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dissertation entitled

SYNTHESIS OF EXTENDED TRIPTYCENES(IPTYCENES)
AND LINEAR POLYCYCLIC ARENES

presented by

Jihmei Luo

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in CHEMISTRY

Harold Hart
Major professor

Date Oct.30,1986

SYNTHESIS OF EXTENDED TRIPTYCENES (IPTYCENES) AND LINEAR POLYCYCLIC ARENES

By

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A DISSERTATION

submitted to

Michigan State University

in partial fulfillment of the requirement

for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1986

ABSTRACT

SYNTHESIS OF EXTENDED TRIPTYCENES (IPTYCENES) AND LINEAR POLYCYCLIC ARENES

By

Jihmei Luo

Triptycene is the first member of a large series of compounds for which we have coined the general term "iptycene". The prefix (tri, pent, etc.) indicates the number of separated arene planes. A general synthetic approach to the iptycene framework and the synthesis of some specific iptycenes are described.

Four useful iptycene synthons can be derived from 1,2,4,5-tetrabromobenzene **31**. Treatment of **31** with either one or two equivalents of n-BuLi and furan gives 6,7-dibromo-1,4-dihydronaphthalene-1,4-epoxide **38** or 1,4:5,8-diepoxy-1,4,5,8-tetrahydroanthracene **40**. Metal-catalyzed deoxygenation of **38** gives 2,3-dibromonaphthalene **49**, which is then treated with one equivalent of n-BuLi and furan to give 1,4-dihydroanthracene-1,4-epoxide **50**. The utility of the above five synthons and of 1,4-dihydronaphthalene-1,4-epoxide **7**, and 11,12-dimethylene-9,10-dihydro-9,10-ethanoanthracene **52** is demonstrated in four new, much improved

syntheses of 5,14[1',2']benzeno-5,14-dihydropentacene **20**, itself a useful iptycene synthon. The versatility of **20** as a synthon for higher iptycenes is illustrated with syntheses of six pentiptycenes, two heptiptycenes and two noniptycenes.

In the second part of this thesis, the synthesis of linear polycyclic epoxyarenes by cycloaddition of benzocyclobutene to the epoxides **7**,**38**,**40** and **50** was investigated. Dehydration followed by dehydrogenation of the corresponding adducts affords a convenient way to prepare linear acenes (i.e. tetracene, 2,3-dibromotetracene and pentacene) in good yields. Cycloaddition of 5,14-dihydropentacene **128** with **50** or **38**, followed by dehydration and dehydrogenation, gives the potential synthon 7,16[1',2']benzeno-7,16-dihydroheptacene **109** or 6,15[1',2']benzeno-2,3-dibromo-6,15-dihydrohexacene **143**. The dual functionalities present in these molecules should permit their use as precursors of complex iptycenes or polyiptycenes.

A synthetic equivalent of furano[3,4-f]benzo[c]furan **133** is described in the third part of this thesis. Cycloaddition of **40** and tetraphenylcyclopentadienone **153** gives bis-adducts **160** in high yield. Thermal decomposition of **160** in the presence of a dienophile (i.e. DMAD, TCNE, naphthaquinone, 1,4-anthraquinone and **7**) provides a novel route to linear polycyclic epoxyarenes in good yields.

With Love, to Thungmei

ACKNOWLEDGEMENTS

I wish to express my sincere appreciation to Professor Harold Hart for his enthusiasm, encouragement and guidance throughout the course of this study.

In addition, I would like to thank Professor E. G. LeGoff, who served as my second reader, and the other members of my Guidance Committee, Professor G. E. Leroi and Professor T. J. Pinnavaia.

Appreciation is extended to Michigan State University, the National Science Foundation, and the National Institutes of Health for financial support in the form of teaching and research assistantships, and the SOHIO company for a summer term fellowship.

Many thanks go to my family, parents-in-law, and friends for their love and support over the past few years.

Last and most, I thank my wife, Thungmei, for her endless love, support, and encouragement during these years.

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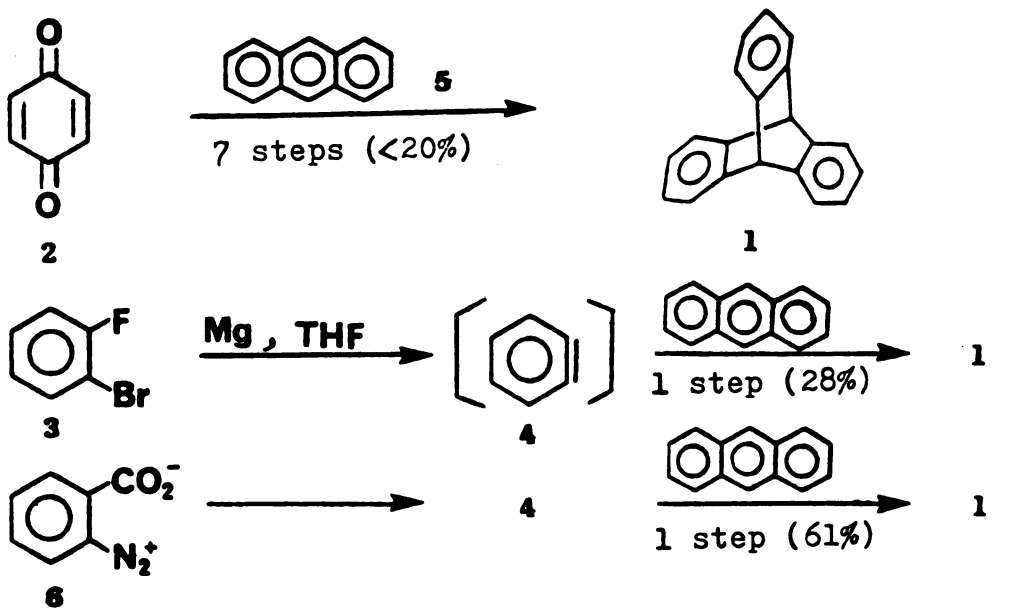
INTRODUCTION

A. Triptycene.

Triptycene 1[1] was first synthesized in 1942 by P. D. Bartlett[2] for the purpose of testing certain concepts in physical-organic chemistry. The trivial name is derived from the triptych of antiquity, a book with three leaves hinged on a common axis. The Bartlett synthesis, which started from 1,4-benzoquinone 2 and anthracene, was lengthy (7 steps) and gave 1 in only a modest overall yield (<20%).

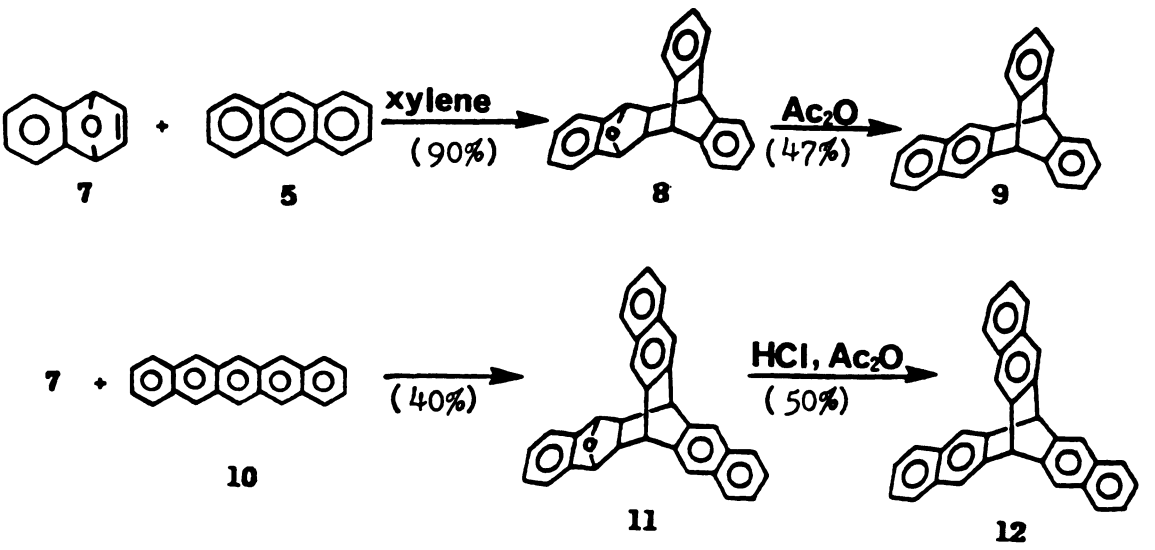


Some years later, a one-step synthesis from benzyne 4 (generated from the Grignard reagent of o-bromofluorobenzene 3) and anthracene 5 was developed by Wittig[3], and really opened the door to triptycene chemistry. With the development of various benzyne precursors, it was found that

the most convenient way to generate benzyne for the preparation of triptycene is to decompose o-benzenediazonium carboxylate 6 (obtained by diazotising anthranilic acid) by heating in an aprotic solvent.[4] This methodology made triptycene readily available for many interesting investigations.

Numerous triptycenes are now known.[5] Their rigid framework has attracted the attention of many research workers. In recent years, triptycenes have been used in mechanistic studies[6] and to study intramolecular charge transfer,[7] restricted rotation about single bond (atropisomerism),[8] and correlated bond rotations (gearing).[9]

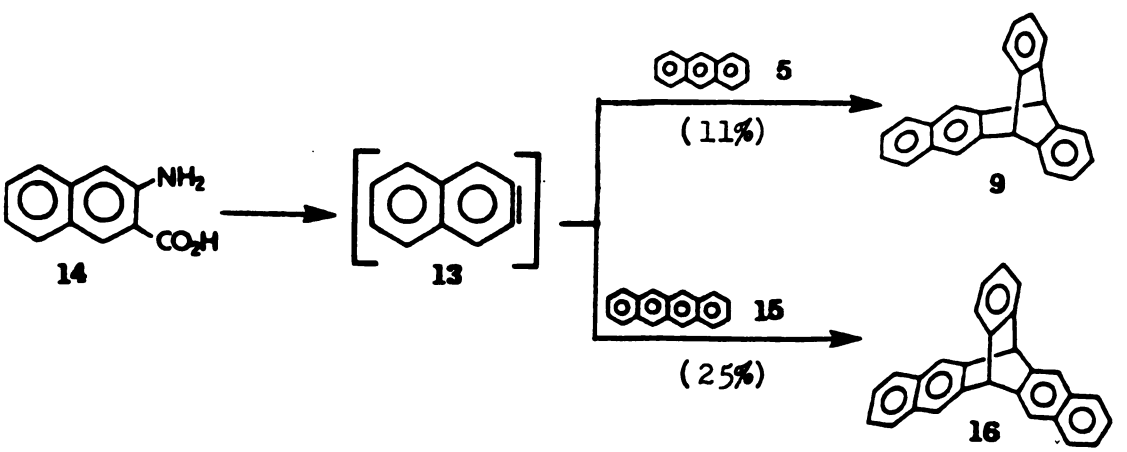
A few triptycene analogues containing naphthalene, anthracene and other fused-rings have also been synthsized. In 1960, Wittig[10] discovered that the furan adduct of benzyne, 1,4-dihydronaphthalene-1,4-epoxide 7 , was an effective dienophile. The double bond of 7 added to the



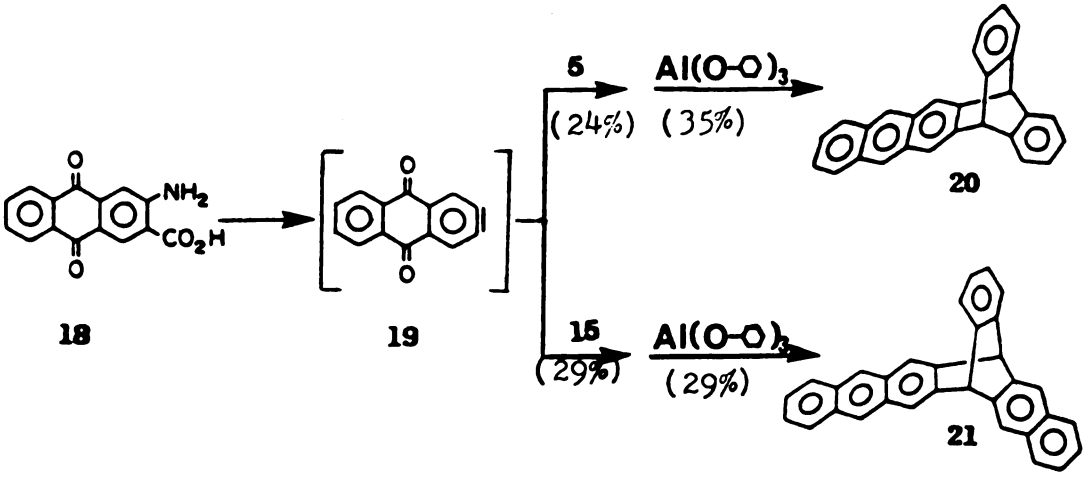
middle ring of anthracene or pentacene to give adducts **8** or **11**, respectively. The oxygen bridges were removed separately by acetic anhydride or hydrochloric acid in acetic anhydride to produce [2^b.1.1]triptycene **9** or [2^b.2^b.2^b]triptycene **12** (the derivation of the trivial names will be described; vide infra). In these two-step sequences, **7** acts as the synthetic equivalent of 2,3-naphthyne **13** in cycloadditions to acenes. This concept is important to us since we will apply this idea to the synthesis of extended triptycenes throughout the course of this study.

7 **13**

Other fused-ring triptycenes were used by Misumi[11] to test the concept of transannular $\pi - \pi$ interactions by examining their spectral properties. The syntheses were generally extensions of the Wittig concept, i.e. cycloaddition reactions of arynes and acenes. Althouugh the



14 **13** **9** **16**



cycloadditions were successful, the yields were rather low. Morever, the aryne precursors (**14** and **18**) are not readily available (especially **18**, which was prepared in five steps from toluene[12] or obtained in a low yield, multi-step route from phthalic anhydride[13]). Compound **20** was attractive to us, since it may serve as a building block in the synthesis of extended triptycenes. We shall describe in this thesis several much better routes to **20**.

We can summarize these literature results by noting that the basic construction of the triptycene framework is generally through aryne (i.e. **4**, **13**, **19**) addition to an acene(i.e. anthracene, tetracene, pentacene).

B. Extended Triptycenes (Iptycenes).

Despite this substantial history,[5] the considerable potential for extending the rigid triptycene framework to larger interesting and useful compounds has only recently been realized.[14] Triptycene **1** is the parent of a large

series of compounds for which Hart has coined the general term " iptycene ".[14a]

The name " iptycene " emphasizes the relationship between these compounds and the parent structure triptycene. A prefix indicates the number of separated arene planes; thus **1**, **9** and **20** are triptycenes (three planes); **22**, **24**, **25** and **26** are pentiptycenes (five planes); **23** and **27** are heptiptycenes (seven planes).

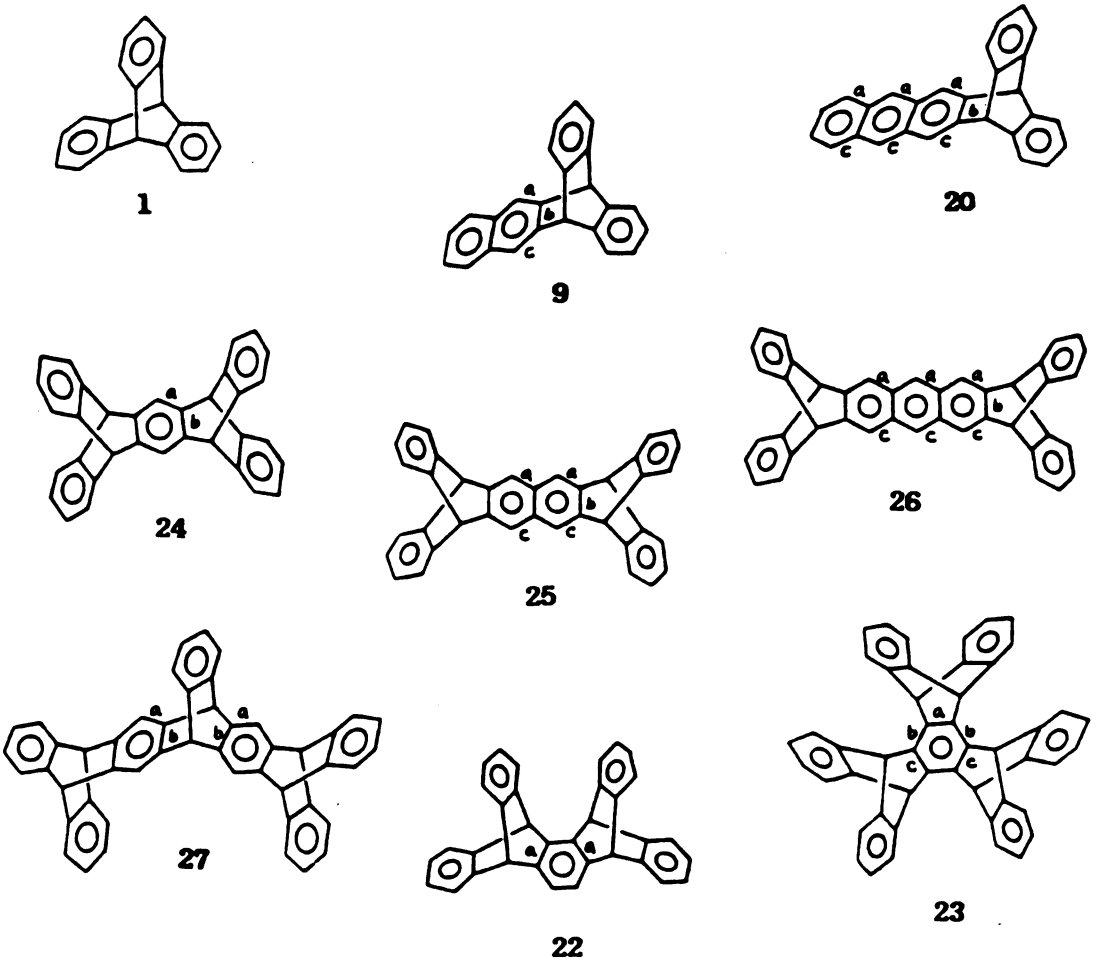
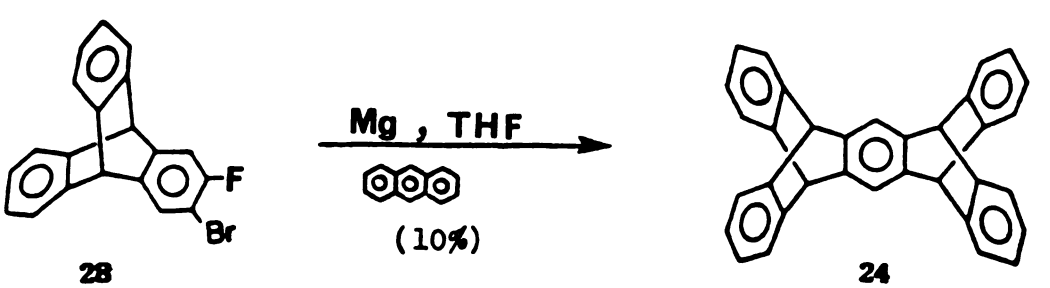


Figure 1. Various iptycenes.

There are three descriptors that need to be added to these names to precisely define the structures. The use of two of these descriptors is illustrated in the following names: for **22**, [1.1.1^{a}.1.1]pentiptycene; **24**, [1.1.1^{b}.1.1]-pentiptycene; **23**, [1.1.1^{a,c}.1.1.1.1]heptiptycene; **27**, [1.1.1^{b}.1.1^{b}.1.1]heptiptycene; **9**, [2^{b}.1.1]triptycene. The 1's indicate that each ring is benzenoid, and this number would be replaced by 2 if naphthalenoid or 3 if anthracenoid or phenanthrenoid, etc. The superscriptors refer to the bond (a, b, or c) to which the sp^{3} carbons are attached.

A third descriptor, to indicate points of ring fusion, may also be necessary. It consists again of a bond (a, b, or c) and is placed in parentheses. For examples: for **25**, [1.1.2(b)^{b}.1.1]pentiptycene; **26**, [1.1.3(b,b)^{b}.1.1]-pentiptycene; **20**, [3(b,b)^{b}.1.1]triptycene.

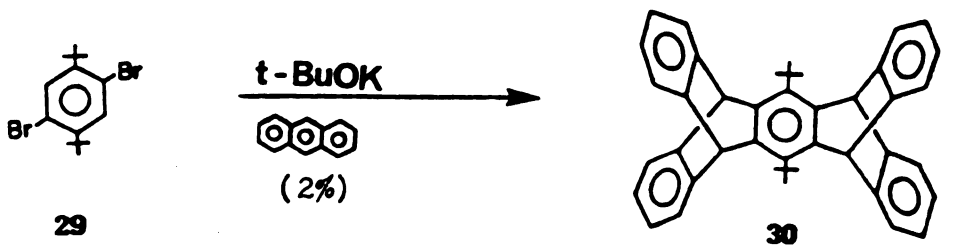
Just as with triptycenes, cycloaddition reactions will also be important in the construction of extended triptycenes (iptycenes). This methodology has been applied to the synthesis of several iptycenes using aryne or di-aryne equivalents. The pentiptycene **24** was first prepared by Russian workers by the reaction of triptycyne equivalent **28** with anthracene, in low yield (10%).[15] The



28 **24**

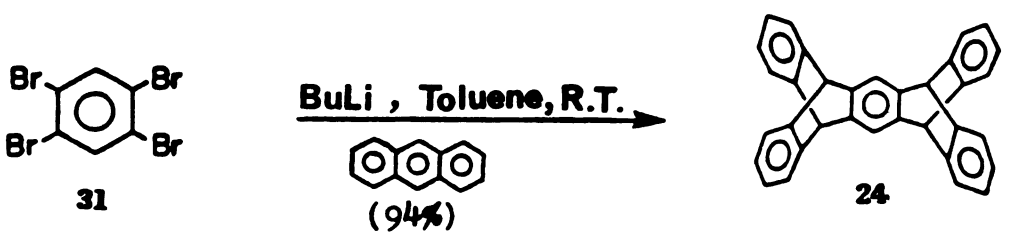
required o-bromofluorotriptycene 28 was synthesized from anthracene in four steps, so that the overall yield of 24 from a readily available starting material was only 1.2% (5 steps).

The di-t-butyl derivative 30 was synthesized from di-aryne precursor 29 but in only a 2% yield.[16]

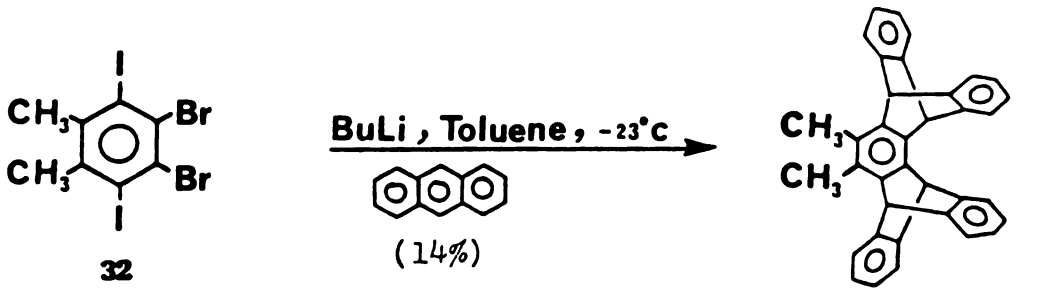


29 30

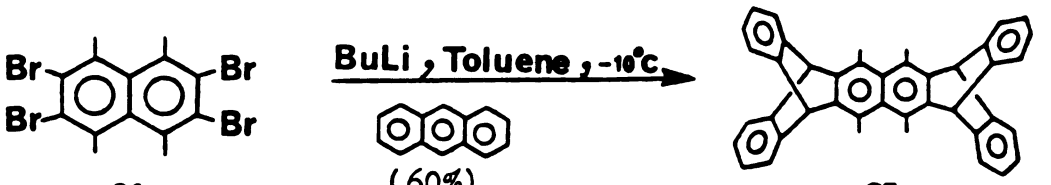
An improved method of generating di-aryne equivalents has been developed in recent years by Hart and coworkers.[17] They described the use of tetrahaloarenes as di-aryne equivalents. When treated with two equivalents of an organolithium reagent in the presence of certain dienes, bis-cycloadducts were readily formed. For example, a simple one-step synthesis of 24[14a] in a much improved yield was executed using tetrabromobenzene 31 as a 1,4-benzadiyne equivalent. The yield in this reaction was 94% based on the consumed anthracene, but only 26% based on the tetrabromobenzene.



31 24



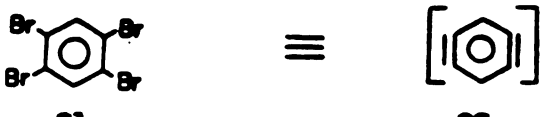
32 33



34 35

Similarly, pentiptycenes 33 and 35 were synthesized via di-aryne equivalents 32 and 34, respectively.[14a]

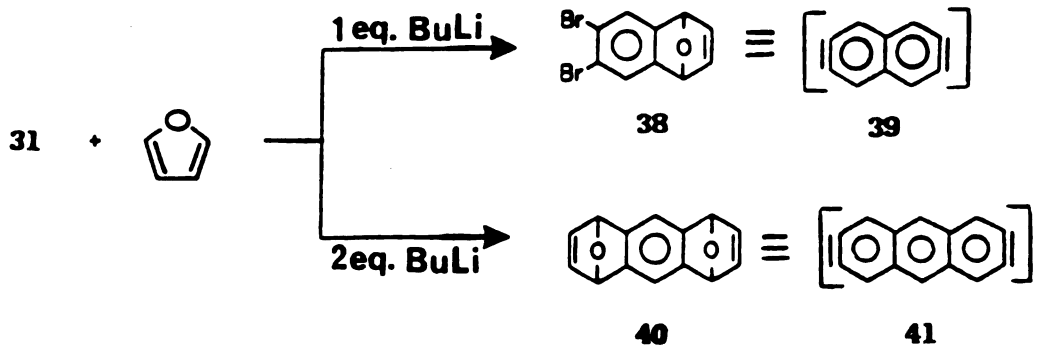
1,2,4,5-Tetrabromobenzene 31 is an especially useful synthon, since it serves not only as the synthetic equivalent of 1,4-benzadiyne 36 and 4,5-dibromobenzyne 37, but also as the precursor of synthetic equivalents of 2,3;6,7-naphthadiyne 39 and 2,3;6,7-anthradiyne 41. Hart and coworkers demonstrated the use of this concept with syntheses of the novel iptycene 27 and the useful synthon 20 (vide infra).



31 36

37

Treatment of 31 with either one or two equivalents of n-butyllithium and furan gave epoxide 38 or bis-epoxide 40.



Since the double bonds in 38 and 40 are effective dienophiles, these aryne equivalents can be used to build fused-ring iptycenes, such as 26 (Fig. 2) and 20 (Fig. 3).

Cycloaddition of 40 with anthracene gave bis-adduct 42, which on dehydration produced pentiptycene 26. Thus, 40 is a synthetic equivalent of 2,3;6,7-anthradiyne 41. The central anthracene moiety in 26 added benzyne to give the novel U-shape heptiptycene 27.[14b]

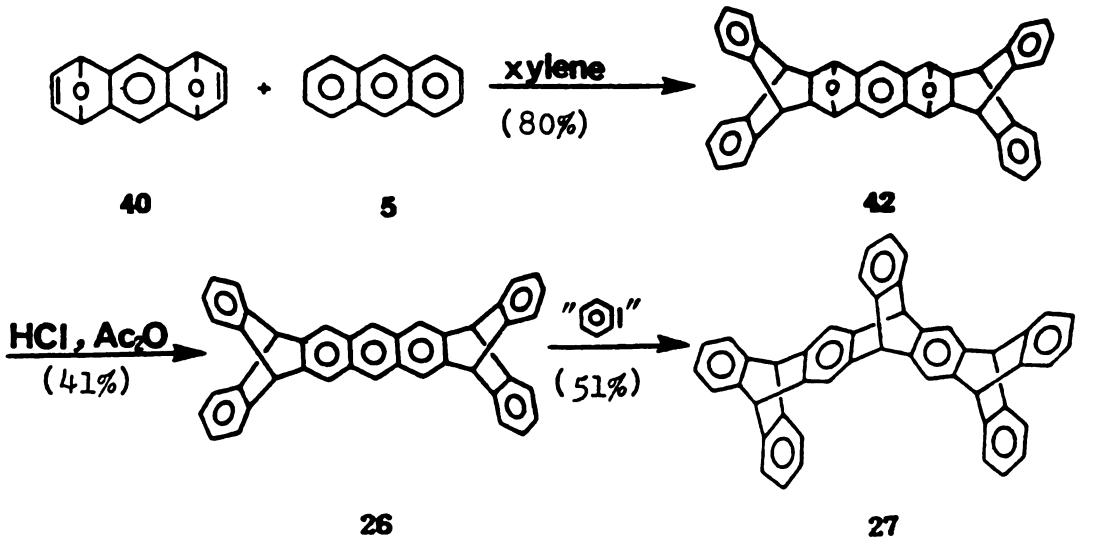


Figure 2. Synthesis of [1.1.1^{b}.1.1^{b}.1.1]heptiptycene 27 via 2,3;6,7-anthradiyne equivalent 40.

Similarly, 38 is a 2,3;6,7-naphthadiyne equivalent. Reaction of 38 with anthracene produced an adduct 43 which on dehydration gave 44. Treatment of 44 with one equivalent of n-butyllithium and furan gave an adduct 45 which was then deoxygenated with low-valent titanium to give [3(b,b)^{b}.1.1]-triptycene 20.[18] This synthesis of 20 gives a much better yield than the literature method.[11a] Since compound 20 will serve as an important building block in the synthesis of higher iptycenes, we shall also describe later three other methods for its synthesis (see Results and Discussion part).

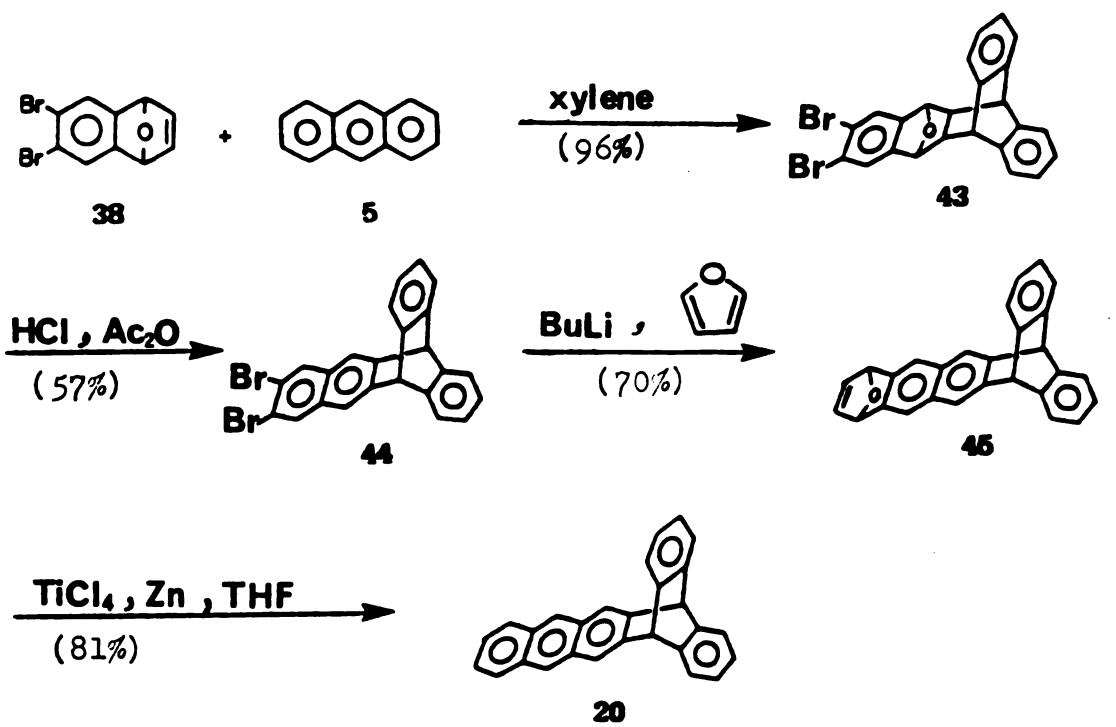


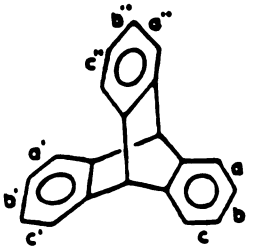
Figure 3. Synthesis of [3(b,b)^{b}.1.1]triptycene 20 via 2,3;6,7-naphthadiyne equivalent 38.

So far we have briefly described the history from triptycene to extended triptycenes (iptycenes). The basic

concepts are summarized as follows:(a) cycloaddtion of an aryne (i.e. **4**, **13**) to an acene (i.e. anthracene, tetracene, pentacene) directly constructs the triptycene framework. (b) di-aryne equivalents (i.e. **31**, **38**, **40**) can be used to build up iptycenes quickly. The main part of this thesis will discuss the application of these concepts to the synthesis of higher iptycenes.

C. Reasons for The Synthesis of Iptycenes.

As we have pointed out, triptycene can be considered as the first member of a large series of compounds, namely "iptycenes". For example, fusion of a single 9,10-anthradiyl moiety **46** to triptycene **1** at an **a** or **b** bond can give pentiptycene **22** or **24**, respectively. Fusion of two



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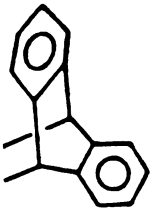
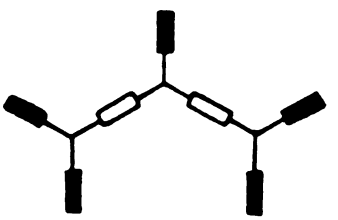


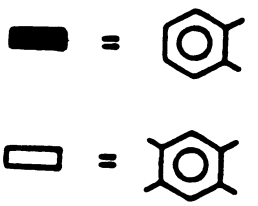
46

9,10-anthradiyl moieties at **b** and **b'** will give heptiptycene **27**, etc. Elaboration of **1** with one to six 9,10-anthradiyl moieties leads to 24 possible different iptycenes.[19] Only a few of these iptycenes are known,[19,20] and the remainder provide a synthetic challenge. Although this thesis does not deal with these particular iptycenes, the general synthetic strategies for attaining such compounds will be discussed.

Besides the synthetic challenge, iptycenes possess a number of interesting properties which make their synthesis worthwhile. One of these properties is high melting points and high thermal stability. For instance, the melting points of triphenylmethane, triptycene **1**, pentiptycene **24**, and heptiptycene **27** increase from 94° to 256° to 483° to >525°. The factors which lead to these unusually high melting points are not obvious. It is important to examine their x-ray structures, particular the packing patterns.[21] Polyiptycenes, like polyphenyls, could be potentially useful heat-resistant materials.[22]

Another interesting feature of these iptycenes is their molecular cavities, which could be useful in forming host-guest compounds. As previously mentioned, heptiptycene **27** has a U-shape cavity with two parallel arene rings, as shown in an end-on view. The cavity may be used to trap metal ions or small organic molecules.





27 (end-on view)

There are many other interesting structural features of iptycenes besides high melting points, high thermal stability, and possibilities as hosts in molecular

complexes. For example, spectral properties involving ring-ring interactions,[11] novel organometallic complexes, novel photochemistry and unusual semi-conductor design.

This thesis will deal mainly with the synthesis of parent iptycenes. First, the synthesis of some useful synthons, including both dienophiles and dienes will be described. Then, it will be shown how these synthons can be applied to improved syntheses of **20**, itself a useful iptycene synthon, and to higher iptycenes.

Like **20**, [3(b,b)^{b}.1.3(b,b)^{b}]triptycene **109** and [3(b,b)^{b}.3(b,b)^{b}.3(b,b)^{b}]triptycene **110** are both potential synthons for the synthesis of higher iptycenes or polyiptycenes. We shall discuss the attemped synthesis of these synthons via heptacene equivalents in the second part of this thesis. The synthesis of linear acenes (i.e. tetracene and pentacene, which are difficult to obtain by literature methods) via cycloaddition of epoxides (**7**, **38**, **50**) and benzocyclobutene will be presented, to demonstrate the versatility of these epoxides. In addition, the use of 5,14-dihydropentacene as a diene in cycloadditions with epoxides **50** and **38**, which leads to the synthesis of potential synthons **109** and [3(b,b)^{b}.1.2^{b}]triptycene **143**, will also be described.

Finally, we shall describe the bis-cycloadduct of epoxide **40** and tetraphenylcyclopentadienone **153**, which is a useful synthetic equivalent of furano[3,4-f]benzo[c]furan **133**. Its synthesis and application to the preparation of linear polycyclic arenes will be presented.

RESULTS AND DISCUSSION

Part I. Synthesis of Extended Triptycenes (Iptycenes).

A. Useful Synthons.

Triptycenes are usually prepared by aryne addition to an anthracene. Cycloaddition will also be important to build up higher iptycenes. A general approach to the construction of iptycenes is shown in Fig. 4.

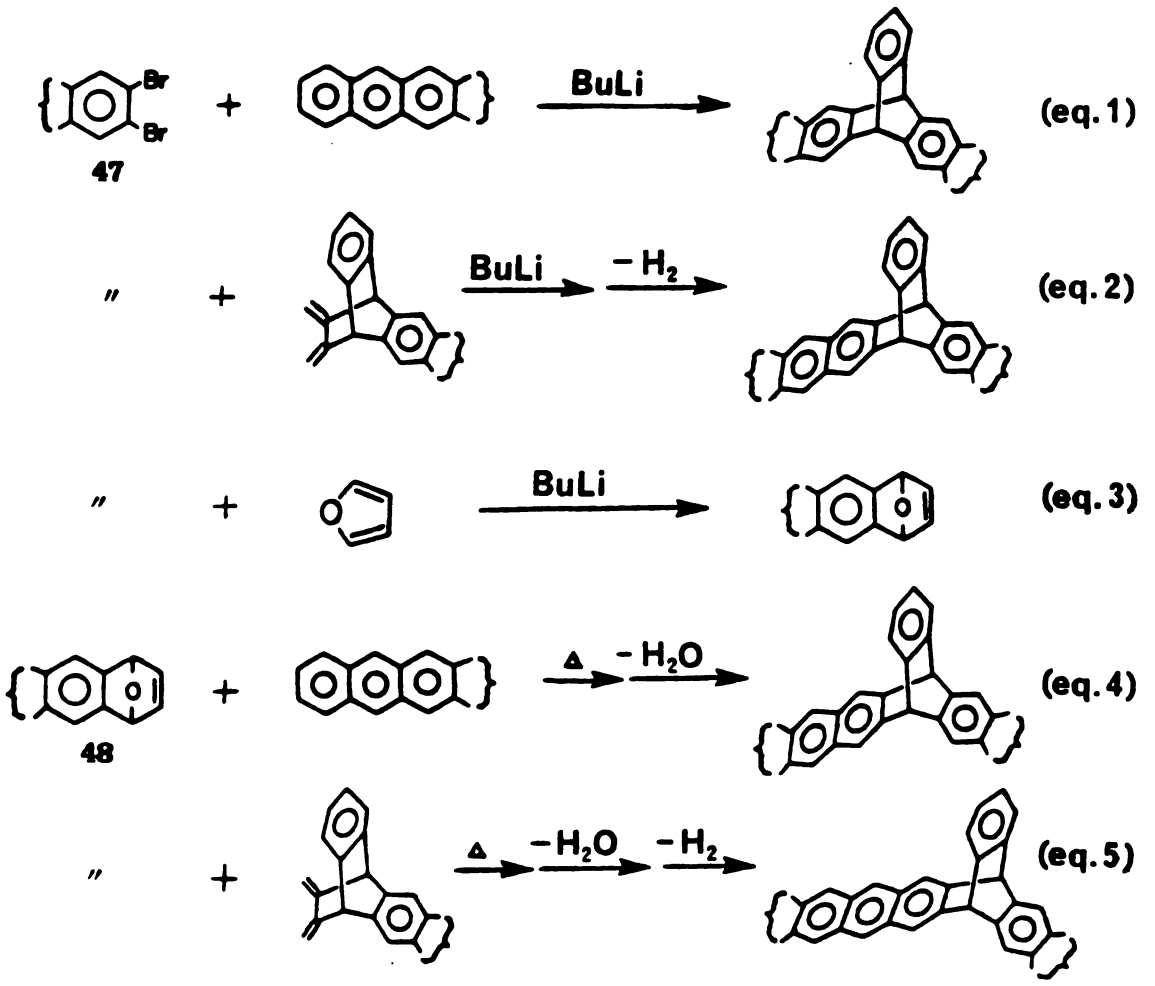
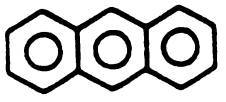


Figure 4. General construction of the iptycene framework.

First, an aryne generated from a 1,2-dibromoarene and trapped with an anthracene moiety will give directly the iptycene framework (eq.1). Second, aryne addition to a bis-methylene moiety, followed by dehydrogenation will then give one additional fused ring in the resulting iptycene system (eq.2). Third, a furan adduct can be generated as in eq.3 and used as an aryne equivalent (epoxide) which, on reaction with an anthracene moiety followed by dehydration gives another route to fused-ring iptycenes (eq.4). Finally, cycloaddition between this aryne equivalent and a bis-methylene moiety, followed by dehydration and dehydrogenation, provides another method for constructing the iptycene backbone, now with three fused rings (eq.5).

Rather than tackle each particular iptycene as a unique synthetic challenge, it is useful to have available a number of building blocks which can be employed in various sequences to construct certain ring systems. Some synthons that we have found useful are listed in Table 1. They are either aryne or di-aryne equivalents. Dienes such as anthracene **5**, [3(b,b)^{b}.1.1]triptycene **20**, and the bis-methylene compound **52** are also needed as building blocks.



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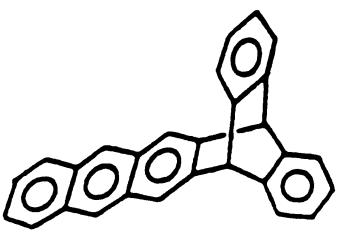

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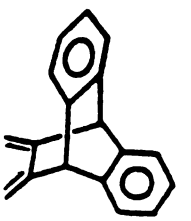

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Table 1. Synthons Useful as Aryne or Di-aryne Equivalents.

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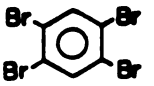
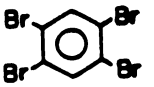
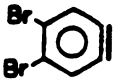
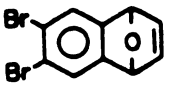
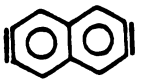
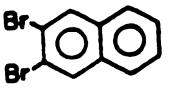
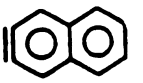
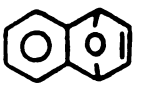
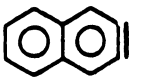
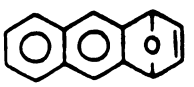
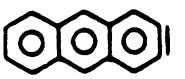
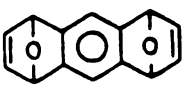
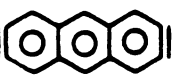
 31	 36
 31	 37
 38	 39
 49	 13
 7	 13
 50	 51
 40	 41

1,2,4,5-Tetrabromobenzene 31,[24] which is useful as the synthetic equivalent of either 4,5-dibromobenzyne 37 or 1,4-benzadiyne 36, is readily prepared in good yield by bromination of commercially available 1,4-dibromobenzene. Various synthons can be derived from 31 (Fig. 5). Treatment

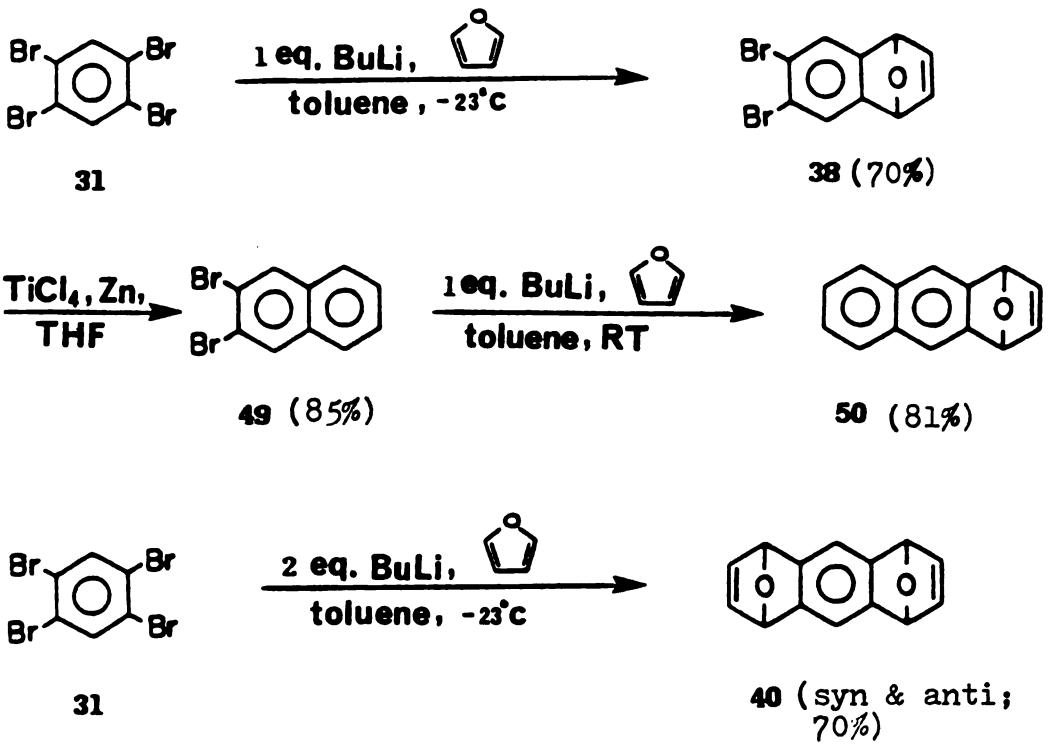
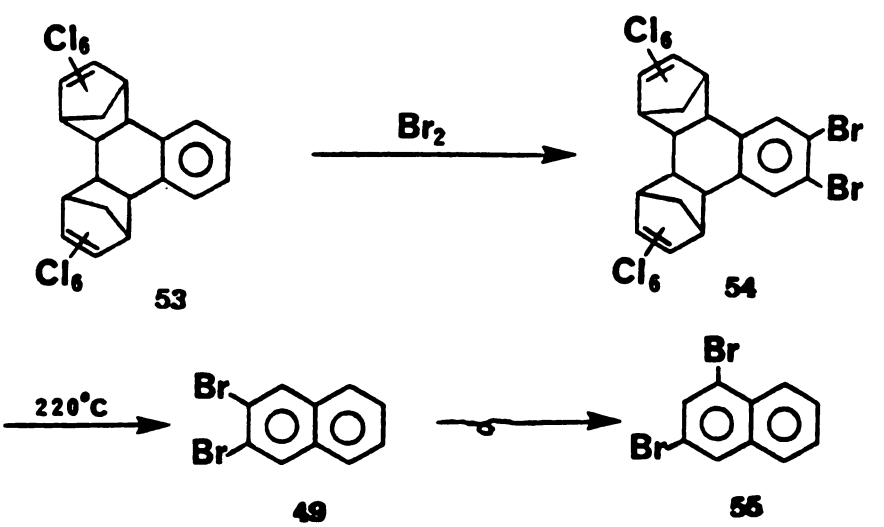


Figure 5. Synthesis of various synthons from 1,2,4,5-tetrabromobenzene 31.

of 31 with either one or two equivalents of n-butyllithium and furan gives synthon 38 or 40.[14b,18] These reactions as described in the literature, were generally carried out at -23°C. At this temperature most of the tetrabromobenzene precipitated; consequently only small scale reactions could be carried out or else large volumes of solvent were necessary. After some trials, we have developed optimum

conditions for these reactions using a minimum amount of solvent so that the reactions can be scaled up to produce ten grams of product(see Experimental Part for details).

