2.2 M n-butyllithium in hexanes. The solution was stirred for two hours, brought to 0°C and stirred at this temperature for 30 minutes. Methyl iodide (excess) was added and the mixture was stirred for another hour. The solvent was

removed and the oily material was taken up in ether. The ether solution was washed with water, saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Evaporation of solvent and chromatography of the oily residue on a silica gel column using hexanes as eluent gave 0.35 g (86%) of **105** as a colorless liquid which was crystallized from pentane upon cooling in the freezer; m.p. 62-63°C; ^{1}H NMR ($CDCl_3$) δ 1.84 (s,3H), 4.56 (dd,1H), 4.67 (dd,1H), 6.90 (m,4H), 7.17 (m,2H); ^{13}C NMR ($CDCl_3$) δ 16.89, 55.09, 56.44, 122.49, 124.49, 129.66, 139.54, 145.19, 146.63; mass spectrum m/e (relative intensity) 204 (12), 202 (36), 168 (17), 167 (100), 166 (22), 165 (41), 152 (43). Anal. Calcd. for $C_{13}H_{11}Cl$: C, 77.03; H, 5.47. Found: C, 76.94; H, 5.43.

3. Attempted trapping of **110** with 1,3-diphenylisobenzofuran

To a solution of 0.37 g (2.0 mmol) of 1,3-diphenylisobenzofuran in 25 mL of anhydrous THF at -78°C under argon was added dropwise 1.0 mL (1.1 equivalent) of 2.2 M n-butyllithium in hexanes. The solution was stirred for two hours, brought to room temperature and heated at reflux for two hours. Methanol (1 mL) was added, the solvent was removed and the oily material was taken up in ether. The ether solution was washed with water, saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was chromatographed on a silica gel column using 3:1 hexanes/ether as eluent. Naphthalene and a compound whose molecular weight corresponded to that of isobenzofuran plus an atom of oxygen were the only products.

4. Attempted trimerization of **110**

To a solution of 0.75 g (4 mmol) of 2-chloro-1,4-dihydro-1,4-ethenonaphthalene in 25 mL of anhydrous THF under argon at -78°C was

added dropwise 2 mL (1.1 equivalent) of 2.2 M n-butyllithium in hexanes. The reaction mixture was stirred for two hours, brought to room temperature and then heated at reflux for two hours. After cooling to room temperature the excess n-butyllithium was quenched with methanol. The solvent was removed and the residue was taken up in methylene chloride. The methylene chloride solution was washed with water, saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Evaporation of the solvent and chromatography of the dark brown residue on a silica gel column using 5:1 hexanes/methylene chloride as eluent gave 0.36 g (70%) of a white crystalline material; m.p. 80-82°C which was found to be naphthalene (mass spectrum, NMR).

5. Thermal decomposition of 2-chloro-1,4-dihydro-1,4-ethenonaphthalene

A solution of 0.19 g (1.0 mmol) of 2-chloro-1,4-dihydro-1,4-ethenonaphthalene in 0.5 mL of hexanes was flashed through a (5 mm diameter, 50 cm length) pyrex column packed with glass helices heated to 400°C. The material collected at the end of the column showed only recovered starting material. In a second experiment the same amount of the neat compound was melted and flashed through the column. The material collected at the end of the tube was found to be the starting material (G.C., NMR). In a third experiment the same amount of the pure compound was placed in a small sealed tube and was heated at 350°C for 5 minutes. The tube was cooled to room temperature and opened. The dark brown material in the tube was dissolved in methylene chloride, absorbed onto a silica gel plate and eluted with hexanes. The polymeric materials were discarded, and the combined hexane soluble materials were analyzed by G.C. The G.C. results showed the presence of four different

compounds, the starting material, naphthalene, 1-chloronaphthalene, and 2-chloronaphthalene with the 1:0.8:2 ratio respectively.

6. 2-Chloro-1,4-dihydro-1,4-ethanonaphthalene 114

To a solution of 1.9 g (10 mmol) of 2-chloro-1,4-dihydro-1,4-ethenonaphthalene in 30 mL of 95% ethanol was added 1 mL (excess) of hydrazine monohydrate solution and a catalytic amount of cupric sulfate. The reaction mixture was stirred for eight hours while air was bubbling through. After the starting material completely disappeared (the course of the reaction was monitored by NMR) petroleum ether (100 mL), along with 50 mL of water, was added. The organic layer was separated, washed with water, saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The solvent was evaporated and the oily residue was vacuum pumped for 24 hours. Chromatography of this oily material on a silica gel column using pentane as the eluent gave 1.65 g (88%) of 114 as a colorless oil. ^{1}H NMR ($CDCl_3$) δ 1.39 (m,2H), 1.57 (m,1H), 1.74 (m,1H), 3.87 (m,2H), 6.25 (dd,1H), 7.06 (m,4H); ^{13}C NMR ($CDCl_3$) δ 26.50, 42.00, 48.92, 122.87, 123.116, 125.65, 126.11, 126.70, 129.65, 137.90, 142.81, 143.46; mass spectrum m/e (relative intensity): 192 (5), 190 (3), 164 (33), 163 (14), 162 (100), 155 (11), 130 (10), 129 (16), 128 (11), 127 (19). Anal. Calcd. for $C_{12}H_{11}Cl$: C, 75.59; H, 5.81. Found: C, 75.42; H, 5.78.

7. Attempted trapping of 115 with 1,3-diphenyl isobenzofuran

To a solution of 0.38 g (2.0 mmol) of 2-chloro-1,4-dihydro-1,4-ethanonaphthalene and 0.60 g (2.2 mmol) of 2,3-diphenylisobenzofuran in 25 mL of anhydrous THF at -78°C under argon was added dropwise 1.0 mL (1.1 equivalent) of 2.2 M n-butyllithium in hexanes. The reaction

mixture was stirred for two hours, brought to room temperature, and heated at reflux for two hours. Methanol (1 mL) was added. The solvent was removed and the oily material was taken up in ether. The ether solution was washed with water, saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was chromatographed on a silica gel column using 3:1 hexanes/ether as eluent. The only identifiable products were a trace of trimer and a compound whose molecular weight corresponded to that of isobenzofuran plus one atom of oxygen.

8. 1,2,3,4,5,6,7,8,9,10,11,12-Dodecahydro-1,4,5.8,9.12-tri-o-benzenotriphenylene 116

To a solution of 0.76 g (4 mmol) of 2-chloro-1,4-dihydro-1,4-ethanonaphthalene in 25 mL of anhydrous THF under argon at -78°C was added dropwise 2.0 mL (1.1 equivalent) of 2.2 M n-butyllithium in hexanes. The solution was stirred for two hours, brought to room temperature and heated at reflux for one hour. The solution was quenched with methanol and the solvent was removed. The residue was taken up in methylene chloride. The methylene chloride solution was washed with water, saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was chromatographed on a silica gel column using 2:1 hexanes/chloroform as eluent. A yellow solid was obtained which was recrystallized several times from hexane-chloroform to afford 55 mg (9%) of a single trimer as a white solid; m.p. 314-316°C. ^{1}H NMR ($CDCl_3$) δ 1.76 (s,12H), 4.71 (s,6H), 6.96 (dd,6H), 7.17 (dd,6H); ^{13}C NMR ($CDCl_3$) δ 27, 39.91, 123.60, 125.75, 134.16, 144.72; mass spectrum m/e (relative intensity), 462 (4),

434 (16), 378 (35), 278 (31), 254 (100), 189 (45), 129 (34). Anal. Calcd. for $C_{36}H_{30}$: C, 93.46; H, 6.53. Found: C, 93.27; H, 6.45.

9. 11-Chloro-9-methyl-9,10-ethenoanthracene; 12-chloro-9-methyl-9,10-ethenoanthracene 118 and 119

To a solution of 5.8 g (20 mmol) of 11,12-dichloro-9-methyl-9,10-ethanoanthracene in 125 mL of THF was added 3.0 g (excess) of potassium t-butoxide. The reaction mixture was heated at reflux for 12 hours. The solvent was removed and the brown oily material was taken up in ether. The ether solution was washed with water, saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Evaporation of the solvent and chromatography of the residue on a silica gel column using hexanes as eluent gave 4.8 g (94%) of a 1:1 (NMR) mixture of two products. The two isomers were separated by fractional recrystallization from hexanes according to the following procedure. A concentrated solution of the mixture was left to stand in the refrigerator for 3-5 days, upon which crystallization occurred. The solution was diluted with hexanes and filtered. The crystals collected were found to be enriched in the 11-chloro-isomer which was further recrystallized from hexanes to give the pure product. The second isomer was purified by removing the hexanes from the mother liquor and recrystallizing from methanol. 11-chloro-9-methyl-9,10-ethenoanthracene; m.p. 132-133°C, ^{1}H NMR ($CDCl_3$) δ 2.15 (s,3H), 5.01 (d,1H), 6.93 (d,1H), 6.97 (m,4H), 7.28 (m,4H); ^{13}C NMR: ($CDCl_3$) δ 15.30, 50.90, 58.57, 120.40, 122.85, 124.69, 125.30, 136.90, 145.30, 145.91, 147.34; mass spectrum m/e (relative intensity) 252 (13), 218 (17), 217 (100), 215 (25), 202 (34), 120 (26), 108 (17). Anal. Calcd. for $C_{17}H_{13}Cl$: C, 80.82; H, 5.14. Found: C, 80.77; H, 5.16.

12-Chloro-9-methyl-9,10-ethenoanthracene: m.p. 108- 109°C. ^{1}H NMR ($CDCl_3$) δ 2.20 (s,3H), 4.94 (s,1H), 6.41 (s,1H), 7.00 (m,4H), 7.28 (m,4H); ^{13}C NMR ($CDCl_3$) δ 13.75, 51.25, 53.45, 120.85, 123.16, 124.58, 125.21, 134.54, 146.45, 147.50, 147.91; mass spectrum m/e (relative intensity), 252 (23), 218 (18), 217 (100), 216 (20), 215 (29), 202 (51), 192 (16). Anal. Calcd. for $C^{17}H^{13}Cl$: C, 80.82; H, 5.14. Found: C, 80.86; H, 5.12.

10. 5,12,-Diphenyl-11-hydro-6-methyl-5.12-oxo-6,11-0-benzenonaphthacene 123

To a solution of 0.50 g (2 mmol) of 11-chloro-9-methyl-9,10-ethenoanthracene and 0.60 g (2.2 mmol) of 1,3-diphenyl-isobenzofuran in 20 mL of anhydrous THF under argon at -78°C was added dropwise 1.0 mL (1.1 equivalent) of 2.2 M n-butyllithium in hexanes. The reaction mixture was stirred for 2 hours, brought to room temperature and heated at reflux for two hours. A small amount of methanol was added (1 mL) and the solvent was removed. The residue was taken up in methylene chloride. The methylene chloride solution was washed with water, saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Removal of the solvent and chromatography of the residue on a silica gel column using 1:2 hexane/methylene chloride as eluent gave 0.22 g of 123; m.p. 259-260°C. ^{1}H NMR ($CDCl_3$) δ 1.65 (s,3H), 5.24 (s,1H), 6.26 (d,1H), 6.72 (m,3H), 6.96 (m,7H), 7.09 (d,2H), 7.15 (m,2H), 7.27 (d,2H), 7.42 (m,3H), 7.58 (m,3H), 7.73 (d,2H); ^{13}C NMR ($CDCl_3$) δ 18.71, 50.60, 51.78, 65.52, 120.40, 122.65, 124.89, 126.66, 127.47, 127.72, 128.03, 128.37, 129.10, 129.48, 130.25, 131.94, 132.54, 133.41, 140.34, 141.28, 142.68, 143.61, 146.12; mass spectrum m/e (relative intensity), 487(35), 486(98), 472(10), 471(17), 409(35), 294(28),

265(88), 194(30), 192(100), 191(59). Anal. Calcd. for $C_{37}H_{26}O$: C, 91.32; H, 5.38. Found: C, 91.26; H, 5.33.

