Tetrahedron Vol. 42, No. 6, pp. 1641 to 1654, 1986
Printed in Great Britain.

0040-4020/86 $3.00+.00

IPTYCENES

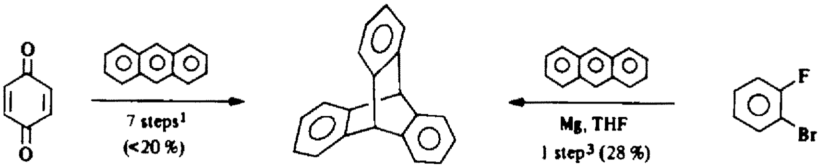
EXTENDED TRIPTYCENES[†]

HAROLD HART,* ABDOLLAH BASHIR-HASHEMI, JIHMEI LUO and MARY ANN MEADOR
Department of Chemistry, Michigan State University, East Lansing, MI 48824, U.S.A.

(*Received in USA 6 May* 1985)

Abstract—Triptycene is the first member of a large series of compounds for which we have coined the general term "iptycenes". The prefix (tri, pent, etc.) indicates the number of separated arene planes. By fusing from one to six 9,10-anthradiyl moieties on the triptycene framework, one can derive a first generation of iptycenes (Table 1). Of these, only 3, 4, 8 and a substituted 2 are known; the remainder provide a synthetic challenge. Potentially interesting practical and theoretical properties of iptycenes and particular structural features of several (i.e. 15, 16 and 24) are briefly discussed, as are certain extensions beyond the compounds in Table 1. Methods for preparing useful synthons 35–41 are described. Three new, much improved syntheses of triptycene 29, itself a useful iptycene synthon, are presented. In addition, improved syntheses of pentiptycenes 3 and 33 are described, as well as the first syntheses of pentiptycenes 32, 34 and 52 and heptiptycene 54. The way is paved for future development of this mini-domain of unnatural products.

Triptycene 1[‡] was first synthesized over 40 years ago by Bartlett[1] to test the idea that its derived bridgehead radical would "have much less tendency to exist" than the analogous triphenylmethyl radical. The Bartlett synthesis, which started with the cycloaddition of 1,4-benzoquinone to anthracene, required seven steps and gave 1 in only a modest overall yield. Parenthetically, the above prediction that prompted its initial synthesis was correct, and triptycene's rigid framework has been useful in other mechanistic studies.[2]



1

It was Wittig's one-step synthesis[3] of 1 some 14 years later, via the addition of benzyne (dehydrobenzene) to anthracene, that really opened the door to triptycene chemistry. A major improvement in yield and convenience came with the generation of benzyne from anthranilic acid,[4] and triptycene formation eventually became a test for the efficacy of various benzyne precursors.[5] Triptycene synthesis even became a standard undergraduate laboratory "experiment".[6]

Numerous triptycenes are now known.[7] The rigid framework is attractive and in recent years has been used to study intramolecular charge transfer,[8] restricted rotation about single bonds (atropisomerism),[9] and correlated bond rotations (gearing).[10]

Iptycenes: 9,10-anthradiyl fusions

In most of the structural variations on triptycenes, its triptych or triplanar geometry has been preserved.[§] However, as we have pointed out briefly,[11] triptycene can be considered as the first member of a large series of compounds for which we coined the general term "iptycenes". For example, fusion of a single 9,10-anthradiyl moiety to triptycene 1 at an a or b bond can give the pentiptycene 2 or 3, respectively. The prefix "pent" indicates the number of separate arene planes in 2 and 3; a trivial nomenclature system which distinguishes 2 from 3 as $[1.1.1^a.1.1]$- and $[1.1.1^b.1.1]$-pentiptycene has been devised.[||]

The possibilities for elaborating 1 with 9,10-anthradiyl moieties are shown in Table 1.

Only a few of the iptycenes listed in Table 1 are known. Hydrocarbon 2 is not yet known although a derivative with two methyl substituents on the central ring has been prepared.[11] Pentiptycene 3 was first prepared in low yield through the addition of 2,3-triptycyne to anthracene.[12] A much shorter, higher yield route from 1,2,4,5-tetrabromobenzene, anthracene and butyllithium has been described, and this method has been extended to various substituted analogs.[11] (We shall describe here an even better, though somewhat longer route to 3; *vide infra*.) Compound 3, in which the central arene ring is a quinone, has long been known.[13]

Of the bis-fused triptycenes, 4 has been prepared via a cycloalkyne "trimerization".[11,14] Compounds 5–7 are not known, but the synthesis of 8 was recently accomplished.[15] (We shall also describe here a better

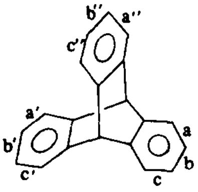
---

[†] This paper is dedicated to Professor Paul D. Bartlett who started it all, in memory of a stimulating year that one of us (H.H.) spent in his Harvard laboratory 30 years ago.

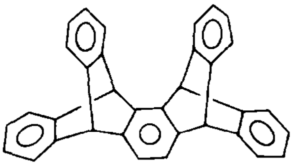
[‡] CA nomenclature is 9,10[1′,2′]-benzenoanthracene.