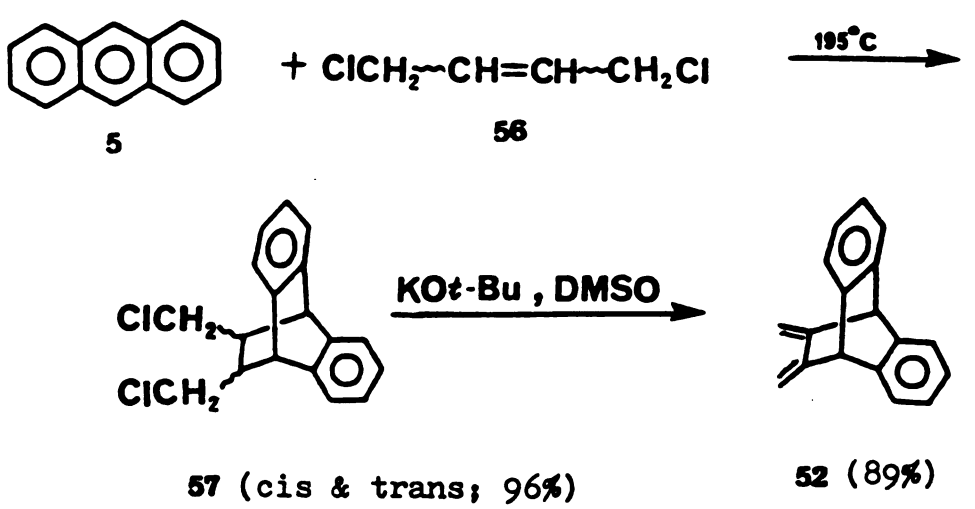
2,3-Dibromonaphthalene **49** is a useful 2,3-naphthyne equivalent. It has been prepared by several methods.[25] The best of these involved bromination of the commercially available naphthalene-hexachlorocyclopentadiene bis-Diels-Alder adduct **53** followed by pyrolysis of the bromination product at 220° C.[25d] The overall yield for the two steps was 46%. However, we found that the pyrolysis step occasionally involved rearrangement of **49** to its isomer 1,3-dibromonaphthalene **55**. The evidence came from the ^{1}H NMR spectrum, which showed two one-proton singlets at δ 8.13 and 7.94 for the halogenated ring protons, and two two-proton doublets of doublets (AA'BB') at δ 7.73 and 7.50 for the non-halogenated ring protons. The expected product **49** showed, on the other hand, a two-proton singlet at δ 8.15 and two two-proton doublets of doublets at δ 7.48 and 7.68 as required by its symmetry.



We describe here an alternate route to **49** involving the metal-catalyzed deoxygenation[29] of **38** with $TiCl_4$ and zinc, which proceeds in excellent yield (86%).

The 2,3-anthryne equivalent **50** is readily prepared from **49**. The literature method[25e] used phenyllithium, whereas we used n-butyllithium instead with equal effect but a simpler purification. Simple recrystallization gave the desired product in high purity without column chromatography.

Butadiene **52**, with a 9,10-anthradiyl unit fused to the 2,3 positions, is a useful diene for iptycene synthesis. The literature syntheses[26] of **52** require four steps from anthracene, except for one[27] which requires only two steps. However, the latter did not report experimental details. We describe here the use of 1,4-dichloro-2-butene[28,31] **56** as a dienophile in the cycloaddition with anthracene. The mixture of cis and trans cycloadducts was dehydrochlorinated using potassium t-butoxide in DMSO.[26b] The overall yield for the two steps was 85%.



As we have described above, the basic synthons are now readily available. We shall discuss later how these synthons can be applied to the synthesis of higher iptycenes.

B. Exo Selectivity in Endoxide Cycloadditions.

In this study, 7-oxabicyclo[2.2.1]hepta-2,5-dienes of the type **48** have been used frequently as dienophiles in cycloadditions with an anthracene moiety, to construct the iptycene framework (see Fig. 4; eq.4). The cycloadduct may have two possible configurations, exo **59** or endo **60**. The

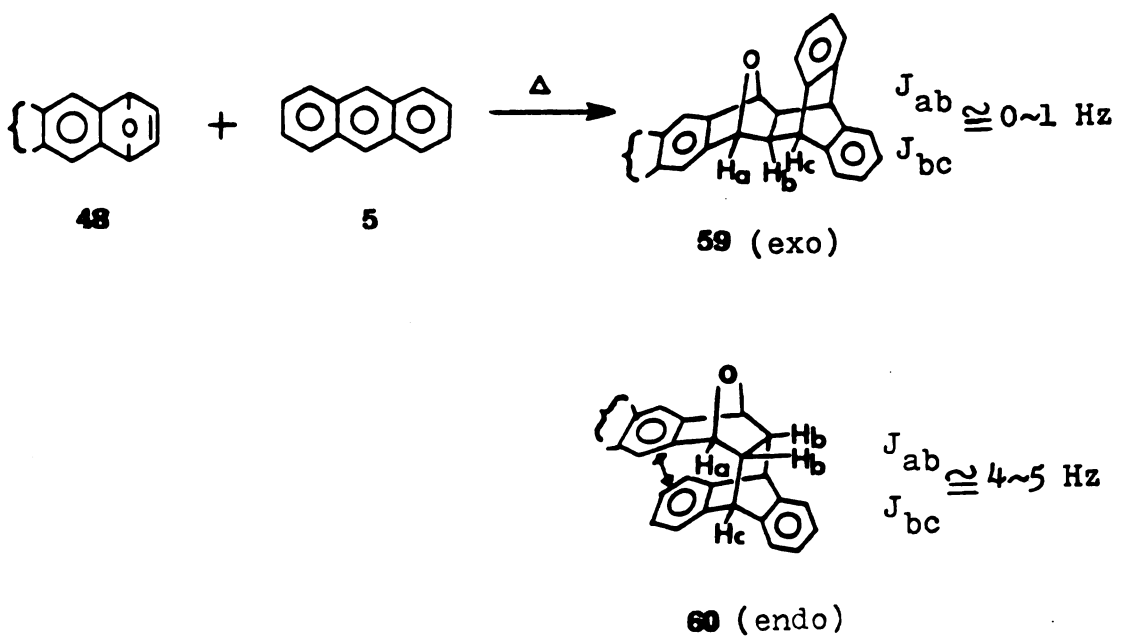


Figure 6. Exo and endo adducts of 7-oxabicyclo[2.2.1]-hepta-2,5-dienes 48 with anthracene.

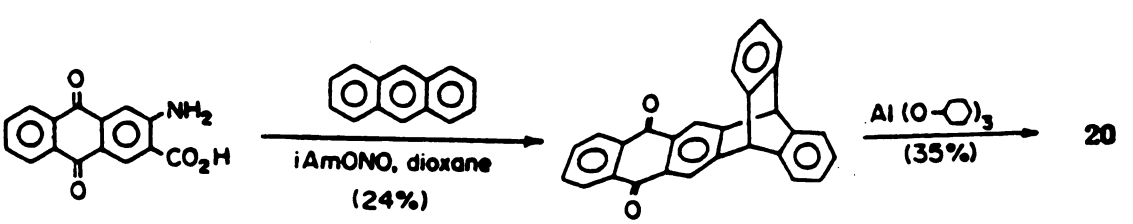
endo adduct is thought to be the kinetic product. However, the severe steric crowding and $\pi-\pi$ repulsion makes this addition mode highly unfavorable. The thermodynamically favored exo adduct is thus the only product formed. The two isomers can be readily distinguished by their proton NMR

spectra.[30] In the exo isomer, the dihedral angle between H_a and H_b or H_b and H_c is close to 90°, so that the bridge methine protons H_a and H_c show no coupling with the H_b protons. Thus we should be able to see three "singlet" aliphatic protons in the exo isomer's spectrum. In the endo isomer, the dihedral angle is about 65°, and J_{ab} or J_{bc} should be about 4-5 Hz.

Exo selectivity is prevalent throughout this study. None of the endo isomer has been found. This selectivity will not be mentioned in most synthetic sequences, but in some cases it is important in assigning structures.

C. An Improved Synthesis of [3(b,b)^b.1.1]Triptycene (20).

Triptycene 20 was previously synthesized by the route shown below.[11a] The overall yield was only 8.4% from 18 which itself is difficult to obtain.[12,13]



Since 20 is potentially a very useful synthon for iptycenes, through cycloadditions to the anthracene moiety, we sought a good short route to it. Four methods will be presented, because they illustrate different uses for the various synthons (Fig. 4) and also because two intermediates (44 and 45) in the longest synthesis (route a) can

themselves be useful synthons. The syntheses of 20 are schematically outlined in Fig. 7.

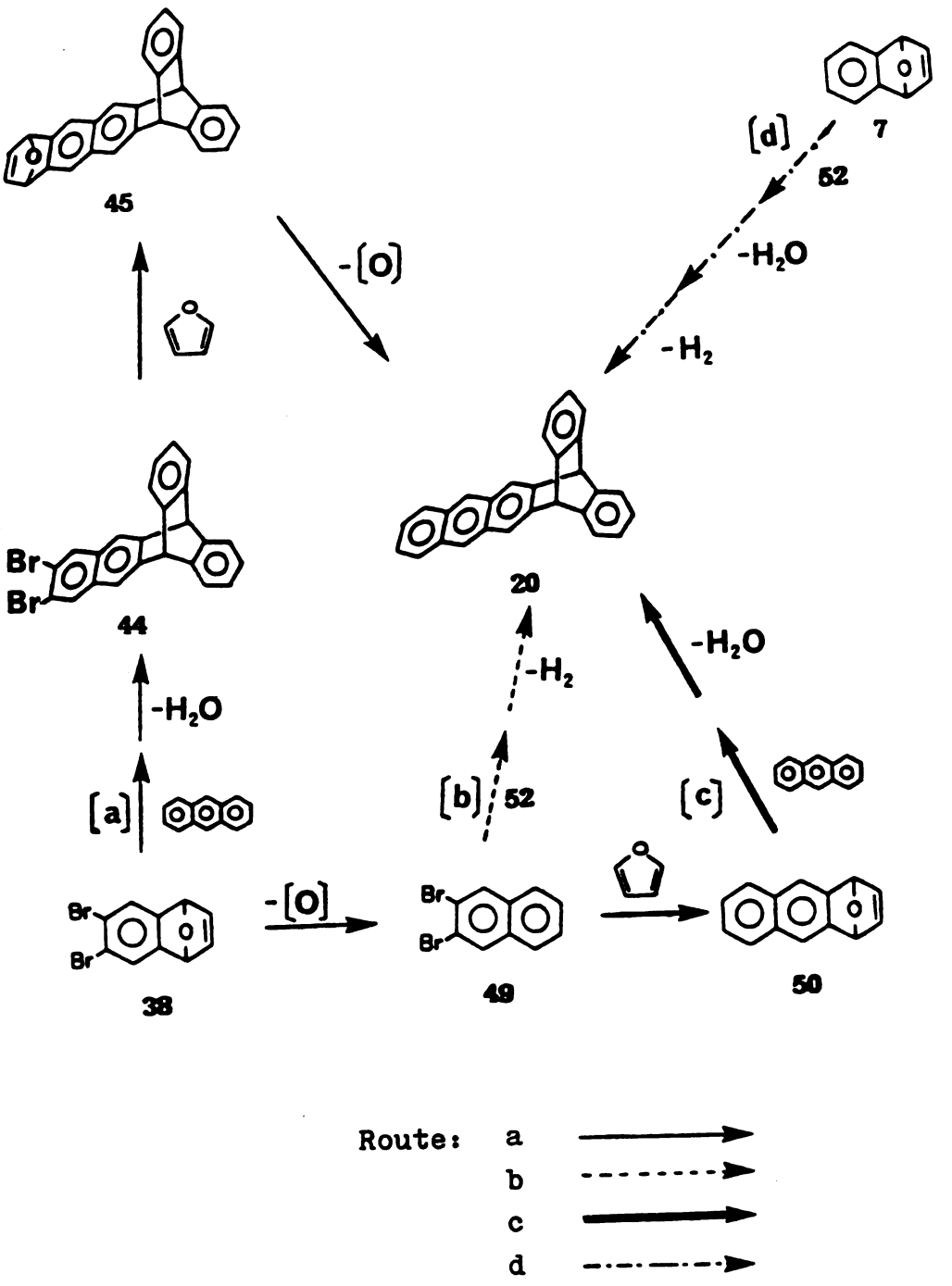
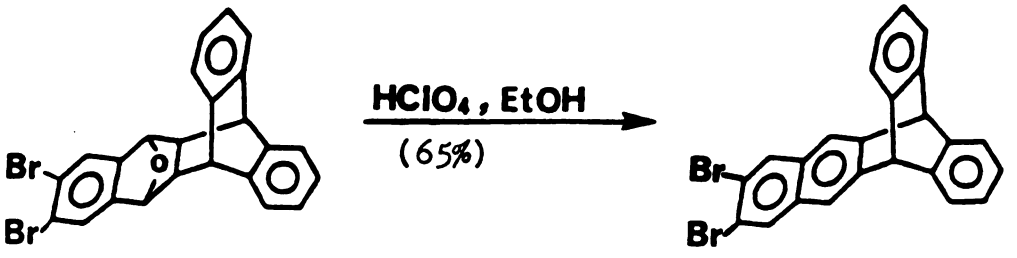


Figure 7. Schematic syntheses of [3(b,b)^{b}.1.1]triptycene 20 via various synthons.

Method A : The first good synthesis of **20** was developed by Hart and Meador[18] from **38**, using di-aryne equivalent methodology (Fig. 3). Treatment of **38** with anthracene in refluxing xylene gave a single exo adduct **43** in 96% yield. Meador used hydrochloric acid and acetic anhydride as the dehydrating reagent to remove the oxygen bridge, but it was found that this reaction was frequently not reproducible. After several different conditions were tried, we found that perchloric acid in ethanol was an effective dehydrating reagent, giving **44** in 65% yield.

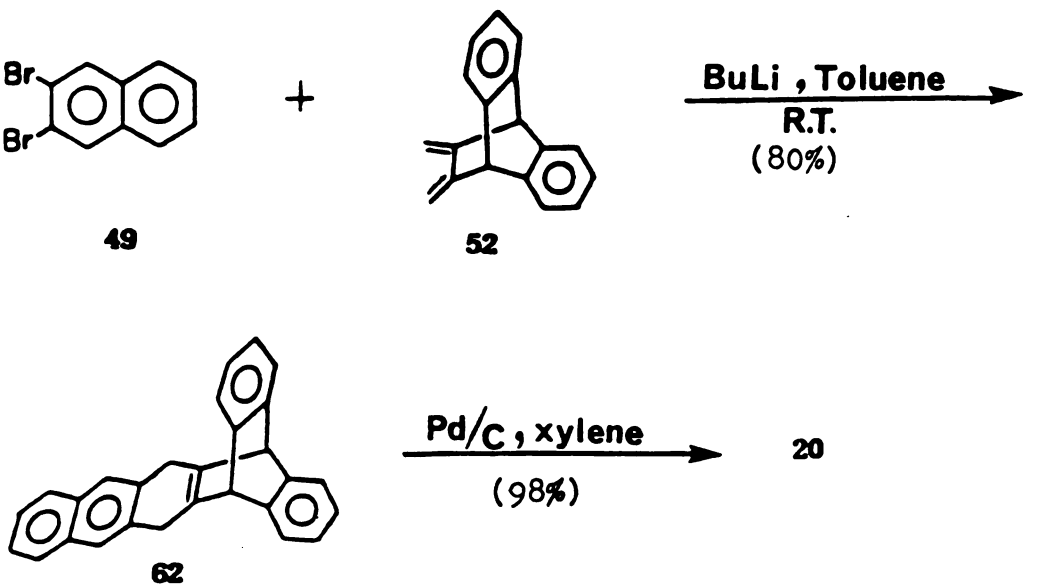


43 **44**

The last ring was added by cycloaddition of the correspounding aryne to furan followed by deoxygenation of the resulting adduct **45** with low valent titanium. The overall yield of **20** in four steps from **38** was 35%. In this way multi-gram amounts of **20** can be obtained quite readily after reaction condition for each step in the sequence were optimized.

Although this route to **20** is somewhat long, two potentially useful iptycene synthons **44** and **45** are generated. Their use in the synthesis of higher iptycenes will be demonstrated later (vide infra).

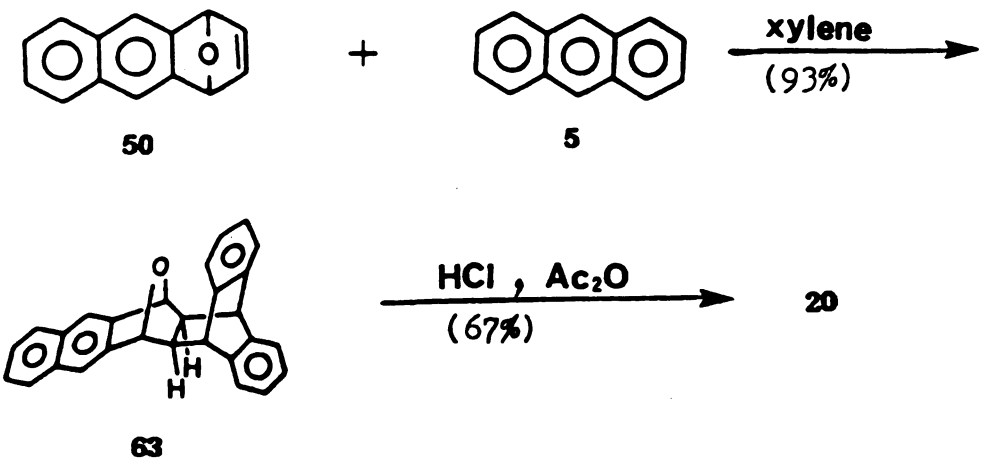
Method B : This route uses 2,3-naphthyne equivalent **49** as the synthon.[19,31] Treatment of 2,3-dibromonaphthalene **49** with one equivalent of n-butyllithium at room temperature generates 2,3-naphthyne **13**, which is trapped with diene **52** in situ (application of Fig. 4; eq.2). The dihydroadduct **62** was then dehydrogenated using 10% Pd/C in refluxing xylene to give **20**. The overall yield for the two-step sequence was 78%.



49 **52** **20** **62**

The structure of the intermediate **62** was confirmed by its spectra. The ^1H NMR spectrum showed a two-proton singlet at δ 4.92 for the bridgehead protons and a four-proton singlet at δ 3.82 for the allylic protons. Also present was a two-proton singlet at δ 7.58 for the uncoupled naphthalene protons, and a two-proton doublet of doublets at δ 7.70 for the coupled naphthalene protons, as well as a doublet of doublets at δ 6.96(4H) and a multiplet at δ 7.34 (6H) for the remaining aryl protons. The mass spectrum had a molecular ion peak at m/e 356.

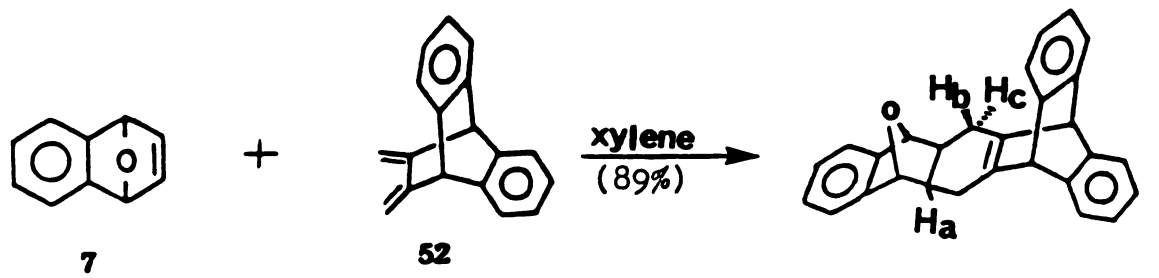
Method C : This route starts with the three-ring precursor **50**, a 2,3-anthryne equivalent (application of Fig. 4; eq.4). Cycloaddition of **50** to anthracene in refluxing xylene gave exo adduct **63** in 93% yield. Acid dehydration using hydrochloric acid and acetic anhydride gave **20** in 67% yield. The overall yield for the two-step sequence was 62%.



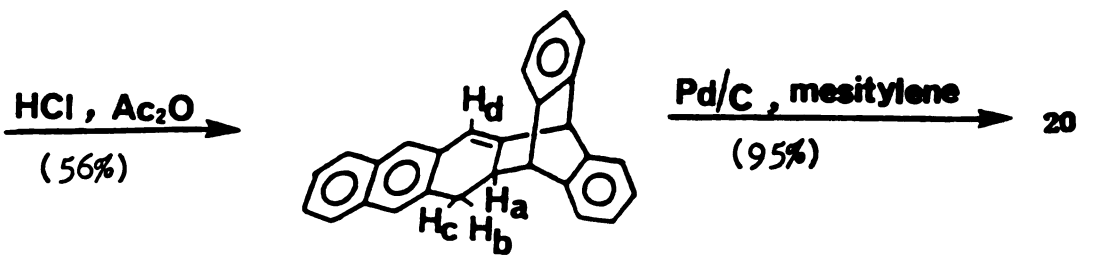
50 **5** **63**

The structure of adduct **63** was confirmed by its spectra. The ^{1}H NMR spectrum showed a two-proton singlet at δ 2.36 for the endo protons, a two-proton singlet at δ 5.08 for the bridgehead protons adjacent to the oxygen , and a two-proton singlet at δ 4.49 for the remaining bridgehead protons. The aromatic region contained a naphthalene moiety which appeared as follows : δ 7.72(dd,2H), 7.52(s,2H), 7.40 (dd,2H). In addition, there were four two-proton doublets of doublets at δ 7.02, 7.17, 7.24 and 7.33 for the remaining aryl protons. The ^{13}C NMR spectrum of **63** showed only fourteeen peaks (three aliphatic carbons at δ 47.52, 49.21, 81.23 and eleven aromatic carbons) as required by symmetry. The mass spectrum showed a molecular ion peak at m/e 372.

Method D : This route starts from another 2,3-naphthyne equivalent, **7**, which was readily available from the reaction of benzyne with furan.[33] Cycloaddition of **7** to **52** gave adduct **64** in 89% yield. The stereochemistry of **64** was not determined, but probably was exo. The ^{1}H NMR



7 **52** **64**



65

spectrum of **64** showed two two-proton singlets at δ 4.78 and 4.92 for the bridgehead protons, and three sets of two-proton doublets of doublets at δ 1.87, 2.20 and 2.82 (J_{bc}=14 Hz; J_{ab}=7 Hz; J_{ac}=5 Hz) for the H_a, H_b and H_c protons. The remaining aryl protons appeared as a four-proton multiplet at δ 6.85-6.91 and an eight-proton multiplet at δ 7.05-7.23. The ^{13}C NMR spectrum had thirteen peaks (four aliphatic carbons at δ 30.47, 42.01, 55.77, 84.98 and nine aromatic carbons) as required by symmetry. The mass spectrum showed a molecular ion peak at m/e 374.

The dehydration of **64** with acid (56%) was accompanied by double-bond isomerization to give vinylnaphthalene **65**, as

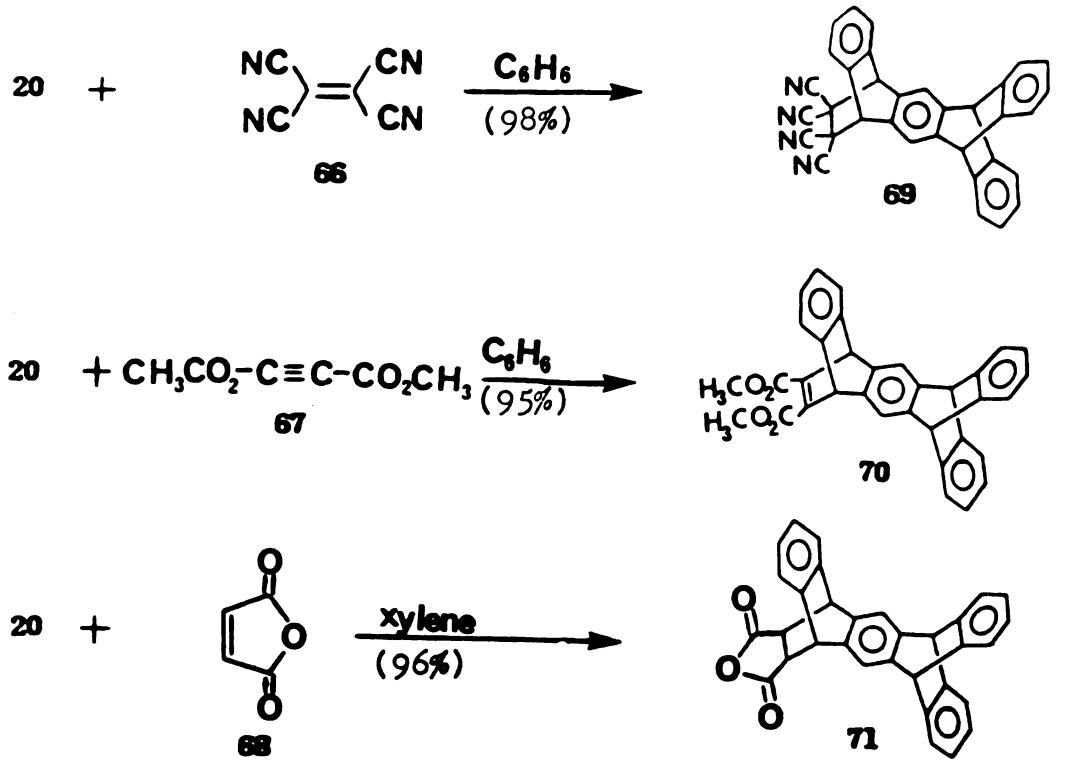
indicated by loss of the symmetry expected in the ^{1}H NMR spectrum. For example, the spectrum contained a triplet at δ 2.32 for the allylic protons (H_a) and two doublets of doublets at δ 2.72 and 2.96 for the benzylic protons (H_b and H_c). Also, the bridgehead protons appeared as two singlets at δ 4.32 and 4.87, and there was a vinyl proton (H_d) at δ 6.55. The remianing aromatic proton signals were also consistent with a structure in which the double bond had moved into conjunction with the naphthalene moiety. The mass spectrum had a molecular ion peak at m/e 356.

Compound **65** was dehydrogenated to **20** in 95% yield by refluxing with 10% Pd/C in mesitylene for 3 days. The overall yield for the three-step sequence from **7** and **52** was 47% (application of Fig. 4; eq.5).

All four methods presented here are improvements over the literature method.[11a] The particular choice will depend on which synthons are available, and whether or not additional functionality (for example, bridgehead substituents) are desired in the final product.

D. Cycloadditions of [3(b,b)^b.1.1]Triptycene (20) with TCNE (66), DMAD (67) and MA (68).

The possible use of **20** as a synthon for higher iptycenes was first tested with simple dienophiles such as tetracyanoethylene (TCNE, **66**), dimethyl acetylene-dicarboxylate (DMAD, **67**), and maleic anhydride (MA, **68**). All three reactions gave a cycloadduct quite readily in high yields.



The structures of the cycloadducts (**69**, **70**, and **71**) were confirmed by their spectra. The most characteristic feature of their ^{1}H NMR spectrum is the disappearance of protons due to the anthracene moiety and the formation of additional bridgehead protons. Two sets of bridgehead protons and the uncoupled benzenoid protons of the central ring are the most obvious features of the spectra. For example, singlet peaks appear at δ 5.69, 5.75 and 7.82 for **69**; at δ 5.31, 5.35 and 7.42 for **70**, and at δ 4.71, 5.40 and 7.39 for **71**.

The reactivity of the anthracene moiety in **20** toward dienophiles in the Diels-Alder reaction is somewhat retarded compared with that of anthracene itself, probably due to additional steric crowding caused by the 9,10-anthradiyl moiety.

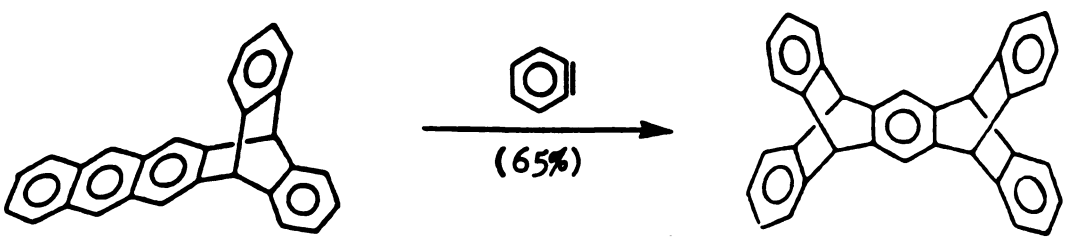
E. Synthesis of a series of [n^{b}.1.1^{b}.1.1]Pentiptycenes via [3(b,b)^{b}.1.1]Triptycene.

With diene **20** now readily available by several good methods (vide supra), it was possible to use this synthon with the various dienophiles shown in Table 1 to synthesize a series of pentiptycenes, as briefly outlined in Fig. 8.

1. Improved Synthesis of [1.1.1^{b}.1.1]Pentiptycene (5,14[1',2']:7,12[1",2"]-Dibenzeno-5,7,12,14-tetrahydro-pentacene)(24).

The first example in Fig. 8 demonstrated here was an improved synthesis of **24**. The previous one-step synthesis of **24** from **31**, anthracene and n-butyllithium proceeded in 94% yield based on the consumed anthracene. In fact, however, the practical yield is only 26% based on **31**.[14a] There are some technical difficulties with this method, and also a substantial amount of anthracene remains which must be separated from the desire **24** by chromatography and/or sublimation. Hence, a better route seemed desirable.

Since we can now make **20** readily by good methods, **24** can be prepared in one step from the reaction of **20** with benzyne (via benzenediazonium-2-carboxylate hydrochloride). The yield was 65%.[19]



20 **24**

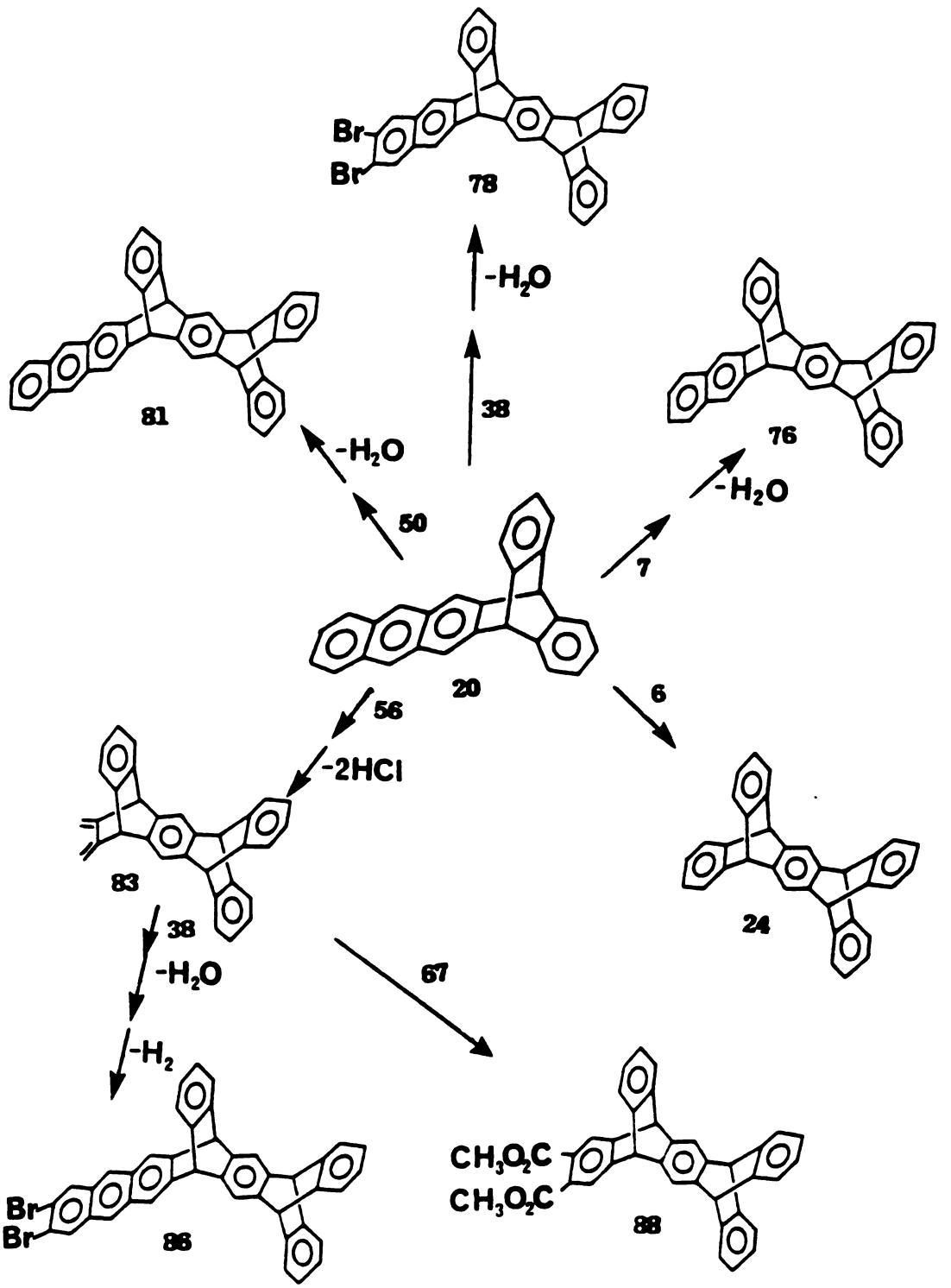
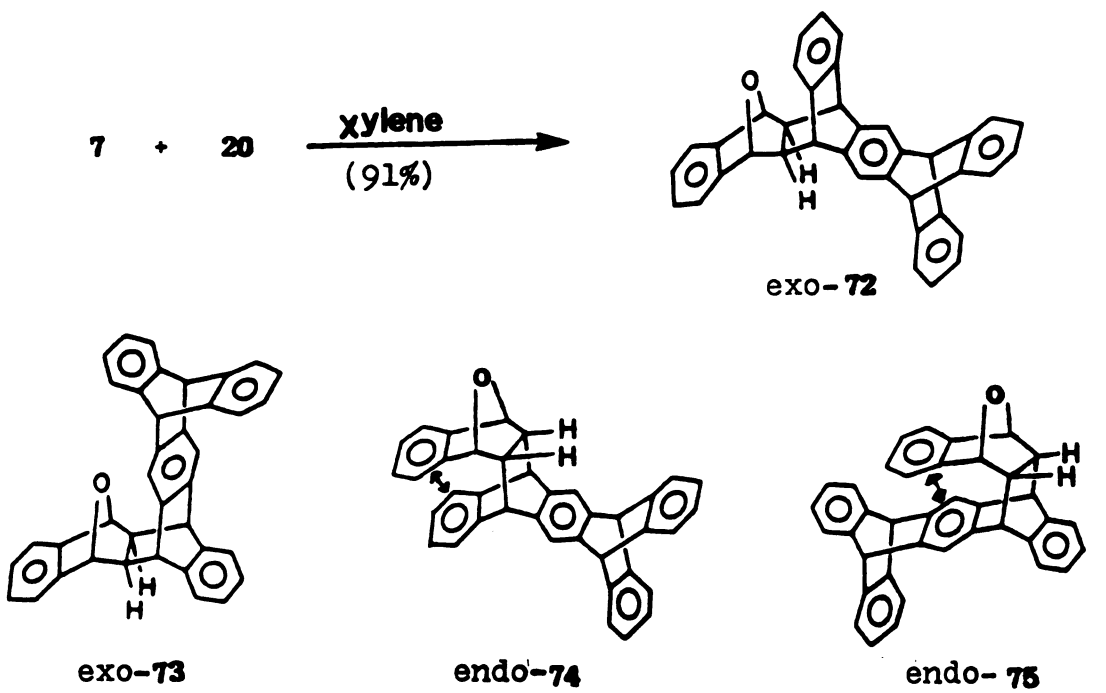


Figure 8. Schematic syntheses of [n^b.1.1^b.1.1]-pentiptycenes via [3(b,b)^b.1.1]triptycene 20.

2. [2^b.1.1^b.1.1]Pentiptycene (5,16[1',2']:7,14[1",2"]-Dibenzeno-5,7,14,16-tetrahydrohexacene)(76)

The availablity of synthons epoxide **48** (i.e. **7**, **38**, **50**) and **20** allowed us to construct pentiptycenes with an "outer" fused-ring moiety (see general approach in Fig. 4, eq.4).

Cycloaddition of **7** and **20** in refluxing xylene for 2 days gave exo adduct **72** in 91% yield. Four possible isomers may be formed (two exo and two endo ; Fig. 9) in this



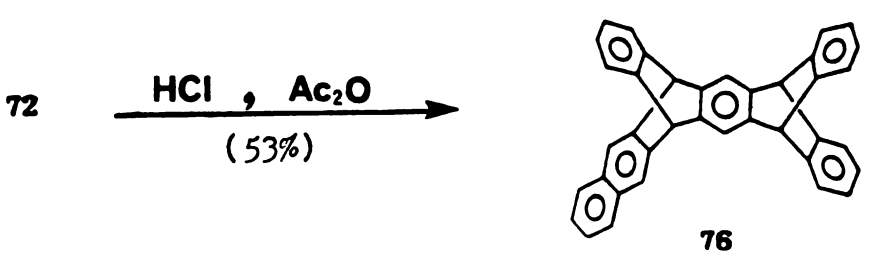


Figure 9. Synthesis of [2^b.1.1^b.1.1]pentiptycene **76**.

reaction. However, only one isomer was actually observed. Structures **74** and **75** can be ruled out easily by looking at the severe steric crowding and lack of observed coupling between the endo protons and the bridgehead protons (see discussion in exo selectivity). The stereochemistry of the adduct was not determined, but probably was **72**, which is less crowded than **73**.

The ^{1}H NMR of **72** showed four two-proton singlets at δ 1.97, 4.22, 4.80, and 5.30 for the bridgehead protons, and a two-proton singlet at δ 7.25 for the uncoupled benzenoid ring protons. The remaining aryl protons appeared as six sets of two-proton and one set of four-proton doublets of doublets at δ 6.88, 6.92, 6.97, 7.18, 7.24, 7.33 and 7.06. The ^{13}C NMR spectrum gave seventeen peaks (two peaks were missing due to quarternary carbons or overlapped signals) with four aliphatic carbons at δ 47.25, 48.85, 53.97, and 81.13. The mass spectrum showed a molecular ion peak at m/e 498.

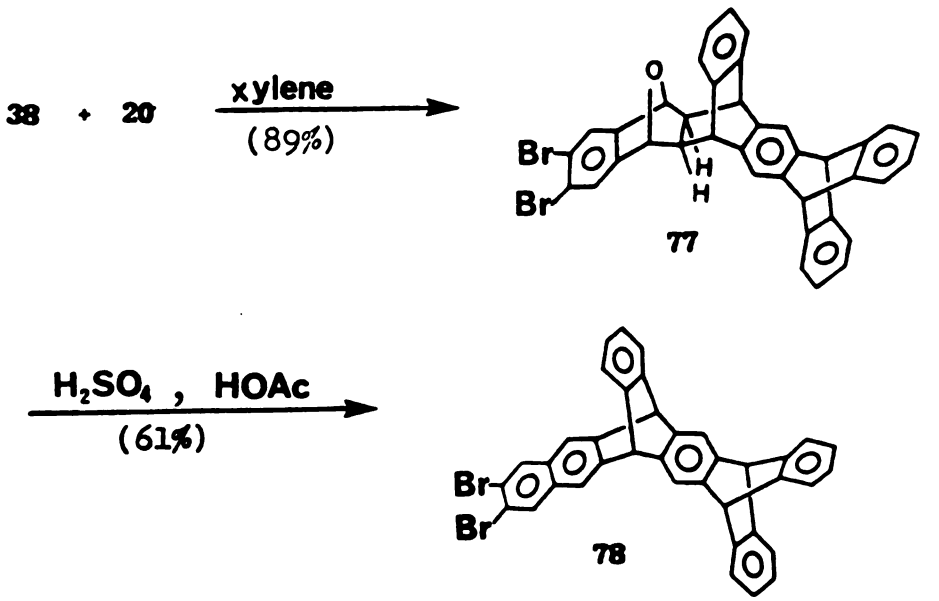
Adduct **72** was dehydrated using hydrochloric acid and acetic anhydride to give the desired pentiptycene **76** in 53% yield. The structure of **76** was assigned from its spectra. The ^{1}H NMR spectrum consisted of two two-proton singlets at δ 5.31 and 5.41 for the bridgehead protons. The aromatic protons appeared as two two-proton singlets at δ 7.48 and 7.68 for the uncoupled benzenoid ring and naphthalene ring protons, a two-proton doublet of doublets at δ 7.63 for the coupled naphthalene peri protons, and two sets of multiplets at δ 6.83-6.95 and 7.25-7.34 for the remaining aryl protons.

The ^{13}C NMR spectrum had nineteen peaks (two aliphatic carbons at δ 53.59 and 53.96 as well as seventeen aromatic carbons), as required by the symmetry. The mass spectrum showed a molecular ion peak at m/e 480.

The overall yield for the two-step synthesis of **76** from the readily available **7** and **20** was 48%.

3. 5,16[1',2']:7,14[1",2"]-Dibenzeno-10,11-dibromo-5,7,14,16-tetrahydrohexacene (78).

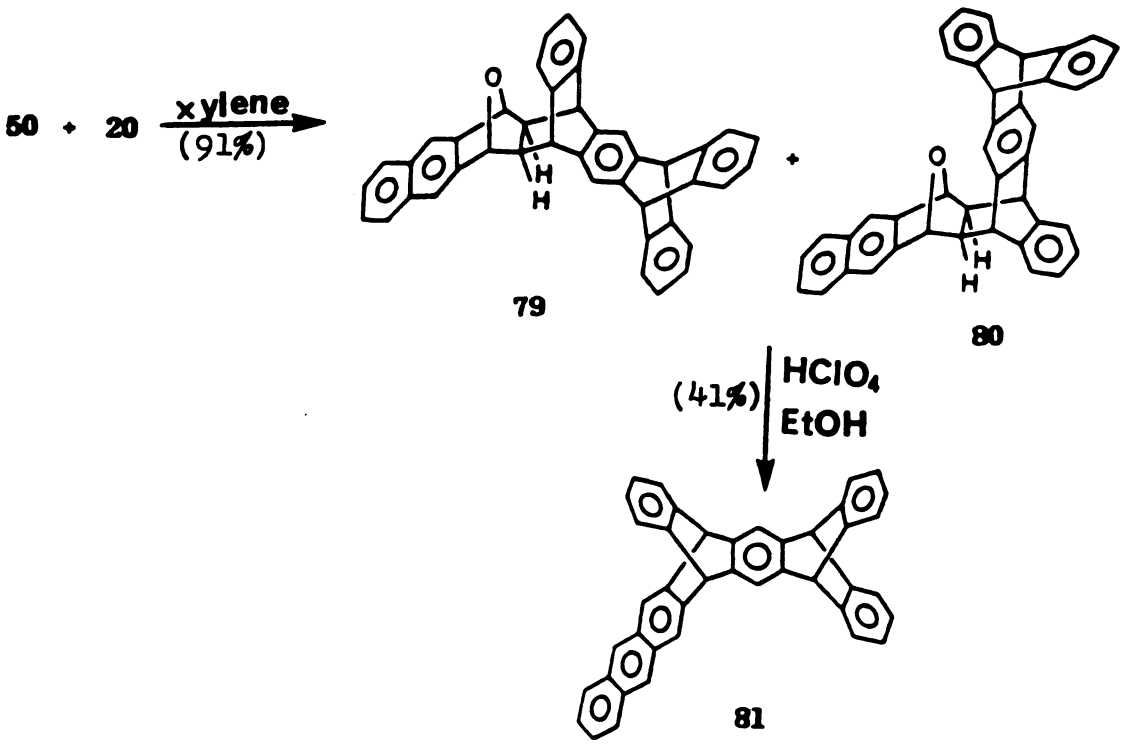
The successful synthesis of **76** led the way to other fused-ring pentiptycenes. Thus, by replacement of synthon **7** with **38** in the synthetic scheme (Fig. 9) one can obtain the target compound **78**. Reflux of **38** and **20** in xylene for 3 days again yielded only a single isomer, **77**, in 89% yield. The adduct was dehydrated using sulfuric acid and acetic acid to give pentiptycene **78** (61%). The overall yield for the two-steps was 54%.



The structures of 77 and 78 were confirmed by their spectra, which were similar to those of 72 and 76. The ^{1}H NMR spectrum of a series of pentiptycenes is listed in Table 2. The ^{13}C NMR spectrum of 78 showed seventeen peaks (two peaks were missing due to quarternary carbons or overlapped signals) with two aliphatic carbons at δ 53.39 and 53.90. The mass spectrum showed a strong molecular ion peak at m/e 638.