11. Trimerization of the bicycloalkyne 122 generated from 11 and 12-chloro-9-methyl-9,10-ethenoanthracene

To a solution of 5.1 g (20 mmol) of a mixture of 11 and 12-chloro-9-methyl-9,10-ethenoanthracene in 100 mL THF under argon at -78°C was added dropwise 8.8 mL (1.1 equivalent) of 2.5 M n-butyllithium in hexanes. The reaction mixture was stirred for one hour, brought to room temperature and heated at reflux for two hours. Methanol (2 mL) was added and the solvent was removed. The residue was taken up in methylene chloride, washed with water, saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Evaporation of the solvent and elution of the solid material with 3:1 hexanes/methylene chloride on a silica gel column gave 3.4 g(78%) of a mixture of three products. Compound A: m.p. 209-210°C; ^{1}H NMR ($CDCl_3$) δ 1.62 (s,3H), 2.11 (s,3H), 4.67 (d,1H), 4.94 (s,1H), 6.14 (d,1H), 6.98 (m,8H), 7.23 (m,8H); ^{13}C NMR ($CDCl_3$) δ 14.30, 15.39, 49.82, 52.71, 53.68, 55.76, 119.96, 120.49, 122.78, 123.40, 124.28, 124.72, 125.07, 140.36, 141.10, 145.51, 145.59, 146.92, 148.36, 150.04; mass spectrum m/e (relative intensity). Anal. Calcd. for $C_{34}H_{25}Cl$: C, 87.10; H, 5.33. Found: C, 86.96; H, 5.30.

Compound B: m.p. 259-261°C, ^{1}H NMR ($CDCl_3$) δ 2.14 (s,3H), 2.16 (s,3H), 4.99 (s,1H), 5.66 (d,1H), 6.68 (d,1H), 6.91 (m,8H), 7.20 (m,8H); ^{13}C NMR ($CDCl_3$) δ 15.45, 15.66, 50.47, 53.53, 56.26, 58.94, 120.28, 120.69, 123.43, 123.54, 124.57, 124.66, 125.16, 125.49, 141.63, 142.36, 144.72, 146.28, 147.78, 147.33, 147.77, 148.10, 148.72; mass spectrum

m/e (relative intensity) same as Compound A. Anal. Calcd. for $C_{34}H_{25}Cl$: C, 87.10; H, 5.33. Found: C, 87.04; H, 5.38.

Compound C was found to be a 3:1 mixture of isomeric trimers which could not be separated. However, the symmetrical trimer (C_3h) was formed exclusively when pure 11-chloro-isomer was used for trimerization. Compound C (C_3h) isomer; m.p. >500°C; ^1H NMR ($CDCl_3$) δ 3.02 (s,9H), 6.73 (s,3H), 6.95 (m,12H), 7.36 (m,12H); ^{13}C NMR ($CDCl_3$) δ 20.19, 48.70, 121.72, 123.48.125.74, 146.21, 148.30; mass spectrum m/e (relative intensity) 649(30), 648(95), 633(43), 456(21), 441(29), 426(28), 262(16), 191(76), 85(100). Anal. Calcd. for $C_{51}H_{36}$: C, 94.45; H, 5.55. Found: C, 94.33; H, 5.51.

12. 11-chloro-9,10-dimethyl-9,10-ethenoanthracene 131

To a solution of 6.1 g (20 mmol) of 11,12-dichloro-9,10-dimethyl-9,10-ethanoanthracene in 125 mL THF was added 3.0 g (excess) of potassium t-butoxide. The reaction mixture was heated at reflux for 16 hours. The solvent was removed and the residue was taken up in ether. The ether solution was washed with water, saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Evaporation of solvent and chromatography of the oily material on a silica gel column using hexanes as eluent gave 4.9 g (91%) of 131 as a white solid; m.p. 106-107°C, ^1H NMR ($CDCl_3$) δ 2.08 (s,3H), 2.12 (s,3H), 6.55 (s,1H), 6.99 (m,4H), 7.24 (m,4H).

13. Attempted Trimerization of 11-chloro-9,10-dimethyl-9,10-ethenoanthracene

To a solution of 1.35 g (5 mmol) of 11-chloro-9,10-dimethyl-9,10-ethenoanthracene in 50 mL of anhydrous THF at -78°C under argon was

added dropwise 2.2 mL (1.1 equivalent) of 2.5 M n-butyllithium in hexanes. The reaction mixture was stirred for one hour, brought to room temperature and heated at reflux for two hours. Methanol (1mL) was added. The solvent was removed and the dark brown material was taken up in methylene chloride. The methylene chloride solution was washed with water, saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Evaporation of the solvent and chromatography of the residue on a silica gel column using 3:1 hexanes, methylene chloride gave compounds A and B as the major products.

Compound A: 320 mg (26%), m.p. 263-264°C; ^{1}H NMR ($CDCl_3$) δ 1.38 (s,3H), 1.44 (s,3H), 2.05 (s,3H), 2.09 (s,3H), 6.07 (s,1H), 7.07 (m,16H); ^{13}C NMR ($CDCl_3$) δ 13.90, 14.74, 15.33, 15.83, 49.49, 52.55, 52.64, 119.84, 120.11, 120.60, 124.29, 124.83, 125.20, 142.49, 145.11, 149.48, 150.02, 151.04; mass spectrum m/e (relative intensity) 498(0.3), 497(0.3), 496(0.9), 373(1.2), 207(19), 206(100), 191(14). Anal. Calcd. for $C_{36}H_{29}Cl$: C, 87.02; H, 5.83. Found: C, 86.95; H, 5.86.

Compound B: 130 mg (11%), m.p. 378-380°C; ^{1}H NMR ($CDCl_3$) δ 1.28 (s,3H), 1.33 (s,3H), 1.51 (s,3H), 1.58 (s,3H), 1.79 (s,3H), 1.82 (s,3H), 5.96 (s,1H), 6.91 (m, 14H); ^{13}C NMR ($CDCl_3$) δ 45.38, 47.85, 48.59, 49.81, 50.59,52.11, 123.17, 123.96, 124.21, 124.67, 125.36, 126.37, 126.66, 127.20, 128.92, 130.75, 140.16, 142.04, 143.37, 144.01, 144.54; no mass spectrum could be obtained. Anal. Calcd. for $C_{54}H_{43}Cl.H_2O$: C, 86.37; H, 5.80. Found: C, 86.28; H, 5.77.

14. 6,11-Dimethyl-5,12-diphenyl-5,12-oxo-6,11-o-benzenotetracene 134

To a solution of 0.54 g (2 mmol) of 11-chloro-9,10-dimethyl-9,10-ethenoanthracene and 0.60 g (2.2 mmol) of 1,3-diphenylisobenzofuran in

25 mL of anhydrous THF at -78°C under argon was added dropwise 1.0 mL (1.1 equivalent) of 2.2 M n-butyllithium in hexanes. The mixture was stirred for two hours, brought to room temperature and heated at reflux for another two hours. The reaction mixture was cooled to room temperature, quenched with a small amount of methanol and the solvent was removed. The residue was taken up in methylene chloride, washed with water, saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Evaporation of the solvent and chromatography of the residue on a silica gel column using 2:1 hexanes/methylene chloride as eluent gave 190 mg (19%) of **134** as a white solid; m.p. 306-308°C, ^{1}H NMR ($CDCl_3$) δ 1.82 (s,6H), 6.64 (m,4H), 6.75 (q,2H), 7.11 (m,4H), 7.31 (q,2H), 7.43 (m,6H), 7.73 (m,4H); ^{13}C NMR ($CDCl_3$) δ 15.53, 51.49, 66.65, 120.83, 123.12, 124.79, 125.22, 125.41, 129.10, 130.00, 130.93, 135.27, 148.10, 149.59, 150.83; mass spectrum m/e (relative intensity) 501(2), 500(6), 396(5), 395(15), 365(8), 194(10), 270(100), 105(35). Anal. Calcd. for $C_{38}H_{28}O$: C, 91.16; H, 5.63. Found: C, 91.11; H, 5.61.

15. 2-Chloro-3-[1-(2-methyl-1-butyne-2-ol)]-1,4-dihydro-1,4-ethenonaphthalene (109)

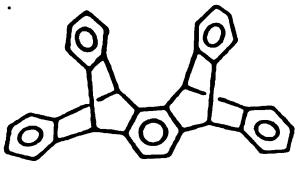
To a solution of 0.38 g (2 mmol) of 2-chloro-1,4-dihydro-1,4-ethenonaphthalene was added 0.9 mL (1.1 equivalent) of 2.5 M n-butyllithium in hexane at -78°C under argon. The reaction mixture was stirred for one hour, brought to room temperature, stirred at this temperature for another hour and heated at reflux for two hours. To this was added 1 mL of acetone and the mixture was heated at reflux for an additional two hours. The solvent was removed by steam distillation. Chromatography of the remaining residue on a silica gel plate using 3:1 hexanes/ methylene chloride as eluent gave 0.12 g (47%) of naphthalene

and 0.24 g (44%) of **106** as a yellow gum. ^{1}H NMR ($CDCl_3$) δ 1.48 (2,6H), 2.16 (broad s,1H), 4.71 (t,1H), 4.78 (6,1H), 6.90 (m,4H), 7.18 (m,2H); ^{13}C NMR ($CDCl_3$) δ 31.83, 54.34, 56.63, 66.27, 123.71, 125.83, 126.11, 128.23, 138.81, 140.06, 145.45, 146.12; mass spectrum, m/e (relative intensity) 272 (4), 270 (16), 191 (15), 176 (15), 128 (35), 86 (31), 84 (46), 43 (100). Anal. Calcd. for $C_{17}H_{15}ClO$: C, 75.41; H, 5.58. Found: C, 75.32; H, 5.60.

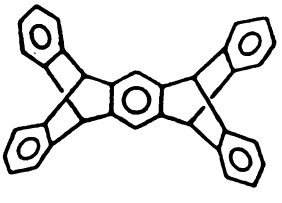
APPENDICES

APPENDIX 1

The name "iptycene" emphasizes the relationship between these compounds and the parent compound triptycene. The prefixes tri, pent, hept, etc. indicate the number of separated arene planes. Besides the prefix, three descriptors enclosed in a bracket are used to precisely define these structures. The first descriptor, a series of numbers, defines the arene ring system (1,2,3, etc. for benzenoid, naphthalenoid, anthracenoid, etc. respectively). The second descriptors are English alphabet letters (a,b and c, . . .), and are placed at the upper and lower right side of the first descriptors. The upper index refers to the bonds to which the sp^3 carbon atoms are attached; and the lower index indicates the bonds involved in ring fusions. Thus, compounds **2**, **3**, **33** and **77** are [1.1.1^{a}.1.1] pentiptycene, [1.1.1^{b}.1.1] pentiptycene, [1.1.3$^{b}_{bb}$.1.1] pentiptycene and [1.1.3$^{a}_{cb}$.1.1] pentiptycene, respectively.