4. [3(b,b)^{b}.1.1^{b}.1.1]Pentiptycene (5,18[1'.2']:7,16[1",2"]-Dibenzeno-5,7,16,18-tetrahydroheptacene)(81)

We have described the synthesis of naphthalene fused-ring pentiptycenes, 76 and 78. The anthracene analog can be similarly prepared. Heating 50 and 20 in xylene for 4 days afforded two regioisomeric adducts, 79 and 80, in 91% yield and approximately 59:41 ratio by NMR.



The structures of the adducts were assigned based on the ^{1}H NMR spectrum. The major isomer had a spectrum which consisted of four two-proton singlets at δ 2.12, 4.28, 4.93 and 5.31 for the bridgehead protons, and two two-proton singlets at δ 7.25 and 7.43 for the uncoupled benzene and naphthalene ring protons. The minor isomer contained corresponding peaks at δ 2.29, 4.36, 4.99, 5.35, and 7.33 and 7.45. The remaining aromatic peaks were too complex to assign.

The mixture was not separated but dehydrated directly using perchloric acid to give pentiptycene **81** in 41% yield. The structure of **81** was also confirmed by its ^{1}H NMR spectrum. The protons of the anthracene moiety were apparent as two two-proton singlets at δ 8.18 and 7.80 and two two-proton doublets of doublets at δ 7.89 and 7.36. In addition, there were two two-proton singlets at δ 5.33 and 5.44 for the bridgehead protons, a singlet at δ 7.51 for the central benzenoid ring protons, and remaining peaks correspounding to the twelve aryl protons (see Table 2). The mass spectrum showed a molecular ion peak at m/e 530 as the base peak. The UV spectrum possessed a set of bands typical of an anthracene, with the longest wavelength absorption at 374 nm.

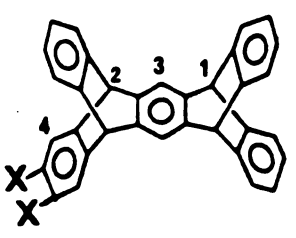
5. Synthesis of 7,12[1',2']-Benzeno-15,16-dimethylene-5,14-ethano-5,7,12,14-tetrahydropentacene (83).

So far we have successfully demonstrated a general route to the synthesis of fused-ring pentiptycenes by

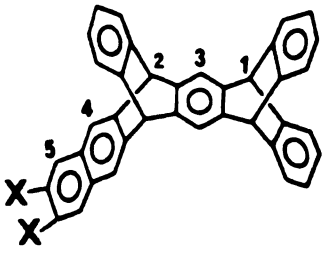
Table 2. ^{1}H NMR Spectra of [n^b.1.1^b.1.1]pentiptycenes.

compound	position[a] 1	2	3	4	5	6	remaining aryl protons
24	5.30	5.30	7.43	7.28[b]			6.92[b]
88	5.29	5.33	7.40	7.58			6.87-6.92(6H)[c] 7.22-7.33(6H)[c]
76	5.31	5.41	7.48	7.68	7.63[b]		6.83-6.95(6H)[c] 7.25-7.34(8H)[c]
78	5.34	5.40	7.49	7.50	7.88		6.86-6.99(6H)[c] 7.25-7.35(6H)[c]
81	5.33	5.44	7.51	7.80	8.18	7.89[b]	(6.86,6.91,6.98)[b] 7.27-7.38(8H)[c]
86	5.32	5.42	7.49	7.77	8.20	8.06	(6.85,6.91,6.98, 7.25,7.29,7.35)[b]

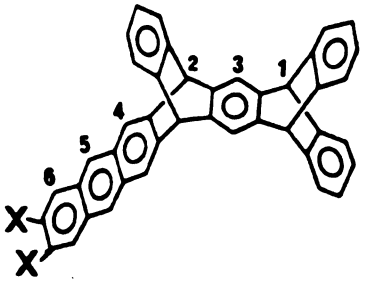
a. Position 1 to 6 refer a two-proton singlets except for b superscript.
b. A two-proton doublet of doublets.
c. Multiplet with assigned protons in parentheses.



24 (X=H)
88 (X=CO_2CH_3)



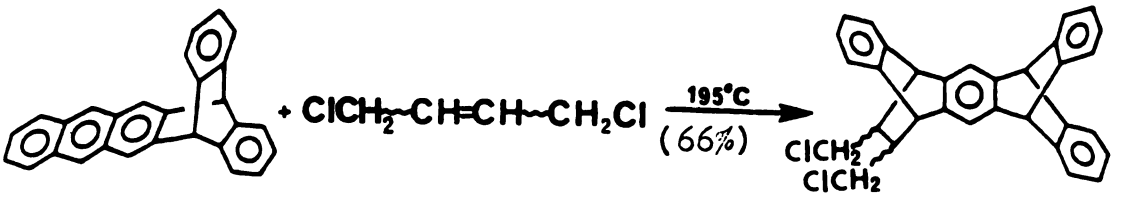
76 (X=H)
78 (X=Br)



81 (X=H)
86 (X=Br)

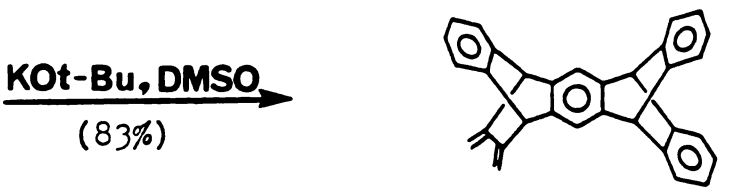
employing the cycloaddition of epoxides (i.e. **7**, **38**, **50**) and synthon **20**, followed by dehydration of the resulting adducts (application of Fig. 4; eq.4). Another method to achieve the goal is to fuse the ring by cycloaddition between the epoxide and a bis-methylene compound (see general approach in Fig. 4; eq.5).

Synthesis of the necessary bis-methylene moiety from anthracene has been described earlier. Similarly, the higher analogue **83** can be prepared from **20**. Reaction of **20**



20 **56** **82**

(cis & trans)



83

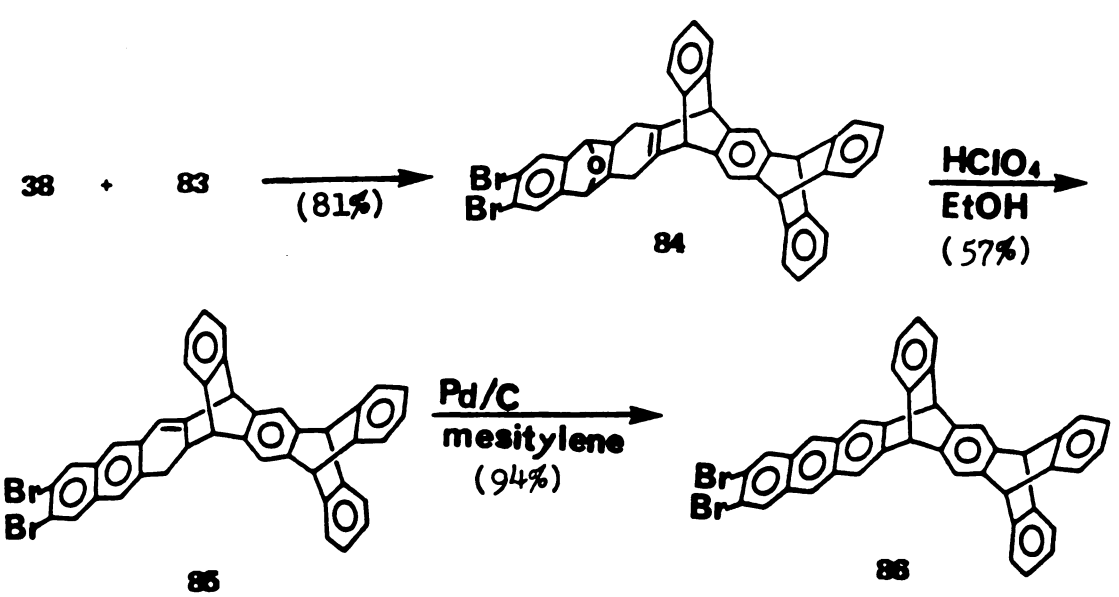
with 1,4-dichloro-2-butene (sealed tube, 195° , 3 days), followed by base-catalyzed elimination gave the bis-methylene compound **83** in 55 % overall yield. The structure of **83** was clear from its ^{1}H NMR spectrum. It showed two-proton singlets at δ 5.20 and 5.34 for the bridgehead protons, and peaks at δ 4.75 and 5.05 for the vinyl protons. The aromatic region contained a two-proton singlet at δ 7.36 for the central benzenoid ring protons and six sets of two-proton doublets of doublets (6.89, 6.96, 7.03, 7.22, 7.28,

7.33) for the remaining aryl protons. The ^{13}C NMR spectrum gave sixteen peaks as required by the symmetry. The mass spectrum showed a strong molecular ion peak at m/e 406.

The use of diene **83** in cycloadditions to synthesize fused-ring or functionalized pentiptycenes will be discussed below.

6. Synthesis of 5,18[1',2']:7,16[1",2"]-Dibenzeno-11,12-dibromo-5,7,16,18-tetrahydroheptacene (86).

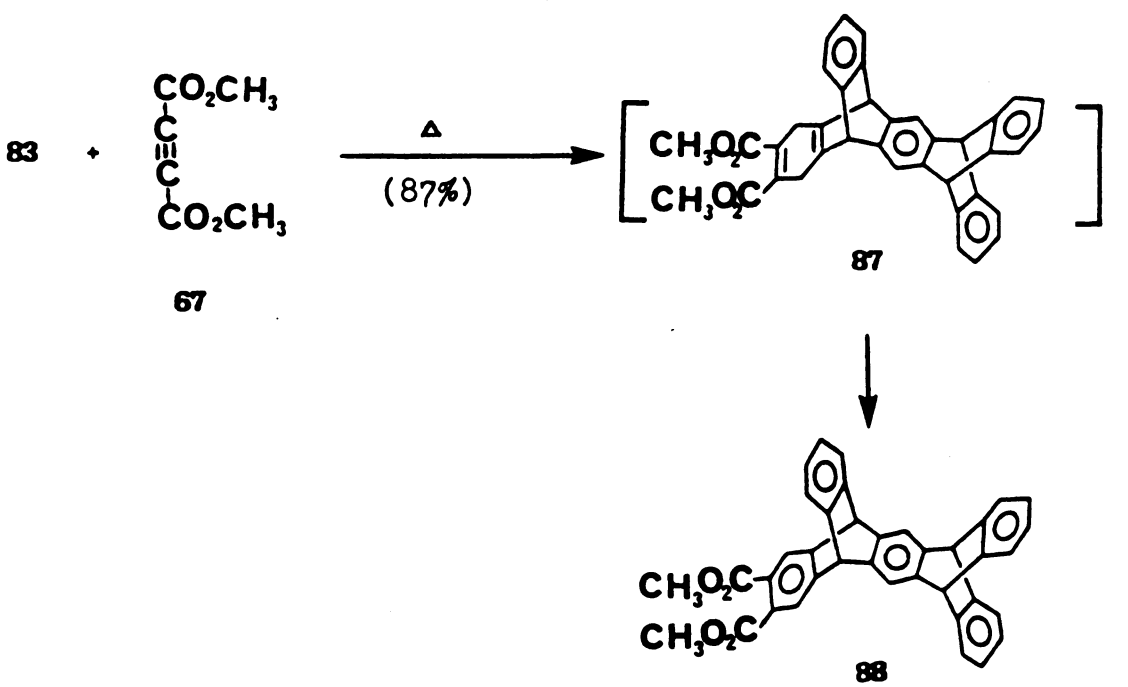
Heating **83** and **38** in refluxing xylene for 60 h gave adduct **84** in 81 % yield. The stereochemistry of **84** was not determined, but probably was exo. Dehydration of **84** using perchloric acid proceeded with double-bond isomerization (a similar phenomenon has been observed; see the synthesis of **20**, method D; vide supra) to give vinyl naphthalene **85** in 57 % yield. Finally, compound **85** was dehydrogenated to dibromoanthracene **86** (94 %) by refluxing with Pd/C in mesitylene for 4 days.



The ^{1}H NMR spectrum of **86** showed two two-proton singlets at δ 5.32 and 5.42 for the bridgehead protons. The anthracene moiety was easily apparent as three two-proton singlets at δ 8.20, 8.06 and 7.77. In addition, a two-proton singlet for the uncoupled benzenoid ring protons and six sets of two-proton doublets of doublets for the remaining aryl protons were present (see Table 2). The ^{13}C NMR spectrum of **86** showed sixteen peaks (five peaks were missing due to quarternary carbons or overlapped signals) with two aliphatic carbons at δ 53.47 and 54.03 . The mass spectrum[65] showed a molecular ion at m/e 688 as base peak.

7. Synthesis of Dimethyl 5,14[1',2']:7,12[1",2"]-dibenzeno-5,7,12,14-tetrahydropentacene-2,3-dicarboxylate (88).

The diene **83** can also be used to synthesize functionalized pentiptycenes. For example, ring fusion between **83** and **67** gave **88** directly in 87 % yield. The



intermediate **87** was automatically dehydrogenated under refluxing xylene conditions.

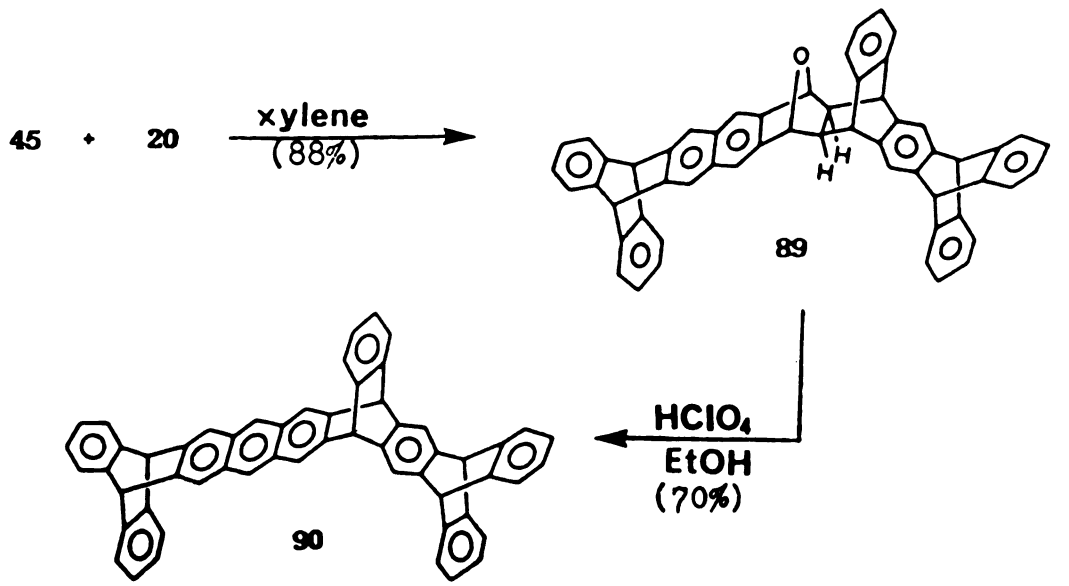
The structure of **88** was confirmed by its spectra. The ^{1}H NMR spectrum (Table 2) showed a six-proton singlet at δ 3.80 for the methyl protons, and two two-proton singlets at δ 5.29 and 5.33 for the bridgehead protons. The aromatic region consisted of two two-proton singlets at δ 7.40 and 7.58 for the uncoupled benzenoid ring protons, as well as two sets of six-proton doublets of doublets for the remaining aryl protons. The ^{13}C NMR spectrum gave only sixteen peaks (three peaks were missing due to either quarternary carbons or overlapped signals) with aliphatic carbons at δ 52.38, 53.53 and 53.88. The mass spectrum showed a strong molecular ion peak at m/e 546.

As discussed in this section, one can see clearly the versatility of **20** as a synthon in the synthesis of a series of pentiptycenes (Fig. 8). Among them, compounds **78**, **81** and **86** are useful potential synthons for even higher iptycenes. The dibromo moiety in **78** and **86** is an aryne equivalent. The anthracene moiety in **81** and **86**, on the other hand, can be utilized as diene.

F. Synthesis of [1.1.3(b,b)^{b}.1.1^{b}.1.1]Heptiptycene (5,22[1',2']:7,20[1",2"]:11,16[1"',2"']-Tribezeno-5,7,11,16,20,22-hexahydrononacene)(90).

As we have mentioned earlier, compound **45** might serve as a useful synthon. The double bond in **45** is an

effective dienophile. Thus, cycloaddition of **45** and **20**, followed by dehydration of the adduct gave heptiptycene **90** in good yield. In this case, mainly one cycloadduct,

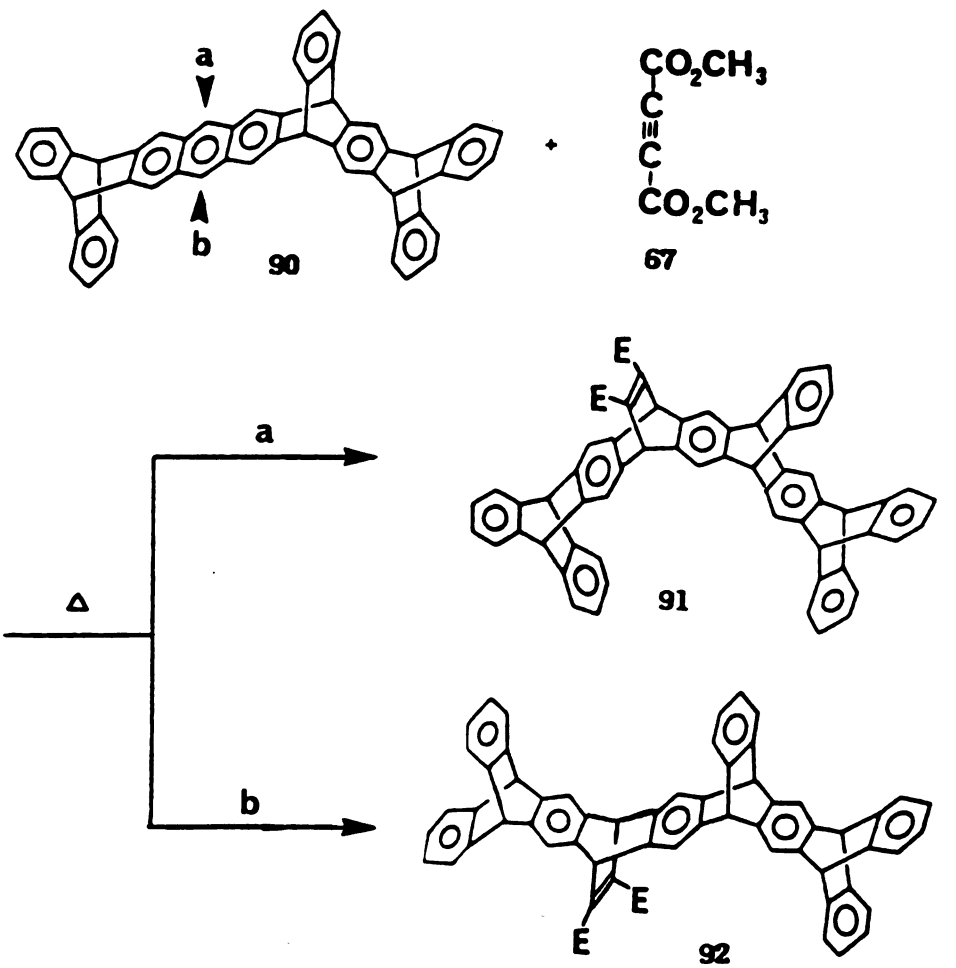


thought to be **89**, was formed in 88 % yield. The ^{1}H NMR spectrum of **89** showed five sets of two-proton singlets at δ 1.85, 4.06, 4.75, 5.30 and 5.47 for the bridgehead protons. In addition, there were two-proton singlets at δ 7.67 and 7.30 for the naphthalene moiety, and at δ 7.21 for the uncoupled benzenoid ring protons. The remaining aryl protons appeared as follows : δ 6.86-7.07 (m,12H), 7.32-7.41(m,8H).

Dehydration of the adduct **89** using perchloric acid gave **90** in 70 % yield. The structure of **90** was confirmed by its spectra. The ^{1}H NMR spectrum showed three two-proton singlets at δ 5.31, 5.39 and 5.47 for the bridgehead protons. The anthracene moiety was apparent as three two-proton singlets at δ 8.01, 7.78 and 7.72. In addition,

there was a two-proton singlet for the uncoupled benzenoid ring protons, and the remaining aryl protons (twenty) appeared as six sets of two-proton doublets of doublets at δ 6.83, 6.90, 6.94, 7.24, 7.28 and 7.33, and two four-proton multiplets at δ 7.00 and 7.40. The ^{13}C NMR spectrum gave twenty-one peaks (seven peaks were missing due to either quarternary carbons or overlapped signals) with three aliphatic carbons at δ 53.44, 53.59 and 53.95. The mass spectrum showed a molecular ion at m/e 706 as the base peak. The UV spectrum of **90** possessed a set of bands typical of an anthracene, with the longest wavelength at 371 nm.

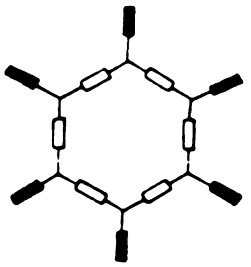
Cycloaddition of DMAD to the anthracene moiety of **90** gave exclusively one regioisomer. If dienophile approaches



from face "a" of the anthracene moiety(less hindered), adduct **91** will be obtained. On the other hand, if dienophile attacks from the more hindered face "b" (an additional 9,10-anthradiyl moiety is on this face), one will get adduct **92**. The product is thought to be **91**. The unusual upfield chemical shift of the bridgehead and uncoupled benzenoid ring protons support structure **91**, even though this structure may be more hindered than **92**, which has a zig-zag extended geometry.

The ^{1}H NMR spectrum of the adduct showed a six-proton singlet at δ 3.65 for the methyl protons, and three singlets at δ 5.14, 5.18 and 5.20 (ratio 2:4:2) for the bridgehead protons. The aromatic region contained two singlets at δ 7.27 and 7.28 (ratio 4:2) for the uncoupled benzenoid ring protons, and the remaining aryl protons appeared as follows: δ 6.78(dd,4H), 6.85(dd,4H), 6.91(dd,2H), 7.15-7.26(m,10H). The ^{13}C NMR spectrum gave only twenty-two peaks (nine peaks were missing due to either quarternary carbons or overlapped signals) with five aliphatic carbons at δ 52.20, 52.21, 52.36, 52.81 and 52.82. The mass spectrum showed a molecular ion peak at m/e 848.

Note that structure **91** completes five of the six sides in hexagonal cycloiptycene **93** (head-on view). Its enclosed cavity could be useful in forming host-guest compounds. The benzyne adduct of **90**, such as **94** or **95** is an attractive synthetic target. However, an attempt to synthesize these compounds was not successful (benzyne generated from benzenediazonium-2-carboxylate hydrochloride). Further



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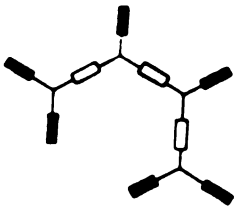

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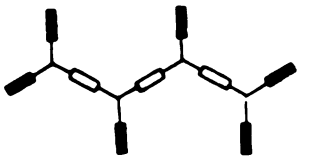


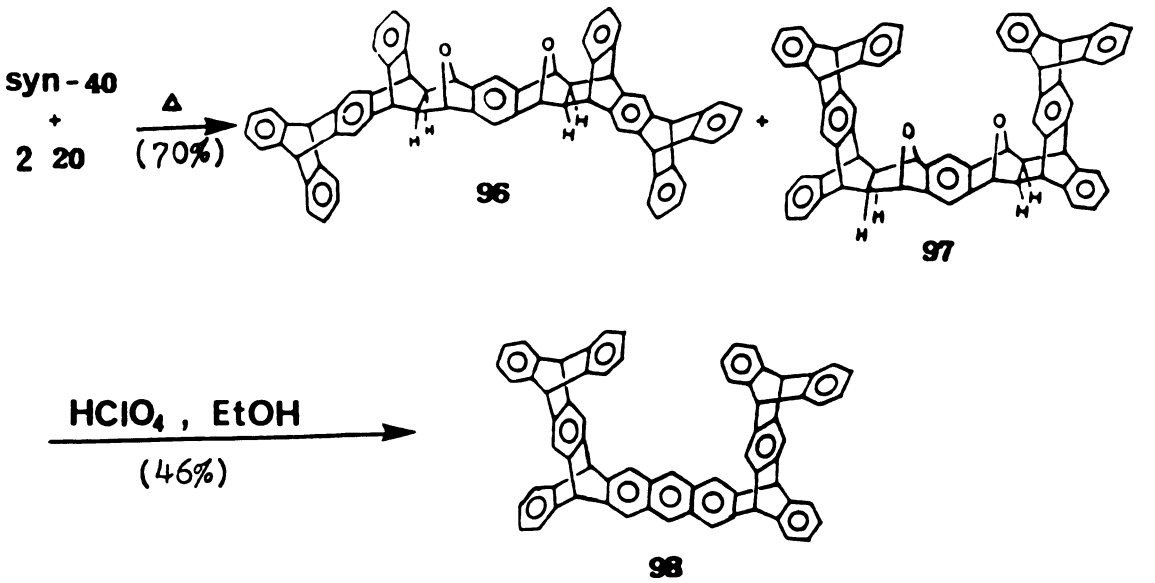
95

investigation on different conditions or with other benzyne precursors seems desirable.

G. Synthesis of [1.1.1^{b}.1.3(b,b)^{b}.1.1^{b}.1.1]Noniptycene (98 and 103).

Bis-epoxide 40, a synthetic equivalent of 2,3;6,7-anthradiyne is a powerful synthon for constructing higher iptycenes (see Fig. 2, p.9). Here we illustrate another synthesis of noniptycenes, to show the versatility of epoxide 40. If the reaction scheme in Fig. 2 is extended by replacing anthracene with triptycene 20, noniptycenes 98 and 103 can be readily obtained.

(1) Syn-noniptycene (98). Heating syn-40 and two equivalents of 20 in a sealed tube (xylene as solvent) at 180°C for 3 days afforded a mixture of regioisomers 96 and 97 (NMR ratio 1:1) in 70 % yield. The stereochemistry of bis-adducts 96 and 97 was assigned as exo, a thermodynamically-controlled product (the endo adducts would be highly hindered sterically). Singlets for the bridgehead protons in the ^{1}H NMR spectrum supported the exo structures (see discussion of exo selectivity, vide supra).

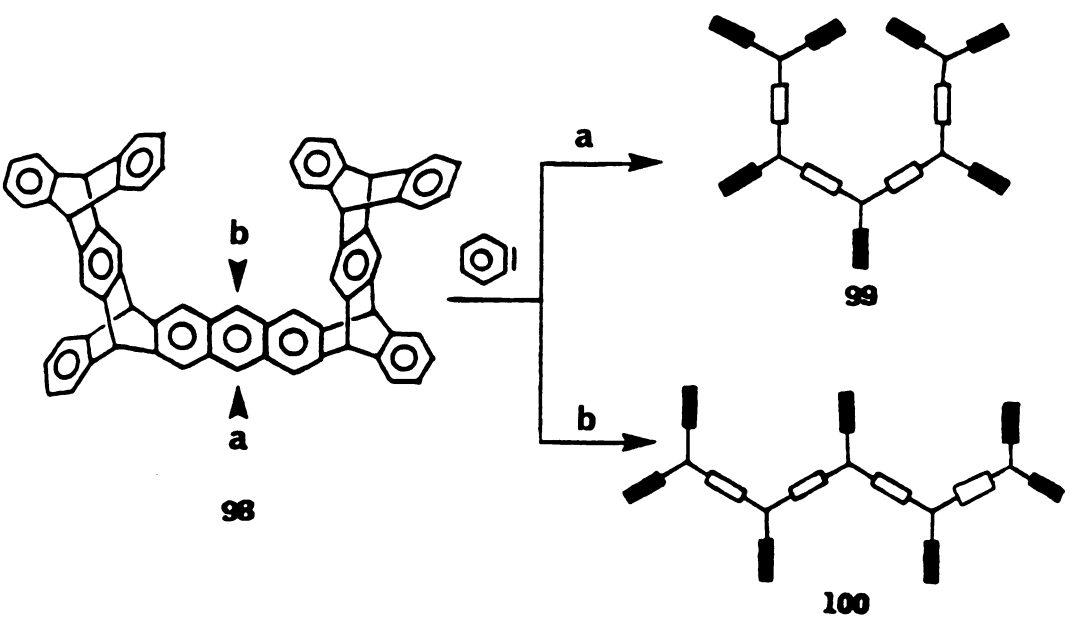


The ^{1}H NMR spectrum of the adducts showed clearly two sets of bridgehead. One set appeared at δ 1.85, 4.19, 4.71, and 5.23 (area ratio 4:4:4:4). Another set of peaks corresponding to the other isomer appeared as δ 1.99, 4.23, 4.74 and 5.28 (area ratio 4:4:4:4). The remaining aryl peaks were too complicated to assign to individual isomers; they appeared as follows : δ 6.76(s), 6.86-6.94(m), 6.95(s), 7.02-7.08(m), 7.12-7.21(m), 7.23(s), 7.25-7.33(m).

The mixture of the adducts was not separated but was dehydrated directly using perchloric acid to give the syn-noniptycene **98** in 46 % yield. The structure of **98** was confirmed by its spectra. The ^{1}H NMR spectrum showed two four-proton singlets at δ 5.290 and 5.361 for the bridgehead protons, and a four-proton singlet at δ 7.449 for the uncoupled benzenoid ring protons. In addition, the anthracene moiety was apparent as singlets at δ 7.946 and 7.688, area ratio 2:4. The remaining aryl peaks appeared as

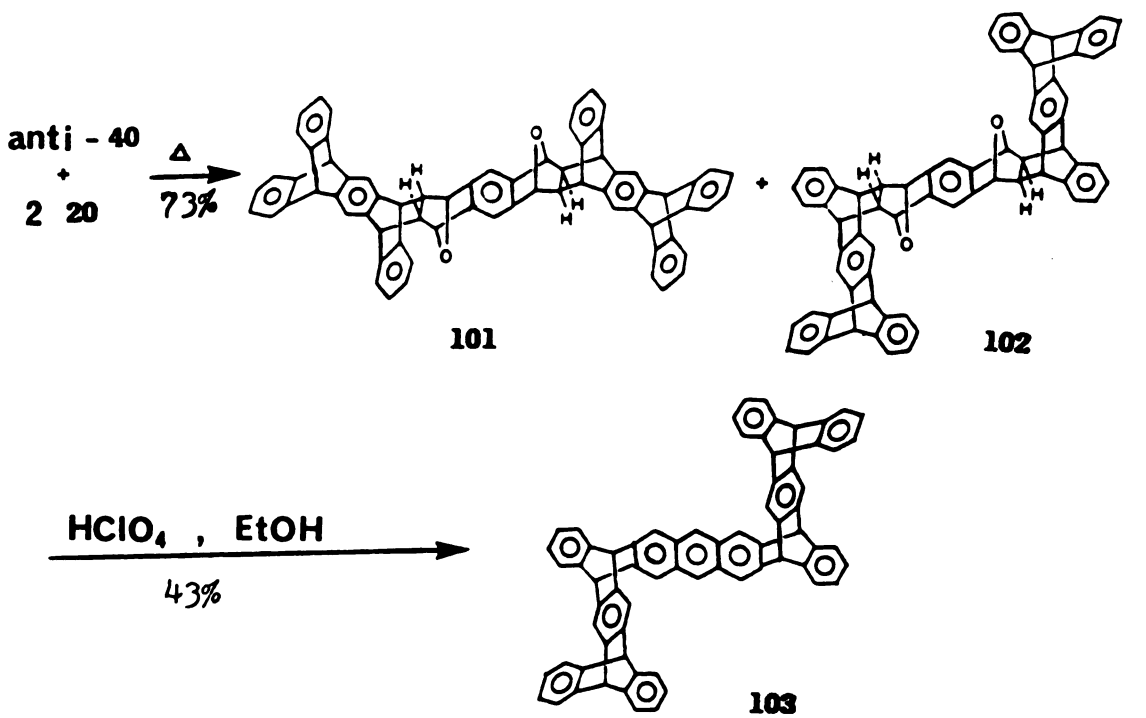
follows : δ 6.802-6.835(dd,4H), 6.878-6.951(m,8H), 7.212-7.328(m,12H). The ^{13}C NMR spectrum showed fourteen peaks (four peaks were missing due to either quarternary carbons or overlapped signals) with two aliphatic carbons at δ 53.502 and 54.006. The UV spectrum of **98** possesed a set of bands typical of an anthracene, with the longest wavelength absorption at 372 nm. The mass spectrum[35] showed a strong molecular ion peak at m/e 882.

If benzyne were to add to **98** from the bottom (face a) of the anthracene moiety, one should obtain undecaiptycene **99** (cyclic form). On the other hand, if benzyne approaches



from the top face b, then undecaiptycene **100** (zig-zag form) will be obtained. However, attempted cycloaddition of benzyne (generated from benzenediazonium-2-carboxylate hydrochloride) to the anthracene moiety of **98** was not successful; the reaction gave mainly recovered starting material.

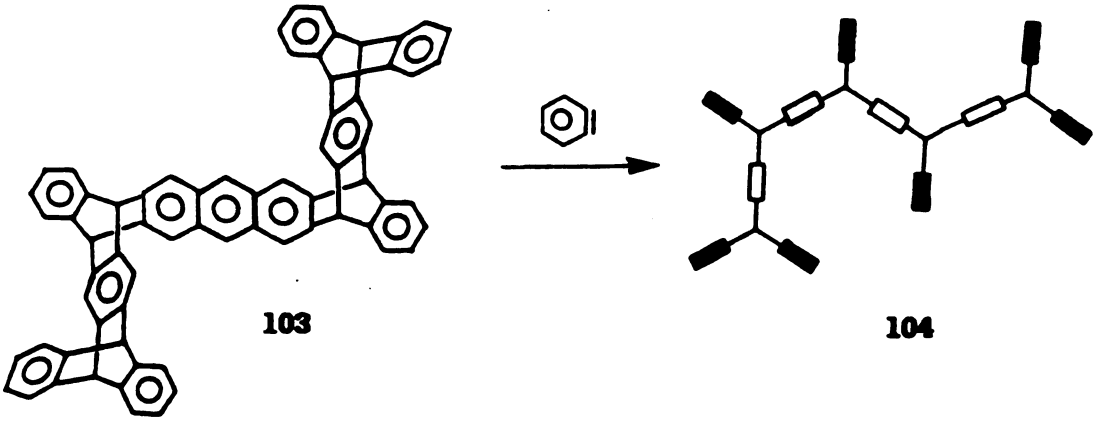
(2) Anti-noniptycene (103). The anti-noniptycene **103** was synthesized in a manner similar to **98**, by cycloaddition of anti-**40** to two equivalents of **20**, followed by dehydration of the mixture of the adducts (**101** and **102**, NMR ratio 1:1) as shown in the equation:



The ^{1}H NMR spectrum of the adducts also showed clearly two sets of bridgehead protons. One set appeared at δ 1.78, 4.10, 4.62 and 5.30 (area ratio 4:4:4:4) and the other at δ 2.02, 4.23, 4.73 and 5.26. The remaining aryl peaks were too complicated to assign; they appeared as follows : δ 6.77(s), 6.82-6.93(m), 6.98-7.01(m), 7.06-7.10(m), 7.18(s), 7.19-7.35(m).

The mixture of adducts was dehydrated using perchloric acid to give **103** in 43 % yield. The spectra of **103** were very similar to those of **98**. The ^{1}H NMR spectrum of **103** showed two four-proton singlets at δ 5.295 and 5.365 for the bridgehead protons, and a four-proton singlet at δ 7.452 for the uncoupled benzenoid ring protons. In addition, the anthracene moiety was apparent as singlets at δ 7.947 and 7.689, area ratio 2:4. The remaining aryl peaks appeared as follows: δ 6.802-6.836(dd,4H), 6.879-6.952 (m,8H), 7.213-7.331(m,12H). The ^{13}C NMR spectrum showed sixteen peaks (two peaks were missing) with two aliphatic carbons at δ 53.442 and 53.959. The UV spectrum of **103** possessed bands similar to those of **98**, with the longest wavelength absorption at 372 nm. The mass spectrum[35] gave a strong molecular ion peak at m/e 882.

Benzyne addition to the anthracene moiety of compound **103** should give only one adduct **104**. The cycloaddition was



103 **104**

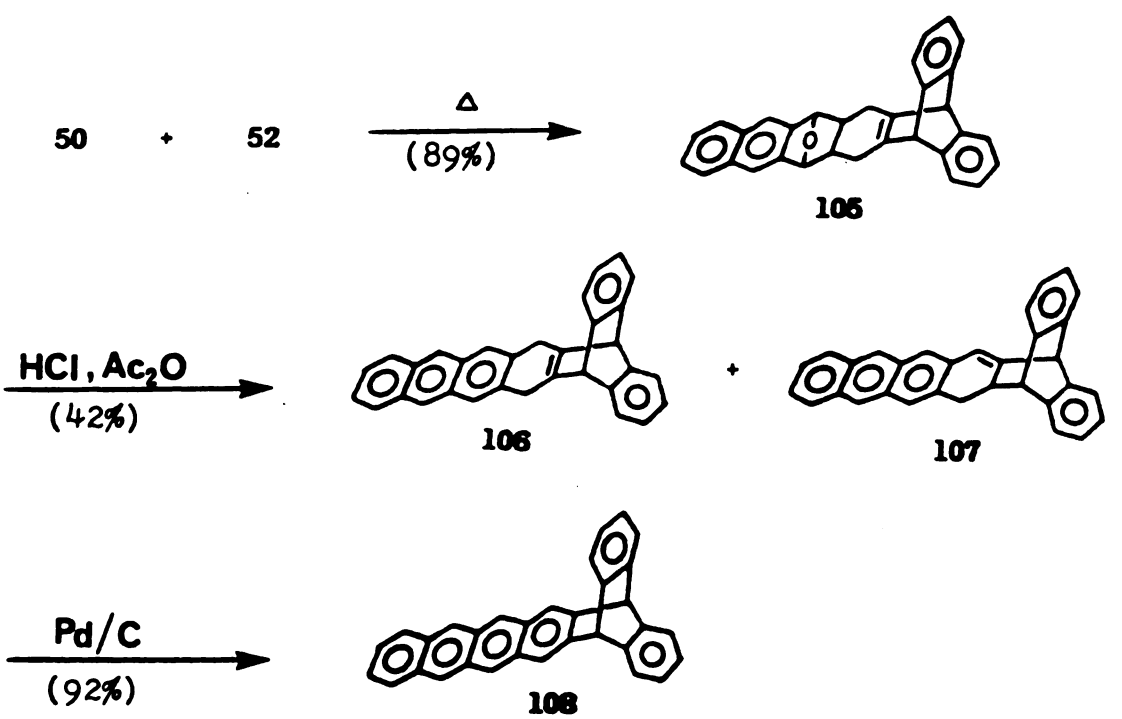
attempted (benzyne generated from o-benzenediazonium-carboxylate hydrochloride); however, no adduct was

successfully isolated.

As we have discussed above, one can see clearly the versatility of bis-epoxide **40** as a powerful synthon for higher iptycenes. In only two steps, reaction of **40** and **20**, can readily extend triptycenes(three planes) to noniptycenes(nine planes). We hope that further careful reinvestigation of the benzyne[53] addition to the noniptycenes **98** and **103** will furnish the novel iptycenes **99**, **100** and **104**.

H. Synthesis of [4(b,b,b)^{b}.1.1]Triptycene (108).

Triptycenes containing naphthalene or anthracene fused ring have been described earlier. The tetracene anolog **108**, however, is not known in the literature. Here we describe its synthesis via three-ring precursor **50** and diene **52**. The



thermal cycloaddition gave a single adduct **105** (89 %). Dehydration using hydrochloric acid in acetic anhydride afforded a mixture of **106** and its double-bond isomer **107** (42 %), which were then dehydrogenated to give the desired tetracene **108**.

The structure of **108** was confirmed by its spectra. The ^{1}H NMR spectrum contained a two-proton singlet at δ 5.53 for the bridgehead protons, and two four-proton doublets of doublets at δ 7.07 and 7.46 for the benzenoid ring protons. In addition, the tetracene moiety appeared as follows : δ 8.56(s,2H), 8.46(s,2H), 7.45(dd,2H), 7.86(s,2H), 7.35 (dd,2H). The ^{13}C NMR spectrum showed twelve peaks (one peak was missing) with the aliphatic carbons at δ 53.52. The mass spectrum had a molecular ion peak at m/e 404. The UV spectrum of **108** possessed a set of bands typical of a tetracene, with longest wavelength absorption at 469 nm.

I. Conclusions.

Iptycenes form a very large class of compounds with rigid well-defined geometries based on elaboration of its simplest member, triptycene. The compounds have novel structures for studying various phenomena in chemistry, such as charge transfer, restricted rotation, thermal stability, host-guest phenomena, factors which contribute to high melting points and many others.

In this part of the thesis, we have described a general approach to the iptycene framework (Fig. 4) via seven important synthons (**7**, **31**, **38**, **40**, **49**, **50**, **52**) and

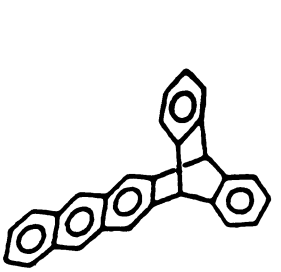
illustrated their utility in improved syntheses of **20** (four routes). We have also demonstrated the versatility of **20** as a synthon in the preparation of some higher iptycenes, including pentiptycenes **24**, **76**, **78**, **81**, **86** and **88**, heptiptycenes **27** and **89**, and noniptycenes **98** and **103**.

The syntheses we have discussed were limited mainly to the unsubstituted carbocyclic framework, but further elaboration, including heterocycles, functional substituents, etc., is clearly possible.

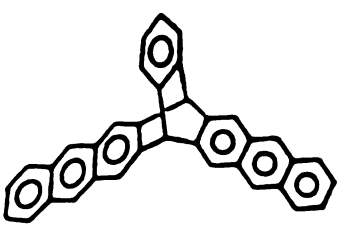
The door to iptycene chemistry has been opened. We anticipate that there will be many delights as we explore its domain.

Part II. Synthesis of Linear Acenes and Polyiptycene Precursors.

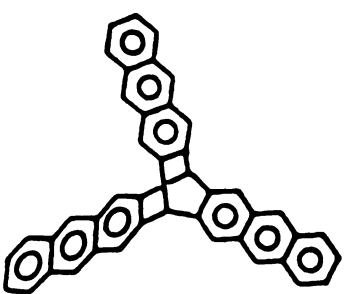
As mentioned earlier, iptycnes are usually prepared via addition of an aryne or aryne equivalent to an acene (i.e. anthracene, tetracene and pentacene). We have demonstrated the utility of synthon **20** in the synthesis of higher iptycenes in part I. Compound **20** contains an anthracene unit in the triptycene framework as a building block. One can imagine that a triptycene with two anthracene moieties (**109**) or even three anthracene moieties (**110**) would be a very useful synthon for the synthesis of complex iptycenes or polyiptycenes.



20



109

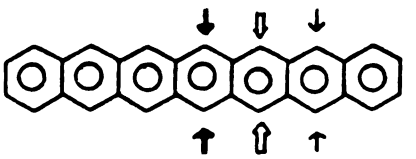


110

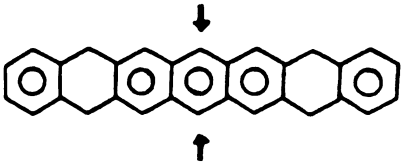
A. Attempted Synthesis of [3(b,b)^{b}.1.3(b,b)^{b}]Triptycene (109) and [3(b,b)^{b}.3(b,b)^{b}.3(b,b)^{b}]Triptycene (110) via Heptacene Equivalents 112 and 121.

Compounds **109** and **110** can be viewed respectively as cycloadducts of benzyne or 2,3-anthryne to the middle ring of heptacene **111**. However, these direct routes have several problems associated with them. First, heptacene is reported to be a very unstable species.[36] Second, heptacene has several possible reactive sites for cycloaddition. Although addition to the middle ring might be preferred,

cycloaddition to the other rings, particularly the other 'internal' rings, could also be quite facile. Thus, cycloadditions of a dienophile to heptacene could give quite a complicated mixture. As an alternative to heptacene, we chose 5,9,14,18-tetrahydroheptacene **112** as a "heptacene equivalent".

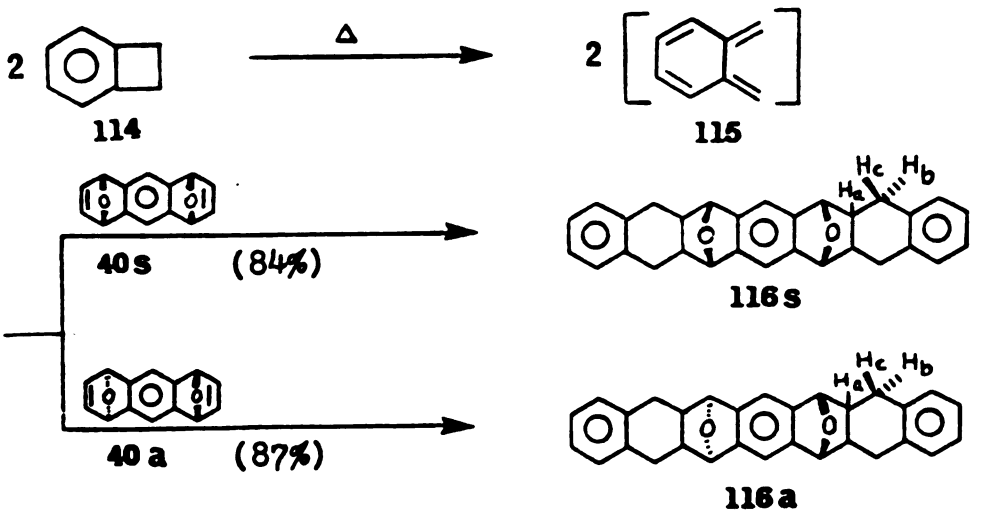


111



112

Cycloadditions to **112** should occur only at the central anthracene moiety, and dehydrogenation of the resulting dihydroanthracene moieties in the cycloadducts should give the desired products. The seven linearly fused rings needed for **112** were constructed by addition of two equivalents of o-xylylene **115** to the anthracene bis-epoxide **40**. Thermal ring opening of benzocyclobutene **114**[37] generated the reactive diene o-xylylene,[38] which then added to dienophile **40** to give the bisadduct **116** in high yield.