2



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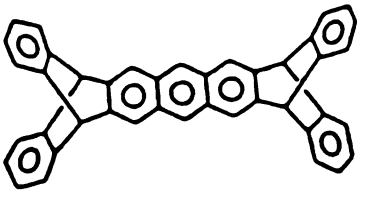

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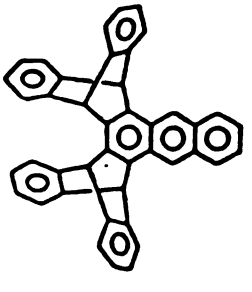
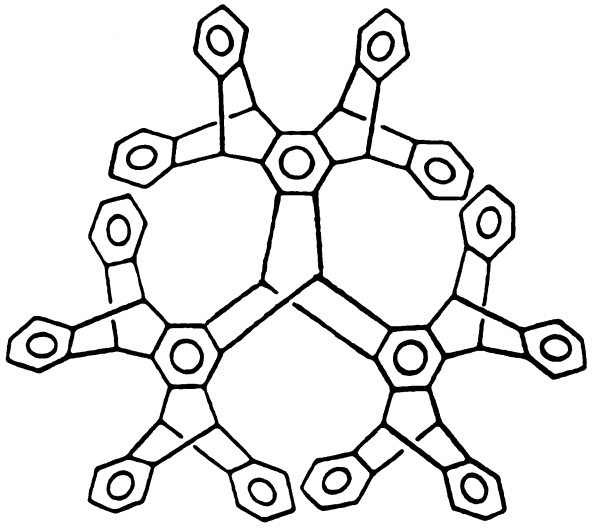


77

Accordingly, "supertriptycene" **24** is named as [1.1.1^{a,c}.1.1.1^{a,c}-.1^{a,c}.1.1.1.1.1.1.1.1] pentadecaiptycene.



24

A simplified or abbreviated definition is possible for the compounds listed in Table I. If the sites of possible fusions on the parent compound triptycene **1** can be designated by the alphabet letters a,b,c, and their primes and seconds. Thus, compounds **2**, **3** and **24** can simply be defined as a-pentiptycene, b-pentiptycene and a,c,a^{1},c^{1},a$^{"}$,c$^{"}$-pentadecaiptycene.

APPENDIX 2

Crystallographic Data for Compound

Crystals of **66**, $C_{32}H_{22}Cl_2$, are triclinic; space group p-1; a=8.229, b=10.641, c=6.837 A, =102.22°, =102.22°, =77.34°; Z-1; M-477.44; P_c=1.410 g cm^{-3}. Lattice dimensions were determined using a Picker-FACS-I diffractometer and M_oK_1 (=0.71073 A) radiation. Intensity data were measured using M_oK radiation (2 max= 45°) yielding 2964 total collected data and, based on I > 25 (I), 1482 observed data. The data were reduced[78]; the structures were solved by direct methods[79]; and the refinement was by full-matrix least-squares techniques.

The final R values were R^1 = 0.032 and R^2 = 0.038. The final difference Fourier map showed densities ranging from +0.221 to -0.248 with no indication of missing or incorrectly placed atoms. Bond lengths and bond angles are given in the following pages (Table 4 and 5).

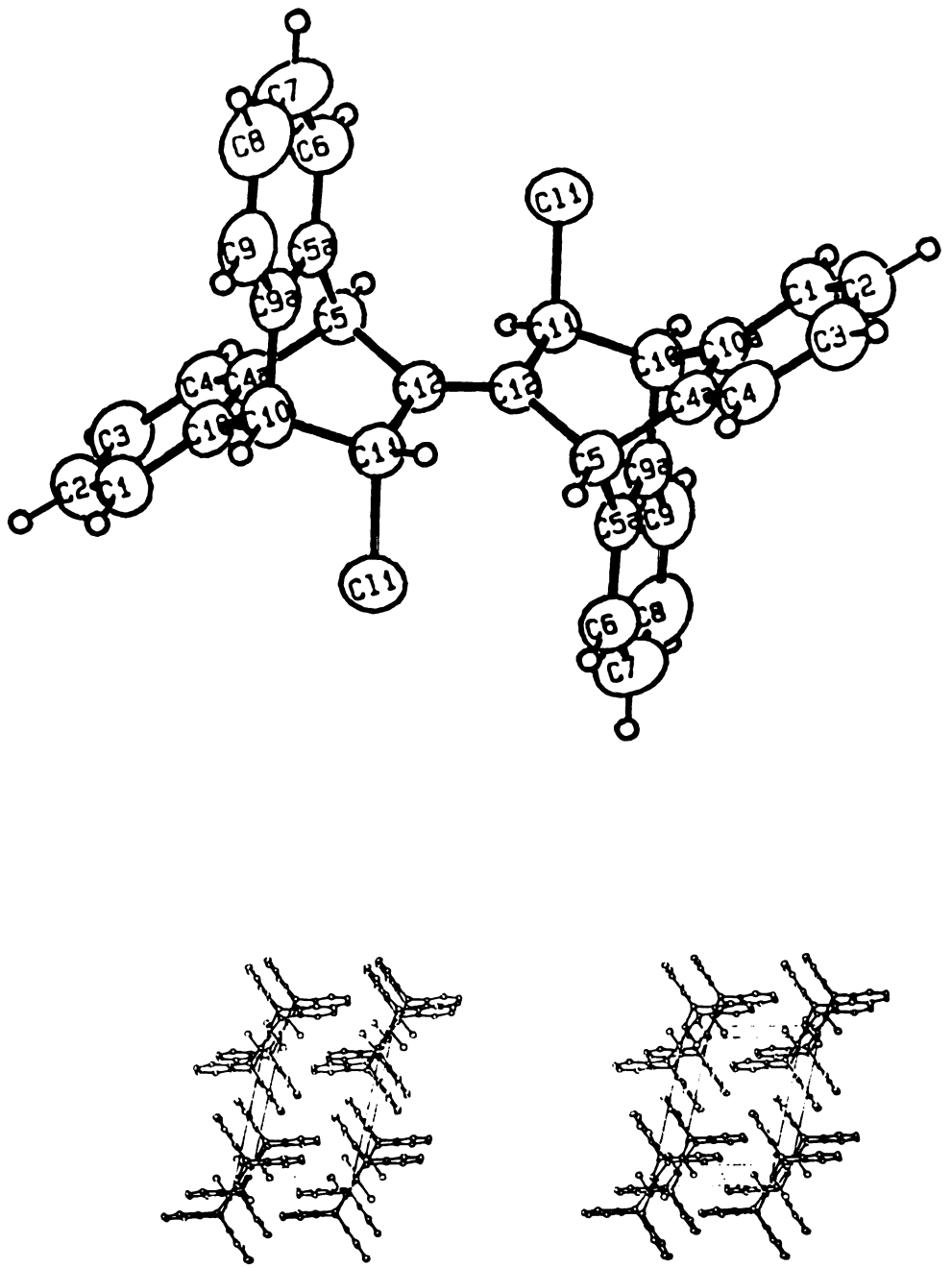


Figure 8. Crystal structure and the packing pattern of the crystals of compound 66.

Table 4. Bond distances (Å) for 66.

Atom1	Atom2	Distance
Cl1	Cl1	1.826(2)
C1	C2	1.384(5)
C1	C10a	1.388(4)
C2	C3	1.373(4)
C3	C4	1.393(4)
C4	C4a	1.384(4)
C4a	C5	1.525(4)
C4a	C10a	1.393(4)
C5	C5a	1.524(3)
C5	C12	1.530(4)
C5a	C6	1.378(4)
C5a	C9a	1.396(4)
C6	C7	1.394(4)
C7	C8	1.377(5)
C8	C9	1.379(4)
C9	C9a	1.384(4)
C9a	C10	1.519(4)
C10	C10a	1.514(4)
C10	C11	1.549(4)
C11	C12	1.513(3)
C1	H1	0.96(3)
C2	H2	0.96(3)
C3	H3	0.92(3)
C4	H4	0.94(2)

Atom1	Atom2	Distance
C5	H5	0.88(2)
C6	H6	0.93(2)
C7	H7	0.91(3)
C8	H8	0.88(3)
C9	H9	0.84(3)
C10	H10	0.88(2)
C11	H11	1.13(3)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 5. Bond Angles (°) for 66.

Atom1	Atom2	Atom3	Angle
C2	C1	C10a	119.0(3)
C1	C2	C3	121.0(3)
C2	C3	C4	120.7(3)
C3	C4	C4a	118.4(3)
C4	C4a	C5	126.0(2)
C4	C4a	C10a	120.9(2)
C5	C4a	C10a	113.0(2)
C4a	C5	C5a	106.6(2)
C4a	C5	C12	108.8(2)
C5a	C5	C12	104.0(2)
C5	C5a	C6	126.6(2)
C5	C5a	C9a	112.8(2)
C6	C5a	C9a	120.6(2)
C5a	C6	C7	119.0(3)
C6	C7	C8	120.3(3)
C7	C8	C9	120.8(3)
C8	C9	C9a	119.4(3)
C5a	C9a	C9	119.9(2)
C5a	C9a	C10	113.3(2)
C9	C9a	C10	126.8(2)
C9a	C10	C10a	107.3(2)
C9a	C10	C11	105.6(2)
C10a	C10	C11	107.0(2)
C1	C10a	C4a	120.0(3)
C1	C10a	C10	126.8(2)

Atom1	Atom2	Atom3	Angle
C4a	C10a	C10	113.3(2)
C11	C11	C10	108.8(2)
C11	C11	C12	110.7(2)
C10	C11	C12	109.5(2)
C5	C12	C11	111.2(2)
C2	C1	H1	123.(2)
C10a	C1	H1	118.(2)
C1	C2	H2	119.(2)
C3	C2	H2	120.(2)
C2	C3	H3	118.(1)
C4	C3	H3	121.(1)
C3	C4	H4	120.(2)
C4a	C4	H4	122.(2)
C4a	C5	H5	112.(1)
C5a	C5	H5	112.(1)
C12	C5	H5	113.(2)
C5a	C6	H6	120.(1)
C7	C6	H6	121.(1)
C6	C7	H7	122.(2)
C8	C7	H7	118.(2)
C7	C8	H8	116.(2)
C9	C8	H8	123.(2)
C8	C9	H9	117.(2)
C9a	C9	H9	124.(2)

Atom1	Atom2	Atom3	Angle
C9a	C10	H10	114.(1)
C10a	C10	H10	113.(2)
C11	C10	H10	109.(2)
C11	C11	H11	101.(1)
C10	C11	H11	110.(1)
C12	C11	H11	116.(1)

Numbers in parentheses are estimated standard deviations in the least significant digits.

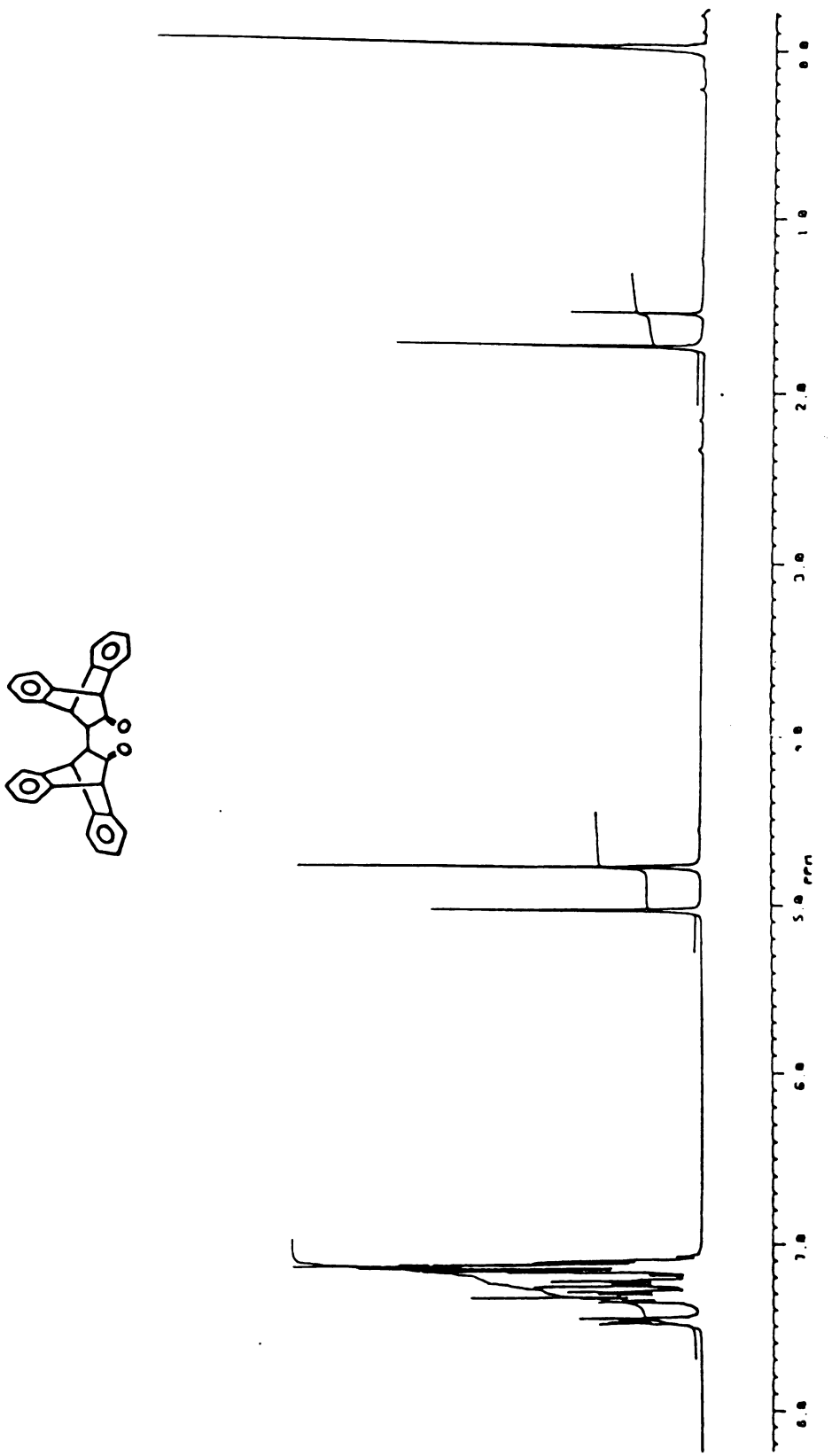


Figure 9. 250 MHz ^1H NMR spectrum of compound 60.

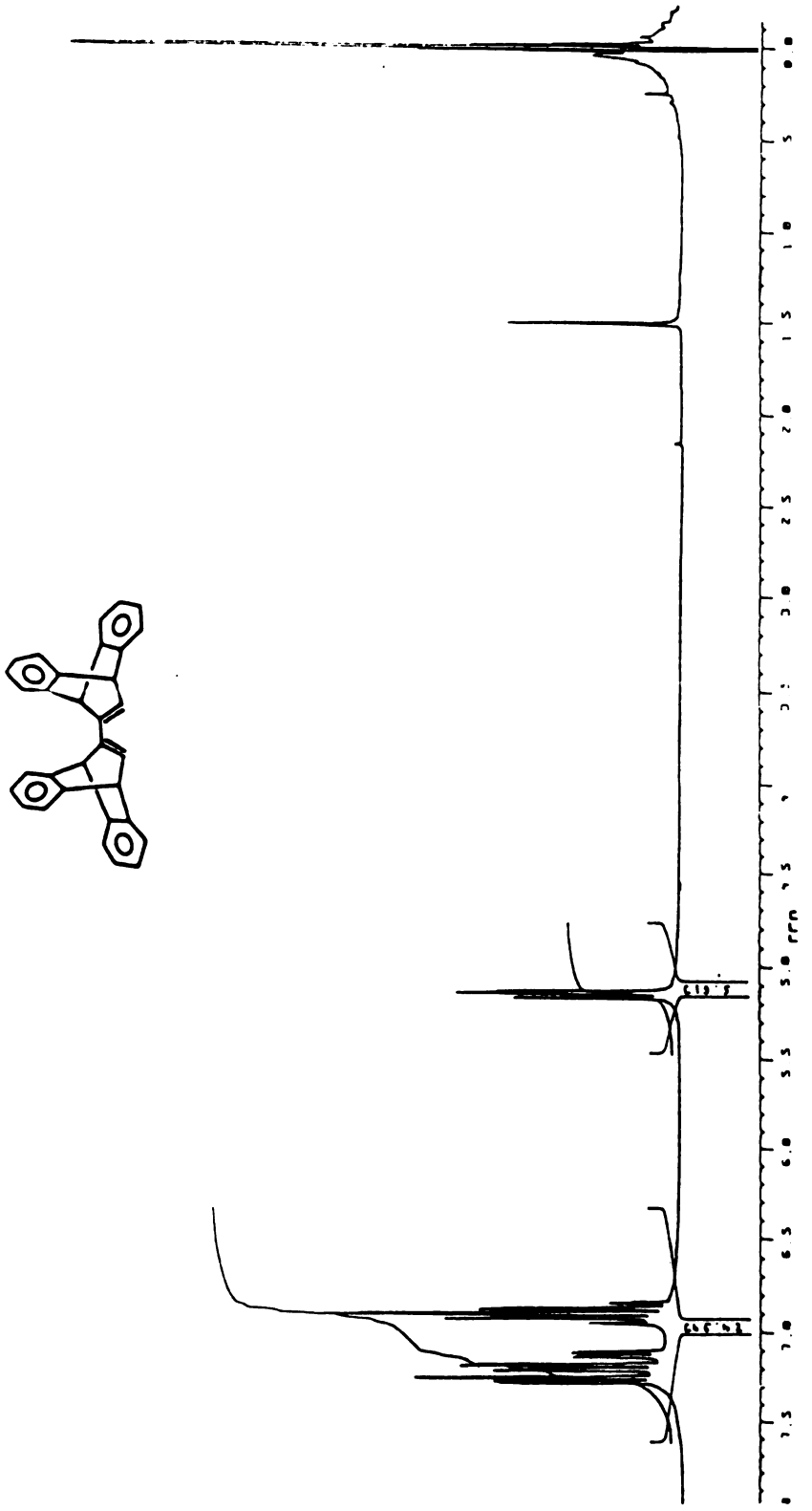


Figure 10. 250 MHz ^{1}H NMR spectrum of compound 56.

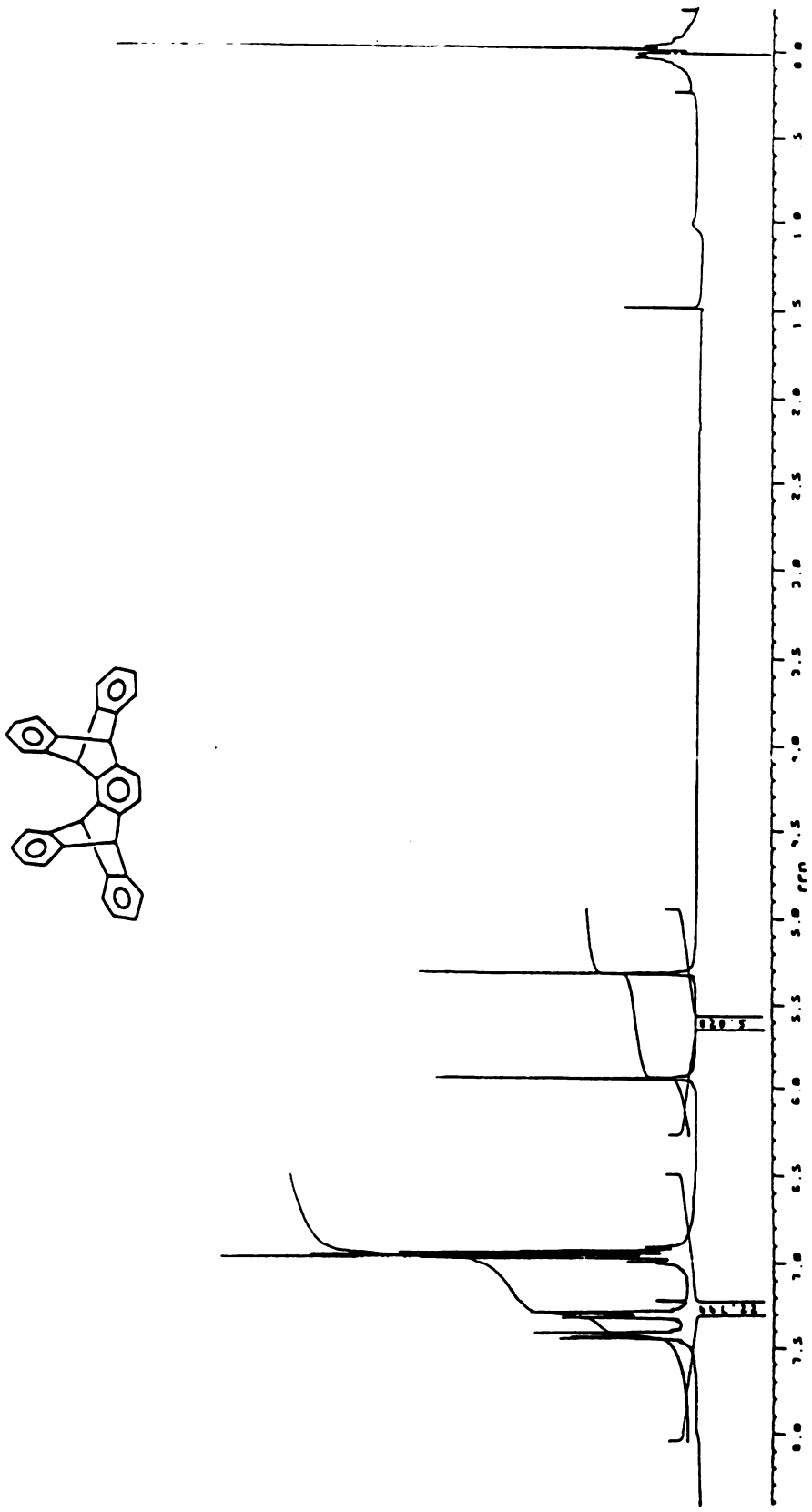
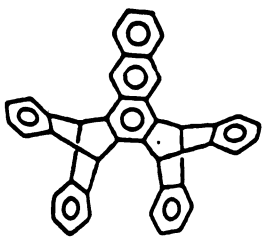


Figure 11. 250 MHz ^{1}H NMR spectrum of [1.1.1.1^a.1.1] pentiptycene 2.