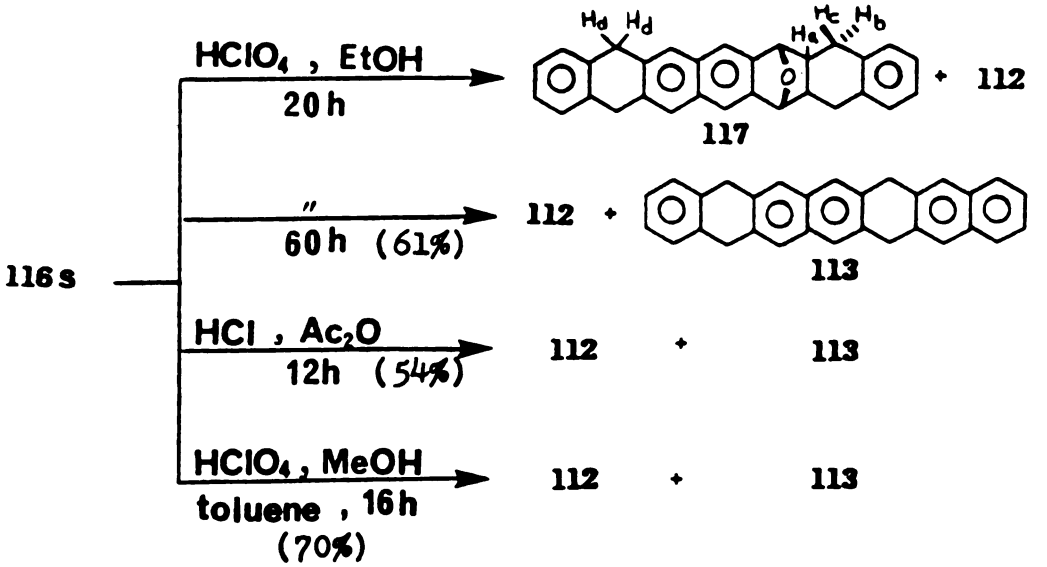
Thus, heating **40** (syn or anti) and two equivalents of **114** in a sealed tube (toluene as solvent) at 190° for 24 h gave bisadduct **116** in 84 or 87 % yield, respectively. The stereochemistry of **116** was not determined unequivocally, but was probably exo (see discussion in part I). For example, the ^{1}H NMR spectrum of syn-bisadduct **116s** had a four-proton singlet at δ 5.06 for the bridgehead protons, an eight-proton broad singlet at δ 7.09 for the "outer" benzenoid ring protons, and a two-proton singlet at δ 7.18 for the central benzenoid ring protons. In addition, there were three sets of four-proton doublets of doublets at δ 1.97, 2.70 and 2.98 for protons H_a, H_b and H_c (J_{ab}= 6 Hz; J_{bc}= 14 Hz; J_{ac}= 11 Hz). The small or zero coupling between H_a and the bridgehead protons suggests exo stereochemistry. The ^{13}C NMR of **116s** showed eight peaks (three aliphatic and five aromatic carbons) as required by the symmetry.

The structure of anti-bisadduct **116a** was also confirmed by its spectra. Its NMR spectra (^{1}H and ^{13}C) were very similar to those of the syn isomer.

Dehydration of **116s** using perchloric acid in refluxing ethanol for 20 h gave mainly the mono-dehydrated compound **117** together with a small amount of desired tetrahydro-heptacene **112**. The ratio, by NMR, was 4:1.

The ^{1}H NMR spectrum of **117** showed a four-proton singlet at δ 4.06 for the H_d protons, a two-proton singlet at δ 5.24 for the bridgehead protons and three sets of two-proton doublets of doublets at δ 2.11, 2.75 and 3.04 for the protons H_a, H_b and H_c respectively. In addition, the

aromatic region showed two two-proton doublets of doublets at δ 7.20 and 7.32 for the "left" benzenoid ring protons, two two-proton singlets at 7.57 and 7.71 for the naphthalene ring protons, and a four-proton broad singlet at δ 7.13 for the "right" benzenoid ring protons.



The ^1H NMR spectrum of **112** contained an eight-proton singlet at δ 4.12 for the benzylic protons. In addition, the anthracene moiety appeared as singlets at δ 8.29 and 7.89, area ratio 2:4. The remaining aryl protons were two four-proton doublets of doublets at δ 7.20 and 7.33.

To further dehydrate **117**, **116s** was heated with the same reagent but for a longer time (60 h). This unfortunately produced a mixture of the desired product **112** and its isomer **113**; the ratio by NMR was 1:2. The isomerization of **112** probably proceeded via either a carbocation rearrangement or a thermal hydrogen walk, since isomer **113** is thermodynamically more stable than **112** by about 3.90 Kcal/mole (calculated difference in aromatic energy).[51]

112 113

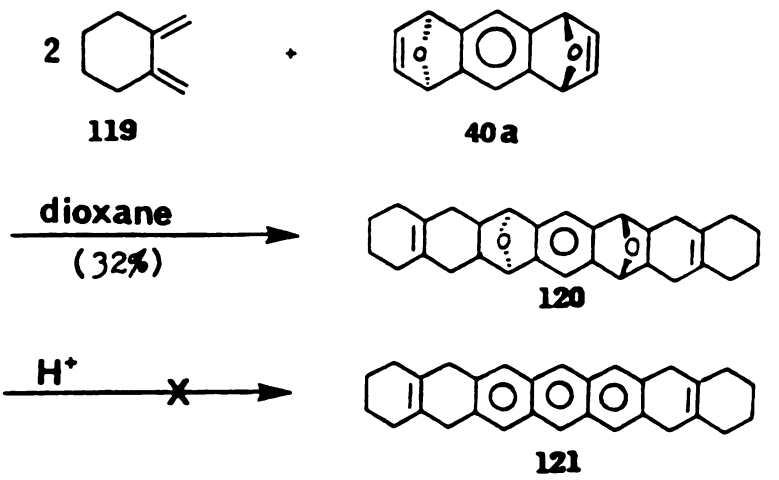
The structure of **113** was determined by its ^1H NMR spectrum. It showed two four-proton singlets at δ 4.06 and 4.21 for the benzylic protons. The aromatic region had peaks typical of two naphthalene units, which consisted of three two-proton singlets at δ 7.69, 7.71 and 7.77 for the uncoupled naphthalenoid ring protons and a two-proton doublet of doublets at δ 7.78 for the coupled peri protons. The remaining six aryl protons appeared as a multiplet at δ 7.15-7.42. The mass spectrum of a mixture of **112** and **113** gave a correct molecular ion peak at m/e 382.

Changes in the dehydrating reagents (for example, using hydrochloric acid in acetic anhydride, or perchloric acid in a mixture of methanol and toluene) gave similar results, as did dehydration of the anti-bisadduct **116a**.

The formation of thermodynamically favored isomer **113**[45] in the dehydration step made this approach fruitless, because separation of **112** from **113** was difficult due to their structural similarity and to the facile conversion of **112** to **113**. Attemped cycloadditions of **112** with several dienophiles (i.e. **6**, **50**) resulted in further isomerization of **112** to **113**.

A possible alternative to **112** as a heptacene equivalent was its octahydro analog **121**. Its construction would involve a similar strategy, but use diene **119** in place of benzocyclobutene **114**. Heating anti-bisepoxide **40a**

with two equivalents of diene **119** in refluxing dioxane gave bis-cycloadducts **120** in modest (32 %) yield.



The structure of **120** was confirmed by its spectra. The ^{1}H NMR spectrum showed a two-proton singlet at δ 7.04 for the central benzenoid ring protons, a four-proton singlet at δ 4.90 for the bridgehead protons and multiplets at δ 1.57(8H), 1.82(4H), 1.93(8H), 2.12(8H) for the remaining aliphatic protons. The ^{13}C NMR spectrum of **120** gave eight peaks (five aliphatic and three aromatic or vinyl carbons) as required by the symmetry.

Dehydration of **120** using various acids gave consistent results which again indicated a mixture of rearranged products. The ^{1}H NMR spectrum was too complicated to analyze. However, it showed several vinyl peaks, suggesting that the double bond had migrated. A naphthalene moiety was also indicated, suggesting that isomerization had occured due to carbocation rearrangements. Although cycloadditions to the dehydration mixture were attemped, no adducts were isolated.

Alternatively we thought that reducing the double bonds in **120** prior to dehydration might eliminate the possibility of rearrangement. Hydrogenation of **120** was attemped using several different reagents (i.e. hydrazine, Pd/C, Pt/C). However, the tetra-substituted double bonds were quite resistant to reduction, and the reactions gave mainly recovered starting materials.

The isomerizations which accompanied the dehydration of **116** or **120** led us to abandon the synthesis of building blocks **109** and **110** by these routes. An alternative approach to compound **109** starting from 5,14-dihydropentacene will be discussed later in this part of the thesis.

B. Synthesis of Tetracenes (15 and 127) and Pentacene (10).

Despite the lack of success in the synthesis of heptacene equivalent **112**, the successful cycloaddition of **40** to benzocyclobutene **114** to construct seven linearly fused rings in one step made it worthwhile to explore this reaction further. Tetracene and pentacene are both known compounds, but they are difficult to prepare.[51]

Here, we digress from the main goals of this research to describe the synthesis of these acenes by exploiting the cycloaddition of **114** to various epoxides (i.e. **7**, **38**, **50**) to build up a linear ring framework.

(1) Tetracene Heating equimolar amounts of epoxide **7** and benzocyclobutene **114** in a sealed tube (toluene as solvent) at 185-195° for 24 hour gave cycloadduct **122** in 86 % yield. The structure of **122** was confirmed by it spectra.

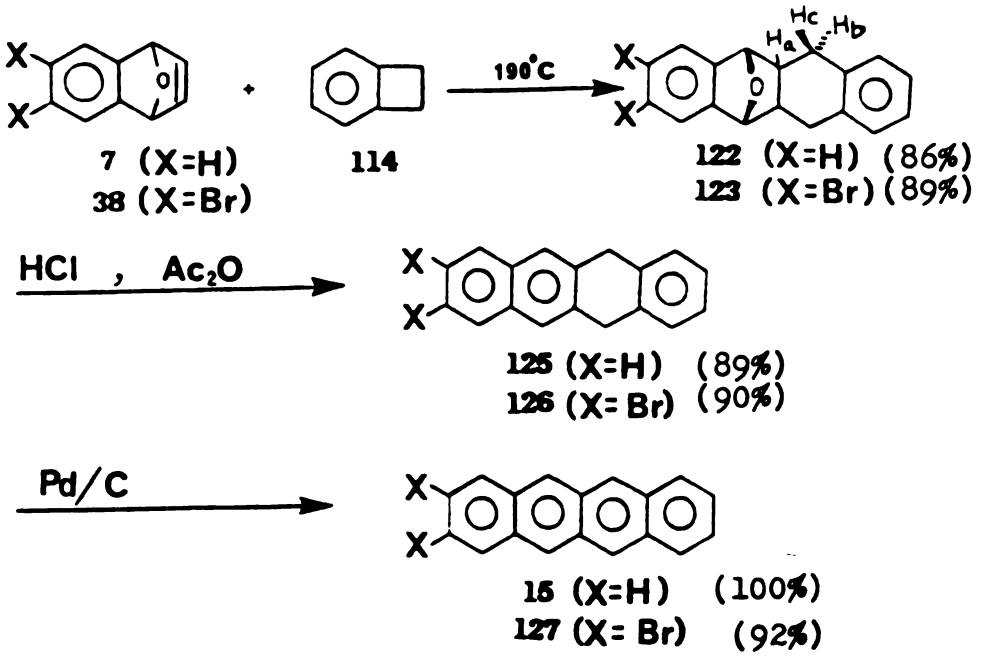


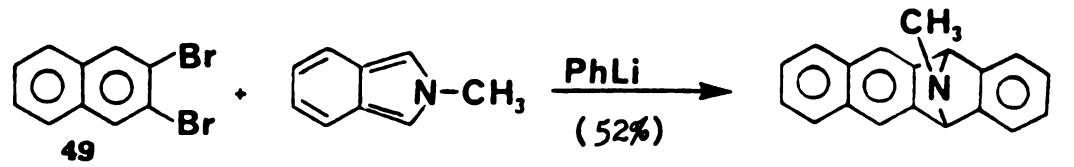
Figure 10. Synthesis of tetracenes via epoxides 7 and 38 and benzocyclobutene 114.

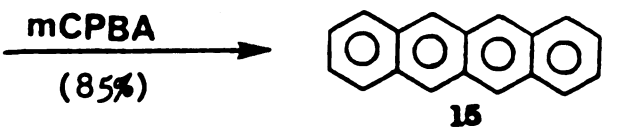
The ^{1}H NMR spectrum showed a two-proton singlet at δ 5.13 for the bridgehead protons, and three sets of two-proton doublets of doublets at δ 2.02, 2.74 and 3.04 for protons H_a, H_b and H_c (J_{ab}=6 Hz; J_{bc}=14 Hz; J_{ac}=11 Hz). In addition, the aromatic region appeared as two two-proton doublets of doublets at δ 7.14 and 7.24 and a four-proton broad singlet at δ 7.12. The small or zero coupling between H_a and the bridgehead protons suggests exo stereochemistry. The ^{13}C NMR spectrum of 122 had nine peaks (three aliphatic and six aromatic carbons) as required by the symmetry.

Dehydration of 122 using hydrochloric acid gave the known dihydrotetracene 125 in 89 % yield; this was then quantitatively dehydrogenated to the corresponding tetracene

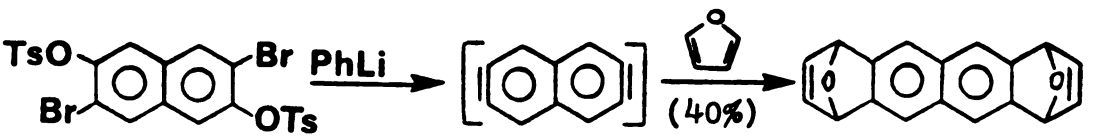
15. The overall yield for the three-step sequence (Fig. 10) was 77 % from 7 and 114, which is superior to the recently reported methods of Gribble[47b,47c] and Rickborn[54].

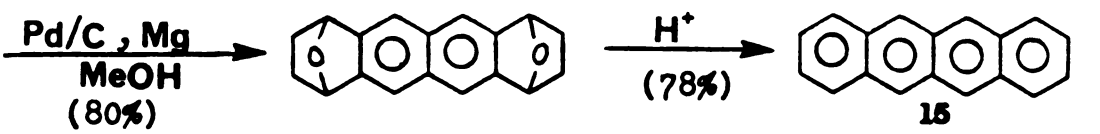
Gribble's[47b] first method involved the cycloaddition of 2,3-naphthyne to 2-methylisoindole followed by deamination of the adduct by m-chloroperbenzoic acid. The yield for the two-step sequence was 44 %.





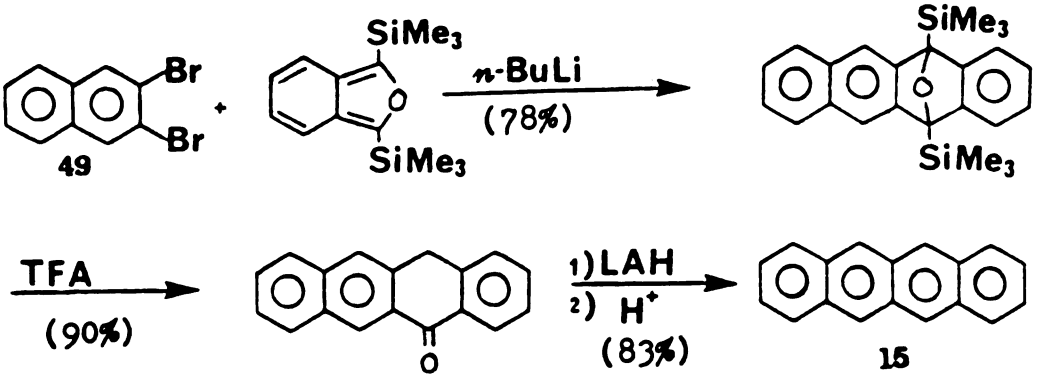
The second synthesis of 15 reported by Gribble[47c] involved the cycloaddition of 2,6-naphthadiyne to furan. Subsequent deoxygenation afforded the tetracene in 25 % overall yield from the dibromo ditosylate.





The third method, described by Rickborn,[54] used the cycloaddition of 1,3-bis(trimethylsilyl)isobenzofuran to 2,3-naphthyne. Trifluoroacetic acid induced conversion of the adduct to the corresponding anthracene followed by reduction/dehydration of the ketone gave tetracene in 58 %

overall yield.



Our method for the synthesis of tetracene is comparatively simple, proceeds in high yield, and can be scaled up easily.

(2) 2,3-Dibromotetracene By employing epoxide **38** in place of **7** in the synthetic sequence, 2,3-dibromotetracene **127** was obtained in a 74 % overall yield (Fig. 10). Intermediates **123**, **126** and the dibromotetracene **127** are all previously unknown compounds.

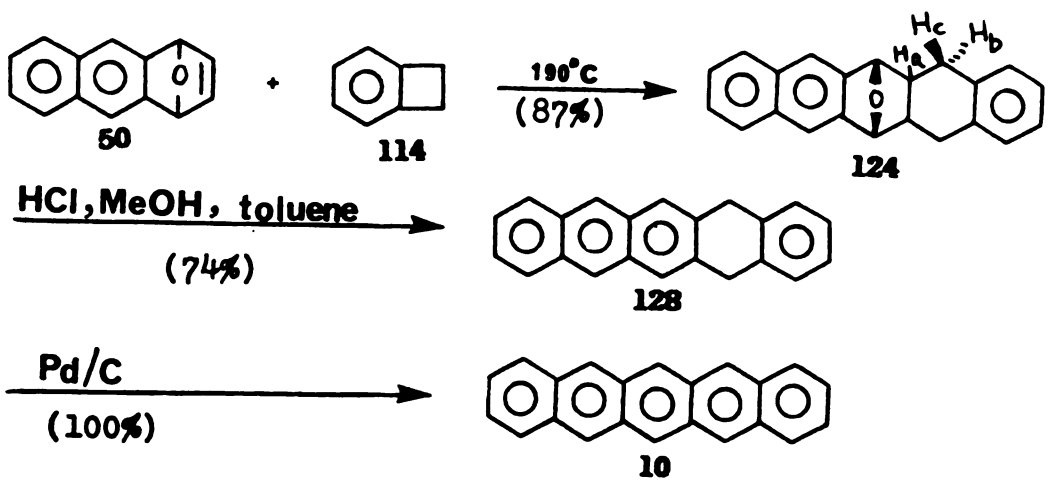
The ^{1}H NMR spectrum of **123** showed two two-proton singlets at δ 5.07 and 7.49 for the bridgehead and the uncoupled benzenoid ring protons, and three sets of two-proton doublets of doublets at δ 1.99, 2.70 and 2.98 for protons H_a, H_b and H_c, and a four-proton broad singlet at δ 7.13 for the remaining aryl protons. The ^{13}C NMR spectrum contained nine peaks (three aliphatic and six aromatic carbons) as required by the symmetry. The mass spectrum gave a correct molecular ion peak at m/e 406.

The ^{1}H NMR spectrum of **126** showed a four-proton singlet at δ 4.06 for the benzylic protons. In addition, the aromatic region consisted of a naphthalene moiety that

appeared as two two-proton singlets at δ 7.63 and 8.07 and a benzene moiety as two two-proton doublets of doublets at δ 7.22 and 7.34. The ^{13}C NMR spectrum had nine peaks (one aliphatic carbon plus eight aromatic carbons) as required by the symmetry. The mass spectrum gave a molecular ion peak at m/e 388.

Dehydrogenation of **126** using 10 % Pd/C gave 2,3-dibromotetracene **127**. Compound **127** is an orange solid (typical tetracene color) which is insoluble in most organic solvents. The insolubility of this material prevented the measurement of its NMR spectrum. The mass spectrum showed a strong molecular ion peak at m/e 386. The UV spectrum of **127** possessed a set of bands typical of a tetracene, with the longest wavelength absorption at 472 nm.

(3) Pentacene In a procedure similar to the synthesis of tetracenes **15** and **127**, pentacene **10** was synthesized in 64 % overall yield via epoxide **50** and benzocyclobutene **114** as shown below.

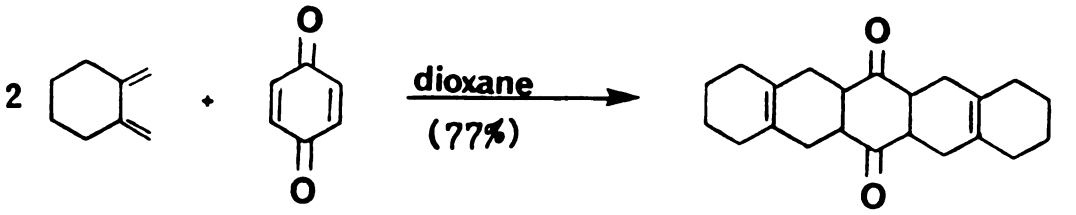


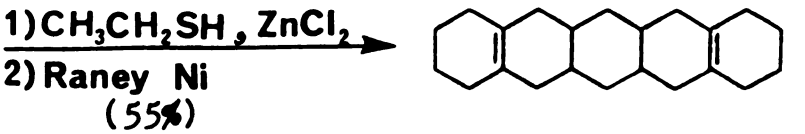
The structure of adduct **124** was confirmed by its spectra. The ^{1}H NMR spectrum showed a two-proton singlet at δ 5.25 for the bridgehead protons, and three sets of two-proton doublets of doublets at δ 2.12, 2.78 and 3.04 for protons H_a, H_b and H_c. In addition, the aromatic region contained a naphthalene moiety that appeared as follows : δ 7.44(dd,2H),7.62(s,2H),7.79(dd,2H). Finally, the remaining aryl protons appeared as a four-proton broad singlet at δ 7.13. The ^{13}C NMR spectrum had eleven peaks (three aliphatic and eight aromatic carbons) as required by the symmetry.

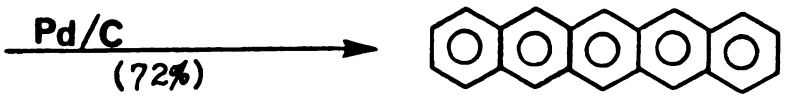
Dehydration of **124** using hydrochloric acid in a mixture of methanol and toluene gave the known 5,14-dihydro-pentacene **128**[48] in 74 % yield. The ^{1}H NMR spectrum (not previously reported) showed a four-proton singlet at δ 4.13 for the benzylic protons, and two two-proton doublets of doublets at δ 7.23 and 7.36 for the benzenoid ring protons. In addition, the anthracene moiety appeared as follows : δ 7.42(dd,2H), 7.92(s,2H), 7.98(dd,2H), 8.36(s,2H).

Compound **128** was quantitatively dehydrogenated to pentacene **10**, whose spectra (IR, UV, mass) were identical to those of a commercial sample.

Pentacene has been synthesized by the fusion of two equivalents of 1,2-dimethylene-cyclohexane to benzoquinone to construct the five ring framework. Reduction of the ketone followed by dehydrogenation gave a 30 % overall yield for the four-step sequence.[55]







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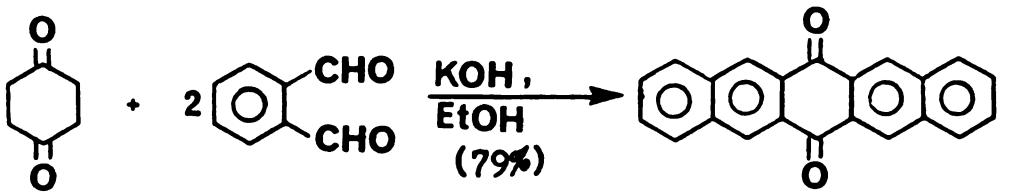
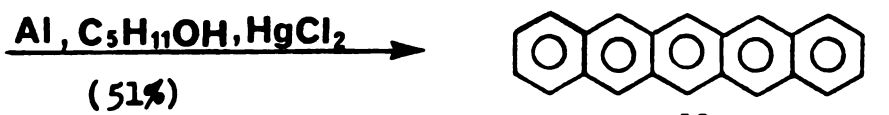
A better route to pentacene was reported by Brucker.[56] This synthesis involved the condensation of two equivalents of o-phthalaldehyde with 1,4-cyclohexanedione to give 6,13-pentacenequinone. Reduction of the quinone by aluminum cyclohexoxide afforded pentacene in a 40 % overall yield.





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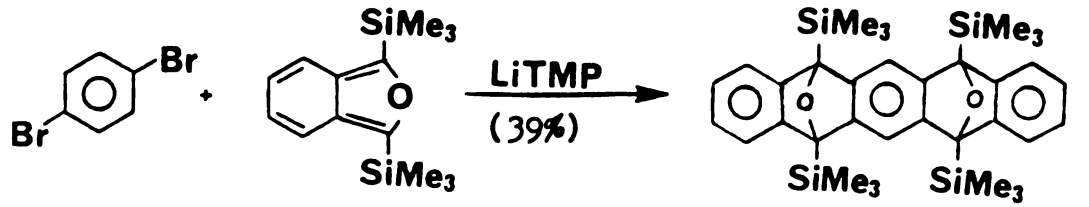
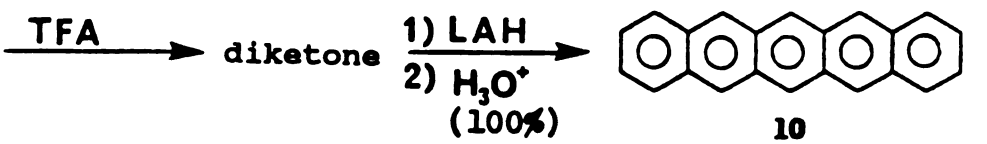
Another recent method reported by Rickborn[54] described the cycloaddition of 1,3-bis(trimethylsilyl)isobenzofuran to 1,4-benzadiyne generated by the LiTMP-induced

dehydrohalogenation of p-dibromobenzene, to give a five-ring cycloadduct. This bisadduct underwent acid-induced conversion to a diketone followed by reduction/dehydration to give pentacene in 39 % overall yield.





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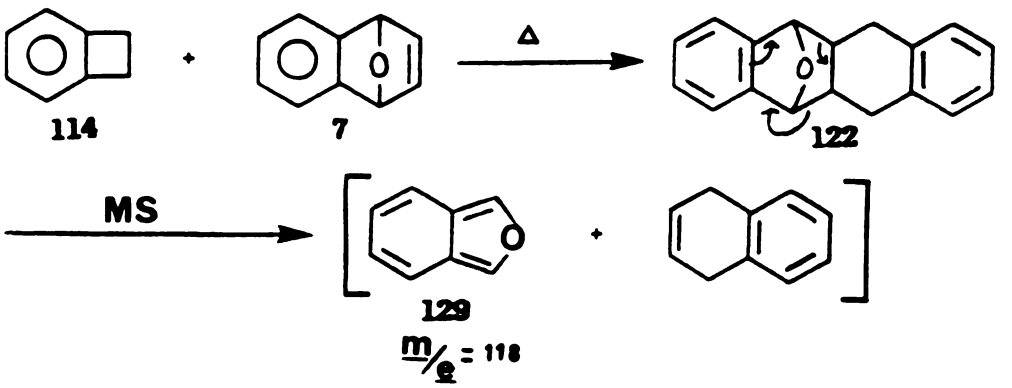
Our synthesis of pentacene is comparable to these literature methods. Besides, the 5,14-dihydropentacene **128** obtained in this synthetic sequence is useful, since it can serve as a synthon for two important polyiptycene precursors, **109** and **143** (vide infra).

We have demontrated the versatility of epoxides (i.e. **7**, **38**, **40**, **50**) as synthons for higher iptycenes in part I. Here again we illustrated the potential usefulness of these epoxides as precursors of linear acenes. Another application of bis-epoxide **40**, to the synthesis of a synthetic equivalent of furano-[3,4-f]benzo[c]furan **160**, will be described in part III of this thesis.

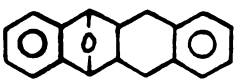
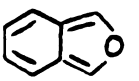
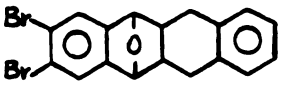
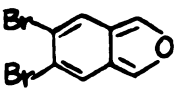
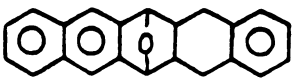
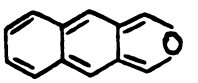
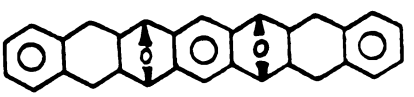
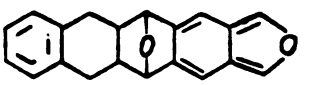
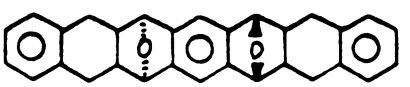
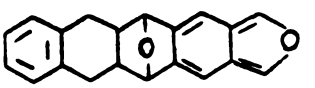
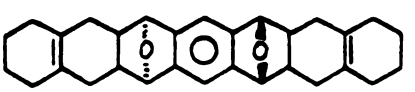
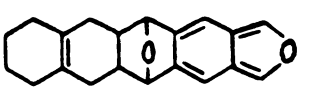
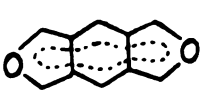
C. Isobenzofuran Intermediates Observed from the Mass Spectra of Epoxyarenes (116, 120, 122, 123 and 124).

In reviewing the mass spectra of a series of epoxyarenes (i.e. 116, 120, 122, 123 and 124) an interesting phenomenon was observed. Isobenzofuran fragments appeared consistently as base peaks in the mass spectra of these adducts, presumably from a retro Diels-Alder reaction.[40]



For example, the mass spectrum of 122 gave a base peak at m/e 118 corresponding to structure 129, which could be explained by β-bond cleavage directed by the oxygen atom in the retro Diels-Alder process. Table 3 summarizes the isobenzofuran fragments observed from mass spectra of epoxyarenes. Among them, species 133 is especially interesting. Although we have not proved the existence of such a species, the possibility suggested the potential use of a furano-[3,4-f]benzo[c]furan equivalent in synthesis, as will be described in more detail in the third part of this thesis.

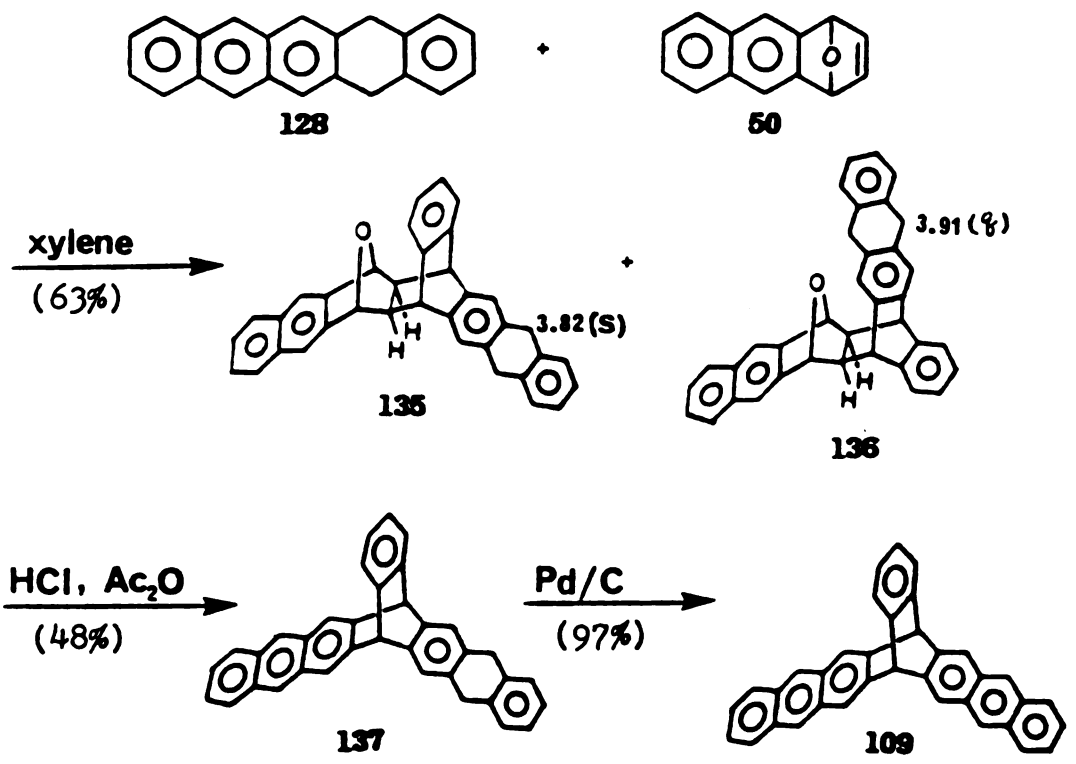
Table 3. Isobenzofuran Intermediates Observed in the Mass Spectra of Epoxyarenes.

compound	isobenzofuran fragment	m/e	rel. intensity
 **122**	 **129**	118	100
 **123**	 **130**	276	100
 **124**	 **131**	168	100
 **116s**	 **132**	288	10
	 **133**	158	100
 **116a**	 **132**	288	15
	 **133**	158	100
 **120**	 **134**	292	21
	 **133**	158	100

D. Synthesis of [3(b,b)^b.1.3(b,b)^b]Triptycene (109) via 5,14-Dihydropentacene.

The heptacene equivalent approach failed to give the desired synthon **109**. Here we describe an alternative and successful approach to **109** and to its analogue **143**, via 5,14-dihydropentacene **128**.

Compound **128** was an intermediate in the synthesis of pentacene (vide supra). The anthracene moiety in this molecule is attractive for use as a diene in cycloaddition reactions. Reflux of equimolar amounts of **128** and **50** in xylene for 5 days gave two regioisomeric adducts **135** and **136** (NMR ratio 3:2) in 63 % yield.



Although four products are in principle possible from this cycloaddition, only two were obtained. Their spectra (lack of coupling with bridgehead protons) suggest that both

are exo isomers. The ^{1}H NMR spectrum of **135** showed three two-proton singlets at δ 2.35, 4.46 and 5.06 for the bridgehead protons and a four-proton singlet at δ 3.82 for the benzylic protons. In addition, the aromatic region consisted of a two-proton singlet at δ 7.49 and two doublets of doublets at δ 7.72 and 7.39 for the naphthalene moiety, a two-proton singlet at δ 7.18 for the uncoupled benzenoid ring protons, and a two-proton doublet of doublets at δ 7.13 as well as a six-proton multiplet at δ 7.20-7.31 for the remaining aryl protons.

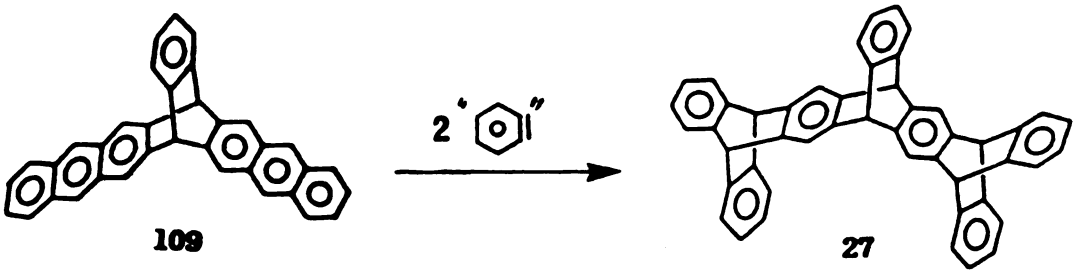
The regioisomer **136** had a very similar ^{1}H NMR spectrum except that the benzylic protons showed a quartet-like splitting (AB type), probably due to the influence of the nearby oxygen bridge.

The mixture of adducts **135** and **136** was dehydrated using hydrochloric acid in acetic anhydride to give a single product **137** (48 %). The structure of **137** was obvious from its ^{1}H NMR spectrum, which showed an anthracene unit and only one set of bridgehead protons. The spectrum consisted of aliphatic singlets at δ 3.84(4H) for the benzylic protons and δ 5.52(2H) for the bridgehead protons. The protons of anthracene moiety were apparent as two two-proton singlets at δ 8.22 and 7.87, and two two-proton doublets of doublets at δ 7.93 and 7.38. The remaining aryl protons appeared as follows : δ 7.03(dd,2H), 7.11(dd,2H), 7.21(dd,2H), 7.36-7.43(m,4H).

Compound **137** was quantitatively dehydrogenated, by refluxing with Pd/C in mesitylene for 60 h, to give **109**.

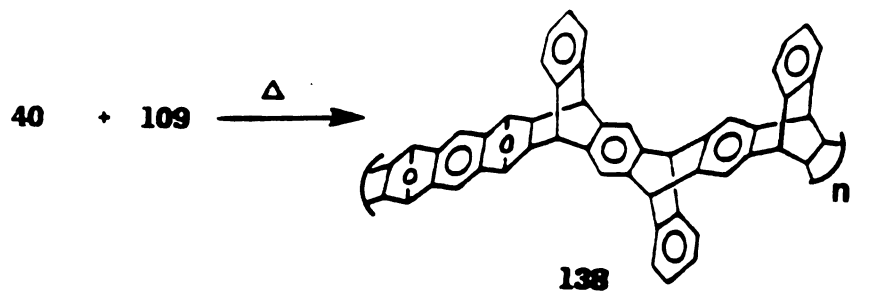
The structure of **109** was obvious from its spectra, which were consistent with the C_{2v} symmetry. The ^{1}H NMR spectrum contained a two-proton singlet at δ 5.68 for the bridgehead protons and two two-proton doublets of doublets at δ 7.11 and 7.52 for the benzenoid ring protons. The protons of the anthracene moieties appeared as two four-proton singlets at δ 8.28 and 7.98 and two four-proton doublets of doublets at δ 7.93 and 7.41. The ^{13}C NMR spectrum gave eleven peaks (one aliphatic carbon and ten aromatic carbons) as required by the symmetry. The mass spectrum of **109** showed a strong molecular ion peak at m/e 454. The UV spectrum possessed a set of bands typical of an anthracene, with the longest wavelength absorption at 378 nm.

The structure of **109** was further confirmed by its cycloaddition reaction with two equivalents of benzyne to give the known heptiptycene **27** in 50 % yield.



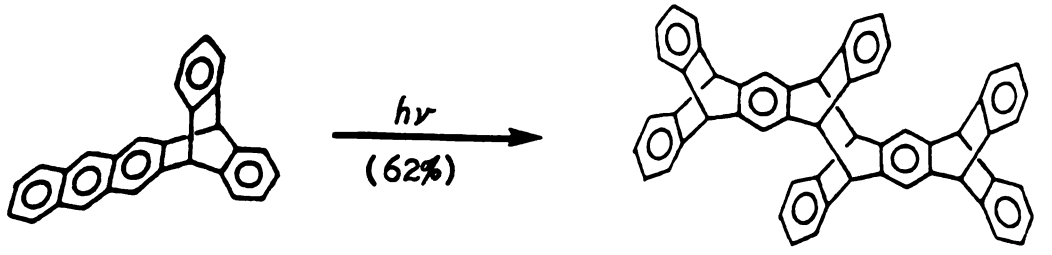
The unique arrangement of the two anthracene moieties in triptycene **109** might be useful for synthesizing complex iptycenes, since such molecules can be built up in two direction. Another possible application will be the synthesis of polyiptycenes, which might be potentially useful polymers for heat-resistant materials. For example, a bifuctional dienophile such as **40**, in a Diels-Alder

cycloaddition with **109**, should give epoxypolyiptycene **138**.[41]



138

A photopolymer from **109** might also be envisioned, via the face-to-face dimerization of its anthracene units. For example, as a model, [3(b,b)^{b}.1.1]triptycene **20** was photodimerized[43,44] to give **139** in 62 % yield. The product is believed to be the head-to-tail isomer. The



20 **139**

characteristic feature of the ^{1}H NMR spectrum of **139** was the disappearance of the anthracene moiety and the additional formation of the bridgehead protons. The spectrum showed two four-proton singlets at δ 4.27 and 5.12 for the bridgehead protons, and a four-proton singlet at δ 6.84 for the uncoupled benzenoid ring protons. The remaining aryl protons appeared as six sets of four-proton doublets of doublets at δ 6.17, 6.60, 6.85, 6.95, 6.98 and 7.21.

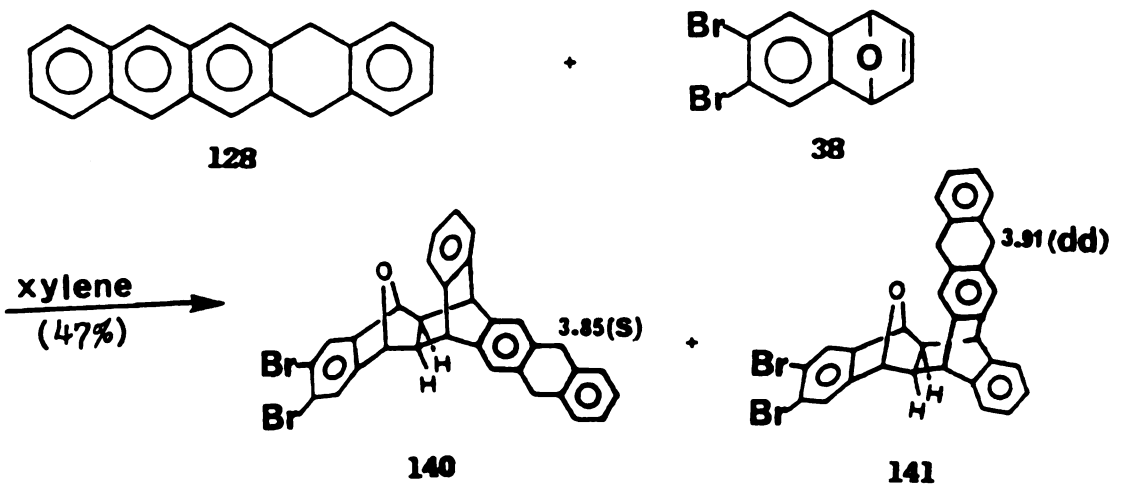
The dimer **139**, unlike **20**, was sparingly soluble in ordinary organic solvents. Upon heating to its melting

point, it dissociated to give **20**.[44]

Similarly, photopolymerization of **109** might afford a useful rigid ladder polymer (The photopolymerization of a similar type of compound, 7,16-bis(1-octynyl-7,16-dihydro-heptacene-7,16-diol has been reported).[41]

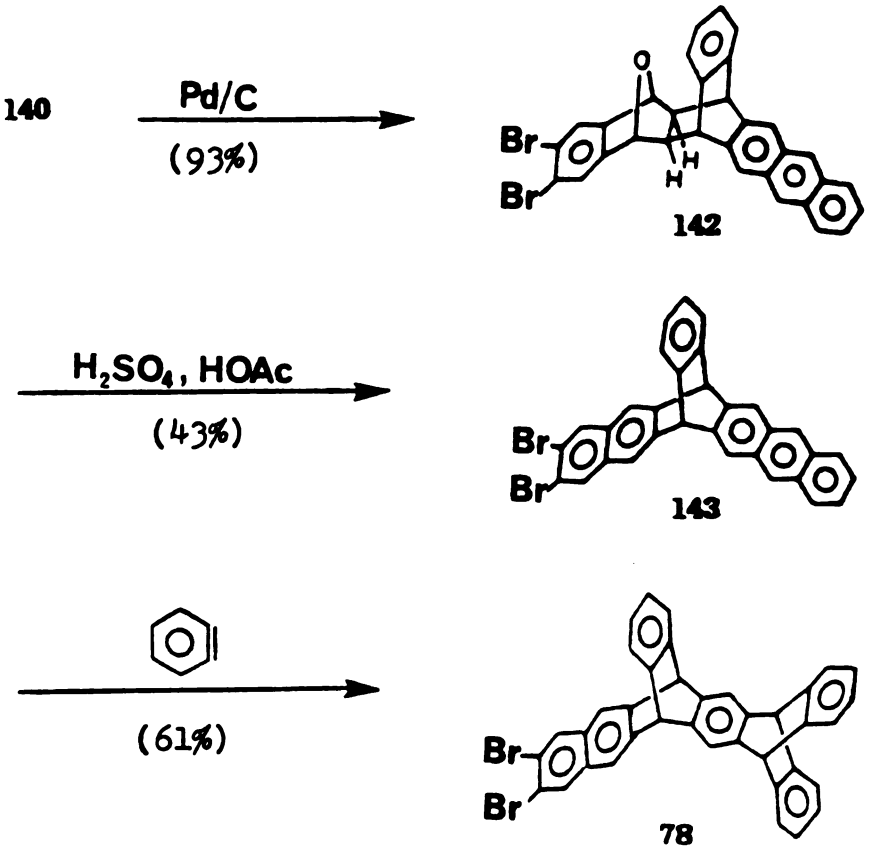
E. Synthesis of 6,15[1',2']-Benzeno-2,3,-dibromo-6,15-dihydrohexacene (143).

The successful synthesis of **109** via 5,14-dihydro-pentacene synthon **128** led us to explore its analogue **143**. Refluxing equivalent amounts of **38** and **128** in xylene for 5 days afforded two regioisomers **140** and **141** (ratio 8:1) in 47 % yield.



The ^{1}H NMR spectra of **140** and **141** were similar to those of **135** and **136**. The benzylic protons of **140** appeared as a singlet at δ 3.85 whereas in **141** these protons appeared as an AB quartet at δ 3.91. The major adduct **140** was then dehydrogenated to give **142** in 93 % yield. The structure of **142** was supported by its ^{1}H and ^{13}C NMR and mass spectra.

Dehydration of **142** using sulfuric acid in acetic acid gave the desired **143** in 43 % yield. The structure of **143** was clear from its spectra and was confirmed by formation of benzyne adduct **78**.