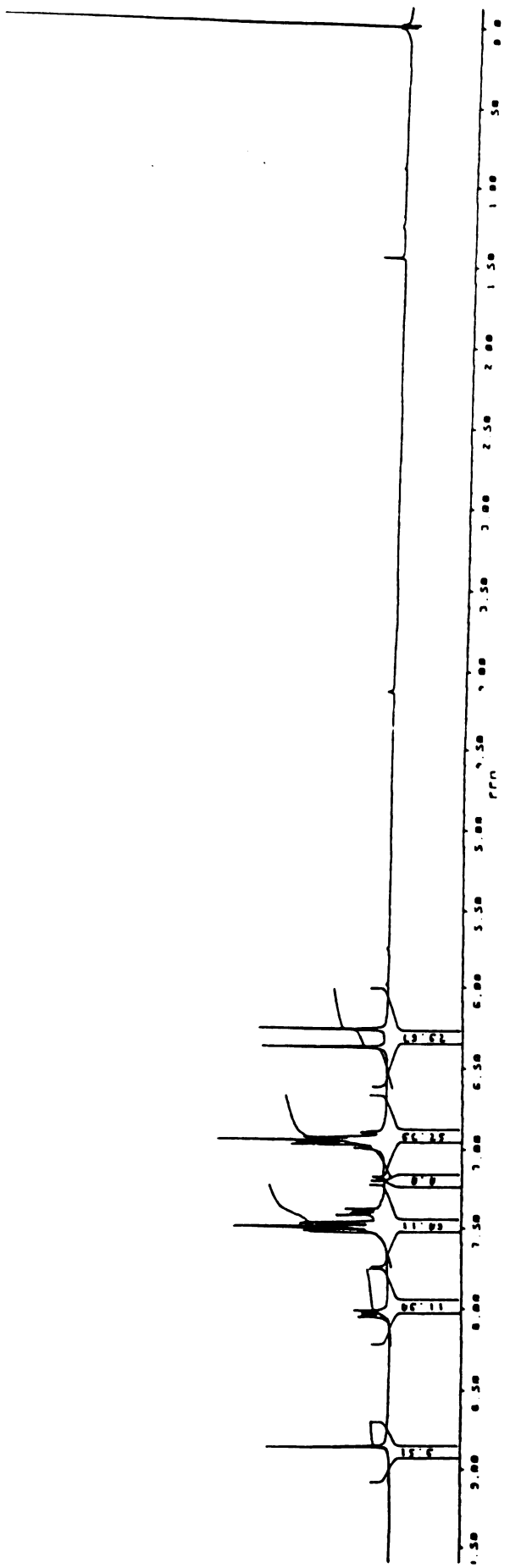


Figure 12. 250 MHz ^{1}H NMR spectrum of [1.1.1.3^{c}$_{bb}$.1.1] pentiptycene 77

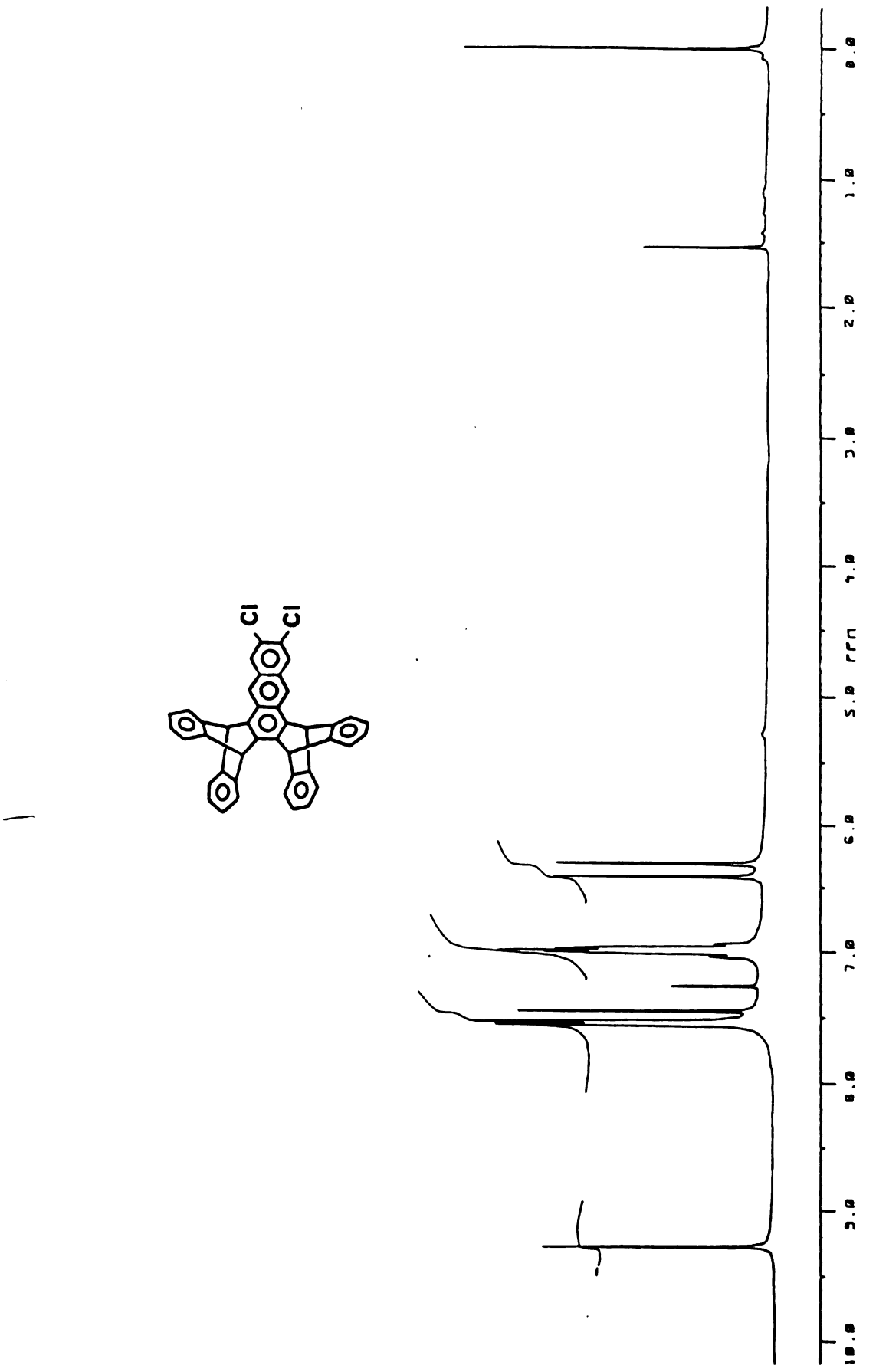


Figure 13. 250 MHz ^{1}H NMR spectrum of compound 81.

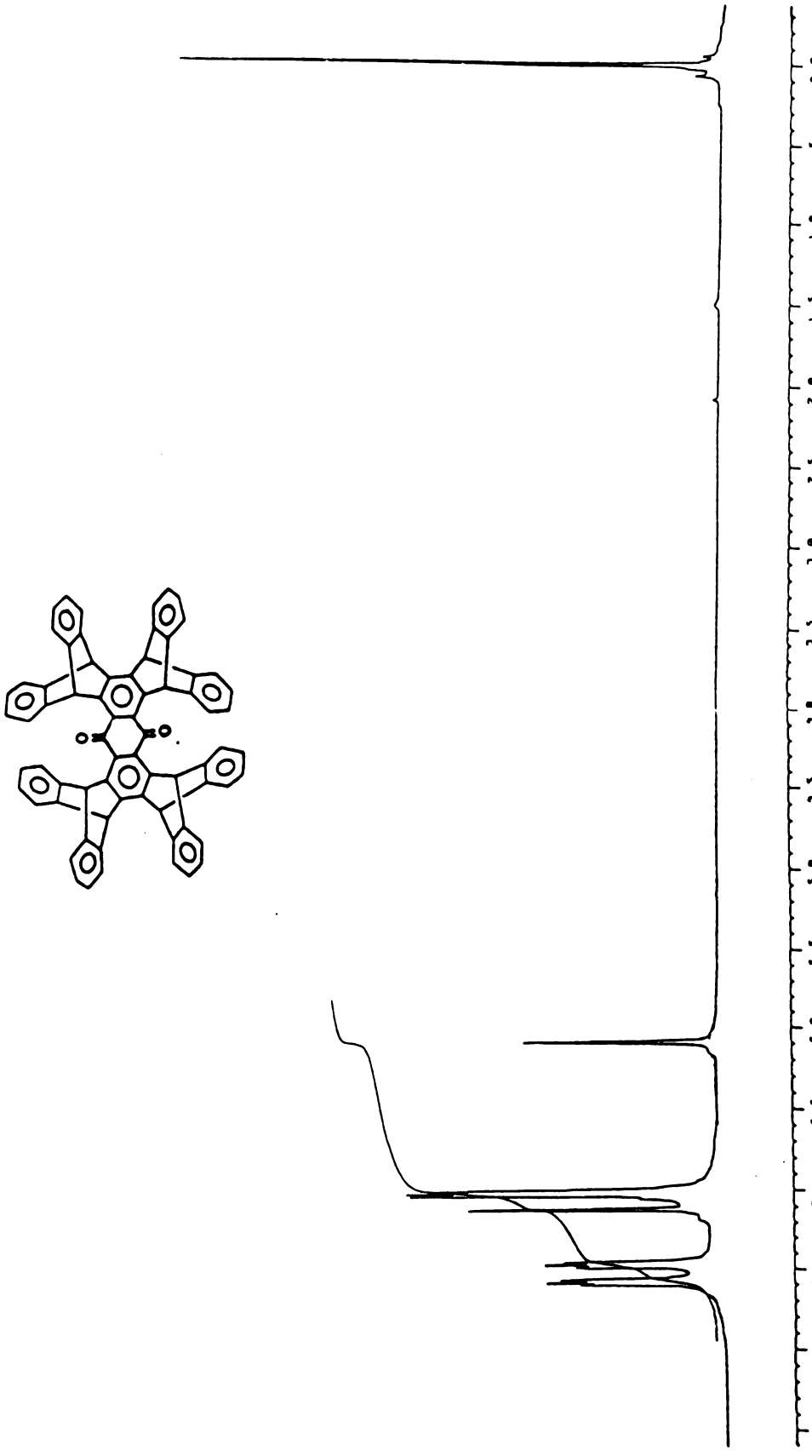
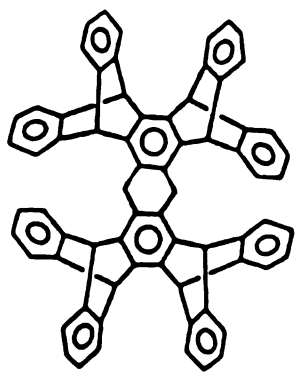


Figure 14. 250 MHz ^{1}H NMR spectrum of compound 83.