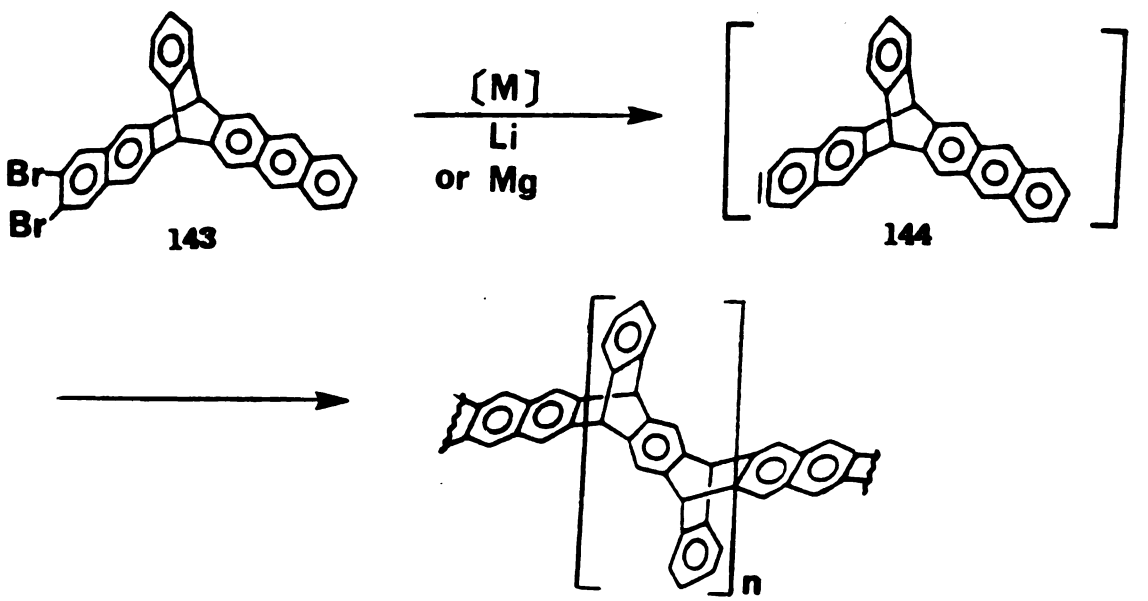


The ^{1}H NMR spectrum of **143** showed a two-proton singlet at δ 5.64 for the bridgehead protons. The aromatic region consisted of two two-proton singlets at δ 7.94 and 7.67 for the naphthalene ring protons, and two two-proton doublets of doublets at δ 7.11 and 7.50 for the benzenoid ring protons. In addition, the anthracene moiety appeared as follows : δ 8.27(s,2H), 7.96(s,2H), 7.92(dd,2H) and 7.40(dd,2H). The ^{13}C NMR spectrum gave fifteen peaks (one peak was missing, possibly overlapped at δ 131.68 due to its double

intensity). The mass spectrum showed a strong molecular ion peak at m/e 562.

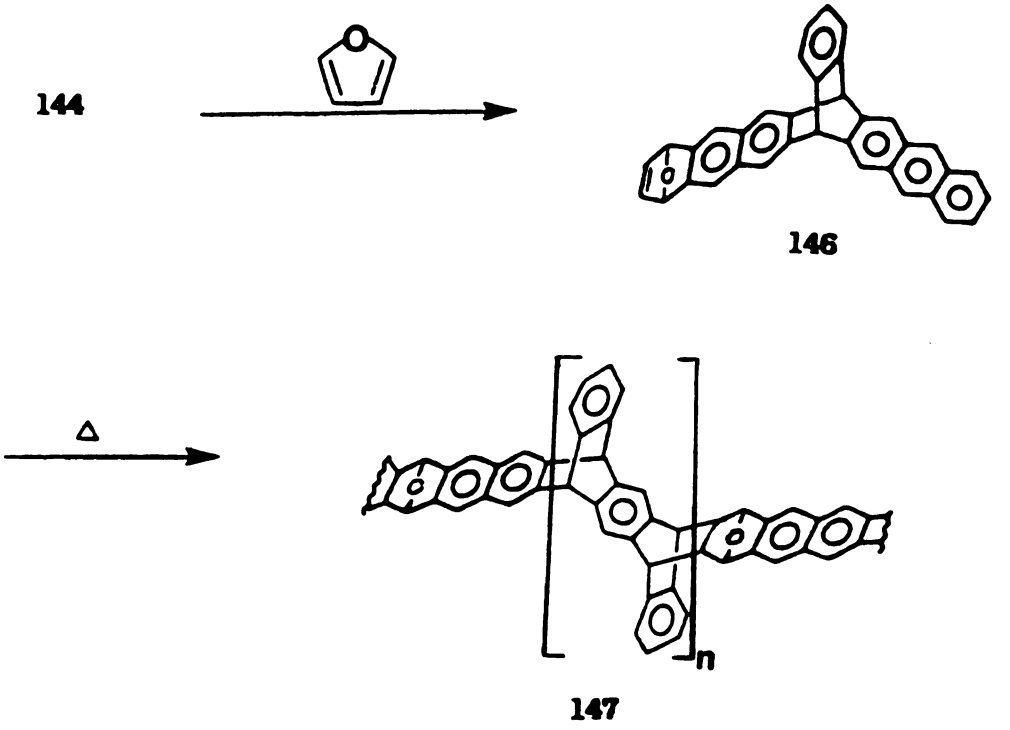
Benzyne addition to the anthracene moiety of **143** gave compound **78** in 61 % yield. Its ^{1}H NMR was identical to that of independently synthesized **78** (vide supra).

Compound **143** is also a potential synthon for the synthesis of complex iptycenes or polyiptycenes. The dual character of the molecule, anthracene moiety as diene and dibromonaphthalene moiety as aryne equivalent, is very attractive. For example, one might use the anthracene moiety to build up higher iptycenes first (as with synthon **20**), then elaborate the aryne equivalent part to make a more complex iptycene. Another possible application might be to use **143** as a monomer to synthesize a polyiptycene. For instance, generation of aryne from the dibromonaphthalene moiety followed by intermolecular Diels-Alder reaction with the anthracene moiety could give polyiptycene **145**.



143 144 145

In addition, one might also trap intermediate **144** with furan to make the potential monomer epoxytriptycene **146**. Heating **146** should then give epoxypolyiptycene **147**.

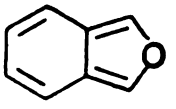


F. Conclusions.

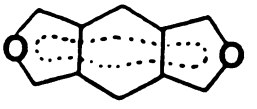
In this part we have demonstrated the successful synthesis of linear acenes by fusion of o-xylylene to the epoxides **7**, **38**, **40** and **50**, followed by dehydration and dehydrogenation. The 5,14-dihydropentacene **128** thus obtained was applied to the synthesis of potential synthons **109** and **143**. The dual fuctionalities in these molecules suggests their use as precursors of complex iptycenes or as monomers to synthesize polyiptycenes.

Part III. Synthesis and Reactions of a Furano[3,4-f]benzo-[c]furan Equivalent.

Isobenzofuran or benzo[c]furan **129**, a reactive species, has been studied extensively in recent years.[57] The application of this compound and its analogues in the Diels-Alder synthesis of polycyclic systems, including natural products, has become recognized.



129



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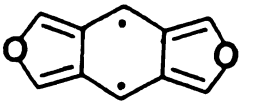
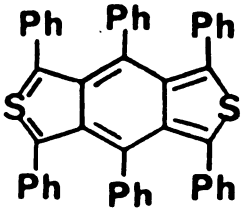


149

Furano[3,4-f]benzo[c]furan (another name is benzo-[1,2-c:4,5-c']difuran) **133** (trial structure), a 14π-electron heterocycle or a biradical species **149**, containing in a sense two units of isobenzofuran is virtually unknown in the literature. The hexaphenyl sulfur analog of **133**, that is thieno[3,4-f]benzo[c]thiophene **150**, was reported to be a stable crystalline compound.[58] The related bicyclic system **151** has also been synthesized.[59]



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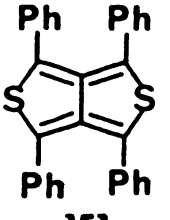


151

Isobenzofuran **129** was first demonstrated to exist as a transient intermediate by Fieser and Haddadin.[60] They reacted **7** with α-pyrone **152** or with tetraphenylcyclopentadienone (tetracyclone) **153** to form Diels-Alder adduct **154** or **155**, respectively (Fig. 11). Upon heating, the adducts

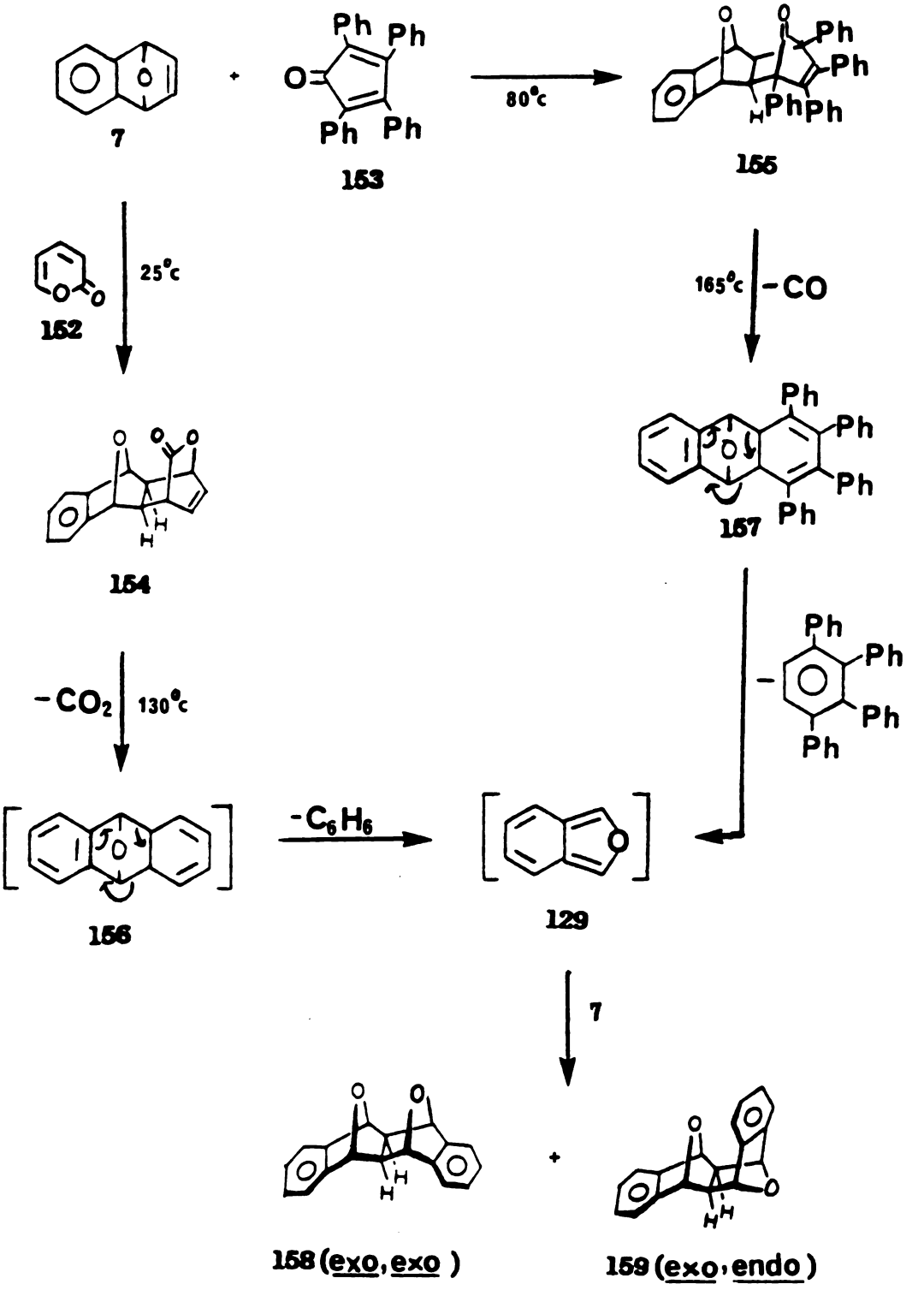
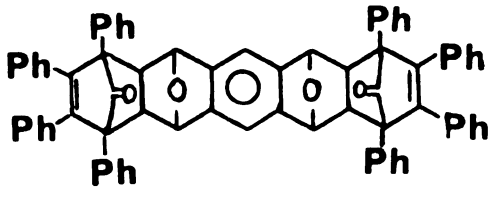


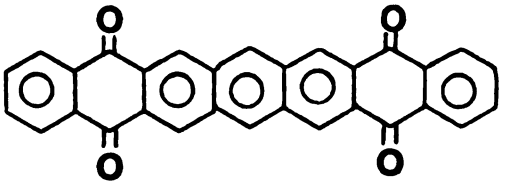
Figure 11. Generation and trapping of isobenzofuran intermediate 129.

spontaneously lost carbon dioxide or carbon monoxide to produce **156** or **157**, which underwent a retro Diels-Alder reaction to give the reactive isobenzofuran intermediate. The isobenzofuran species thus generated was trapped in situ by epoxide **7** to give two adducts, **158** (exo,exo) and **159** (exo,endo). The precursors **154** and **155** thus acted as isobenzofuran equivalents.

In this part of the thesis, we shall describe the use of furano[3,4-f]benzo[c]furan equivalent **160** to synthesize some novel linearly fused polycyclic compounds.

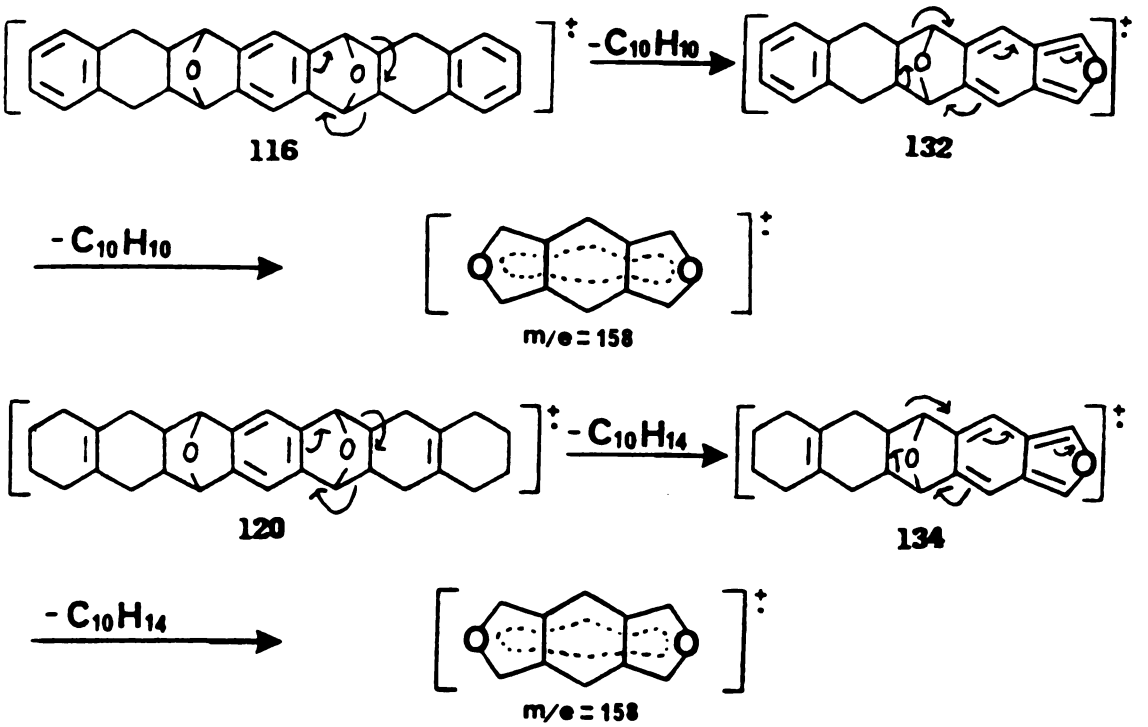


160



161

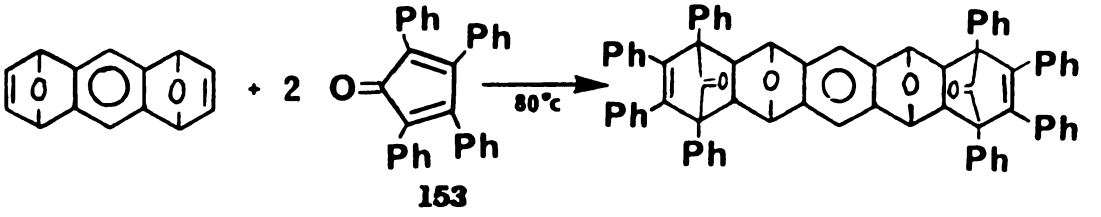
The idea of extending isobenzofurans to the furano-[3,4-f]benzo[c]furan **133** came from our needs and observations during this study. First, the failure of being able to use heptacene equivalents **112** and **121** to synthesize the important building blocks **109** and **110** (see discussion in part II) suggested that a third candidate, 5,18;9,14-heptacenediquinone **161**, might be necessary. This would eliminate the possible phenomenon of hydrogen walks or rearrangements. Second, the mass spectra of epoxyarenes **116** and **120** (Table 3) showed a base peak at m/e 158, possibly due to a transient intermediate that could be formed by a



retro Diels-Alder reaction. The unusually strong base peak of m/e 158 suggested that species 133 might be aromatic (14 π electrons). Third, using a synthetic equivalent of 133 (i.e. 160) we might be able to synthesize 161 via a short route. Finally, the structure and properties of species 133 would be worthwhile to investigate, especially to determine whether or not it could be isolated.

A. Synthesis of Furano[3,4-f]benzo[c]furan Equivalent (160).

Bis-epoxide 40 and tetracyclone 153 are both readily available materials. Thus, cycloaddition of 40 with two equivalents of 153 in refluxing benzene gave bis-adducts 160s or 160a in high yields. Only one isomer was formed in each case, depending on the stereochemistry of the



153

40s	90%	**160s**
40a	92%	**160a**

bis-epoxide precursor. The ^{1}H NMR spectrum of the syn adduct **160s** showed two four-proton singlets at δ 3.16 and 5.81 for the bridgehead protons, and two sets of multiplets at δ 6.87-6.99 and 7.26-7.47 for the aryl protons. The anti adduct **160a** had a similar spectrum, with the bridgehead protons at δ 3.06 and 5.84 , and the central aromatic protons at δ 7.58 as well as remaining aryl protons at δ 6.87-7.04 and 7.27-7.52.

The lack of coupling between the two sets of bridgehead protons indicated that the stereochemistry of both adducts was exo. However, the stereochemistry of the carbonyl groups was not determined.

B. Trapping Various Dienophiles With Furano[3,4-f]benzo-[c]furan Equivalent.

The easy synthesis of **160a** makes it a very useful intermediate for the preparation of some linearly fused polycyclic systems. For example, thermal decomposition of **160a** followed by trapping of the isobenzofuran moiety with a dienophile in situ would afford compounds with bis-fusion on the furano-[3,4-f]benzo[c]furan **133** backbone (Fig. 12).

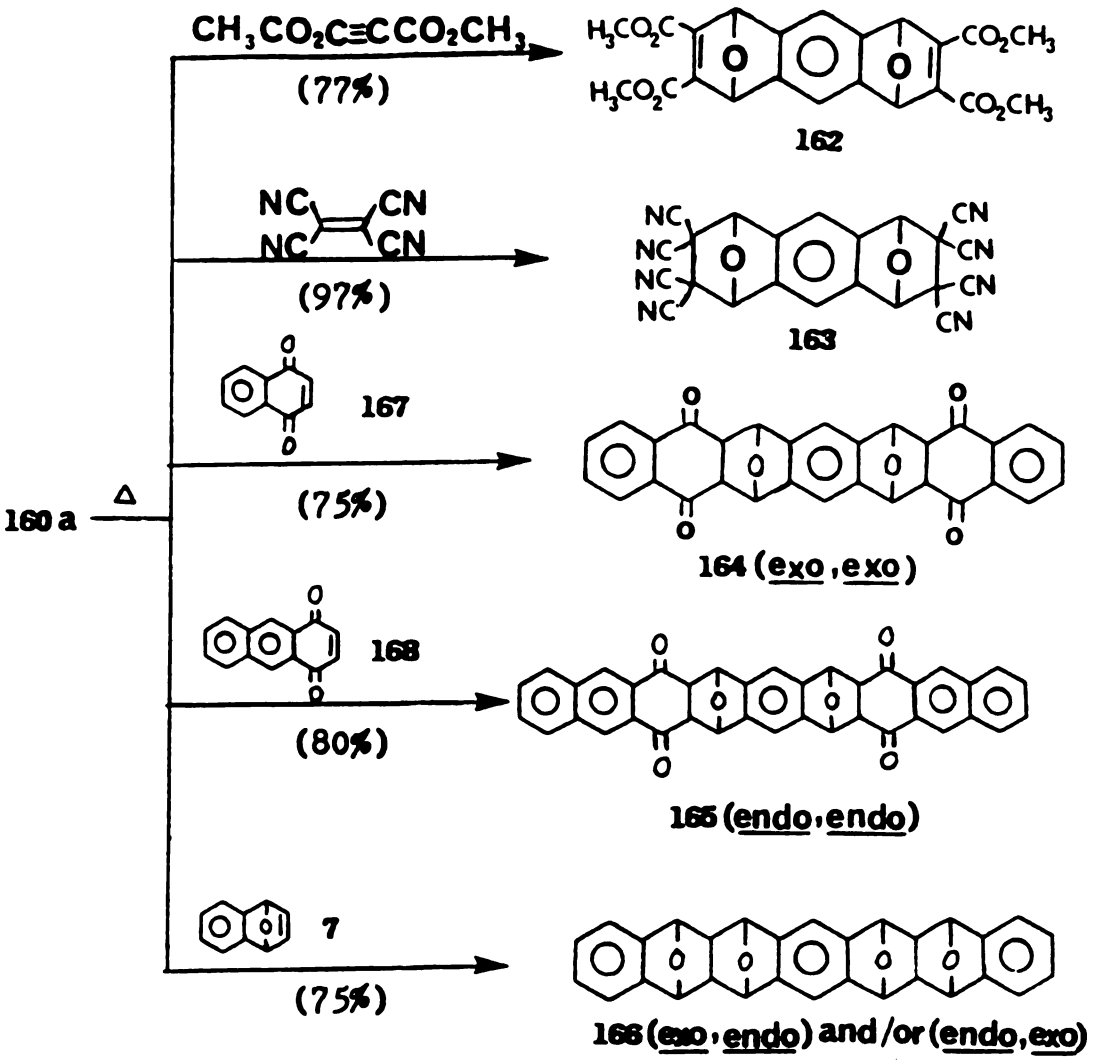


Figure 12. Trapping various dienophiles with furano-[3,4-f]benzo[c]furan equivalent **160a**.

Thus, heating **160a** with two equivalents of a dienophile in a sealed tube (xylene as solvent) at 170° for 13 h gave bis-adducts in good yield. The structure of each individual adduct was assigned by its spectra. However, the stereochemistry of the oxygen bridge (syn or anti) was not determined.

In the case of adduct **162**, both syn and anti isomers were found. The ^{1}H NMR spectrum of anti isomer showed a four-proton singlet at δ 5.91 for the bridgehead protons, a twelve-proton singlet at δ 3.81 for the methyl protons, and a two-proton singlet for the aromatic protons at δ 7.53. The syn adduct had a similar spectrum, whose aromatic protons appeared at δ 7.49. The ^{13}C NMR spectrum of each adduct gave six peaks as required by the symmetry. The mass spectrum of **162** showed a correct molecular ion peak at m/e 442.

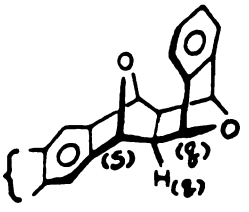
The simple spectra of TCNE adduct **163**[66] indicated that only one isomer was found. The ^{1}H NMR spectrum appeared as two singlets at δ 6.93 and 7.98, area ratio 4:2. The ^{13}C NMR gave only six peaks as required by the C_{2v} symmetry.

The naphthaquinone adduct **164** was isolated in 75 % yield. The ^{1}H NMR spectrum showed two four-proton singlets at δ 3.05 and 5.84 for the bridgehead protons, a two-proton singlet at δ 7.55 for the central aromatic protons, and two sets of four-proton doublets of doublets at δ 7.81 and 8.17 for the "outer" benzenoid ring protons. The stereochemistry of **164** was assigned as exo/exo, the likely thermodynamic product, because the bridgehead protons showed virtually no coupling to each other.

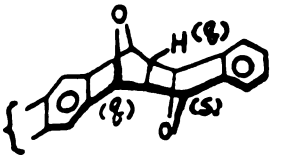
The anthraquinone adduct **165**, on the other hand, was found to be the endo/endo isomer, a kinetically-controlled product, since the ^{1}H NMR spectrum showed obvious coupling between the bridgehead protons. Its spectrum appeared as two four-proton quartets at δ 3.95 and 5.92 for the

bridgehead protons, and a two-proton singlet at δ 7.07 for the central aromatic protons. In addition, the naphthalene moiety appeared as follows : δ 8.55(s,4H), 8.07(dd,4H), and 7.71(dd,4H). The reason for the formation of the kinetic product was probably due to the insolubility of the product (precipitation from the reaction mixture at 170°), which prevented its further conversion to the more stable <u>exo</u>/<u>exo</u> adduct.

Trapping of **160a** in presence of epoxide **7** gave adduct **166** in 73 % yield. The ^{1}H NMR spectrum contained two sets of bridgehead protons. One set appeared at δ 2.77(q,4H), 4.68(s,4H) and 5.32(q,4H). The corresponding peaks of the other set appeared at δ 2.90(q,4H), 4.78(s,4H) and 5.44(q,4H). The remaining aryl protons gave a multiplet at δ 7.02-7.26. The complicated spectrum of **166** indicated that it was possibly a mixture of the <u>exo</u>/<u>endo</u> isomer **169** and the <u>endo</u>/<u>exo</u> isomer **170**.[61] The mass spectrum showed a correct molecular ion peak at <u>m</u>/<u>e</u> 446.



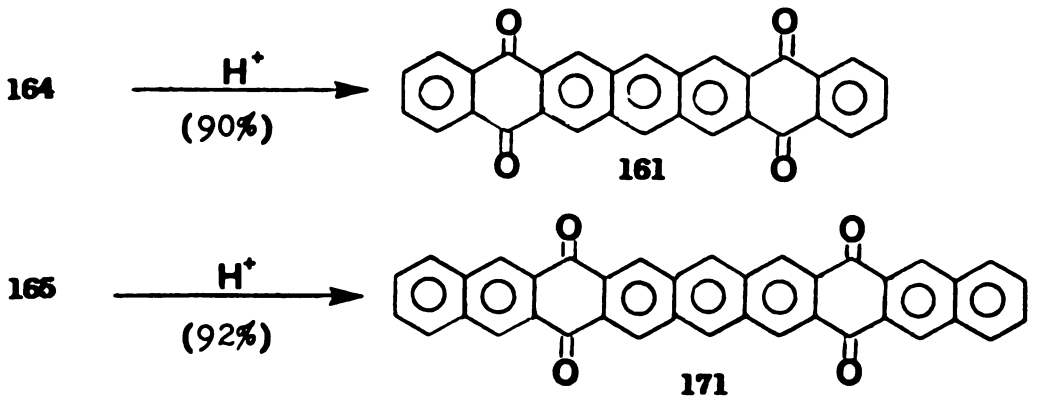
169



170

Fig. 12 summarizes the successful examples of the trapping of furano[3,4-f]benzo[c]furan equivalent **160** with various dienophiles to construct novel linearly fused polycyclic compounds. Among them, adducts **164** and **165** were

dehydrated using sulfuric acid and acetic acid to give the corresponding anthracenes 161 and 171 in high yields.



The insolubility of these compounds in ordinary organic solvents prevented the measurement of their NMR spectra but their structures were supported by IR and mass spectral data as well as by their mode of formation.

The mass spectrum of 161 showed a molecular ion peak at m/e 438. The IR spectrum possessed a typical quinone peak at 1680 cm^{-1}. It gave a brownish-orange vat dye with alkaline sodium dithionite, similar to the result reported by Marschalk.[64] In concentrated sulfuric acid it gave a dark green solution. Although compound 161 can be synthesized readily, the insoluble property of this compound limited its use as a heptacene equivalent.

The structure of 171 was assigned similarly to that of 161. The mass spectrum showed a molecular ion peak at m/e 538. An IR peak of the quinone moiety appeared at 1670 cm^{-1}. The compound gave a dark green solution in concentrated sulfuric acid.

C. Mechanism for the Generation of Isobenzofuran or Furano-[3,4-f]benzo[c]furan from 160a.

The trapping reactions of **160a** with various dienophiles described above possibly proceeded via a stepwise mechanism (via two isobenzofuran moieties) or possibly through the furano[3,4-f]benzo[c]furan **133**. For example, possible mechanisms for the formation of the DMAD bis-adduct **162** are illustrated in Fig. 13.

Upon heating, compound **160a** can lose carbon monoxide to produce **173**, which can undergo a retro Diels-Alder reaction to give the isobenzofuran intermediate **174**. Species **174** can either be trapped with one equivalent of DMAD to afford monoadduct **175**, or undergo further eliminations to generate the furano[3,4-f]benzo[c]furan intermediate **133**. In the former case, loss of carbon monoxide and tetraphenylbenzene **177** will produce another isobenzofuran intermediate **176**, which can then be trapped with DMAD to give the observed bis-adduct **162**. In the latter case, no monoadduct would be involved.

Although it seems that a stepwise pathway has more precedent, the intermediate **133** cannot be ruled out. More evidence supporting the existence of species **133** came from the mass spectra of adducts **162-165**, all of which showed a base or strong peak at m/e 158.

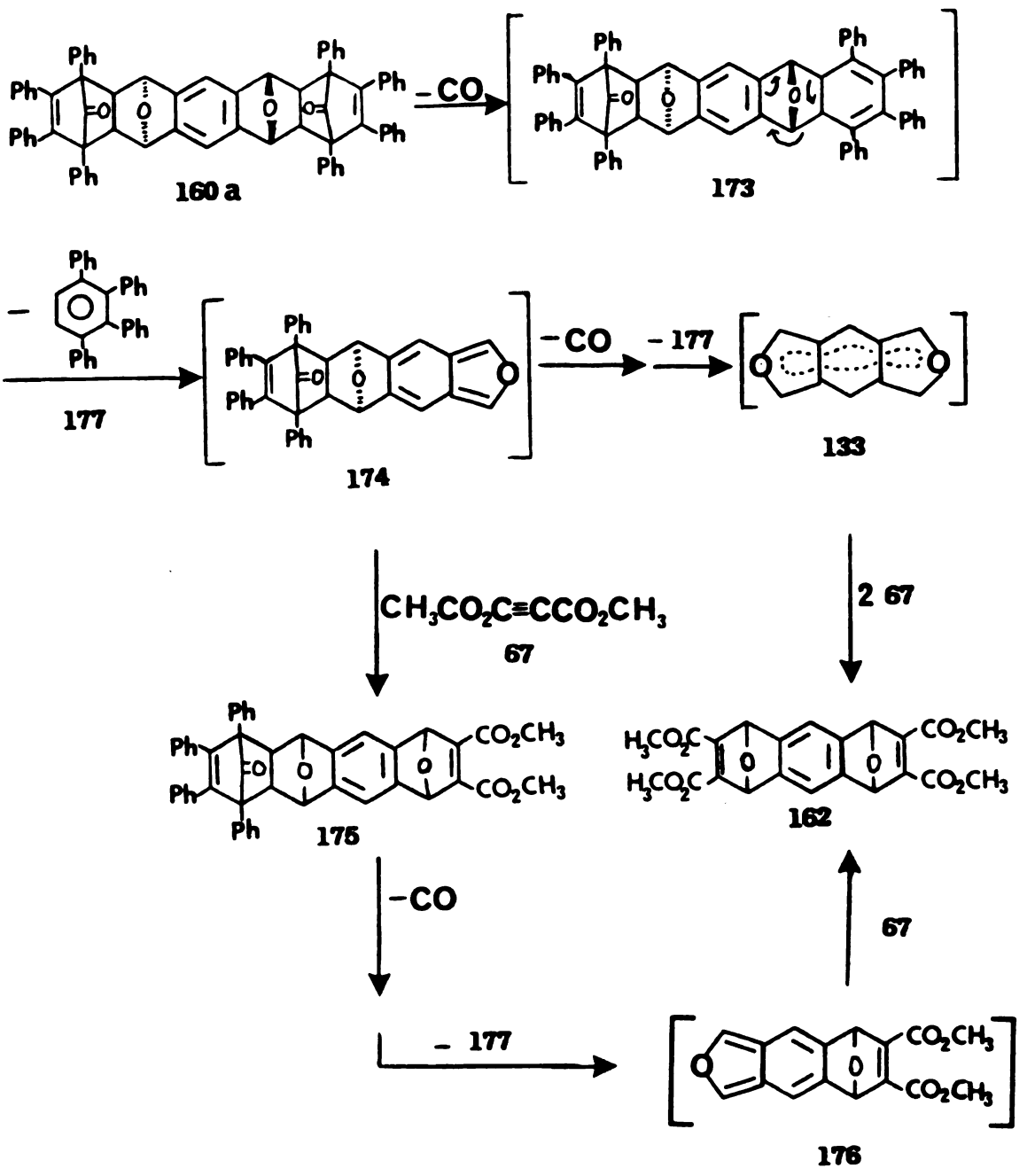
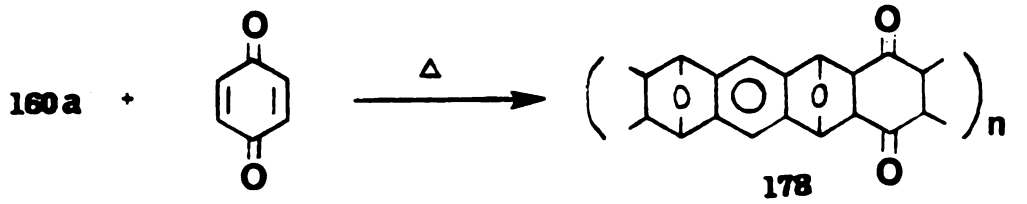
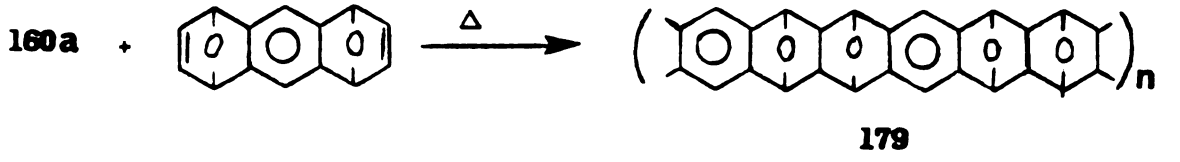


Figure 13. Possible mechanisms for the generation of isobenzofuran or furano[3,4-f]benzo[c]furan 133 from 160a.

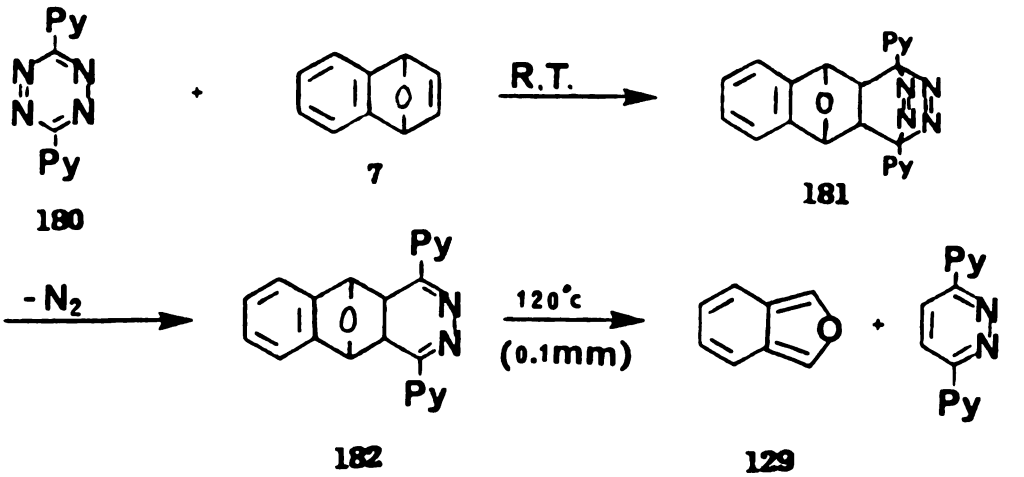
D. Suggestions for Further Studies.

As discussed above, the utility of compound **160a** as a synthetic equivalent of furano[3,4-f]benzo[c]furan **133** for the synthesis of linearly fused polycyclic systems was demonstrated. This methodology can be applied to construct novel polycyclic compounds if a suitable dienophile is chosen. To extend the sucessful examples of adducts **164-166**, one can imagine that a Diels-Alder type of polymer might be synthesized choosing benzoquinone or bisepoxide **40** as the dienophiles. For example,

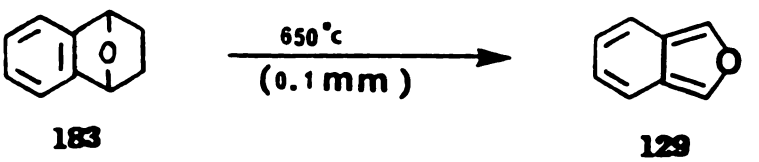




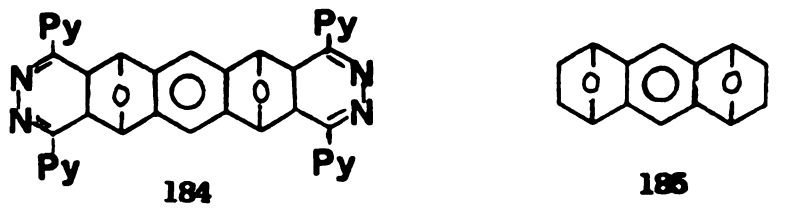
Another feature worthwhile to explore is the isolation of species **133**. Isobenzofuran **129** has been isolated via retro Diels-Alder reaction with derivatives of **7**. Warrener[62] applied 3,6-di(2'-pyridyl)-s-tetrazine **180** as the diene component with **7** to prepare adduct **181**, which spontaneously lost nitrogen to form **182**. By controlled pyrolysis of **182** at 120° under reduced pressure (0.1 mm), **129** was trapped on a cold finger.



Wiersum[63] used 1,4-epoxy-1,2,3,4-tetrahydronaphthalene **183** as a starting material. Flash-vaccum pyrolysis (FVP) of **183** at 650° and 0.1 torr in an unpacked quartz tube resulted in the quantitative formation of **129**.



The successful isolation of isobenzofuran by FVP suggests that furano[3,4-f]benzo[c]furan **133** might be isolated through similar experiments. For example, compounds **184** or **185** could be used as its precursors.



This preliminary study of compound **160** in the synthesis of some linear polycyclic systems opens up a new field to explore. First, by choosing a proper dienophile one can design novel polycyclic compounds. Second, the heterocyclic species related to **133**, or its analogs, is a theoretically interesting subject. We expect to see some achievements in this field in the near future.

Experimental

1. General Procedure. NMR spectra (^{1}H and ^{13}C) were recorded on a Bruker WM 250 MHz spectrometer using $CDCl_3$ as solvent and $(CH_3)_4Si$ as the internal reference. UV spectra were obtained on a Perkin-Elmer 200 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. Some very high melting materials were measured either on a Hitachi M-80A spectrometer with a direct inlet temperature of 300-400 at Ube Industries, Japan, or JEOL HX110 HF spectrometer using field desorption (FD) technique at Michigan State University Mass Spectrometry Facility. Melting points were determined with an electro-thermal melting point apparatus (Fisher Scientific) and are uncorrected. Anhydrous $MgSO_4$ was the drying agent throughout, silica gel for chromatography was either 70-200 or 230-400 mesh. Microanalysis were performed by Spang Microanalytical Laboratory, Eagle Harbor, Michigan.

2. 1,2,4,5-Tetrabromobenzene (31).

To a solution of 1,4-dibromobenzene (236 g, 1 mole) in 1200 mL CCl_4 containing iron filings (4.8 g) was added bromine (206 mL, 4 mole) and the mixture was heated at reflux for 20 h. The cooled mixture was slowly added to a stirred, cold saturated Na_2SO_3 soln (2 L) until the bromine

color disappeared. The resulting ppt was filtered, washed with water, then methanol and saved. The organic layer of the combined filtrates was separated, dried, and evaporated. The residue was combined with the above ppt and recrystallized from benzene to give 275.8 g (70 %) of **31**, m.p. 180-182 (lit.[24] 181); ^{1}H-NMR : δ 7.87 (s).

3. 6,7-Dibromo-1,4-dihydronaphthalene-1,4-epoxide (38).

To a stirred soln of 1,2,4,5-tetrabromobenzene (90 g, 228 mmole) and furan (115 mL) in dry toluene (2 L) at -23° C under argon was added n-butyllithium (250 mmole in 150 mL hexane) dropwise over 4 h. After the mixture slowly came to room temperature, water (50 mL) was added, and the mixture was washed with water, dried, and the solvent removed (rotavap). The resulting yellowish oily solid was recrystallized from methanol to give 48.20 g (70 %) of **38**, m.p. 115-117°; ^{1}H-NMR : δ 5.64(s,2H), 6.98(s,2H), 7.45(s,2H) ; ^{13}C-NMR : δ 81.76, 120.61, 125.43, 142.68, 150.19 ; mass spectrum, m/e (relative intensity) 302 (M^{+},9), 276(19), 193(100), 113(46), 87(21), 63(25). Anal. Calcd. for $C_{10}H_6Br_2O$: C, 39.78 ; H, 2.00. Found : C, 39.86 ; H, 2.07.

4. 2,3-Dibromonaphthalene (49).

To ice-cold dry THF (500 mL) was added carefully 18 mL of $TiCl_4$, followed by 20 g of Zn powder, and the gray mixture was heated at reflux for 30 minutes. Then a soln of **38** (35 g, 116 mmole) in 225 mL of THF was added dropwise. The mixture was refluxed overnight, cooled and poured into 1 L

of cold 10 % HCl. The resulting ppt was filtered, washed with water and air-dried. Recrystallization of the crude product from heptane gave 28.20 g (85 %) of **49**, m.p. 138-140° (lit.[25d] 139-140°); ^{1}H-NMR: δ 7.48(dd,2H), 7.68(dd,2H), 8.15(s,2H).

5. 1,3-Dibromonaphthalene (55).

One hundred and ten grams of **54**[25d] was introduced into 100 mL flask and heated. When all the materials was molten, the flask was mounted with a Claisen head, a condenser and a receiver and the distillation system was evaculated to an absolute pressure of 70-200 mm. The flask contents were heated at a pot temperature of 220°; hexachlorocyclopentadiene distilled over. Distillation was continued until the production of hexachlorocyclopentadiene became very slow and small amounts of solid appeared in the condenser. The dark residue left in the flask was column chromatographed over silica gel using hexane as the eluent to give **55** (9.12 g, 24 %), m.p. 64-66° (Lit.[67] 64°); ^{1}H-NMR : δ 7.50(dd,2H), 7.73(dd,2H), 7.94(s,1H), 8.13(s,1H) ; mass spectrum, m/e (rel. intensity) 288(M+4,27), 286(M+2,48), 284(M^+,23), 276(19), 242(100), 205(8), 196(39), 161(46), 126(91).

6. 1,4-Dihydroanthracene-1,4-epoxide (50).

To a stirred soln of 2,3-dibromonaphthalene (18.2 g, 63.6 mmole) and furan (120 mL) in dry toluene (450 mL) at room temperature under argon was added n-butyllithium (70 mmole in 70 mL hexane) dropwise over 3 h. The mixture was stirred

at room temperature for another 16 h. Methanol (2 mL) was added, and the mixture was washed with water, dried and the solvent removed (rotavap). The resulting ppt was recrystallized from petroleum ether (b.p. 60-90°) to give 10.0 g (81 %) of **50**, m.p. 163-165° (lit.[25e] 164-165°); ^{1}H-NMR : δ 5.80(s,2H), 6.97(s,2H), 7.43(dd,2H), 7.59(s,2H), 7.72(dd,2H).

7. 11,12-Dimethylene-9,10-dihydro-9,10-ethanoanthracene (52)

A mixture of anthracene (10.68 g, 60 mmole) and 1,4-dichloro-2-butene[28] (50 mL, cis/trans mixture) was heated in a sealed tube at 190-195° for 48 h. Solvent removal (distillation) gave a black product which was preabsorbed onto alumina. Column chromatography over silica gel and alumina (1:1, alumina on top) using CH_2Cl_2-hexane (1:2) as eluent gave 16.8 g (96 %) of a cis/trans mixture of 11,12-bis-chloromethyl-9,10-dihydro-9,10-ethanoanthracene **57**, m.p. 144-146° (hexane) ; ^{1}H-NMR : (cis) δ 1.74(m,2H), 2.96(m,2H), 3.30(m,2H), 4.43(s,2H), 7.15(dd,4H), 7.32(dd,4H) ; (trans) 2.46(m,2H), 2.85(m,2H), 3.44(m,2H), 4.55(s,2H), 7.14(dd,4H), 7.32(dd,4H) ; mass spectrum, m/e (relative intensity) 302(M^+,13), 229(3), 215(14), 202(19), 189(7), 178(100), 165(5).

To a soln of **57** (15.15 g, 50 mmole) in DMSO (160 mL) and THF (40 mL) was added t-BuOK (16.5 g, 150 mmole) and the brown soln was stirred at room temperature overnight, then poured into ice-water, and extracted with ether. The organic layer was washed with brine, dried and the solvents

removed (rotavap). The resulting ppt was recrystallized from hexane to give 10.24 g (89 %) of diene **52**, m.p. 156-157° (lit.[26] 157-157.5°) ; ^{1}H-NMR : δ 4.87(s,2H), 5.06(s,2H), 5.16(s,2H), 7.12(dd,4H), 7.31(dd,4H).

8. 1,4;5,8-Diepoxy-1,4,5,8-tetrahydroanthracene (40).

To a stirred soln of 1,2,4,5-tetrabromobenzene **31** (39.4 g, 0.1 mole) and furan (freshly distilled, 120 mL) in dry toluene (1400 mL) at -23° C under argon was slowly added n-BuLi (0.22 mole in 150 mL hexane) for 4 h. After addition the mixture was slowly allowed to warm to room temperature and stirred overnight. Water (50 mL) was added and the mixture was stirred for a few minutes. The organic layer was washed with water and dried. Solvent removal (rotavap) gave a gummy yellow solid which partially dissolved on addition of methanol (120 mL). The off-white crystals which remained (7.03 g) were recrystallized from acetone to give small white plates of anti isomer **40a**. The methanol soln was evaporated to dryness. The residue was either recrystallized from methanol two to three times or column chromatographed over silica gel using EtOAc as the eluent to give the pure syn isomer **40s** (6.62 g). The total yield of both isomers was 65 %. Their ^{1}H NMR spectrum were identical to those of the literature[14b].