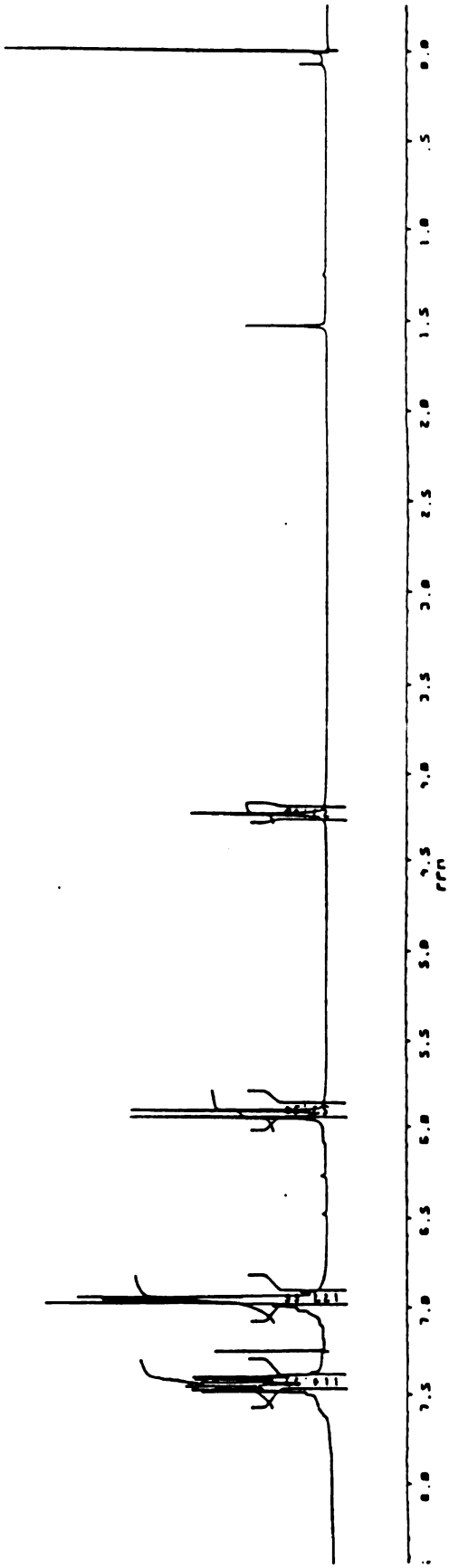


Figure 15. 250 MHz ^{1}H NMR spectrum of compound 84.

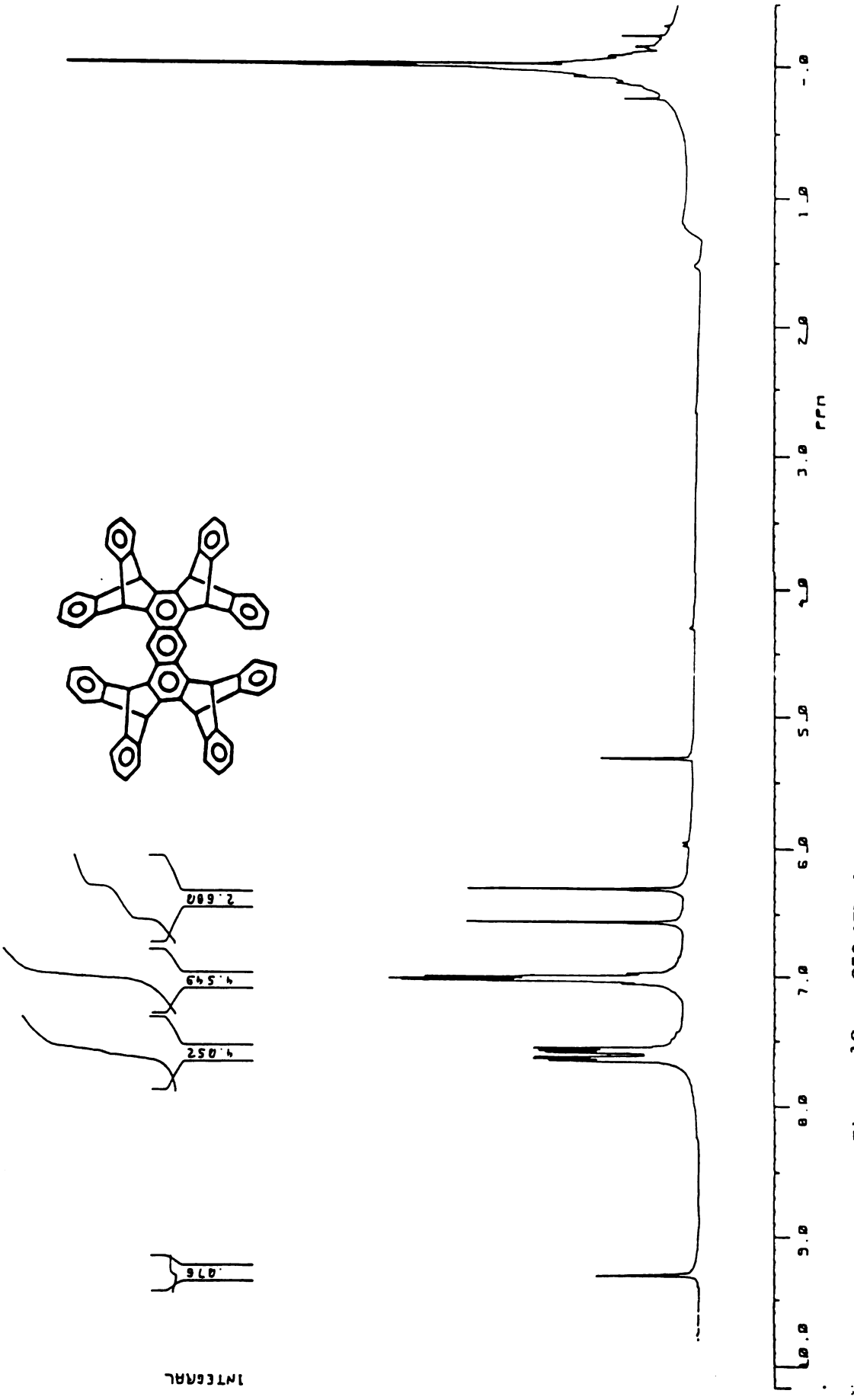


Figure 16. 250 MHz ^{1}H NMR spectrum of compound 58 .

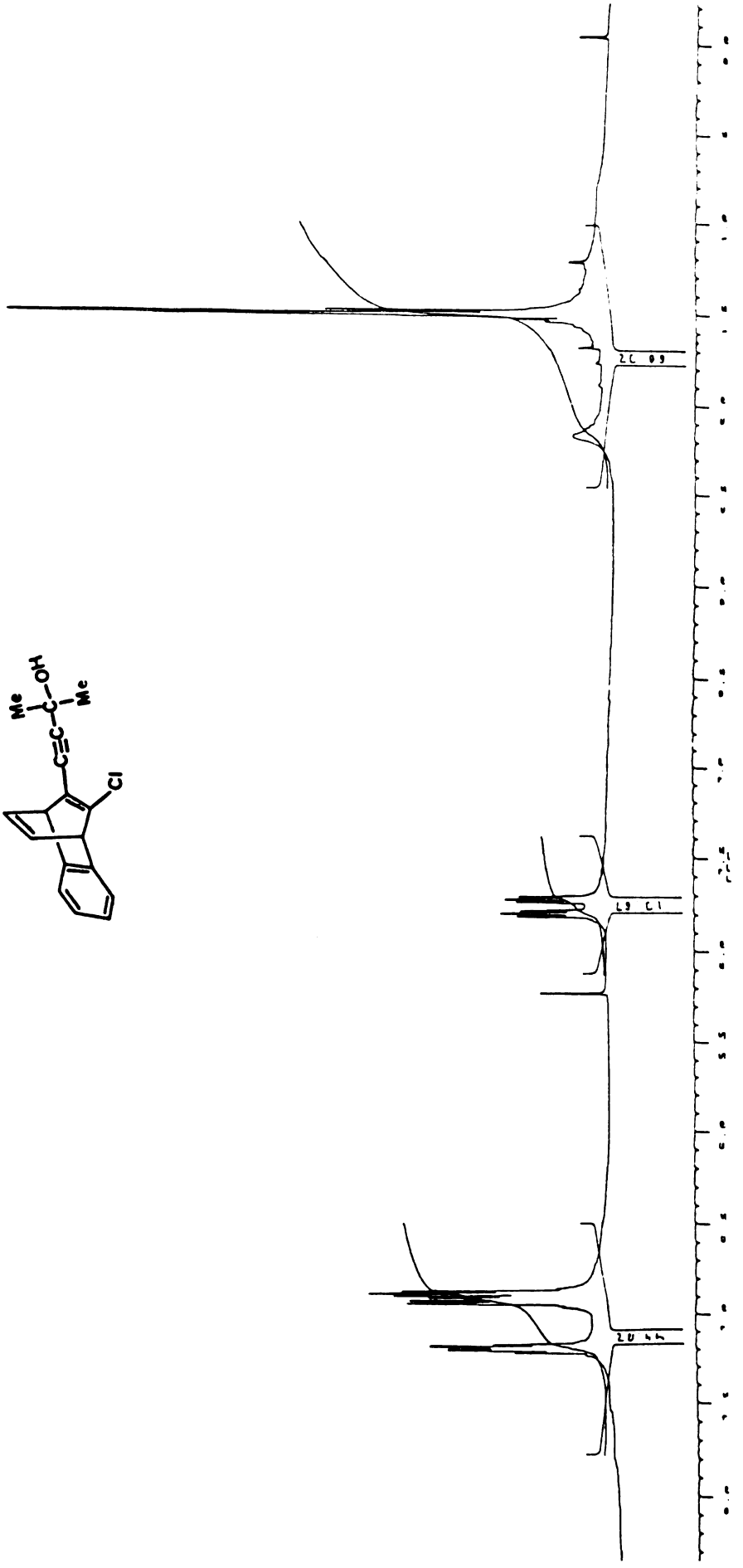


Figure 17. 250 MHz ^{1}H NMR spectrum of compound 109.