9. 5,14[1',2']Benzeno-5,14-dihydropentacene (20).

Method A : A soln of **38** (18.12 g, 60 mmole) and anthracene (10.68 g, 60 mmole) in xylene (700 mL) was heated

at reflux for 4 days. The solvent was removed (rotavap) and the residue was recrystallized from THF-MeOH to give **43** (27.65 g, 96 %) as fine off-white crystals, m.p. 264-266°; ^{1}H-NMR : δ 2.24(s,2H), 4.41(s,2H), 4.89(s,2H), 7.03(dd,2H), 7.16(dd,2H), 7.24(m,4H), 7.40(s,2H) ; ^{13}C-NMR : δ 47.21, 48.25, 80.82, 123.61, 123.81, 124.17, 125.31, 125.90, 126.17, 128.17, 140.10, 143.84 ; mass spectrum, m/e (rel. intensity) 480(M^{+},4), 462(1), 302(2), 289(7), 276(9), 203(26), 191(100), 178(53).

To a suspension of **43** (19.2 g, 40 mmole) in EtOH (1400 mL) was added dropwise 45 mL of 72 % perchloric acid and the soln was heated at reflux overnight. The cooled soln was poured into ice-water (1.5 L). The resulting solid was filtered, washed with water, methanol and dried. Recrystallization from THF-MeOH gave a tan solid, which was further recrystallized from toluene to give **44** (12.01 g, 65%) as colorless flakes, m.p. 386-388°(dec.) ; ^{1}H-NMR : δ 5.51(s,2H), 7.04(dd,4H), 7.43(dd,4H), 7.60(s,2H), 7.94(s,2H) ; ^{13}C-NMR : δ 53.62, 120.68, 123.84, 125.78, 131.64, 144.02, 155.16 (two peaks were missing due to quarternary carbons) ; mass spectrum^{65}, m/e (rel. intensity) 464(35), 462(100), 460 (85).

To a stirred soln of **44** (6.93 g, 15 mmole) and furan (60 mL) in dry THF (1200 mL) at -78° under argon was added n-BuLi (17.25 mmole in 150 mL hexane) dropwise over 5 h. The mixture was allowed to come slowly to room temp and stirred overnight. MeOH (2 mL) was added, and the mixture was washed with water, dried and concentrated. The residue was

chromatographed using CH_2Cl_2-hexane (1:2) as eluent to give **45** (3.89 g, 70 %) as light yellow crystals, m.p. 188-190° (MeOH) ; ^{1}H-NMR : δ 5.48(s,2H), 5.72(s,2H), 6.88(s,2H), 6.99(m,4H), 7.39(m,4H), 7.44(s,2H), 7.65(s,2H) ; ^{13}C-NMR : δ 53.92, 81.88, 118.37, 121.64, 122.17, 123.70, 125.52, 125.61, 127.43, 141.75, 145.82 ; mass spectrum, m/e (rel. intensity) 370(M^+,1), 341(1), 303(1), 170(2), 149(4), 84(5), 40(100).

To a suspension of $TiCl_4$ (6.38 mL) in dry THF (500 mL) under argon at 0° was added 8.9 g of Zn powder. The gray suspension was heated at reflux for 30 minutes and a soln of **45** (4.44 g, 12 mmole) in 100 mL THF was added dropwise. After 8 h at reflux, the cooled mixture was poured into dil. HCl (1 L). The purple mixture was extracted with CH_2Cl_2 and the organic layer was washed with water and dried. Solvent removal gave a solid which was recrystallized from cyclohexane to give **20** (3.44 g, 81 %), m.p. 221-222°[32] ; ^{1}H-NMR : δ 5.54(s,2H), 7.05(dd,4H), 7.38(dd,2H), 7.46(dd,4H), 7.88(s,2H), 7.91(dd,2H), 8.23(s,2H) ; ^{13}C-NMR : δ 53.65, 121.31, 123.81, 124.96, 125.61, 125.75, 127.99, 130.52, 131.69, 141.10, 144.19 ; mass spectrum, m/e (rel. intensity) 354(M^+,100), 353(66), 278(3), 176(69) ; Anal : Calcd. for $C_{28}H_{18}$: C, 94.88; H, 5.12. Found : C, 94.81; H, 5.15.

Method B : To a soln of diene **52** (11.50 g, 50 mmole) and **49** (14.30 g, 50 mmole) in dry toluene (1 L) under argon was added n-BuLi (55 mmole in 150 mL hexane) dropwise over 3 h. The mixture was stirred at room temperature overnight, then quenched with methanol (3 mL). The resulting ppt was

filtered and saved. The filtrate was washed with water, dried and concentrated. The resulting solid was combined with the above ppt and recrystallized from CH_2Cl_2-hexane to give **62** (14.24 g, 80 %), m.p. 298-300°: ^{1}H-NMR : δ 3.82 (s,4H), 4.92(s,2H), 6.96(dd,4H), 7.34(m,6H), 7.58(s,2H), 7.70(dd,2H) ; mass spectrum, m/e (rel. intensity) 356(M^+,4), 290(6), 215(3), 202(3), 191(5), 180(5), 179(100), 178(32).

A soln of **62** (14.60 g, 41 mmole) in xylene (400 mL) containing 1 g of 10 % Pd/C under argon was heated at reflux for 48 h. The hot soln was filtered, and the catalyst was washed with methylene chloride (100 mL). The combined filtrate was concentrated (rotavap) to give colorless crystals of **20** (14.22 g, 98 %), m.p. 220-222°.

Method C : A soln of **50** (786 mg, 4.05 mmole) and anthracene (712 mg, 4.0 mmole) in xylene (20 mL) was heated at reflux for 72 h. The solvent was removed (rotavap) and the residue was recrystallized from $CHCl_3$-hexane to give **63** (1.38 g, 93 %) as tan crystals, m.p. > 310°(dec.) ; ^{1}H-NMR : δ 2.36(s,2H), 4.49(s,2H), 5.08(s,2H), 7.02(dd,2H), 7.17(dd,2H), 7.24(dd,2H), 7.33(dd,2H), 7.40(dd,2H), 7.52(s,2H), 7.72(dd,2H) ; ^{13}C-NMR : δ 47.52, 49.21, 81.23, 116.84, 123.53, 123.79, 125.64, 125.76, 126.08, 128.08, 132.61, 141.41, 144.01, 144.57 ; mass spectrum, m/e (rel. intensity) 372(M^+,1), 354(2), 353(3), 203(10), 191(28), 181(100), 178(39), 168(57), 139(10), 106(9), 91(18).

A soln of **63** (744 mg, 2 mmole) and conc. HCl (5 mL) in acetic anhydride (20 mL) was heated at reflux for 5 h. The cooled mixture was poured into 100 mL ice-water, and the

resulting solid was filtered, washed with water and dried. The solid was column chromatographed over silica gel, first elueting with hexane, then with CH_2Cl_2-hexane (1:4) to give **20** (474 mg, 67 %), m.p. 221-222°.

Method D : A soln of 1,4-dihydronaphthalene-1,4-epoxide[33] (1.44 g, 10 mmole) and **52** (2.30 g, 10 mmole) in toluene (40 mL) was heated at reflux for 72 h. The solvent was removed (rotavap) and the soln was triturated with hexane to give **64** (3.33 g, 89 %), m.p. 209-211° (toluene) ; ^{1}H-NMR : δ 1.87(dd,2H), 2.20(dd,2H), 2.82(dd,2H), 4.78(s,2H), 4.92(s,2H), 6.85-6.91(m,4H), 7.05-7.23(m,8H) ; ^{13}C-NMR : δ 30.47, 42.01, 55.77, 84.98, 118.66, 122.39, 122.50, 124.09, 124.22, 126.40, 143.06, 145.46, 146.39 ; mass spectrum, m/e (rel. intensity) 374(M^+,11), 356(6), 256(68), 215(26), 202(23), 178(92), 90(20).

A soln of **64** (2.99 g, 8 mmole) and conc. HCl (15 mL) in acetic anhydride (60 mL) was heated at reflux for 12 h. The cooled mixture was poured into 300 mL ice-water, and the resulting ppt was filtered, washed with water and dried. Column chromatography using CH_2Cl_2-hexane (1:4) as the eluent gave **65** (1.59 g, 56 %) as colorless crystals, m.p. 217-219°; ^{1}H-NMR : δ 2.32(m,1H), 2.72(m,1H), 2.96(m,1H), 4.32(s,1H), 4.87(s,1H), 6.55(s,1H), 7.11(m,4H), 7.31(m,6H), 7.32(s,1H), 7.38(s,1H), 7.64(m,2H) ; mass spectrum, m/e (rel. intensity) 356(M^+,29), 354(7), 353(5), 352(4), 278(2), 176(13).

A soln of **65** (1.07 g, 3 mmole) in mesitylene (50 mL) containing 150 mg of 10 % Pd/C was heated under argon at reflux for 72 h. The hot soln was filtered and the catalyst

was washed with methylene chloride (20 mL). The combined filtrate was concentrated under reduced pressure to give **20** (1.01 g, 95 %), m.p. 220-222°.

10. Diels-Alder adduct of 20 with tetracyanoethylene (69).

A soln of **20** (354 mg, 1 mmole) and TCNE (128 mg, 1 mmole) in benzene (50 mL) was heated at reflux for 3 h. The green soln (charge transfer complex) gradually faded and a white ppt formed. The cooled soln was filtered, and washed with benzene to give **69** (472 mg, 98 %) as a colorless powder, m.p. ca 288° (dec.) (acetone-hexane) ; ^{1}H-NMR : δ 5.69(s,2H), 5.75(s,2H), 6.90(dd,2H), 7.00(dd,2H), 7.37(dd,2H), 7.39 (dd,2H), 7.48(dd,2H), 7.64(dd,2H), 7.82(s,2H) ; mass spectrum (retro Diels-Alder reaction), m/e (rel. intensity); 354(98), 353(67), 352(57), 128(53), 76(52), 58(28), 43(100). Anal : Calcd. for $C_{34}H_{18}N_4$: C, 84.63 ; H, 3.76. Found : C, 84.41 ; H,3.90.

11. Diels-Alder adduct of 20 with dimethyl acetylene-dicarboxylate (70).

A soln of **20** (531 mg, 1.5 mmole) and DMAD (147 mg, 1.5 mmole) in benzene (20 mL) was heated at reflux for 5 h. The resulting ppt was filtered, washed with hexane to give **70** (707 mg, 95 %), m.p. 304-306° ; ^{1}H-NMR : δ 3.73(s,6H), 5.31(s,2H), 5.35(s,2H), 6.89-6.98(m,6H), 7.27-7.35(m,6H), 7.42(s,2H) ; mass spectrum, m/e (rel. intensity) 496(M^+,11), 481(5), 437(13), 398(17), 370(21), 354(94), 341(22), 243(32), 213(39), 178(51), 165(43), 149(67), 121(59),

105(94), 91(87), 85(82), 44(100) ; Anal : Calcd. for $C_{34}H_{24}O_4$: C, 82.24; H, 4.87. Found : C, 82.07; H, 4.95.

12. Diels-Alder adduct of 20 with maleic anhydride (71).

A soln of **20** (708 mg, 2 mmole) and MA (196 mg, 2 mmole) in xylene (20 mL) was heated at reflux for 5 h. The resulting white ppt was filtered, washed with hexane to give **71** (868 mg, 96 %) as colorless crystals, m.p. 320-322° ; ^{1}H-NMR : δ 3.38(s,2H), 4.71(s,2H), 5.40(s,2H), 6.92(dd,2H), 7.02(dd,2H), 7.13(dd,2H), 7.25(dd,2H), 7.32(dd,2H), 7.39 (s,2H), 7.41(dd,2H) ; mass spectrum (EI), m/e (rel. intensity) 453(M+1,2), 384(2), 355(7), 251(4), 99(100), 85(65) ; Anal : Calcd. for $C_{32}H_{20}O_3$: C, 84.94; H, 4.45. Found : C, 84.70; H, 4.59.

13. Improved synthesis of 5,14[1',2']:7,12[1",2"]dibenzeno-5,7,12,14-tetrahydropentacene (24).

A mixture of **20** (354 mg, 1 mmole), benzenediazonium-2-carboxylate hydrochloride (185 mg, 1 mmole) and propylene oxide (2 mL) in 10 mL of 1,2-dichloroethane was heated at reflux for 3 h. Diethyl carbitol (5 mL) was added and the solvents distilled until the head temperature reached 150° . Maleic anhydride (110 mg) was added and the mixture refluxed for 15 minutes. To the cooled mixture was added a soln of 0.4 g of KOH in 6 mL of MeOH-H_2O (2:1). The mixture was chilled in ice, and the resulting solid was filtered, washed with MeOH-H_2O (4:1) and dried. Recrystallization from CCl_4 gave **24** (280 mg, 65 %) as colorless needles, m.p. ca 465°

(dec.) (lit.[14a] 483°) ; ^{1}H-NMR[34] : δ 5.30(s,4H), 6.92(dd,8H), 7.28(dd,8H), 7.43(s,2H).

14. 5,16[1',2']:7,14[1",2"]Dibenzeno-5,7,14,16-tetrahydrohexacene (76).

A soln of **20** (708 mg, 2 mmole) and 1,4-dihydronaphthalene 1,4-epoxide[33] (317 mg, 2.2 mmole) in xylene (60 mL) was heated at reflux for 72 h. The solvent volume was reduced (rotavap) and the soln was triturated with hexane. The resulting ppt was collected to give **72** (906 mg, 91 %) as a tan solid, m.p. ca 367° (dec.) ; ^{1}H-NMR : δ 1.97(s,2H), 4.22(s,2H), 4.80 (s,2H), 5.30(s,2H), 6.88(dd,2H), 6.92(dd,2H), 6.97(dd,2H), 7.06(dd,4H), 7.18(dd,2H), 7.24(dd,2H), 7.25(s,2H), 7.33 (dd,2H) ; ^{13}C-NMR : δ 47.25, 48.85, 53.97, 81.13, 118.63, 119.62, 123.41, 123.53, 125.01, 125.89, 126.16, 141.17, 141.54, 142.94, 145.29, 145.58, 146.71 (two peaks were missing) ; mass spectrum, m/e (rel. intensity) 498(M^+,43), 480(10), 472(42), 457(100), 380(31), 367(76), 354(29), 353(33), 352(29), 265(6), 252(7), 239(9), 178(10), 131(19), 118(13).

To a soln of **72** (747 mg, 1.5 mmole) in acetic anhydride (30 mL) was added slowly 4 mL of conc. HCl, and the mixture was heated at reflux for 10 h. The cooled soln was poured into ice-water, and extracted with methylene chloride. The extract was washed with 10 % Na_2CO_3, water, dried and concentrated. The residue was column chromatographed using CH_2Cl_2-hexane (1:4) as eluent to give **76** (382 mg, 53 %) as colorless crystals, m.p.>335° (dec.) ; ^{1}H-NMR : δ 5.31(s,2H),

5.41(s,2H), 6.83-6.95(m,6H), 7.25-7.34(m,8H), 7.48(s,2H), 7.63(dd,2H), 7.68(s,2H) ; ^{13}C-NMR : δ 53.59, 53.96, 119.80, 121.44, 123.38, 123.51, 124.06, 125.03, 125.41, 125.55, 125.85, 127.35, 131.66, 141.73, 142.07, 142.89, 144.65, 145.24, 145.33 ; mass spectrum, m/e (rel. intensity) 480 (M^+,8), 472(8), 457(16), 396(6), 384(14), 178(100), 144(56), 115(26), 84(27), 43(58) ; UV (cyclohexane) λ_{max} 324 nm (ϵ 30,452), 310(30,408), 289(31,876), 279(32,103), 272 (32,057), 251(33,348), 227(55,284) ; Anal : Calcd. for $C_{38}H_{24}$: C, 94.97; H, 5.03. Found : C, 95.13; H, 4.95.

15. 5,16[1',2']:7,14[1",2"]Dibenzeno-10,11-dibromo-5,7,14,16-tetrahydrohexacene (78).

A soln of **20** (1.062 g, 3 mmole) and **38** (997 mg, 3.3 mmole) in xylene (160 mL) was heated at reflux for 72 h. The soln was cooled, and the resulting ppt collected and saved. The filtrate was concentrated (rotavap), then triturated with acetone (15 mL). The solid was filtered, washed with a small amount of acetone and combined with the above ppt. Recrystallization from xylene gave **77** (1.75 g, 89 %) as a colorless solid, m.p. ca 410° (dec.) ; ^{1}H-NMR : δ 1.57(s,2H), 4.08(s,2H), 4.54(s,2H), 5.36(s,2H), 6.91 (dd,2H), 6.99(dd,2H), 7.05(dd,2H), 7.14(dd,2H), 7.27(s,2H), 7.28(s,2H),7.30(dd,2H), 7.41(dd,2H) ; ^{13}C-NMR : δ 46.80, 48.25, 54.05, 80.47, 119.47, 121.83, 123.43, 123.51, 123.58, 124.16, 125.11, 125.23, 126.01, 140.78, 141.07, 143.16, 145.15, 145.68, 147.69.

A mixture of **77** (1.312 g, 2 mmole), acetic acid (300 mL)

and conc. H_2SO_4 (8 mL) was heated at reflux overnight. The cooled soln was poured into ice-water and extracted with methylene chloride. The extract was washed with 20% Na_2CO_3, water, dried, and concentrated. Flash column chromatography using CH_2Cl_2-hexane (1:3) as eluent gave **78** (778 mg, 61 %) as a colorless solid, m.p. >430°(dec.); ^{1}H-NMR: δ 5.34(s,2H), 5.40(s,2H), 6.86-6.99(m,6H), 7.25-7.35(m,6H), 7.49(s,2H), 7.50(s,2H), 7.88(s,2H) ; ^{13}C-NMR : δ 53.39, 53.90, 119.94, 120.28, 121.30, 121.54, 123.43, 123.65, 125.11, 125.67, 131.37, 131.56, 141.12, 143.13, 143.59, 144.08, 145.17 (two peaks were missing) ; mass spectrum,[65] m/e (rel. intensity) 640(47), 638(100), 636(35) ;UV (cyclohexane) λ_{max} 337 nm (ϵ 20,274), 323 (20,175), 293(21,412), 282(21,371), 273 (21,091), 249(28,068), 228(25,580), 221(25,288) ; Anal : Calcd. for $C_{38}H_{22}Br_2$: C, 71.49; H,3.47. Found : C, 71.32; H, 3.40.

16. 5,18[1',2']:7,16[1",2"]Dibenzeno-5,7,16,18-tetrahydroheptacene (81).

A soln of **20** (708 mg, 2 mmole) and **50** (407.4 mg, 2.1 mmole) was heated at reflux for 4 days. Evaporation of the solvent (rotavap) gave a tan solid which was recrystallized from $CHCl_3$-petroleum ether (30-60°) to yield a mixture of **79** and **80** (997 mg, 91 %) as light yellow crystals, m.p. 304-306° (dec.) ; ^{1}H-NMR : (major product) δ 2.12(s,2H), 4.28 (s,2H), 4.93(s,2H), 5.31(s,2H), 7.25(s,2H),7.43(s,2H) ; (minor product) 2.29(s,2H), 4.36(s,2H), 4.99(s,2H), 5.35 (s,2H), 7.33(s,2H), 7.45(s,2H). The remaining peaks were too

complex to assign to individual isomers. They appeared as follows, with areas assigned for the sum of both products : δ 6.84-6.96(m,8H), 7.08(dd,2H), 7.13(dd,2H), 7.21(dd,2H), 7.24(dd,2H), 7.30(dd,2H), 7.37(m,8H), 7.69(m,6H).

To a suspension of **79** and **80** (548 mg, 1 mmole) in 20 mL ethanol was added 2 mL of 72 % perchloric acid and the mixture was heated at reflux for 5 h. The cooled soln was poured into 100 mL ice-water, extracted with CH_2Cl_2, dried, and concentrated. Column chromatography of the crude product over silica gel using benzene-hexane (1:2) as eluent gave **81** (217 mg, 41 %)as a colorless solid which was recrystallized from 1,2-dichloroethane, m.p. >430° (dec.) ; ^{1}H-NMR : δ 5.33 (s,2H), 5.44(s,2H), 6.86(dd,2H), 6.91(dd,2H), 6.98(dd,2H), 7.27-7.38(m,8H), 7.51(s,2H), 7.80(s,2H), 7.89(dd,2H), 8.18 (s,2H) ; ^{13}C-NMR : δ 53.49, 54.03, 121.08, 122.85, 123.41, 123.48, 125.03, 125.62, 128.99, 129.16, 132.53, 138.67, 140.75, 141.43, 141.89, 145.39, 146.02 ; mass spectrum,[35] m/e (rel. intensity) 530(M^+,100), 354(12), 353(12), 352(36), 278(8), 62(69), 59(25), 27(76) ; UV (cyclohexane) λ_{max} 374 nm (ε 3590), 355(5310), 337(4770), 320(3125), 295(20,080),286 (21,450), 278(23,520) ; Anal Calcd. for $C_{42}H_{26}$: C, 95.06; H, 4.94. Found : C, 94.77; H,5.22.

17. 7,12[1',2']Benzeno-15,16-dimethylene-5,14-ethano-5,7,12,14-tetrahydropentacene (83).

A mixture of **20** (7.08 g, 20 mmole) and 1,4-dichloro-2-butene (50 mL, cis/trans mixture) was heated in a sealed tube at 190-195 °C for 3 days. The solvent was removed by

distillation to give a black product which was preabsorbed onto silica gel. Column chromatography using CH_2Cl_2-hexane (1:3) as eluent yielded 6.31 g (66 %) cis/trans mixture of **82**, m.p. ca 265° (dec.) ; ^{1}H-NMR : (cis) δ 2.32(dd,2H), 2.92 (dd,2H), 3.25(dd,2H), 4.32(s,2H), 5.35(s,2H) ; (trans) 2.31 (dd,2H), 2.75(dd,2H), 3.36(dd,2H), 4.43(s,2H), 5.36(s,2H). The remaining aromatic peaks were too complex to assign to individual isomers. They appeared as follows : δ 6.89(dd), 7.01(dd), 7.06(dd), 7.24(dd), 7.29(dd), 7.36(s), 7.39(dd) ; mass spectrum, m/e (rel. intensity) 480(5), 478(M^+,5), 379(9), 365(5), 354(62), 334(15), 297(9), 178(39), 121(32), 106(100), 105(90).

To a soln of **82** (5.74 g, 12 mmole) in DMSO (80 mL) and THF (20 mL) was added t-BuOK (4.03 g, 36 mmole) and the soln was stirred at room temperature overnight. The mixture was poured into ice-water and extracted with ether. The organic layer was washed with brine, dried and the solvent removed (rotavap). Column chromatography using CH_2Cl_2-hexane (1:4) as eluent gave **83** (4.29 g, 88 %) as light yellow crystals, m.p. ca 266° (dec.) ; ^{1}H-NMR : δ 4.75(s,2H), 5.05(s,2H), 5.20(s,2H), 5.34(s,2H), 6.89(dd,2H), 6.96(dd,2H), 7.03 (dd,2H), 7.22(dd,2H), 7.28(dd,2H), 7.32(dd,2H), 7.36(s,2H) ; ^{13}C-NMR : δ 40.83, 54.99, 105.02, 119.30, 123.07, 123.33, 123.44, 125.00, 125.07, 126.18, 138.64, 141.79, 143.54, 143.82, 145.28, 145.33 ; mass spectrum, m/e (rel. intensity) 406(M^+,76), 391(9), 354(80), 228(34), 203(26), 195(35), 178(100), 163(17), 151(15), 91(53), 43(39).

18. 5,18[1',2']:7,16[1'',2'']Dibenzeno-11,12-dibromo-5,7,16,18-tetrahydroheptacene (86).

A soln of **83** (1.218 g, 3 mmole) and **38** (0.997 g, 3.3 mmole) in xylene (60 mL) was heated at reflux for 60 h. The cooled soln was concentrated and triturated with hexane. The resulting ppt was filtered and washed with hexane to give **84** (1.72 g, 81%) as a tan solid, m.p. 327-328° (dec.) ; ^{1}H-NMR: δ 1.78(dd,2H), 2.13(dd,2H), 2.72(dd,2H), 4.67(s,2H), 4.83(s,2H), 5.28(s,2H), 6.79(dd,2H), 6.89(dd,2H), 6.96 (dd,2H), 7.10(dd,2H), 7.28(s,2H), 7.34(dd,4H), 7.37(s,2H) ; mass spectrum, m/e (rel. intensity) 710(M+4,1), 708(M+2,2), 706(M^+,1), 432(2), 354(1), 276(1), 252(2), 178(3), 105(4), 91(8), 44(100).

To a soln of **84**(1.416 g, 2 mmole) in ethanol (300 mL) was added slowly 15 mL of 72 % perchloric acid and the mixture was heated at reflux for 16 h. The cooled mixture was poured into ice-water, extracted with methylene chloride and dried. Evaporation of the solvent and column chromatography of the crude product using CH_2Cl_2-hexane (1:3) as eluent gave **85** (787 mg, 57 %), m.p. >360° (dec.) ; ^{1}H-NMR : δ 2.25 (dd,1H), 2.68(dd,1H), 2.87(dd,1H), 4.23(s,1H), 4.77(s,1H), 5.34(s,2H), 6.43(s,1H), 6.92(m,4H), 7.08(dd,2H), 7.14(s,1H), 7.19(s,1H), 7.25(m,4H), 7.32(dd,2H), 7.35(s,1H),7.36(s,1H), 7.86(s,1H), 7.89(s,1H).

A soln of **85** (690 mg, 1 mmole) in mesitylene (20 mL) containing 100 mg of 10 % Pd/C under argon was heated at reflux for 4 days. The hot soln was filtered and the solvent removed under reduced pressure to give **86** (647 mg,

94 %), m.p. >415° (dec.) ; ^{1}H-NMR : δ 5.32(s,2H), 5.42(s,2H), 6.85(dd,2H), 6.91(dd,2H), 6.98(dd,2H), 7.25(dd,2H), 7.29 (dd,2H), 7.35(dd,2H), 7.49(s,2H), 7.77(s,2H), 8.06(s,2H), 8.20(s,2H) ; ^{13}C-NMR : δ 53.47, 54.03, 119.92, 120.93, 121.06, 123.43, 123.70, 123.99, 124.77, 125.11, 125.81, 130.86, 132.09, 141.00, 145.34, 147.50 (five peaks were missing due to its low solubility) ; mass spectrum,[65] m/e (rel. intensity) 690(65), 688(100), 686(40) ; Anal : Calcd. for $C_{42}H_{24}Br_2$: C, 73.27; H, 3.51. Found : C, 73.02, H, 3.69.

19. Dimethyl 5,14[1',2']:7,12[1",2"]dibenzeno-5,7,12,14-tetrahydropentacene-2,3-dicarboxylate (88).

A soln of **83** (812 mg, 2 mmole) and dimethyl acetylene-dicarboxylate (2 mL) in xylene (20 mL) was heated at reflux for 56 h. Solvent removal (rotavap) gave a yellow oil which was column chromatographed using EtOAc-hexane (1:3) as eluent to yield **88** (950 mg,87 %) as colorless crystals, m.p. 240-242° ; ^{1}H-NMR : δ 3.80(s,6H), 5.29(s,2H), 5.33(s,2H), 6.87-6.92(m,6H), 7.22-7.33(m,6H), 7.40(s,2H), 7.58(s,2H) ; ^{13}C-NMR : 52.38, 53.53, 53.88, 119.93, 123.41, 123.63, 123.71, 125.07, 125.42, 129.04, 141.11, 143.03, 143.99, 145.18, 148.77, 167.86 (three peaks were missing) ; mass spectrum, m/e (rel. intensity) 546(M^+,52), 487(3), 428(13), 427(14), 263(24), 258(28), 252(89), 213(44), 206(24), 178 (31), 59(80), 44(100) ; Anal : Calcd. for $C_{38}H_{26}O_4$: C, 83.50; H, 4.79. Found : C, 83.66; H, 4.58.

20. 5,22[1',2']:7,20[1",2"]:11,16[1''',2''']Tribenzeno-5,7,11,16,20,22-hexahydrononacene (90).

A soln of **20** (1.77 g, 5 mmole) and **45** (1.887 g, 5.1 mmole) in xylene (50 mL) was heated at reflux for 5 days. Evaporation of the solvent and recrystallization of the residue from 1,2-dichloroethane-hexane gave adduct **89** (3.19 g, 88 %) as light yellow crystals, m.p. ca 335° (dec.) ; ^{1}H-NMR : δ 1.85(s,2H), 4.06(s,2H), 4.75(s,2H), 5.30(s,2H), 5.47 (s,2H), 6.86-7.07(m,12H), 7.21(s,2H), 7.30(s,2H), 7.32-7.41 (m,8H), 7.67(s,2H).

To a suspension of **89** (2.172 g, 3 mmole) in 70 mL EtOH was added dropwise 6 mL of 72 % perchloric acid, and the soln was heated at reflux for 5 h. The cooled mixture was poured into 200 mL ice-water. The resulting solid was extracted with methylene chloride, dried and evaporated to dryness. The crude product was chromatographed over silica gel with benzene-hexane (1:2) as eluent to give **90** (1.48 g, 70 %) as colorless crystals from toluene, m.p. ca 430° (dec.) ; ^{1}H-NMR : δ 5.31(s,2H), 5.39(s,2H), 5.47(s,2H), 6.83 (dd,2H), 6.90(dd,2H), 6.94(dd,2H), 7.00(m,4H), 7.24(dd,2H), 7.28(dd,2H), 7.33(dd,2H), 7.40(m,4H), 7.47(s,2H), 7.72 (s,2H), 7.78(s,2H), 8.01(s,2H) ; ^{13}C-NMR : δ 53.45, 53.59, 53.95, 119.84, 121.08, 121.25, 123.41, 123.58, 123.75, 125.03, 125.30, 125.64, 128.24, 129.06, 130.39, 140.68, 141.34, 142.96, 144.27, 145.19, 145.34 ; mass spectrum, m/e (rel. intensity) 706(M^{+},100), 528(17), 462(10), 446(5), 354 (48), 286(8), 252(10), 178(10) ; UV (cyclohexane) λ_{max} 371 nm (ε 5650), 352(6895), 335(6265), 319(4840), 286(80,000),

277(62,600), 266(65,910), 260(63,025), 248(36,975), 238 (35,695) ; Anal : Calcd. for $C_{56}H_{34}$: C, 95.15; H, 4.85. Found : C, 94.81; H, 5.19.

21. Diels-Alder adduct of 90 and DMAD (91).

A mixture of **90** (706 mg, 1 mmole) and dimethyl acetylene-dicarboxylate (1 mL) in 1,2-dichloroethane (20 mL) was heated at reflux for 3 days. The cooled soln was concentrated and triturated with hexane. The resulting solid was filtered and recrystallized from $CHCl_3$-hexane to give **91** (704 mg, 83 %) as colorless crystals, m.p. > 360° ; ^{1}H-NMR : δ 3.65(s,6H), 5.14(s,2H), 5.18(s,4H), 5.20(s,2H), 6.78(dd,4H), 6.85(dd,4H), 6.91(dd,2H), 7.15-7.26(m,10H), 7.27(s,4H), 7.28(s,2H) ; ^{13}C-NMR : δ 52.20, 52.21, 53.67, 53.81, 53.82, 119.52, 119.66, 123.26, 123.36, 124.91, 141.12, 142.30, 142.70, 142.84, 145.00, 145.11, 145.36, 145.43, 145.54, 147.19, 147.41, 165.88 (nine peaks were missing) ; the mass spectrum[65] showed M^+ at m/e 849.

22. Syn-5,26[1',2']:7,24[1",2"]:11,20[1"',2"']:13,18[1"",2""]-tetrabenzeno-5,7,11,13,18,20,24,26-octahydroundecacene (98).

A mixture of syn-**40** (1.05 g, 5 mmole), **20** (3.54 g, 10 mmole) and xylene (40 mL) in a sealed tube was heated at 180° for 72 h. The ppt that deposited in the cooled soln was filtered and saved. The filtrate was reduced to half volume (rotavap), and the resulting solid in the cooled soln was filtered and combined with the above ppt to give a mixture

of **96** and **97** (NMR ratio 1:1, 3.21 g, 70 %) as a tan solid, m.p. > 400° (dec.) ; ^{1}H-NMR : (**97**) δ 1.85(s,4H), 4.19(s,4H), 4.71(s,4H), 5.23(s,4H) ; (**96**) δ 1.99(s,4H), 4.23(s,4H), 4.74 (s,4H), 5.28(s,4H); the remaining aryl peaks were too complicated to assign to individual isomers, they appeared as follows : δ 6.76(s), 6.86-6.94(m), 6.95(s), 7.02-7.08(m), 7.16(s), 7.12-7.21(m), 7.23(s), 7.25-7.33(m) ; mass spectrum[35] (retro Diels-Alder reaction), m/e (rel. intensity) 564 (M^{+}-20,4), 538(3), 380(100), 354(64), 210(5).

To a suspension of a mixture of **96** and **97** (2.75 g, 3 mmole) in ethanol (250 mL) was added slowly 15 mL of 72 % perchloric acid and the soln was heated at reflux for 8 h. The cooled soln was poured into ice-water and the resulting ppt filtered, washed with water, dried. The crude product was column chromatographed over silica gel using benzene-hexane (1:2) as eluent to give **98** (1.22 g, 46 %) as colorless crystals, m.p. > 450° ; ^{1}H-NMR : δ 5.290(s,4H), 5.361(s,4H), 6.802-6.835(dd,4H), 6.878-6.951(m,8H), 7.212-7.328(m,12H), 7.449(s,4H), 7.688(s,4H), 7.946(s,2H) ; ^{13}C-NMR : δ 53.502, 54.006, 119.840, 121.053, 123.404, 123.554, 125.040, 125.578, 130.371, 140.675, 142.989, 144.430, 145.225, 145.402 (four peaks were missing); mass spectrum,[35] m/e (rel. intensity) 883(M^{+},12), 882(40), 704(2), 446(10), 384(52), 354(100), 268(4), 252(4), 178(2), 57(15) ; UV (cyclohexane) λ_{max} 372 nm (ε 6634), 353(8230), 335(8230), 320(7588), 296(96,811), 280(59,910), 271(66,075), 264 (112,466), 255(82,616), 249(69,408), 242(65,498) ; Anal. Calcd. for $C_{70}H_{42}$: C, 95.21; H, 4.79. Found : C, 94.97; H,

5.02.

23. Anti-5,26[1',2']:7,24[1",2"]:11,20[1"',2"']: 13,18[1"",2""]tetrabenzeno-5,7,11,13,18,20,24,26-octahydroundecacene (103).

A mixture of anti-**40** (1.05 g, 5 mmole), **20** (3.54 g, 10 mmole) and xylene (40 mL) in a sealed tube was heated at 180° for 72 h. Work up as above gave a mixture of **101** and **102** (NMR ratio 1:1, 3.35 g, 73 %), m.p. ca 425° (dec.) ; ^{1}H-NMR : δ 1.78(s,4H), 4.10(s,4H), 4.62(s,4H), 5.30(s,4H) ; 2.02 (s,4H), 4.23(s,4H), 4.73(s,4H), 5.26(s,4H), the remaining aryl peaks were too complicated to assign to individual isomers; they appeared as follows : δ 6.77(s), 6.82-6.93(m), 6.98-7.01(m), 7.06-7.10(m), 7.18(s), 7.19-7.35(m) ; mass spectrum[35] (retro Diels-Alder reaction), m/e (rel. intensity) 564(M^{+}-**20**,4), 538(17), 380(100), 354(60), 252(3), 210(5).

To a suspension of a mixture of **101** and **102** (2.75 g, 3 mmole) in ethanol (250 mL) was added slowly 15 mL of 72 % perchloric acid and the soln was heated at reflux for 8 h. Work up as for **98** gave **103** (1.14 g, 43 %) as colorless crystals, m.p. > 450° ; ^{1}H-NMR : δ 5.295(s,4H), 5.365(s,4H), 6.802-6.836(dd,4H), 6.879-6.952(m,8H), 7.213-7.331(m,12H), 7.452(s,4H), 7.689(s,4H), 7.947(s,2H) ; ^{13}C-NMR : δ 53.442, 53.959, 119.817, 121.030, 123.502, 123.456, 125.008, 125.047, 125.542, 128.332, 130.321, 141.335, 142.936, 144.367, 145.265, 145.402 (two peaks were missing) ; mass spectrum[35], m/e (rel. intensity) 883(M^{+},58), 882(72),704(3),

446(85), 354(100), 268(25), 252(17) ; UV(cyclohexane) λ_{max} 372(ε 4467), 353(5730), 335(5730), 320(5307), 296(71,372), 280(44,386), 271(50,880), 264(86,828), 261(73,747), 258 (61,317), 254(64,469), 250(53,947), 243(50,730); Anal. : Calcd. for $C_{70}H_{42}$: C, 95.21; H, 4.79. Found : C, 94.87 ; H, 5.13.

24. 5,16[1',2']Benzeno-5,16-dihydrohexacene (108).

A soln of 1,4-dihydroanthracene-1,4-epoxide[33] (854 mg, 4.4 mmole) and **52** (920 mg, 4 mmole) in xylene (60 mL) was heated at reflux for 72 h. The solvent was removed (rotavap), and the residue was recrystallized from MeOH to give **105** (1.51 g, 89 %), m.p. ca 245°(dec.) ; ^{1}H-NMR : δ 1.98(dd,2H), 2.27(dd,2H), 2.86(dd,2H), 4.80(s,2H), 5.05 (s,2H), 6.84(dd,2H), 6.91(dd,2H), 7.18(dd,2H), 7.23(dd,2H), 7.40(dd,2H), 7.52(s,2H), 7.73(dd,2H) ; ^{13}C-NMR : δ 30.37, 42.63, 55.79, 84.98, 116.86, 122.42, 122.52, 124.12, 124.26, 125.59, 128.07, 132.75, 142.84, 143.55, 146.41, 146.92 ; mass spectrum, m/e (rel. intensity) 424(M^+,1), 406(2), 350(4), 253(3), 228(5), 215(7), 202(6), 178(25), 168(100), 152(4), 139(10).

To a soln of **105** (1.27 g, 3 mmole) in acetic anhydride (100 mL) was added slowly 12 mL of conc. HCl, and the mixture was heated at reflux for 10 h. The cooled soln was poured into ice-water and extracted with methylene chloride. The extract was washed with 10 % sodium carbonate, water, and dried. Solvent removal followed by column chromatography using CH_2Cl_2-hexane (1:3) as the eluent gave a mixture of

106 and 107 (511 mg, 42 %), m.p. > 250° (dec.) ; ^{1}H-NMR : (**107**) δ 2.35(dd,1H), 2.79(1H), 3.07(dd,1H), 4.38(s,1H), 4.92 (s,1H), 6.64(s,1H), 7.06(dd,2H), 7.12(dd,2H), 7.37(dd,4H), 7.46(dd,2H), 7.50(s,1H), 7.55(s,1H), 7.90(dd,2H), 8.18 (s,1H), 8.21(s,1H) ; (**106**) δ 3.90(s,4H), 4.95(s,2H), 6.97 (dd,4H), 7.37(dd,4H), 7.46(dd,2H), 7.76(s,2H), 7.92(dd,2H), 8.27(s,2H) ; mass spectrum (mixture), m/e (rel. intensity) 406(M^+,2), 354(4), 228(9), 212(28), 191(12), 178(46), 119 (20), 94(99), 56(63), 41(100).

A soln of **106 and 107** (406 mg, 1 mmole) in mesitylene (30 mL) containing 50 mg of 10 % Pd/C was heated at reflux for 48 h. The hot soln was filtered and the catalyst was washed with 20 mL toluene. The combined filtrate was concentrated under reduced pressure to give **108** (372 mg, 92 %) as orange crystals, m.p. 362-364° (dec.) ; ^{1}H-NMR : δ 5.53(s,2H), 7.07 (dd,4H), 7.35(dd,2H), 7.46(dd,4H), 7.86(s,2H), 7.95(dd,2H), 8.46(s,2H), 8.56(s,2H) ; ^{13}C-NMR : δ 53.52, 121.18, 123.81, 124.98, 125.58, 125.86, 126.04, 128.20, 130.58, 131.27, 140.60, 143.88 (one peak was missing) ; mass spectrum, m/e (rel. intensity) 404(M^+,11), 403(5), 402(4), 202(2), 201(6), 69(2), 55(2), 44(5), 33(100) ; UV (cyclohexane) λ_{max} 469 nm (ϵ 16,363), 440(16,283), 415(15,129), 404(14,992), 392 (14,685), 382(14,517), 370(14,425), 302(81,787), 291 (72,602), 281(69,551) ; Anal : Calcd. for $C_{32}H_{20}$: C, 94.86; H, 5.32. Found : C, 94.62; H, 5.48.

25. Bis-cycloadducts of 40 and 114 (116).

(a) Syn-adduct A mixture of benzocyclobutene[37] (5.20 g,

50 mmole), **40s**[14b] (5.25 g, 25 mmole) and toluene (60 mL) in a sealed tube was heated at 185-195° for 24 h. The ppt that deposited in the cooled soln was filtered and saved. The filtrate was concentrated (rotavap) and triturated with hexane. The resulting solid was then filtered, washed with hexane and combined with the above ppt to give **116s** (8.78 g, 84 %), m.p. 238-240° ; ^{1}H-NMR : δ 1.97(dd,4H), 2.70(dd,4H), 2.98(dd,4H), 5.06(s,2H), 7.09(bs,8H), 7.18(s,2H) ; ^{13}C-NMR : δ 33.11, 42.82, 84.57, 110.46, 126.15, 126.83, 138.96, 144.66 ; mass spectrum, m/e (rel. intensity) 288(10), 270(1), 158(100), 130(7), 129(11), 128(9), 115(8), 102(4), 40(51) ; Anal : Calcd. for $C_{30}H_{26}O_2$: C, 86.09; H, 6.26. Found : C, 85.96; H, 6.30.

(b) Anti-adduct A mixture of benzocyclobutene (4.16 g, 40 mmole), **40a** (4.20 g, 20 mmole) and toluene (50 mL) in a sealed tube was heated at 185-195° for 24 h. Work up as above gave **116a** (7.27 g, 87 %), m.p. ca 272° (dec.) ; ^{1}H-NMR : δ 1.94(dd,4H), 2.69(dd,4H), 3.01(dd,4H), 5.08(s,4H),7.12 (bs,8H), 7.15(s,2H) ; ^{13}C-NMR : δ 33.10, 42.77, 84.53, 110.70, 126.20, 126.87, 138.87, 144.66 ; mass spectrum, m/e (rel. intensity) 288(15), 270(1), 158(100), 130(7), 129(11), 128(9), 115(7), 102(6).

26. Dehydration of 116s.

(a) $HClO_4$-EtOH To a suspension of **116s** (1.254 g, 3 mmole) in ethanol (200 mL) was added slowly 15 mL of 72 % perchloric acid. The resulting soln was heated at reflux for 20 h. The cooled soln was poured into ice-water and the

ppt was filtered, washed with water and dried. The crude product was recrystallized from benzene to give a mixture of **117** and **112** (NMR ratio 4:1, 690 mg) ; ^{1}H-NMR of **117** : δ 2.11 (dd,2H), 2.75(dd,2H), 3.04(dd,2H), 4.06(s,4H), 5.24(s,2H), 7.13(bs,4H), 7.20(dd,2H), 7.32(dd,2H), 7.57(s,2H), 7.71(s,2H).

To a suspension of **116s** (1.672 g, 4 mmole) in ethanol (300 mL) was added slowly 20 mL of 72 % perchloric acid. The soln was heated at reflux for 60 h, and worked up as above. Recrystallization of the crude product from 1,2-dichloroethane gave a mixture of **112** and **113** (NMR ratio 1:2, 932 mg, 61 %). ^{1}H-NMR of **112** : δ 4.12(s,8H), 7.20(dd,4H), 7.33(dd,4H), 7.89(s,4H), 8.29(s,2H) ; ^{1}H-NMR of **113** : δ 4.06 (s,4H), 4.21(s,4H), 7.15-7.42(m,6H), 7.69(s,2H), 7.71(s,2H), 7.77(s,2H), 7.78(dd,2H) ; mass spectrum (mixture of **112** and **113**), m/e (rel. intensity) 382(M^+,1), 280(6), 165(4), 149(5), 139(6), 108(8), 99(100), 55(46).

(b) HCl-Ac_2O To a suspension of **116s** (1.254 g, 3 mmole) in acetic anhydride (70 mL) was added slowly 14 mL of conc. hydrochloric acid through the condenser. The mixture was heated at reflux for 12 h. The cooled soln was poured into cold 10 % sodium carbonate (400 mL) and the ppt filtered, washed with water, ethanol and dried. Recrystallization of the crude product from benzene gave a mixture of **112** and **113** (619 mg, 54 %). The ^{1}H NMR spectrum was similar to that shown above.

(c) $HClO_4$-MeOH-toluene To a suspension of **116s** (2.09 g, 5 mmole) in methanol (30 mL) and toluene (120 mL) was added

slowly 15 mL of 72 % perchloric acid. The soln was then heated at reflux for 16 h. The resulting ppt in the cooled soln was filtered, washed with water, methanol and dried. Recrystallization from 1,2-dichloroethane gave a mixture of **112** and **113** (1.34 g, 70 %).

27. Attemped cycloaddition of 50 with 112.

A soln of **50** (485 mg, 2.5 mmole) and a mixture of **112** and **113** (obtained from dehydration of **116**, 955 mg, 2.5 mmole) in xylene (120 mL) was heated at reflux for 3 days. The solvent was evaporated (rotavap). Column chromatography of the residue over silica gel using CH_2Cl_2-hexane (1:3) as eluent gave **113** (760 mg) and **50** (370 mg). ^{1}H NMR of **113** was identical to that shown above.

28. Bis-cycloadducts of 40a and 119 (120).

A soln of 1,2-bis-methylenecyclohexane **119**[39] (1.08 g, 10 mmole) and **40a**[14b] (1.05 g, 5 mmole) in dioxane (80 mL) was heated at reflux for 14 h. The solid that deposited in the cooled soln was filtered, washed with a small amount of dioxane and dried to give **120** (682 mg, 32 %) as colorless crystals, m.p. > 278° (dec.) ; ^{1}H-NMR : δ 1.57(m,8H), 1.82 (m,4H), 1.93(m,8H), 2.12(m,8H), 4.90(s,4H), 7.04(s,2H) ; ^{13}C-NMR : δ 23.28, 29.94, 33.17, 42.35, 84.76, 110.31, 129.96, 144.66 ; mass spectrum, m/e (rel intensity) 292(21), 274(4), 158(100), 91(13) ; Anal : Calcd. for $C_{30}H_{34}O_2$: C, 84.47; H, 8.03. Found : C, 83.98; H, 7.87.

29. Tetracene (15).

A mixture of benzocyclobutene (1.04 g, 10 mmole), 1,4-dihydronaphthalene-1,4-epoxide[33] (1.44 g, 10 mmole) and toluene (45 mL) in a sealed tube was heated at 190° for 24 h. Work up as for **116s** gave **122** (2.13 g, 86 %) as colorless crystals, m.p. 161-163° ; ^{1}H-NMR: δ 2.02(dd,2H), 2.74(dd,2H), 3.04(dd,2H), 5.13(s,2H), 7.12(bs,4H), 7.14(dd,2H), 7.24 (dd,2H) ; ^{13}C-NMR : δ 33.07, 42.84, 84.57, 118.90, 126.17, 126.55, 126.84, 138.93, 145.62 ; mass spectrum, m/e (rel. intensity) 248(M^+,1), 128(6), 118(100), 90(5).

To a soln of **122** (1.86 g, 7.5 mmole) in acetic anhydride (40 mL) was added slowly 8 mL of conc. hydrochloric acid through the condenser. The soln was heated at reflux for 8 h. The cooled soln was poured into ice-water, and the ppt was filtered, washed with water, methanol and dried. The crude product was recrystallized from toluene to give **125** (1.54 g, 89 %), m.p. 207-208 (lit.[46] 209-210) ; ^{1}H-NMR : 4.09 (s,4H), 7.21(dd,2H), 7.34(dd,2H), 7.41(dd,2H), 7.76(s,2H), 7.78(dd,2H) ; mass spectrum, m/e (rel. intensity) 230 (M^+,100), 229(97), 228(74), 226(18), 215(10), 202(5), 114 (54), 107(16), 101(22), 88(7).

A soln of **125** (1.15 g, 5 mmole) in xylene (30 mL) containing 150 mg 10 % Pd/C under argon atmosphere was heated at reflux for 2 days. The hot soln was filtered to remove the catalyst. Solvent removal (rotavap) gave tetracene **15** (1.08 g, 95 %) as orange crystals, m.p. 339-341° (lit.[47] 340-341°) ; ^{1}H-NMR : δ 7.40(dd,4H), 8.00 (dd,4H), 8.67(s,4H).

30. 2,3-Dibromotetracene (127).

A mixture of benzocyclobutene (1.04 g, 10 mmole), **38** (3.02 g, 10 mmole) and toluene (60 mL) in a sealed tube was heated at 190° for 24 h. Work up as for **116s** yielded **123** (3.61 g, 89 %) as colorless crystals, m.p. 179-181° (CH_2Cl_2-hexane) ; ^{1}H-NMR : δ 1.99(dd,2H), 2.70(dd,2H), 2.98(dd,2H), 5.07(s,2H), 7.13(bs,4H), 7.49(s,2H) ; ^{13}C-NMR : δ 32.75, 42.47, 83.96, 122.32, 124.38, 126.35, 126.90, 138.35, 146.65 ; mass spectrum, m/e (rel. intensity) 278(62), 276(100), 274(55), 248(1), 195(5), 169(10), 167(8), 128(18), 115(13).

To a soln of **123** (2.84 g, 7 mmole) in acetic anhydride (70 mL) was added slowly 15 mL of conc. hydrochloric acid through condenser. The soln was then heated at reflux for 8 hour. Work up as for **125** gave **126** (2.44 g, 90 %) as light yellow crystals, m.p. 224-226° (toluene) ; ^{1}H-NMR : δ 4.06 (s,4H), 7.22(dd,2H), 7.34(dd,2H), 7.63(s,2H), 8.07(s,2H) ; ^{13}C-NMR : δ 36.78, 124.11, 126.49, 127.27, 131.54, 132.07, 136.44, 137.46, 137.77 ; mass spectrum, m/e (rel. intensity) 390(M+4,65), 388(M+2,100), 386(M^+,55), 309(39), 307(42), 228(87), 226(74), 114(38), 113(34).

A soln of **126** (1.16 g, 3 mmole) in xylene (50 mL) containing 150 mg 10 % Pd/C under argon was heated at reflux for 2 days. The hot soln was filtered to remove the catalyst. Solvent removal (rotavap) gave 2,3-dibromotetracene **127** (1.10 g, 96 %) as orange crystals, m.p. 336-338°. It was too insoluble to obtain an NMR spectrum. Mass spectrum, m/e (rel. intensity) 388(M+4,4), 386(M+2), 384

(M^+,4), 308(4), 306(4), 228(9), 226(13), 113(10), 33(100). Anal : Calcd. for $C_{18}H_{10}Br_2$: C, 55.60; H, 2.61. Found : C, 55.26; H, 2.78.

31. Pentacene (10).

A mixture of benzocyclobutene (2.08 g, 20 mmole), **50** (3.88 g, 20 mmole) and toluene (70 mL) in a sealed tube was heated at 190 for 24 h. Work up as for **116s** gave **124** (5.18 g, 87 %), m.p. 235-237 (toluene) ; ^{1}H-NMR : δ 2.12(dd,2H), 2.78 (dd,2H), 3.04(dd,2H), 5.25(s,2H), 7.13(bs,4H), 7.44(dd,2H), 7.62(s,2H), 7.79(dd,2H) ; ^{13}C-NMR : δ 32.89, 43.50, 84.55, 117.13, 125.69, 126.25, 126.90, 128.12, 132.82, 138.69, 143.67 ; mass spectrum, m/e (rel. intensity) 298(M^+,1), 168 (100), 140(5), 129(3), 91(7).

To a soln of **124** (2.98 g, 10 mmole) in methanol (40 mL) and toluene (160 mL) was added slowly 15 mL of conc. HCl. The soln was heated at reflux for 14 h. The resulting solid in the cooled soln was filtered, washed with methanol and dried. Recrystallization of the crude product from 1,2-dichloroethane gave **128** (2.07 g, 74 %) as yellowish crystals, m.p. 305-307° (lit.[48] 300-310°) ; ^{1}H-NMR : δ 4.13 (s,4H), 7.20-7.44(m,6H), 7.92(s,2H), 7.98(dd,2H), 8.36(s,2H) ; mass spectrum, m/e (rel. intensity) 280(M^+,100), 279(73), 278(49), 265(6), 139(9), 133(6), 91(33), 81(14).

A soln of **128** (560 mg, 2 mmole) in xylene (20 mL) containing 80 mg of 10 % Pd/C under argon was heated at reflux for 3 days. The hot soln was carefully filtered to remove the catalyst. The red purple filtrate was quickly

concentrated (rotavap) to give pentacene (512 mg, 92 %) as violet blue crystals. The spectra (IR, UV and mass) were identical to those of a commercial sample.

32. 7,16[1',2']Benzeno-7,16-dihydroheptacene (109).

A soln of **128** (1.40 g, 5 mmole) and **50** (0.97 g, 5 mmole) in xylene (160 mL) was heated at reflux for 5 days. The solid that deposited in the cooled soln was filtered as unreacted **128** (0.21 g). The filtrate was concentrated (rotavap). Column chromatography of the residue using CH_2Cl_2-hexane (1:3) as the eluent gave a mixture of **135** and **136** (1.49 g, 63 %), m.p. 294-296 ; ^{1}H-NMR : (**135**) 2.35 (s,2H), 3.82(s,4H), 4.46(s,2H), 5.06(s,2H), 7.13(dd,2H), 7.18(s,2H), 7.20-7.31(m,6H), 7.39(dd,2H), 7.49(s,2H), 7.72 (dd,2H) ; (**136**) 2.32(s,2H), 3.91(dd,4H, AB type), 4.45 (s,2H), 5.07(s,2H), 6.99(dd,2H), 7.15-7.30(m,8H), 7.39 (dd,2H), 7.50(s,2H), 7.72(dd,2H) ; mass spectrum, m/e (rel. intensity) 474(M^+,9), 456(4), 388(6), 374(4), 305(9), 293(46), 280(16), 278(19), 207(21), 194(26), 181(67), 168 (56), 139(13), 44(100).

To a mixture of **135** and **136** (1.422 g, 3 mmole) in acetic anhydride (60 mL) was added slowly 12 mL of conc. HCl through condenser. The soln was heated at reflux for 12 h. The cooled mixture was poured into ice-water, and extracted with methylene chloride. The extract was washed with 10 % sodium carbonate, water and dried. Solvent removal (rotavap) followed by column chromatography using CH_2Cl_2-hexane (1:4) as the eluent gave **137** (656 mg, 48 %), m.p.

>205° (dec.) ; ^{1}H-NMR: δ 3.84(s,4H), 5.52(s,2H), 7.03(dd,2H), 7.11(dd,2H), 7.21(dd,2H), 7.36-7.43(m,6H), 7.87(s,2H), 7.93 (dd,2H).

A soln of **137** (547 mg, 1.2 mmole) in mesitylene (20 mL) containing 80 mg of 10 % Pd/C was heated at reflux for 60 h. The hot soln was filtered to remove the catalyst. Solvent removal by reduced pressure distillation gave **109** (528 mg, 97 %) as light yellowish crystals, m.p. > 360° (dec.) ; ^{1}H-NMR : δ 5.68(s,2H), 7.11(dd,2H), 7.41(dd,4H), 7.52(dd,2H), 7.93(dd,4H), 7.98(s,4H), 8.28(s,4H) ; ^{13}C-NMR : δ 53.30, 121.66, 123.95, 125.02, 125.72, 126.24, 127.99, 130.69, 131.71, 140.35, 143.35 ; mass spectrum, m/e (rel. intensity) 454(M^{+},59), 453(35), 452(24), 290(4), 274(13), 227(100), 226 (97), 213(34), 197(11), 165(6), 149(6), 105(5) ; UV (cyclohexane) λ_{max} 378 nm (ε 14,298), 358(14,480), 342 (14,361), 325(14,217), 283(31,700), 254(20,762), 212(15,070). Anal : Calcd. for $C_{36}H_{22}$: C, 95.12; H, 4.88. Found : C, 94.87; H, 5.04.

33. Benzyne adduct of 109 (27).

A mixture of **109** (227 mg, 0.5 mmole), benzenediazonium-2-carboxylate hydrochloride (222 mg, 1.2 mmole) and propylene oxide (2 mL) in 20 mL of 1,2-dichloroethane was heated at reflux for 5 h. Work up as for **24** gave **27** (152 mg, 50 %). The ^{1}H NMR spectrum was identical to that of independently synthesized **27** [14b].

34. 6,15[1',2']Benzeno-2,3-dibromo-6,15-dihydrohexacene (143).

A soln of **128** (1.40 g, 5 mmole) and **38** (1.51 g, 5 mmole) in xylene (200 mL) was heated at reflux for 5 days. The solid that deposited in the cooled soln was filtered as 6,13-dihydropentacene (284 mg, rearranged from **128**), m.p. 269-271° (lit.[49] 270-271°) ; ^{1}H-NMR (not previously recorded) : δ 4.25(s,4H), 7.42(dd,4H), 7.79(dd,4H), 7.80(s,4H). The filtrate was concentrated (rotavap). Column chromatography of the residue using CH_2Cl_2-hexane (1:3) as the eluent gave a mixture of **140** and **141** (ratio 8:1, 1.37 g, 47 %), m.p. > 220° (dec.) ; ^{1}H-NMR : (**140**) δ 2.14(s,2H), 3.85(s,4H), 4.35 (s,2H), 4.85(s,2H), 7.15(dd,2H), 7.17(dd,2H), 7.18(s,2H), 7.24(m,4H), 7.38(s,2H) ; (**141**) δ 2.24(s,2H), 3.91(dd,4H, AB type splitting), 4.38(s,2H), 4.91(s,2H), 7.01(dd,2H), 7.14 (dd,2H), 7.21(s,2H), 7.22(m,4H), 7.40(s,2H) ; mass spectrum, m/e (rel. intensity) 584(M+4,6), 582(M+2,24), 580(M^+,15), 564(3), 502(1), 305(29), 293(78), 280(77), 278(100), 276(37), 274(12), 265(9), 195(15), 114(11).

A soln of **140** (1.164 g, 2 mmole) in xylene (150 mL) containing 150 mg of 10 % Pd/C was heated at reflux for 3 days. The hot soln was filtered to remove the catalyst. Solvent removal (rotavap) gave **142** (1.08 g, 93 %), m.p. ca 228° (dec.) ; ^{1}H-NMR : δ 2.35(s,2H), 4.57(s,2H), 5.00 (s,2H), 7.19(dd,2H), 7.34(dd,2H), 7.41(dd,2H), 7.42(s,2H), 7.77 (s,2H), 7.94(dd,2H), 8.27(s,2H) ; ^{13}C-NMR : δ 47.23, 47.62, 81.12, 121.37, 124.07, 124.21, 125.06, 125.69, 126.66, 126.90, 128.00, 130.91, 131.61, 140.34, 140.63, 147.57 ;

spectrum, m/e (rel. intensity) 582(M+4,7), 580(M+2,17), 578 (M^+,12), 562(5), 500(1), 304(32), 302(47), 291(22), 280(44), 278(100), 276(27), 274(12), 195(27), 193(31), 139(19), 126 (28), 114(27).

To a soln of **142** (928 mg, 1.6 mmole) in acetic acid (60 mL) was added slowly 8 mL conc. sulfuric acid. The mixture was heated at reflux for 8 h. The cooled soln was poured into ice-water and extracted with methylene chloride. The extract was washed with 10 % sodium carbonate, water and dried. Evaporation of the solvent followed by column chromatography using CH_2Cl_2-hexane (1:4) as the eluent gave **143** (387 mg, 43 %), m.p. > 230° (dec.) ; ^{1}H-NMR : δ 5.64 (s,2H), 7.11(dd,2H), 7.40(dd,2H), 7.50(dd,2H), 7.67(s,2H), 7.92(dd,2H), 7.94(s,2H), 7.96(s,2H), 8.27(s,2H) ; ^{13}C-NMR : δ 53.27, 120.76, 121.44, 121.76, 124.04, 125.16, 125.76, 126.27, 127.99, 130.52, 131.68, 131.80, 139.86, 142.62, 143.16 ; mass spectrum, m/e (rel. intensity) 564(M+4,9), 562 (M+2,22), 560(M^+,12), 482(4), 480(5), 402(5), 400(8), 201(8), 200(10), 44(100).

35. Benzyne adduct of 143 (78).

A mixture of **143** (168.6 mg, 0.3 mmole), benzenediazonium-2-carboxylate hydrochloride (56 mg, 0.3 mmole) and propylene oxide (2 mL) in 15 mL of 1,2-dichloroethane was heated at reflux for 3 h. Work up as for **24** gave **78** (117 mg, 61 %). The ^{1}H NMR was identical to that of independently synthesized **78**.

36. Photodimer of [3(b,b)^{b}.1.1]triptycene (139).

Triptycene **20** (10 mg) was dissolved in 0.5 mL benzene-d_6, placed in a 5 mm NMR tube and flushed with argon. Irradiation of the sample for 90 minutes using a Hanovia 450 W medium pressure lamp with a Pyrex filter was carried out by taping the sample tube directly to the water-cooled jacket of the lamp.

After irradiation, the sample tube was immediately transfered to the Bruker WM 250 NMR spectrometer, and the spectrum was recorded. ^{1}H-NMR (benzene-d_6) : δ 4.27(s,4H), 5.12(s,4H), 6.17(dd,4H), 6.60(dd,4H), 6.84(s,4H), 6.85 (dd,4H), 6.95(dd,4H), 6.98(dd,4H), 7.21(dd,4H).

A larger scale reaction (**20**, 354 mg) was carried out using a Pyrex test tube instead of the NMR tube, in dry benzene (15 mL). After irradiation for 3 hour as described above, the resulting ppt was filtered, washed with benzene and dried to give **139** (219 mg, 62 %) as a colorless powder, m.p. 281-283°, sparingly soluble in organic solvents. Mass spectrum (thermal reversal to **20**), m/e (rel. intensity) 354 (100), 353(70), 352(57), 276(3), 176(45). Anal : Calcd. for $C_{56}H_{36}$: C, 94.88; H, 5.12. Found : C, 94.69, H, 5.23.

37. Bisadducts of 40 and 153 (1,4:8,11-dicarbonyl-5,14:7,12-diepoxy-1,2,3,4,8,9,10,11-octaphenyl-1,4,4a,5,7,7a,8,11-12,14,14a-didecahydropentacene)(160).

(a) Syn-adduct A mixture of **40s** (1.05 g, 5 mmole) and tetraphenylcyclopentadienone **153** (3.84 g, 10 mmole) in benzene (80 mL) was heated at reflux for 12 h until the

purple color disappeared. The solvent was evaporated (rotavap). The residue was triturated with methanol to give a colorless ppt. The solid was filtered, washed with methanol and dried to yield **160s** (4.40 g, 90 %) as a colorless powder, m.p. > 240° (dec.) ; ^{1}H-NMR : δ 3.16(s,4H), 5.81(s,4H), 6.87-6.99 (m,20H), 7.26-7.47(m,22H).

(b) Anti-adduct In a similar experiment, **40a** (2.10 g, 10 mmole), **153** (7.68 g, 20 mmole) and benzene (180 mL) gave **160a** (8.99 g, 92 %) as a colorless powder, m.p. ca 280° (dec.) ; ^{1}H-NMR : δ 3.06(s,4H), 5.84(s,4H), 6.87-7.04(m,20H), 7.27-7.52(m,20H), 7.58(s,2H) ; IR (nujol) 1775, 1470, 1380 cm^{-1}. Anal : Calcd. for $C_{72}H_{50}O_4$: C, 88.32; H, 5.15. Found : C, 88.31; H, 4.87.

38. Reaction of 160a with dimethyl acetylenedicarboxylate (162).

A mixture of **160a** (1.956 g, 2 mmole), dimethyl acetylene-dicarboxylate (568 mg, 4 mmole) and xylene (60 mL) was heated in a sealed tube at 170° for 13 h. The solvent was evaporated (rotavap). Column chromatography of the residue on flash silica gel using benzene-chloroform (1:1) as the eluent gave tetraphenylbenzene (1.47 g, 96 %). Further elution with EtOAc then gave **162** (681 mg, 77 %) as a mixture of syn and anti adducts, m.p. 276-278° (dec.) from EtOAc ; ^{1}H-NMR : (anti) δ 3.81(s,12H), 5.91(s,4H), 7.53(s,2H) ; (syn) δ 3.81(s,12H), 5.91(s,4H), 7.49(s,2H) ; ^{13}C-NMR : (anti) δ 52.45, 84.85, 115.90, 146.37, 151.55, 162.69 ; mass spectrum, m/e (rel. intensity) 442(M^{+},7), 382(5), 353(10), 335(44), 334(29), 322(71), 300(42), 295(17), 268(14), 240

(100), 228(30), 211(16), 158(20) ; IR (nujol) 1730, 1710, 1460, 1440, 1310, 1280, 1230, 1115, 970, 860 cm^{-1} ; Anal : Calcd. for $C_{22}H_{18}O_{10}$: C, 59.73; H, 4.10. Found : C, 59.70; H, 4.06.

39. Reaction of 160a with tetracyanoethylene (163).

In a similar experiment to **162**, a sealed tube was charged with **160a** (1.956 g, 2 mmole), tetracyanoethylene (512 mg, 4 mmole) and xylene (60 mL). The ppt that deposited in the cooled soln was filtered, washed with benzene and dried to give **163** (803 mg, 97 %) as tan crystals, m.p. > 205° (dec) ; ^{1}H-NMR (DMSO-d_6) : δ 6.93(s,4H), 7.98(s,2H) ; ^{13}C-NMR (DMSO-d_6) : δ 49.38, 87.73, 110.28, 112.28, 119.30, 140.80.

40. Reaction of 160a with naphthaquinone (164).

In a similar experiment to **162**, a sealed tube was charged with **160a** (1.956 g, 2 mmole), naphthaquinone (632 mg, 4 mmole) and xylene (60 mL). Work up as for **162** gave tetraphenylbenzene (1.44 g, 94 %) and **164** (711 mg, 75 %). M.p. of **164** : > 320° (dec.) ; ^{1}H-NMR : δ 3.05(s,4H), 5.84(s,4H), 7.55(s,2H), 7.81(dd,4H), 8.17(dd,4H) ; mass spectrum (rel. intensity), m/e 474(M^{+},2), 316(2), 278(40), 158(100), 130 (14), 125(12) ; IR (nujol) 1680, 1595, 1470, 1380, 1275 cm^{-1} ; Anal : Calcd. for $C_{30}H_{18}O_6$: C, 75.94; H, 3.82. Found : C, 76.07; H, 3.97.

41. Reaction of 160a with 1,4-anthraquinone (165).

In a similar experiment to **162**, a sealed tube was charged

with **160a** (1.956 g, 2 mmole), 1,4-anthraquinone (832 mg, 4 mmole) and xylene (60 mL). The ppt that deposited in the cooled soln was filtered, washed with benzene and dried to give **165** (918 mg, 80 %) as a light yellow solid, m.p. 326-328° (dec.) ; ^{1}H-NMR : δ 3.95(q,4H), 5.92(q,4H), 7.07(s,2H), 7.71(dd,4H), 8.07(dd,4H), 8.55(s,4H) ; mass spectrum (retro Diels-Alder fragment), m/e (rel. intensity) 366(M^+-anthraquinone,1) 208(anthraquinone,32), 158(100), 152(29), 126(32) ; IR (nujol) 1680, 1620, 1580, 1465, 1380, 1270, 1195, 975, 860, 760 cm^{-1}.

42. Reaction of 160a with 1,4-dihydronaphthalene-1,4-epoxide (166).

In a similar experiment to **162**, a sealed tube was charged with **160a** (1.956 g, 2 mmole), 1,4-dihydronaphthalene-1,4-epoxide[33] (576 mg, 4 mmole) and xylene (60 mL). Work up was as described for **162**. Column chromatography using benzene-chloroform (1:1) and then chloroform as eluents gave tetraphenylbenzene (1.39 g, 91 %) and **166** (651 mg, 73 %). M.p. of **166** : 306-308° (dec.) ; ^{1}H-NMR : δ 2.77(q,4H), 4.68(s,4H), 5.32(q,4H); 2.90(q,4H), 4.78(s,4H), 5.44(q,4H), 7.02-7.26(m,10H) ; mass spectrum, m/e (rel. intensity) 446(M^+,1), 428(1), 302(62), 273(17), 184(21), 158(100), 131(31), 118 (61) ; Anal : Calcd. for $C_{30}H_{22}O_4$: C, 80.70; H, 4.97. Found : C, 80.48; H, 5.04.

43. 5,18;9,14-Heptacenediquinone (161).

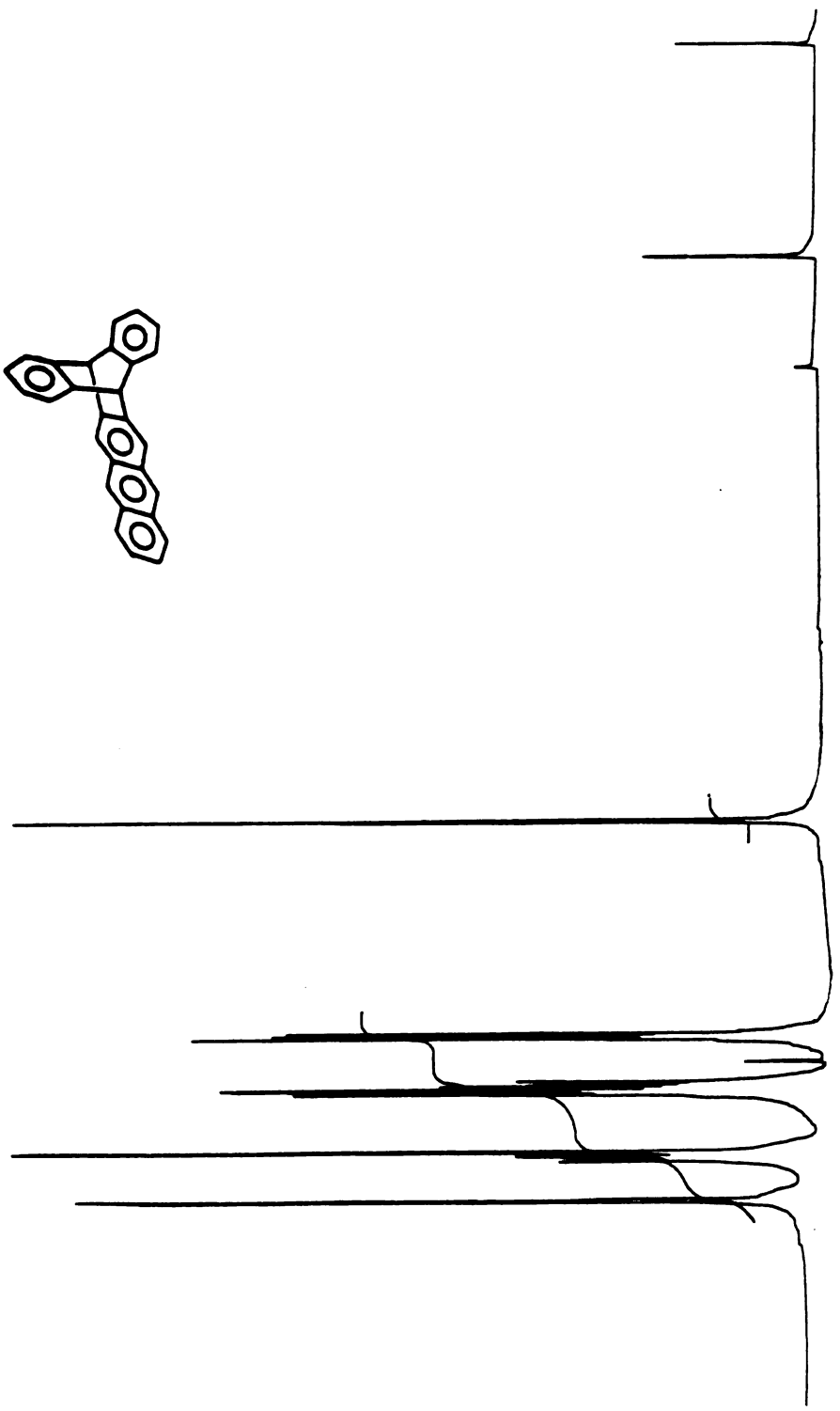
To a suspension of **164** (474 mg, 1 mmole) in acetic acid

(30 mL) was added 4 mL of conc. sulfuric acid and the mixture was heated at reflux for overnight. The cooled soln was poured into ice-water. The resulting ppt was filtered, washed with water, methanol and dried to give **161** (394 mg, 90 %), m.p. > 350° (nitrobenzene) ; owing to the insufficient solubility in all solvents tried, no NMR spectrum was recorded ; the mass spectrum[67] showed M^+ at m/e 438 ; IR (nujol) 1680, 1590, 1285, 890 cm^{-1}. The quinone gave a dark green solution in conc. sulfuric acid. It also gave a brownish-orange vat dye with alkaline sodium dithionite[66].

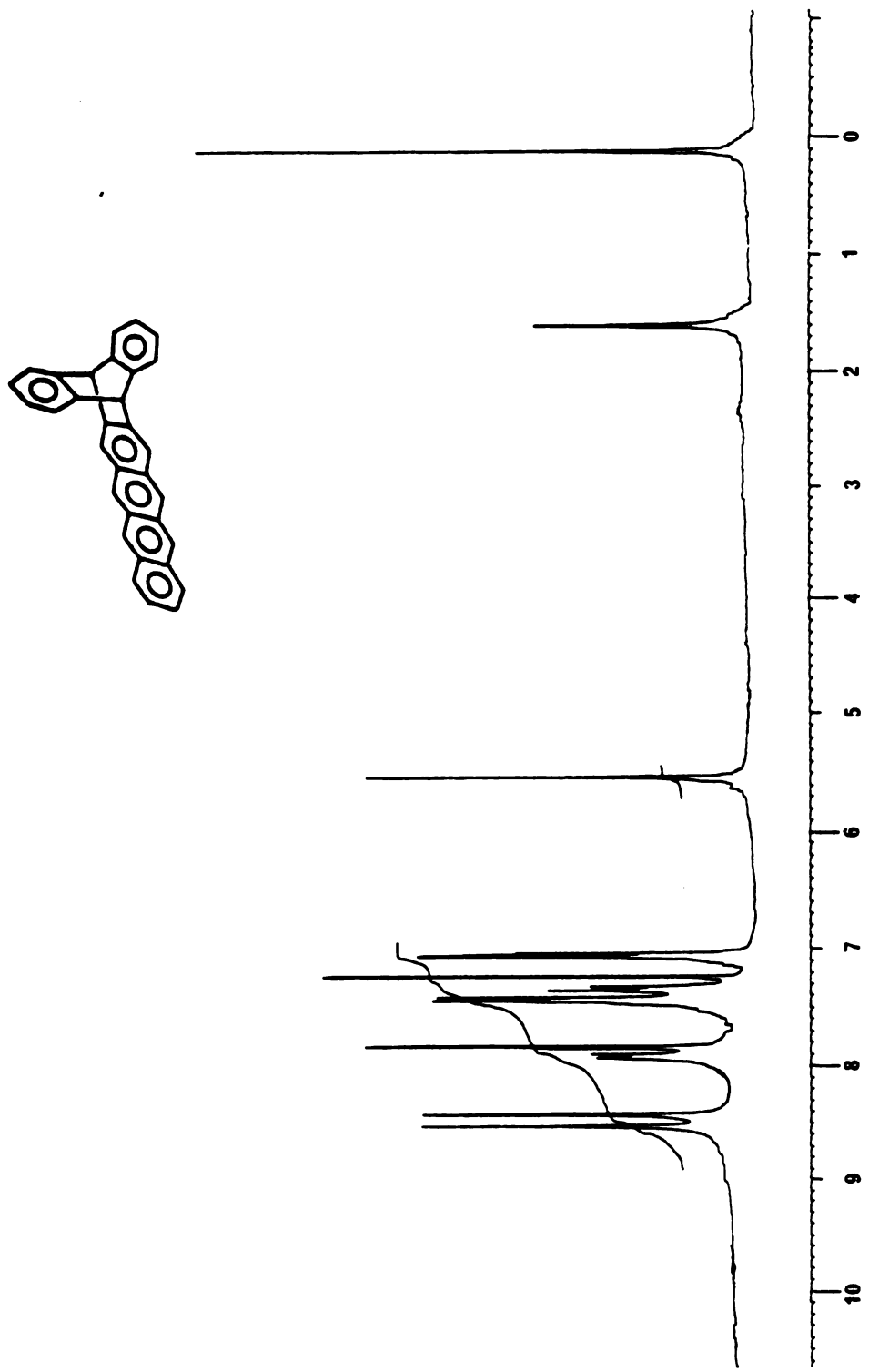
44. 6,21;10,17-Nonacenediquinone (171).

In a similar experiment to **161**, a mixture of **165** (574 mg, 1 mmole), acetic acid (40 mL) and conc. sulfuric acid (5 mL) was heated at reflux overnight. Work up as for 161 gave **171** (495 mg, 92 %) as golden needles from nitrobenzene, m.p. > 360 ; this compound was too insoluble to record an NMR spectrum ; the mass spectrum[67] showed M^+ at m/e 538 ; IR (nujol) 1670, 1610, 1595, 1280, 995 cm^{-1}. In conc. sulfuric acid it showed a dark green solution. Anal : Calcd. for $C_{38}H_{18}O_4$: C, 84.75, H, 3.37. Found : C, 84.58, H, 3.49.

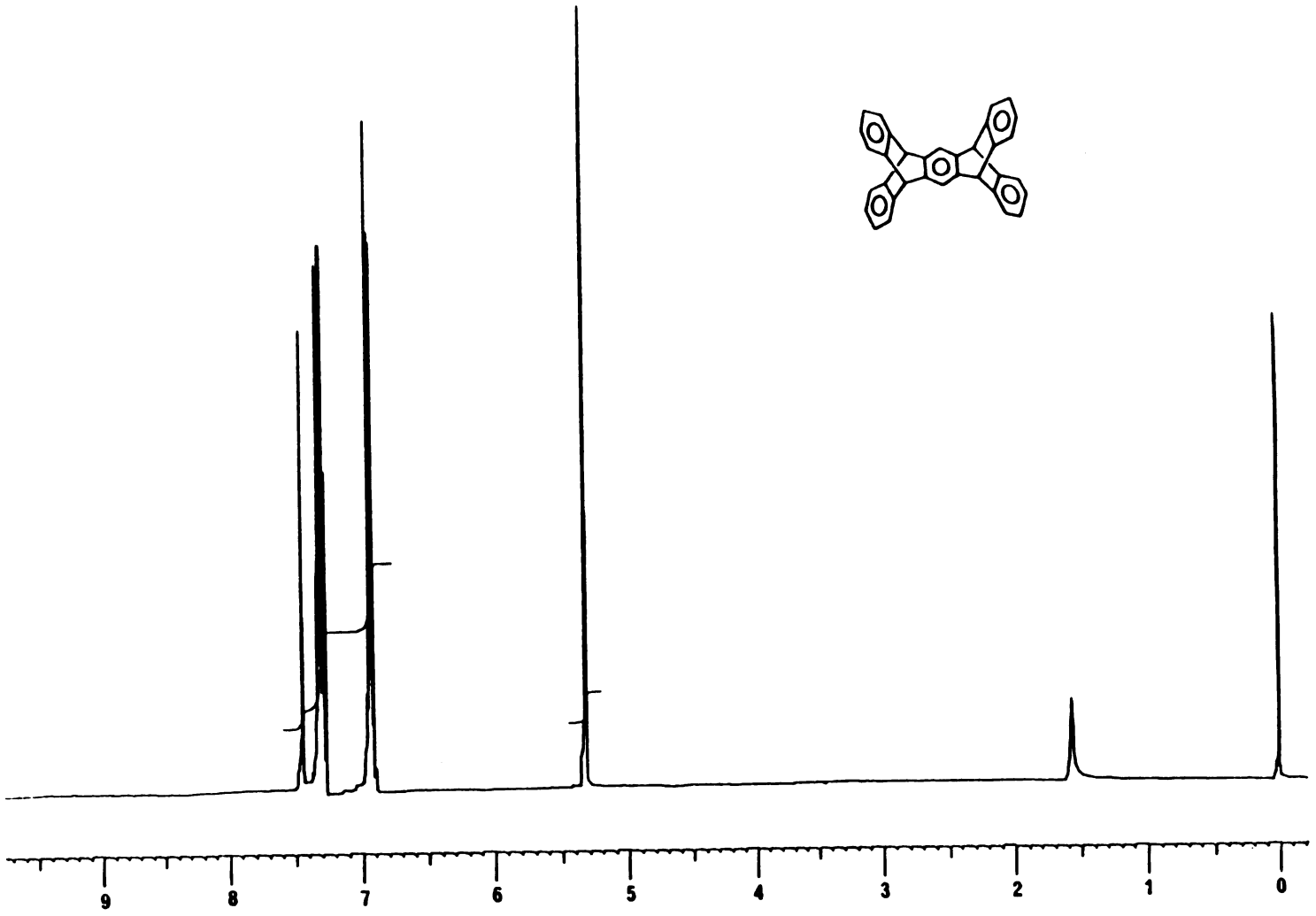
APPENDICES



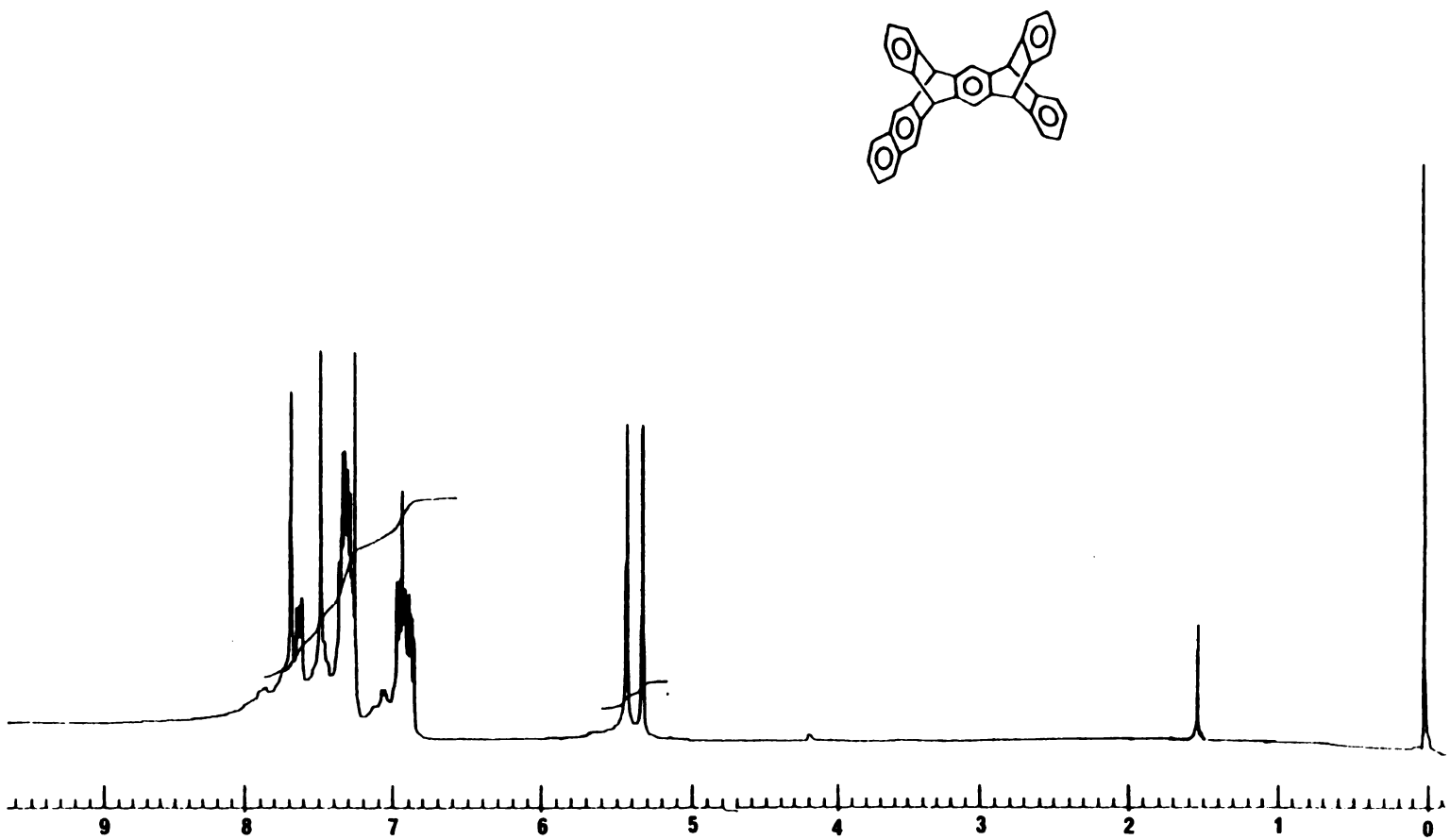
1. 250 MHz ^{1}H NMR of 5,14[1',2']Benzeno-5,14-dihydropentacene (20).



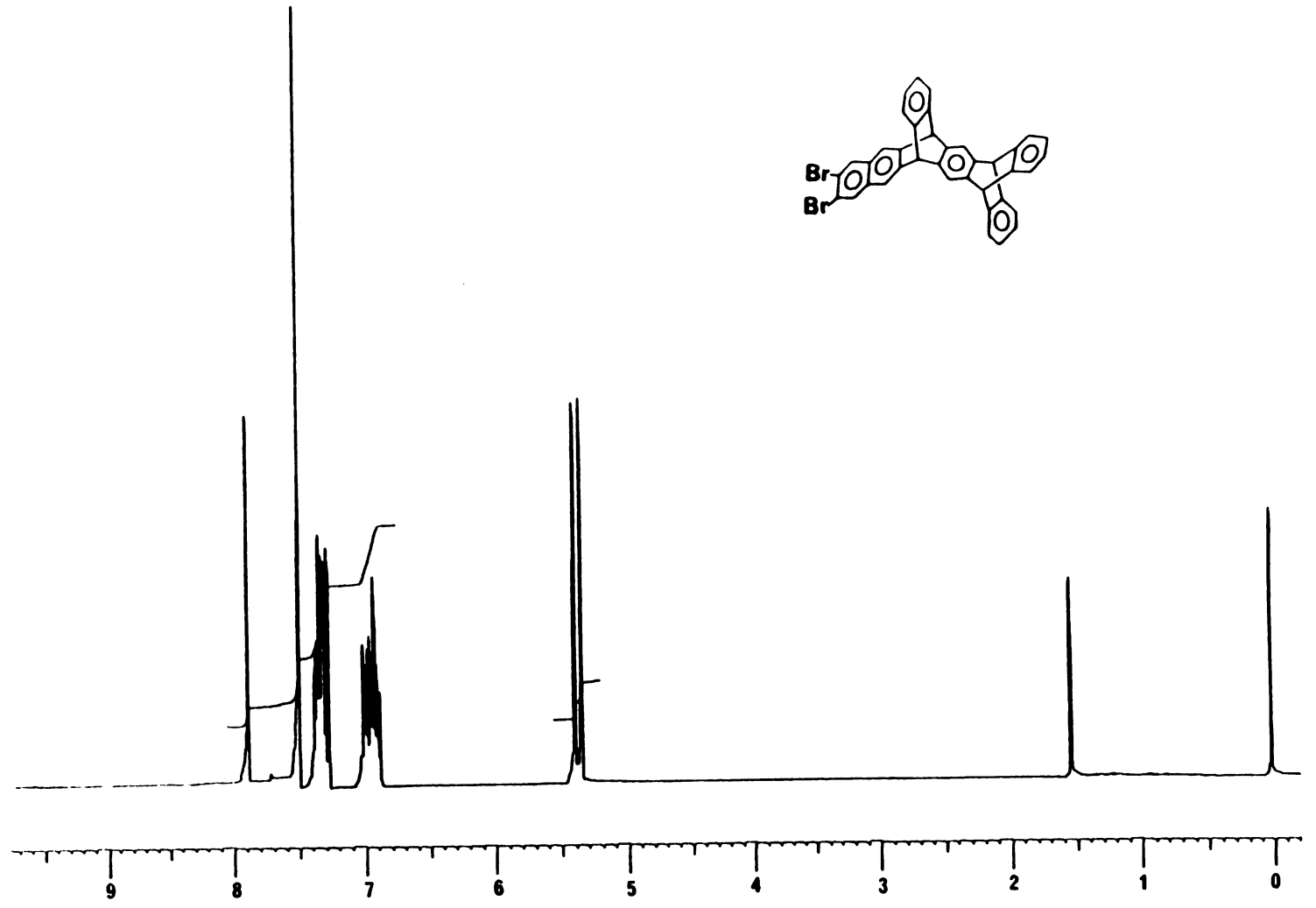
2. 250 MHz ^{1}H NMR of 5,16[1',2']Benzeno-5,16-dihydrohexacene (108).



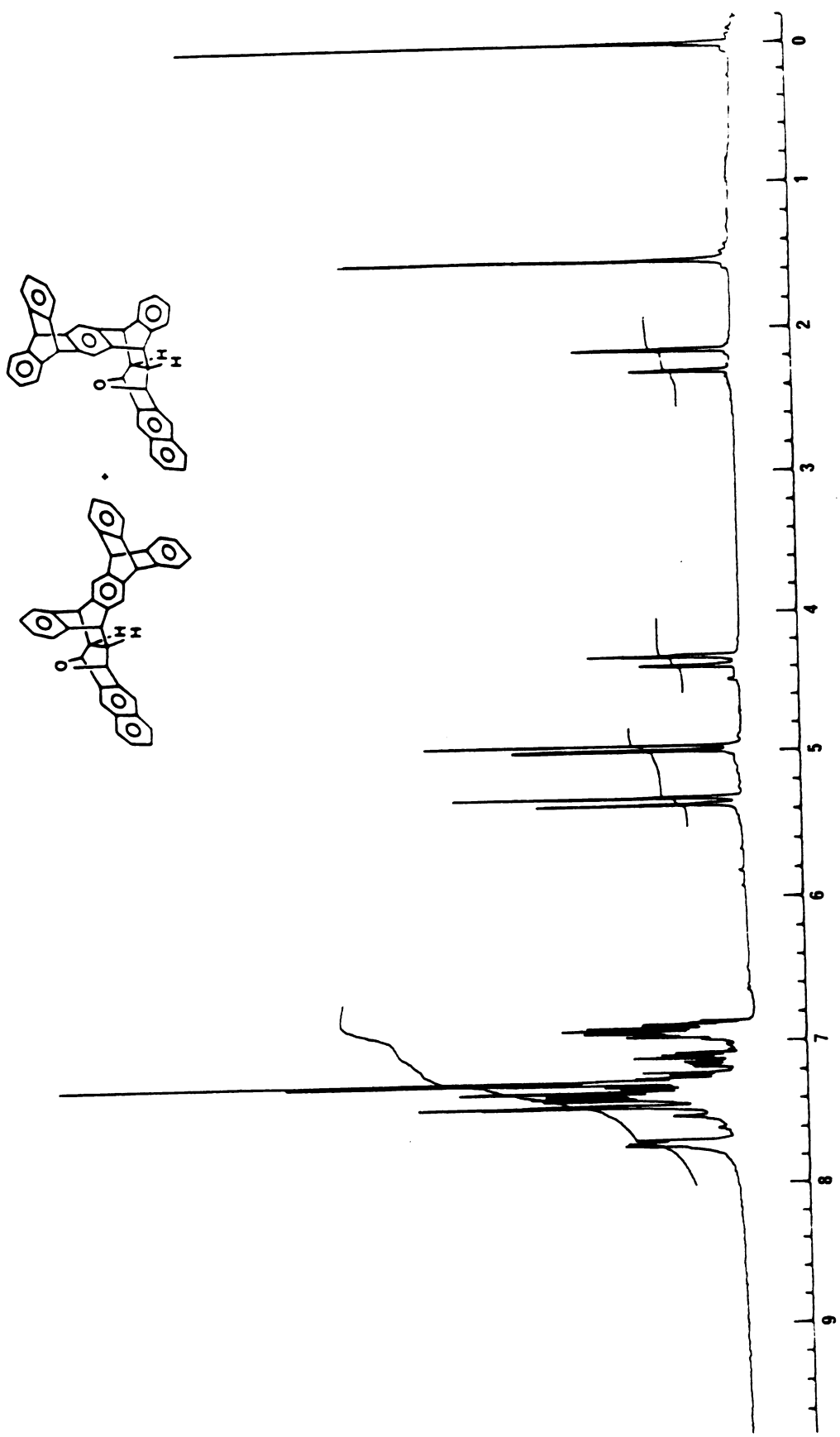
3. 250 MHz ^{1}H NMR of 5,14[1',2']:7,12[1",2"]Dibenzeno-5,7,12,14-tetrahydro-pentacene **(24)**.