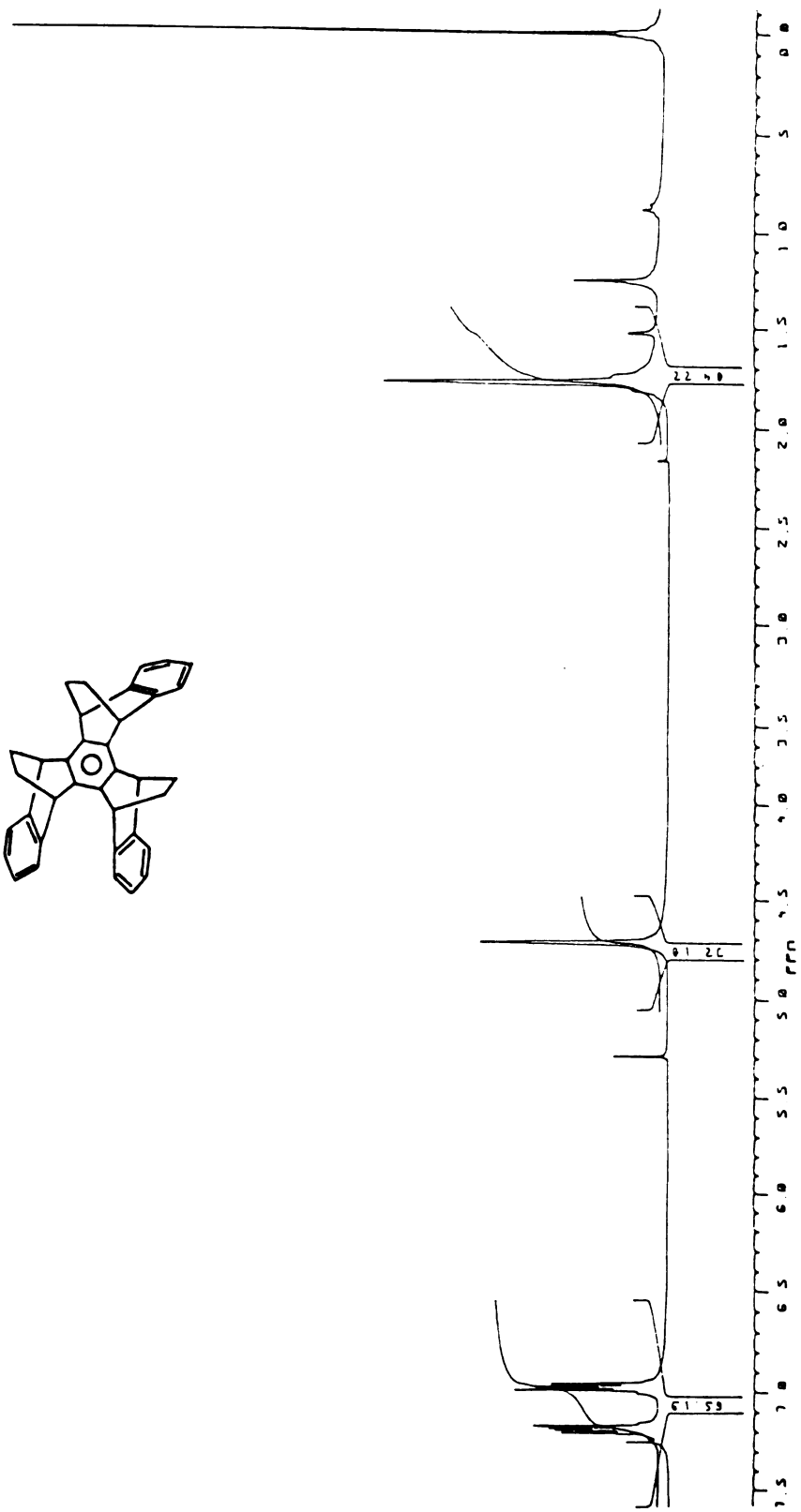


Figure 18. 250 MHz ^{1}H NMR spectrum of compound 116.

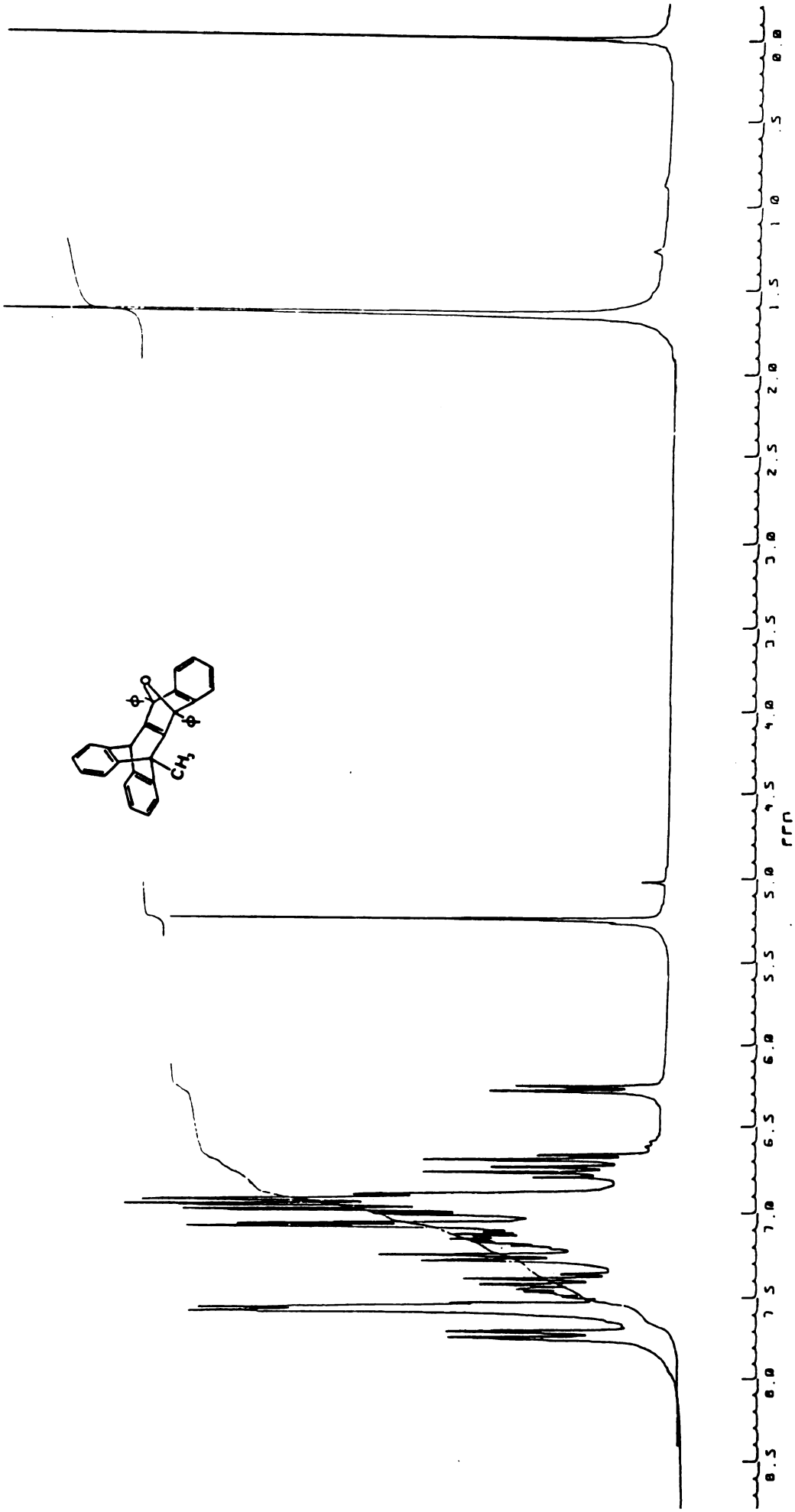


Figure 19. 250 MHz ^{1}H NMR spectrum of compound 123.

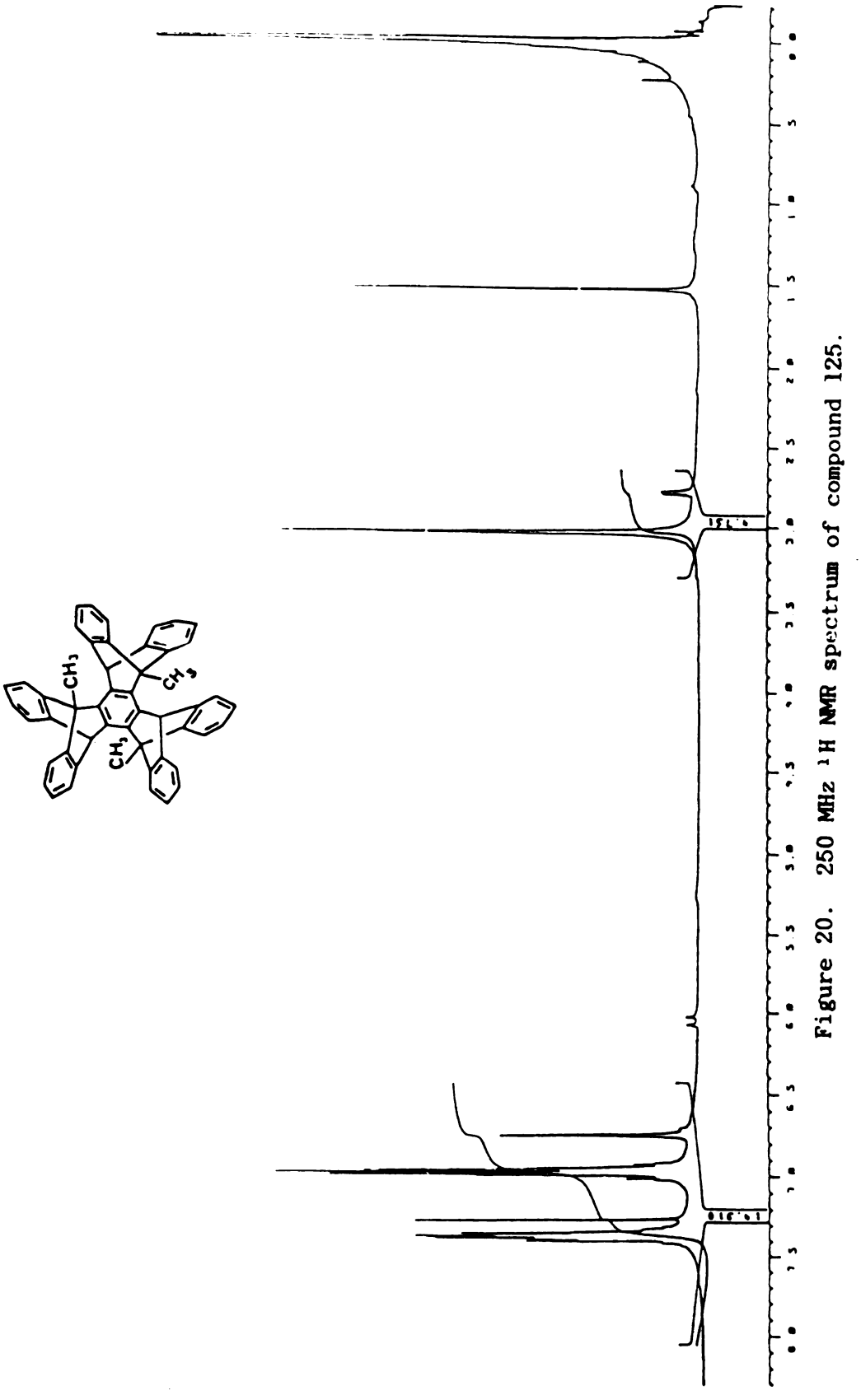


Figure 20. 250 MHz ^{1}H NMR spectrum of compound 125.