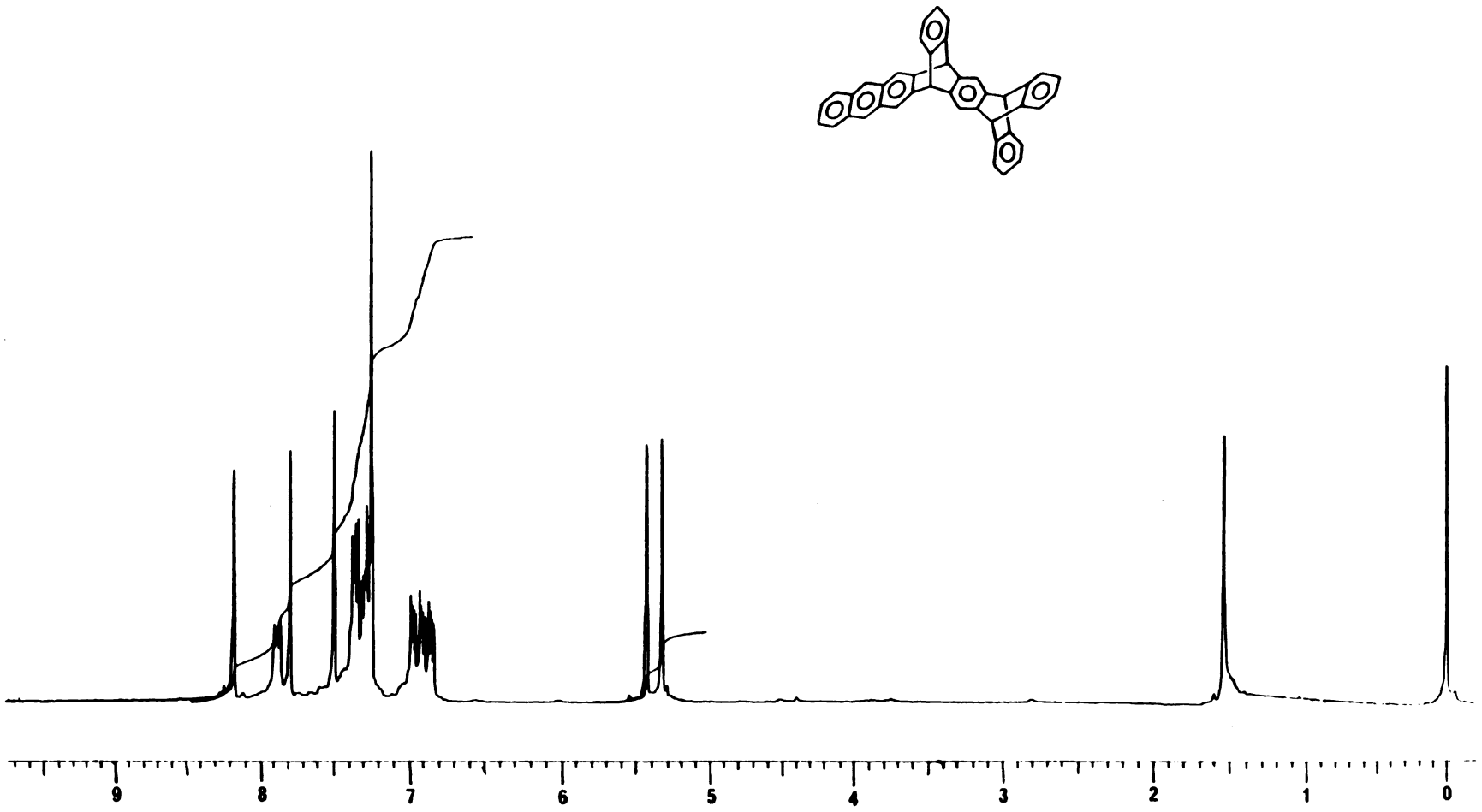
4. 250 MHz ^{1}H NMR of 5,16[1',2']:7,14[1",2"]Dibenzeno-5,7,14,16-tetrahydrohexacene (**76**).



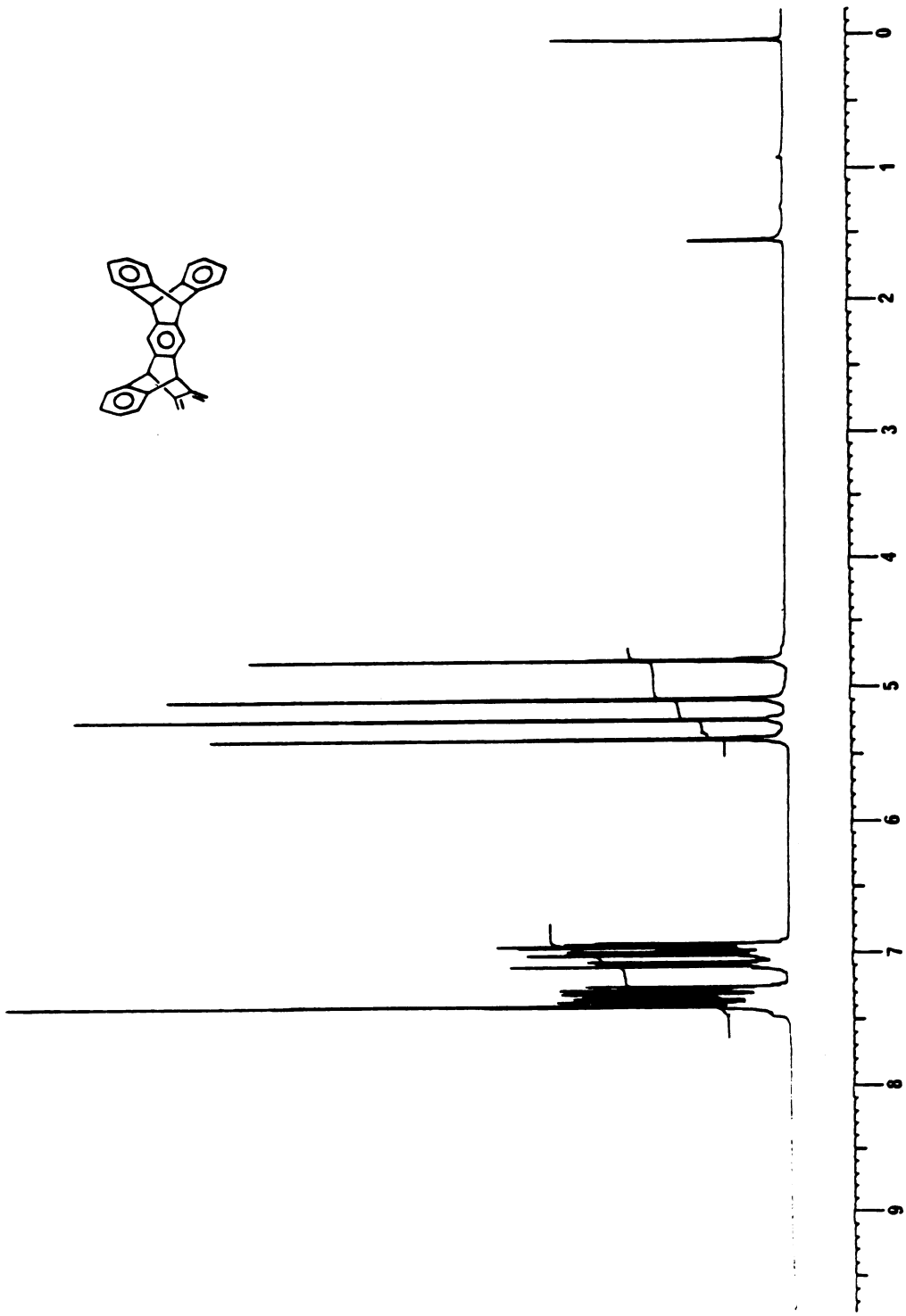
5. 250 MHz ^{1}H NMR of 5,16[1',2']:7,14[1",2"]Dibenzeno-10,11-dibromo-5,7,14,16-tetrahydrohexacene **(78)**.



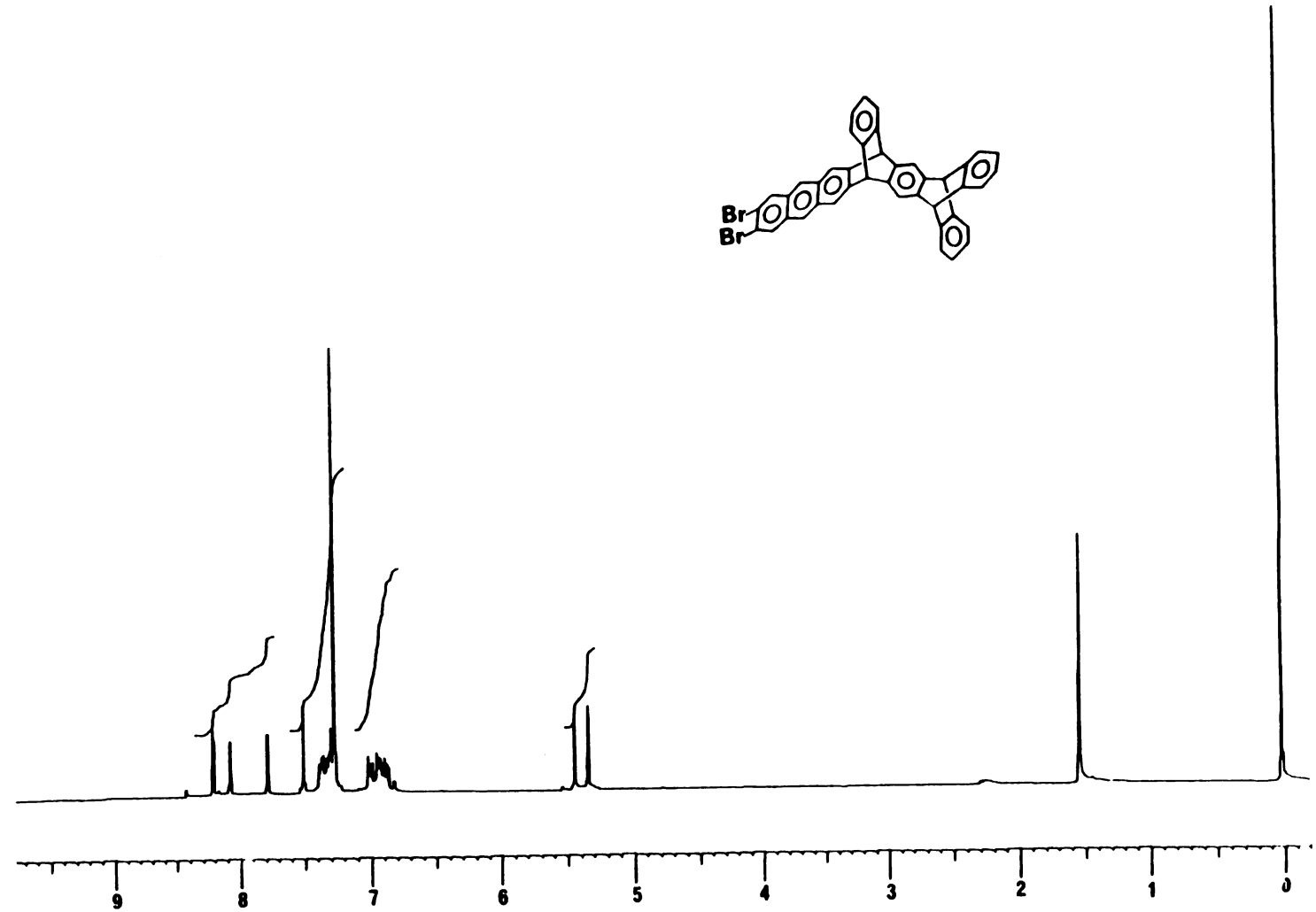
6. 250 MHz ^{1}H NMR of Adducts 79 and 80.



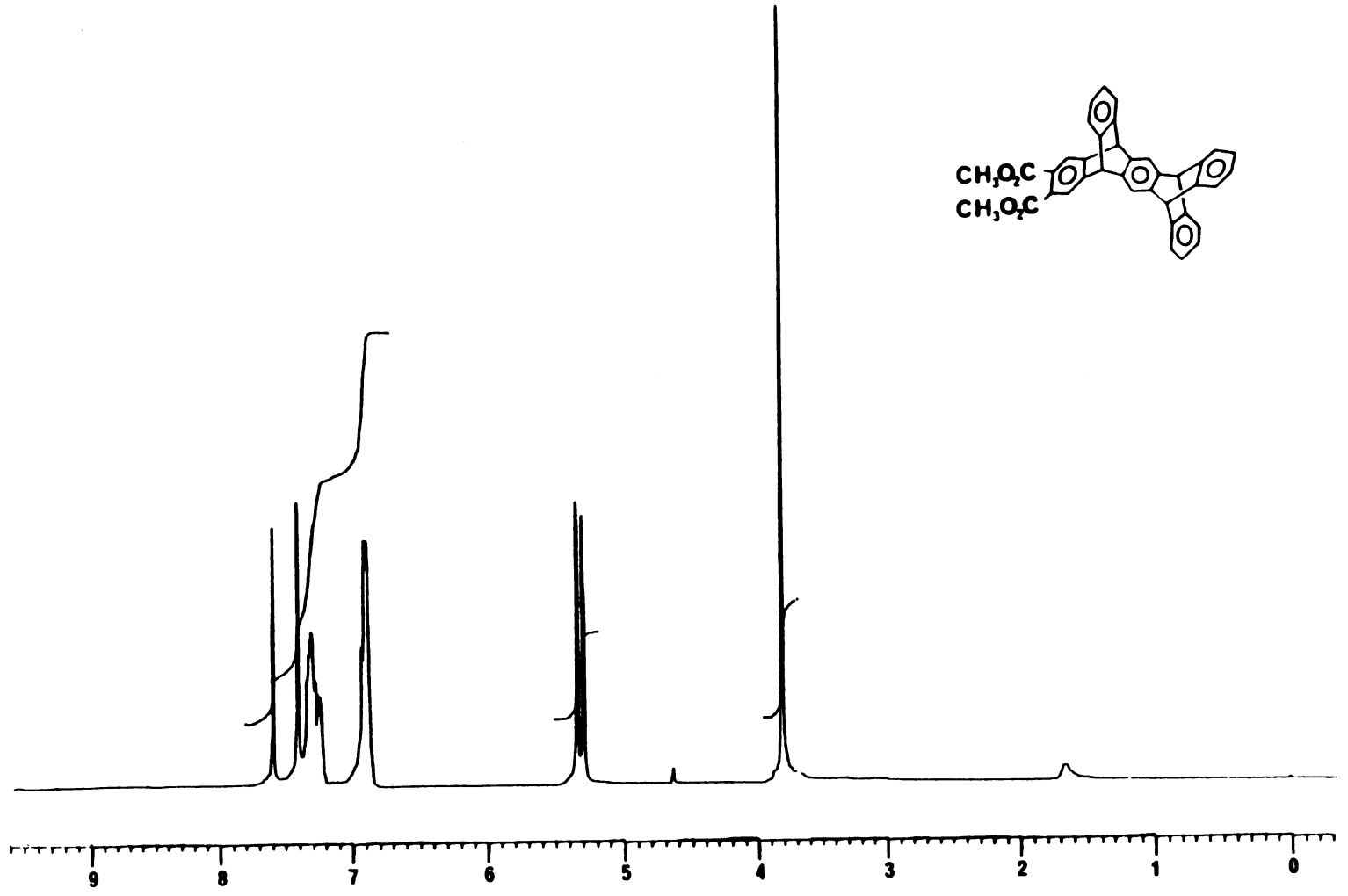
7. 250 MHz ^{1}H NMR of 5,18[1',2']:7,16[1",2"]Dibenzeno-5,7,16,18-tetrahydroheptacene **(81)**.



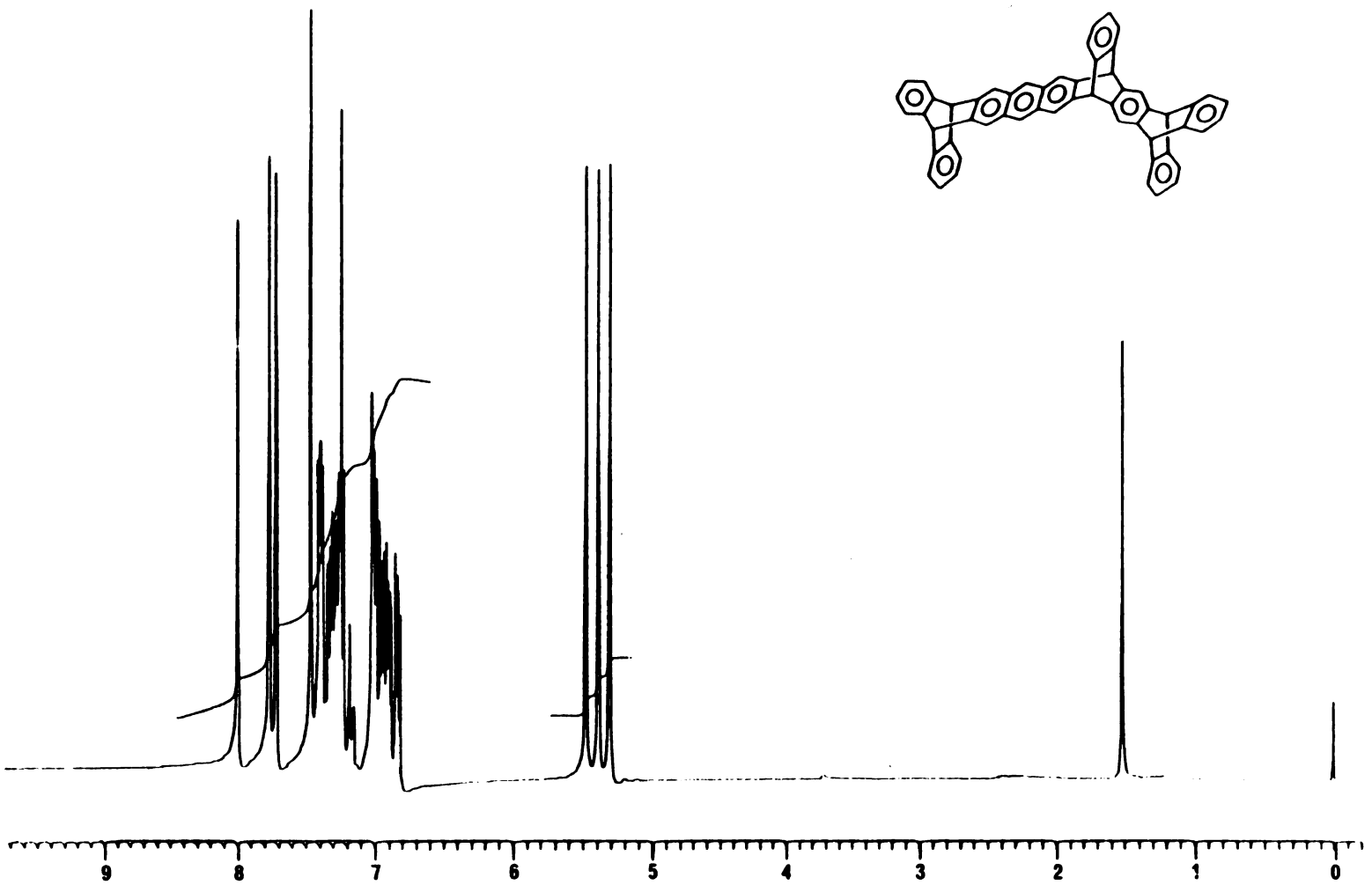
8. 250 MHz ^{1}H NMR of 7,12[1',2']Benzeno-15,16-dimethylene-5,14-ethano-5,7,12,14-tetrahydropentacene (**83**).



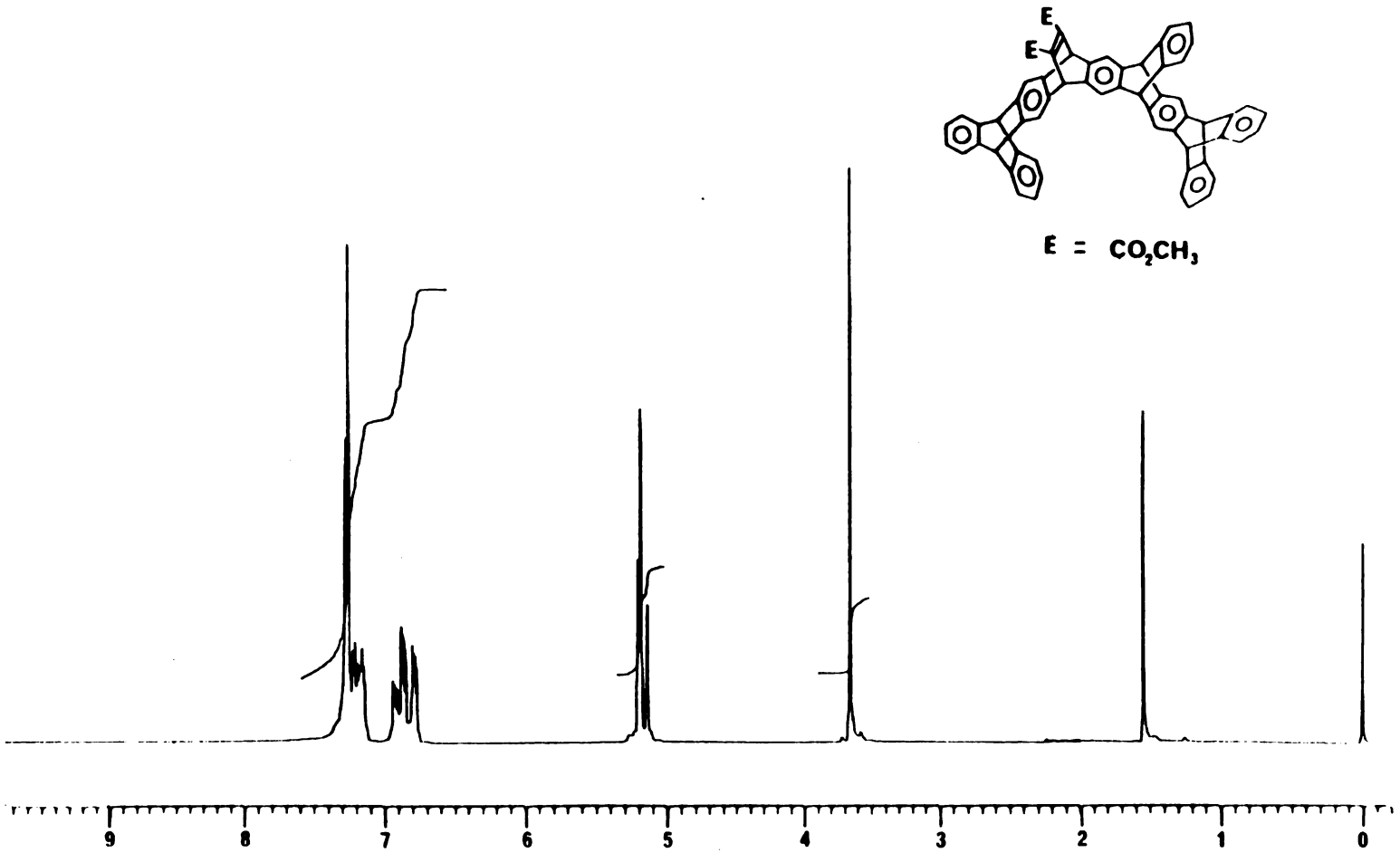
9. 250 MHz ^{1}H NMR of 5,18[1',2']:7,16[1",2"]Dibenzeno-11,12-dibromo-5,7,16,18-tetrahydroheptacene (**86**).



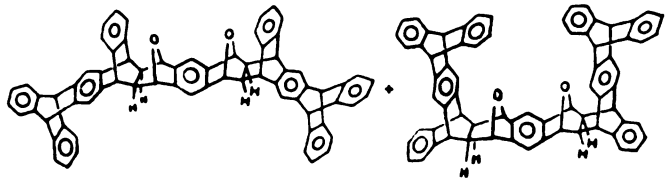
10. 250 MHz ^{1}H NMR of Dimethyl 5,14[1',2']:7,12[1",2"]dibenzeno-5,7,12,14-tetrahydropentacene-2,3-dicarboxylate (88).

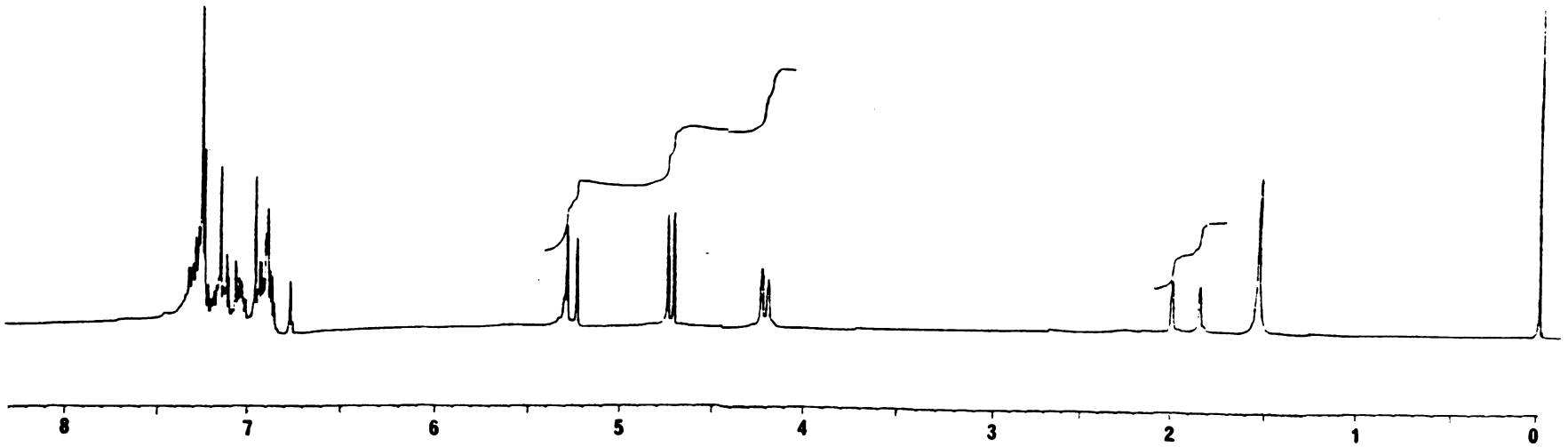


11. 250 MHz ^{1}H NMR of 5,22[1',2']:7,20[1",2"]:11,16[1^{III},2^{III}]Tribenzeno-5,7,11,16,20,22-hexahydrononacene (90).

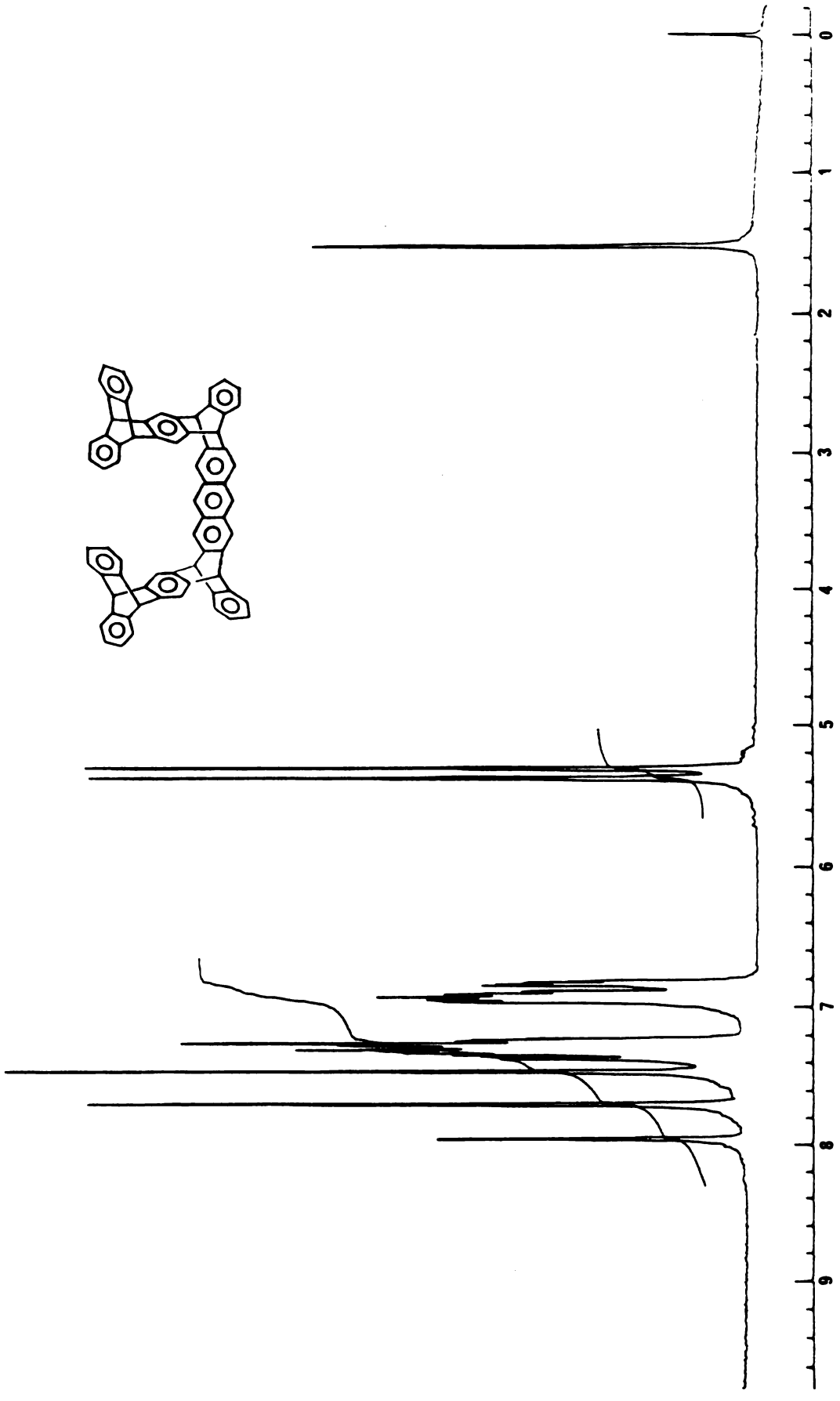


12. 250 MHz ^{1}H NMR of DMAD adduct of **90** (**91**).

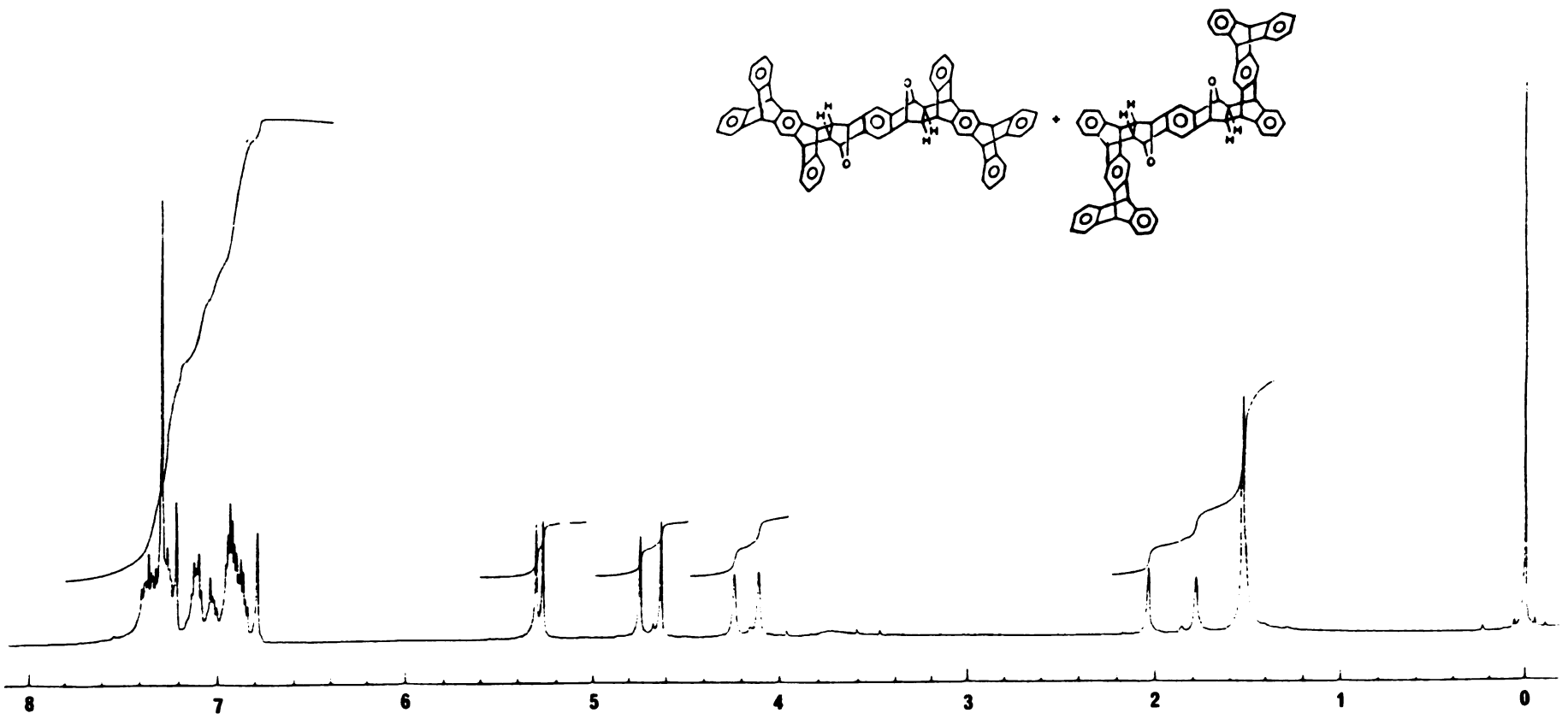




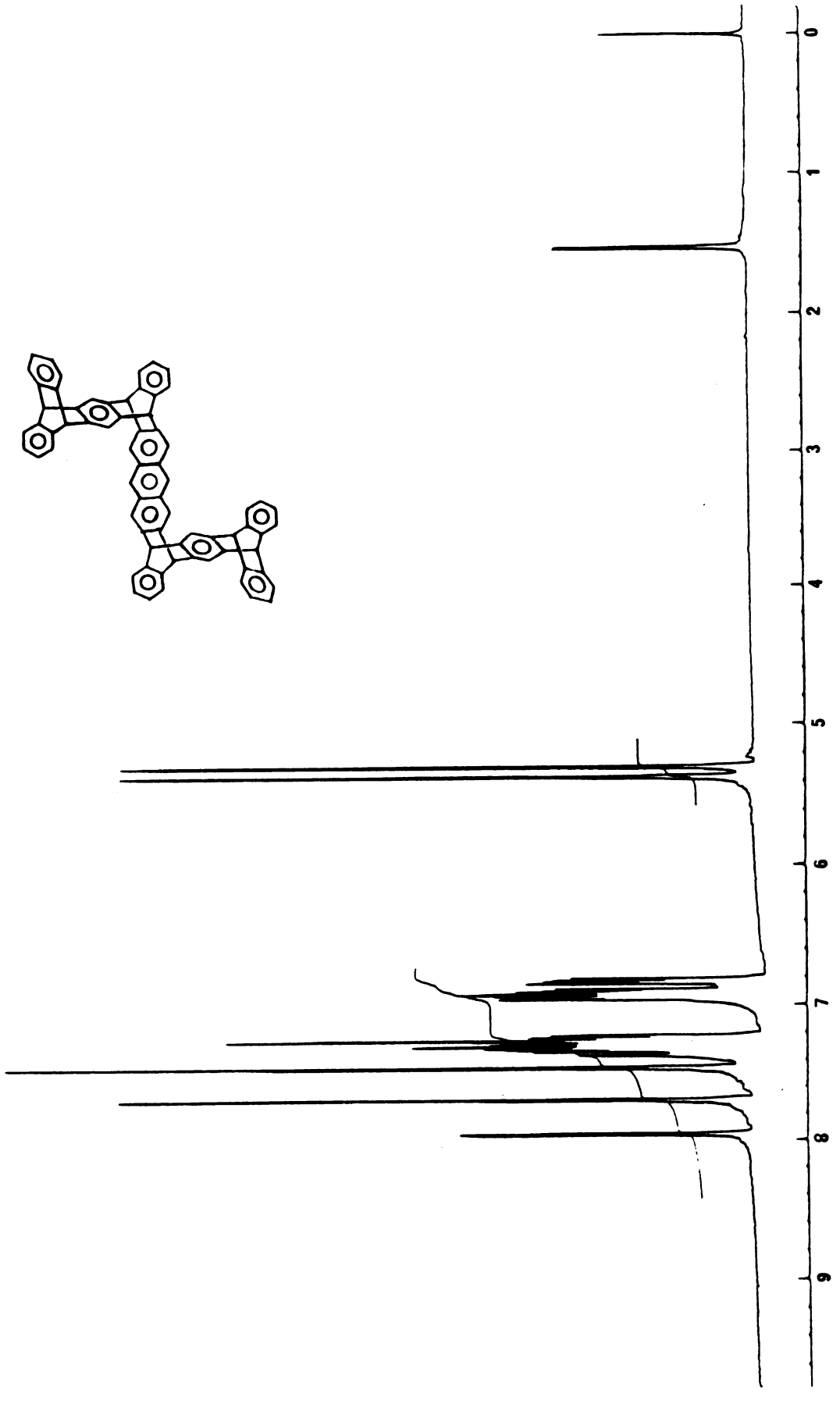
13. 250 MHz ^{1}H NMR of Adducts **96** and **97**.



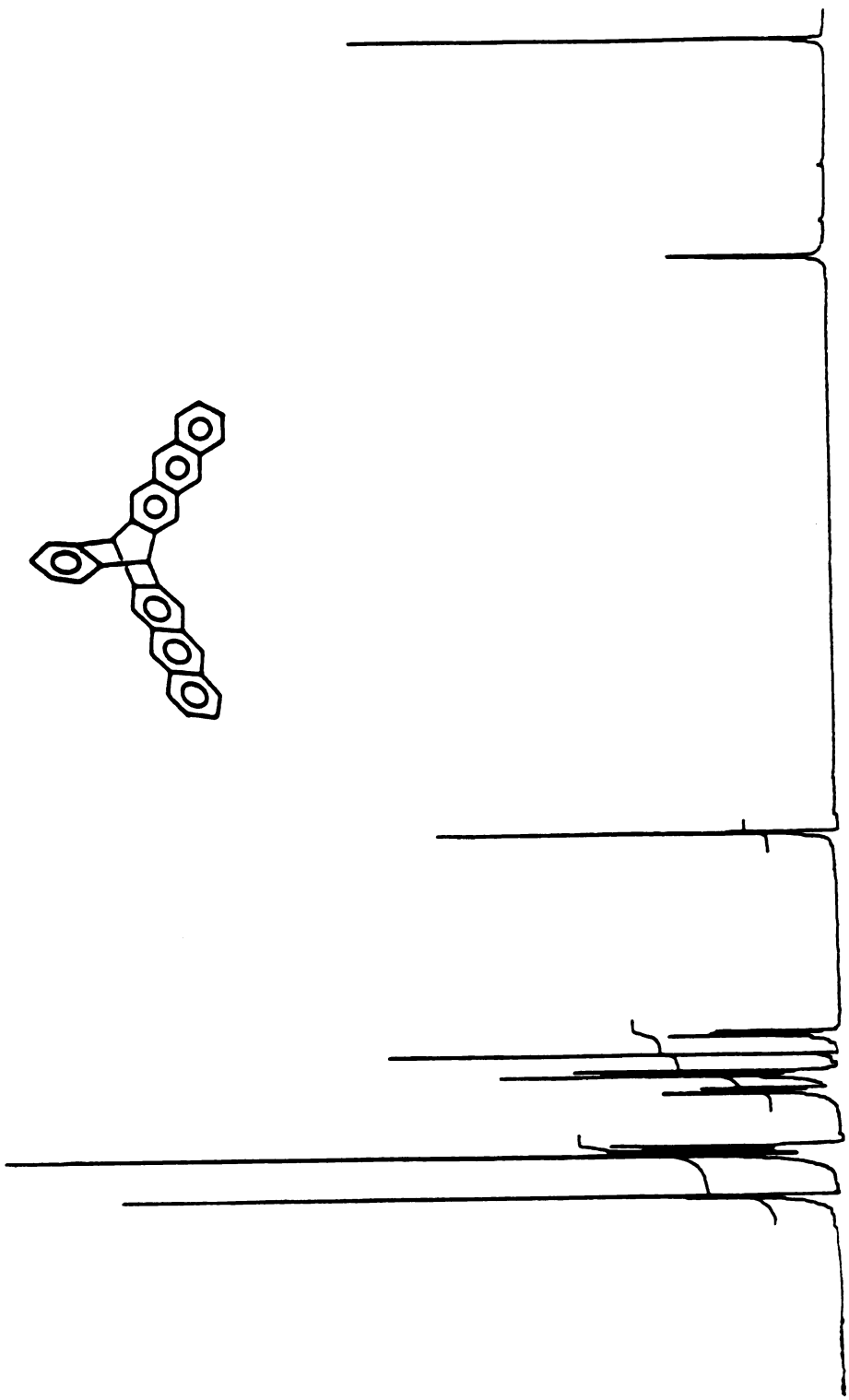
14. 250 MHz ^{1}H NMR of Syn-5,26[1',2']:7,24[1",2"]:11,20[1'''',2''''']:13,18[1"",2""]-tetrabenzeno-5,7,11,13,18,20,24,26-octahydroundecacene (**98**).



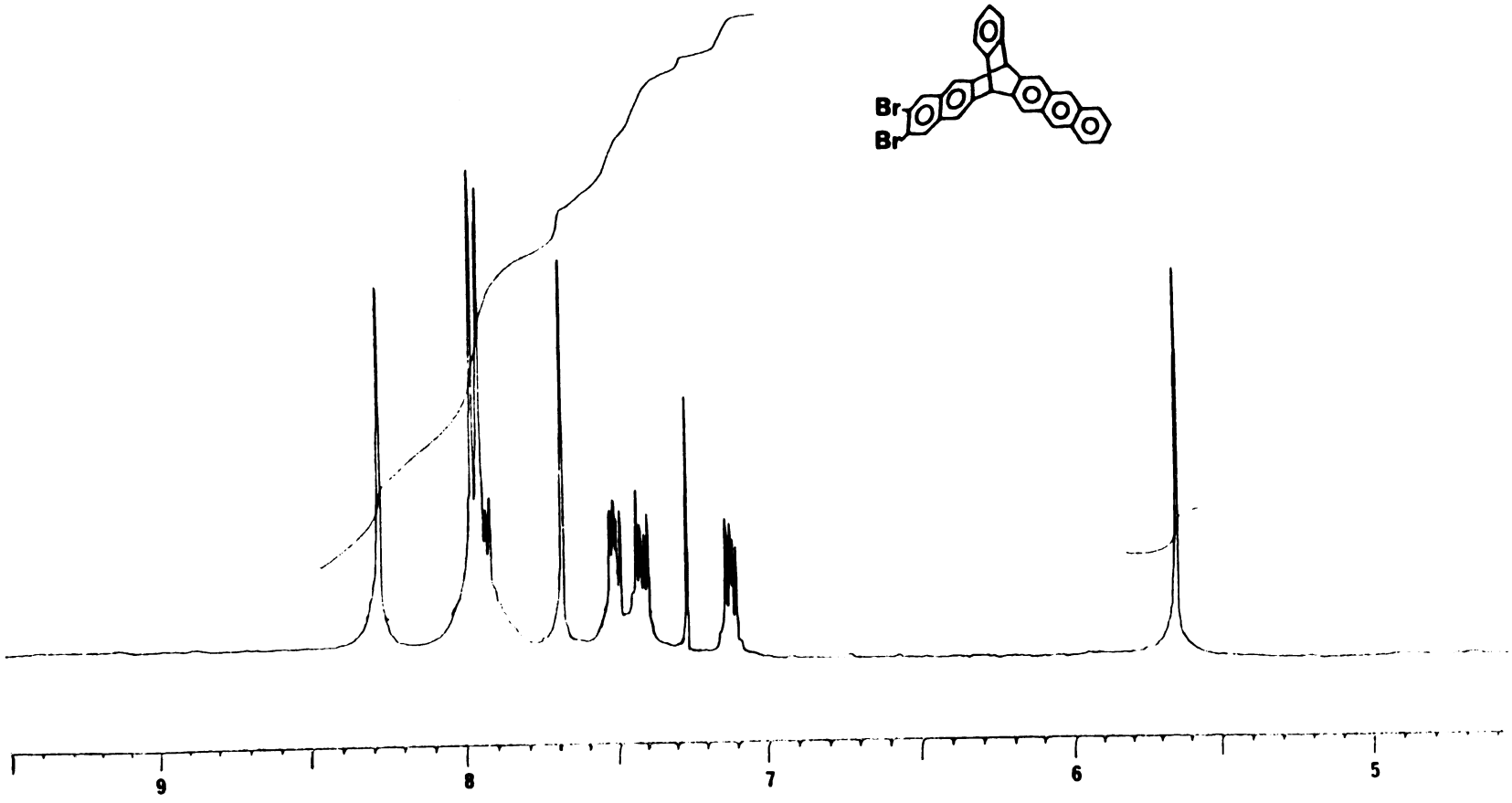
15. 250 MHz ^{1}H NMR of Adducts 101 and 102.



16. 250 MHz ^{1}H NMR of Anti-5,26[1',2']:7,24[1",2"]:11,20[1'",2'"]:13,18[1"",2""]-tetrabenzeno-5,7,11,13,18,20,24,26-octahydroundecacene (**103**).



17. 250 MHz ^{1}H NMR of 7,16[1',2']Benzeno-7,16-dihydroheptacene (109).



18. 250 MHz ^{1}H NMR of 6,15[1',2']Benzeno-2,3-dibromo-6,15-dihydrohexacene (143).

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BIBLIOGRAPHY

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