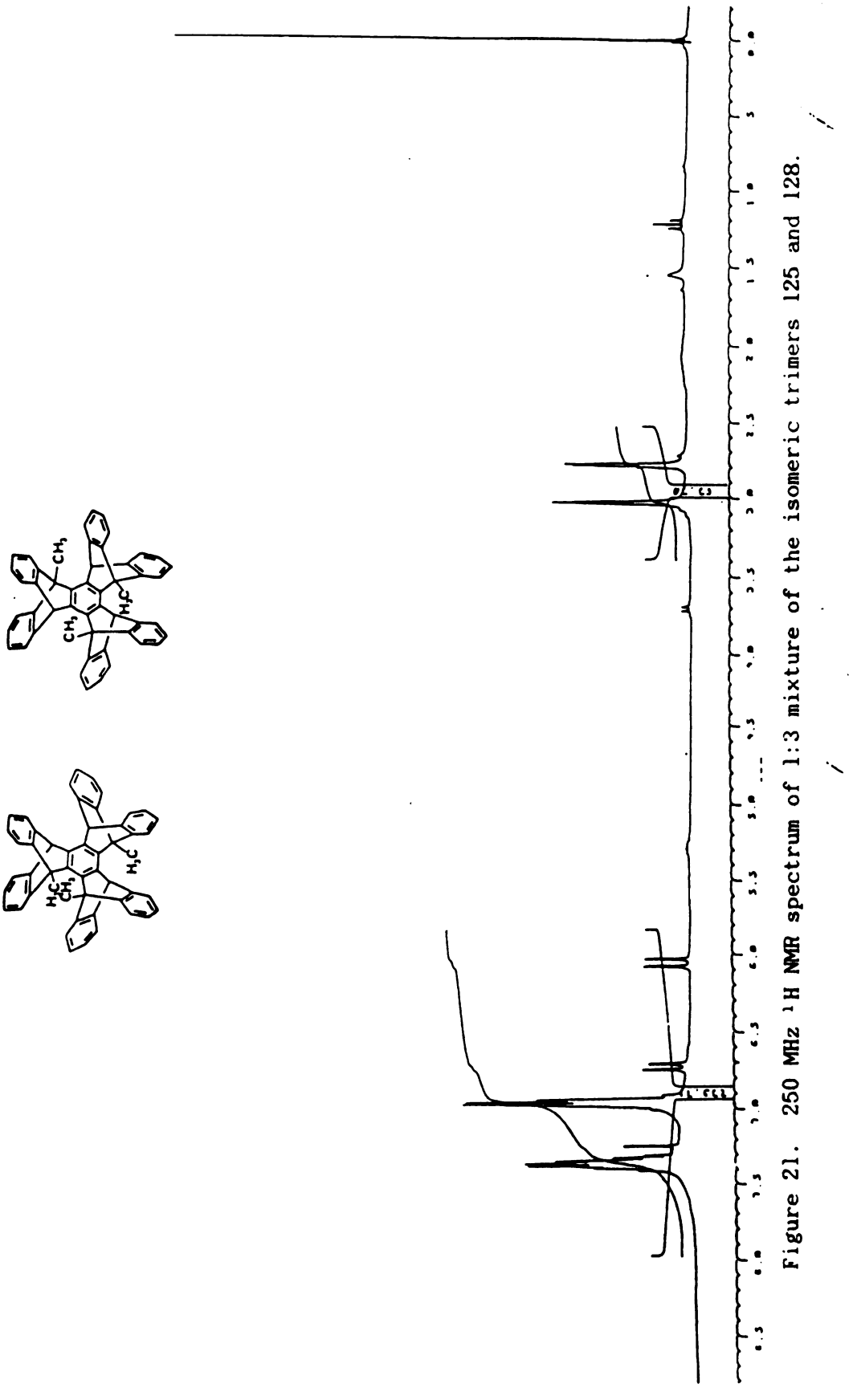


Figure 21. 250 MHz ^{1}H NMR spectrum of 1:3 mixture of the isomeric trimers 125 and 128.

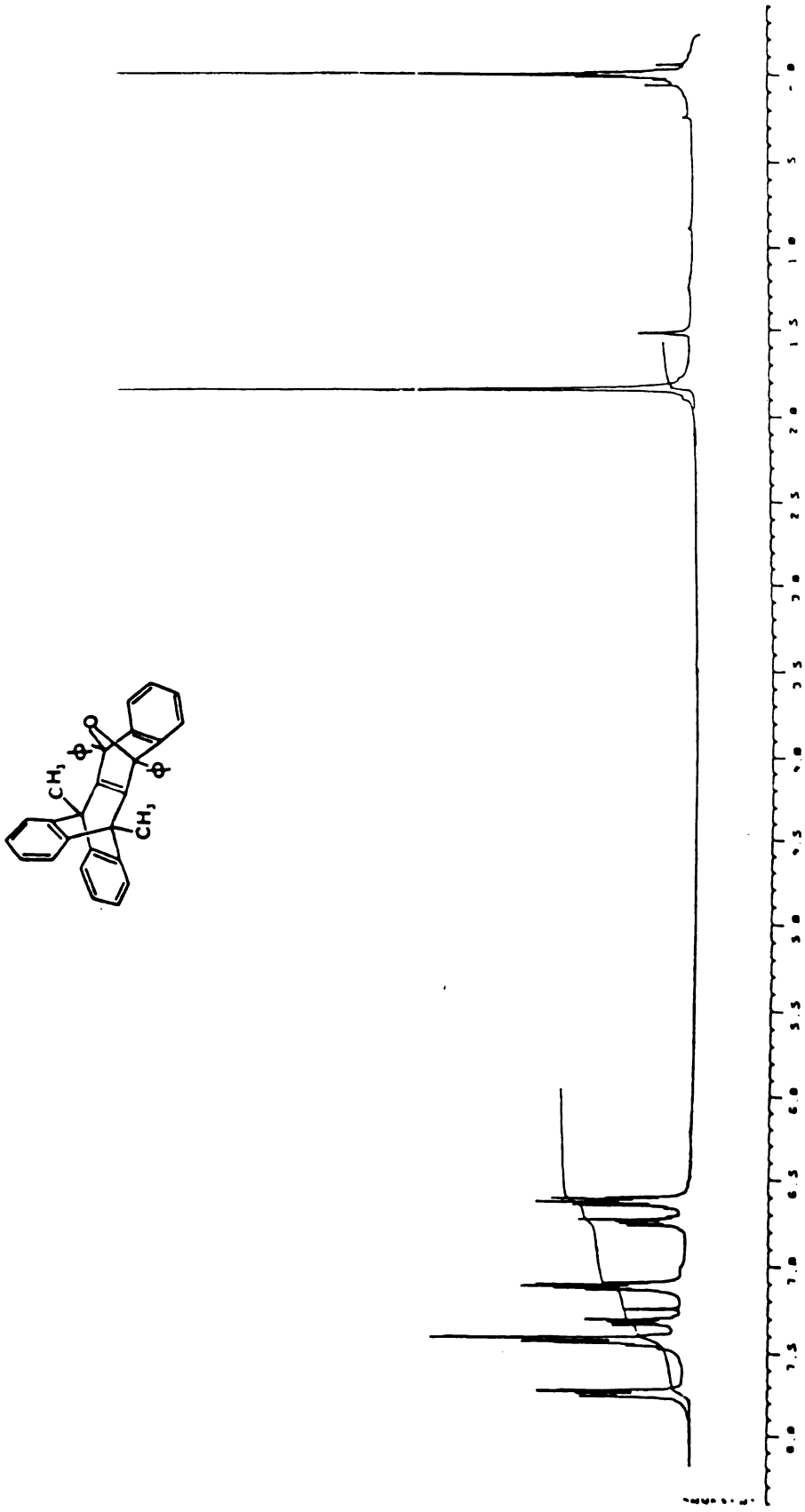
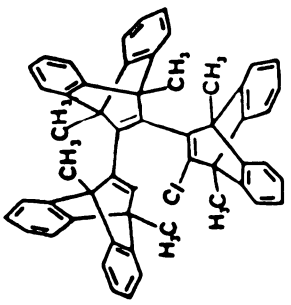


Figure 22. 250 MHz ^{1}H NMR spectrum of the cycloadduct 134.



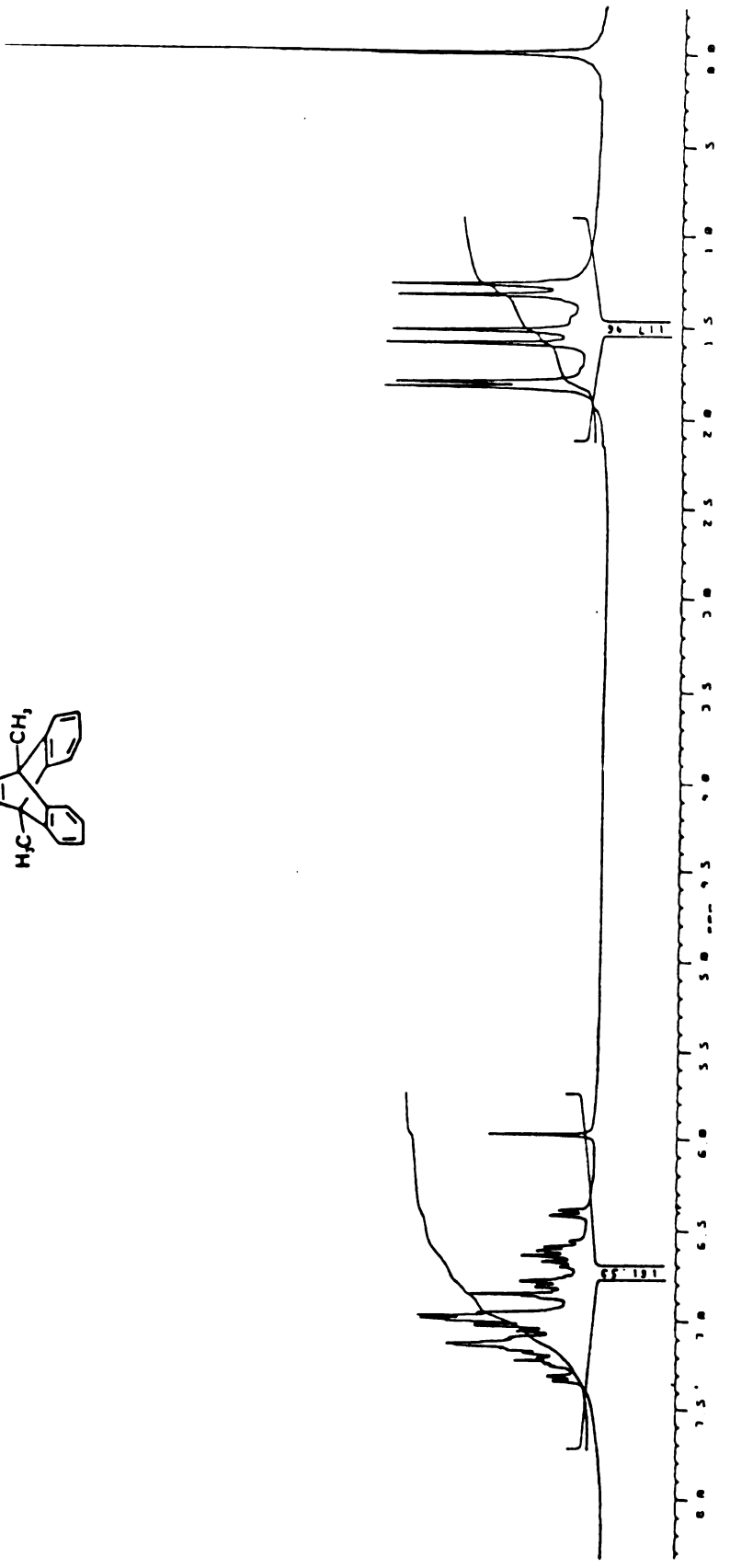


Figure 23. 250 MHz ^{1}H NMR spectrum of 136

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