[§] The trivial name was derived from the triptych of antiquity, a book with three leaves hinged on a common axis.[1]

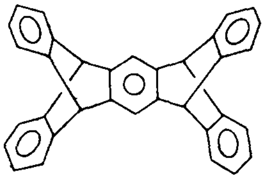
[||] See Ref. 12, footnote 12.


b''
a''
c''
a'
b'
c'
a
b
c

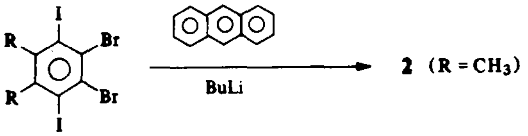
1

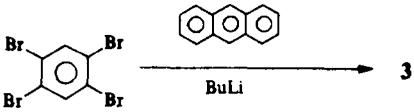


2

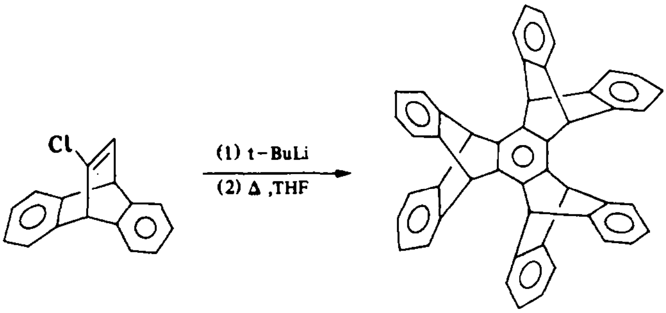


3


I
R
Br
R
Br
I
BuLi
2 (R = CH3)


Br
Br
Br
Br
BuLi
3

35


Cl
(1) t-BuLi
(2) Δ ,THF

4

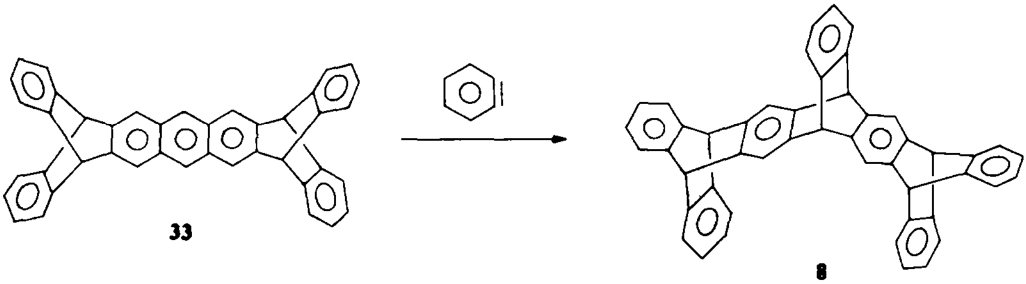

33
8

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

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

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

route to **33**, the immediate precursor of **8**; *vide infra*.) Polyquinones structurally related to **8** have been described.[16]

None of the remaining iptycenes in Table 1 have been reported, although some derivatives of **16** have been prepared by Webster† starting with triptycene trisquinone,[17] and we have recently synthesized the parent hydrocarbon.[18]

Reasons for interest in the iptycenes in Table 1

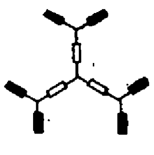
Aside from the synthetic challenge, the iptycenes listed in Table 1, and their derivatives, are likely to possess a number of interesting properties which make their synthesis worthwhile. One of those properties is high melting points and thermal stability. For example, the melting points of triphenylmethane, triptycene, pentiptycene **3**, and heptiptycene **8** increase from 94° to 256° to 483° to > 525°; and the melting point of heptiptycene **4** is reported[14] to be 580° ! The nature of the intermolecular attractions in these hydrocarbon crystals that lead to such high melting points is not obvious. It will be important to determine their X-ray structures, particularly to examine the packing patterns.[19] Polyiptycenes (like polyphenyls) could well be useful heat-resistant materials.[20]

Another interesting feature of these iptycenes is their molecular cavities which could be useful in forming host–guest compounds. As will be mentioned below, we have already begun to encounter this phenomenon. Among the more interesting molecules in this regard are **4**, **8**, **15**, **16** and **24**.

Compound **4** has two equivalent cup-like cavities above and below the central arene ring; viewed in another sense, it has three equivalent cavities disposed symmetrically about axes that lie in the plane of the central ring and bisect its non-fused bonds.

As previously pointed out,[15] **8** has two types of cavities, as shown in an end-on view. The larger, more enclosed cavity is U-shaped with two parallel arene rings, whereas the more open cavities are similar to those in **3**. Compound **16**[18] has three analogous U-shaped cavities. We will (*vide infra*) describe

8 (end - on view)

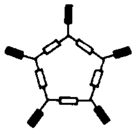


16 (end - on view)

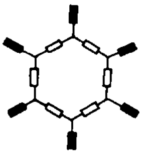
---

† Seminar, Michigan State University, 25 October (1984); work done at the Central Research and Development Department, E. I. duPont de Nemours and Company, Wilmington, Delaware.

compounds analogous to **8** but with more enclosed cavities. Ultimate challenging targets of this type are cycloiptycenes such as **25** and **26** (shown in end-on views).



25



26

Iptycene **24** has the same symmetry as triptycene itself but is a beautiful molecule with three large cavities symmetrically located around the three C_2 axes (Fig. 1). Efforts directed toward the synthesis of **24** are underway.

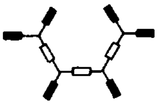
There are six chiral iptycenes listed in Table 1. Three have C_2 axes. Of special interest is **15**, in which the central triptycene moiety is used as a framework to attach a helical array of three 9,10-anthradiyl moieties, resulting in three helically-disposed cavities (Fig. 2).

There are many other interesting structural features of iptycenes besides high melting points, high thermal stability and possibilities as hosts in molecular complexes. We only mention here the possibilities for novel organometallic complexes,[21] novel photochemistry, unusual semi-conductor designs, as well as interesting spectral properties involving ring–ring interactions.

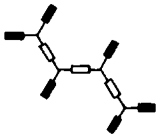
Other interesting iptycenes

Compounds **1**–**24** are all based on elaboration of triptycene itself by fusion of 9,10-anthradiyl moieties, but each compound derived from this analysis can also serve as the starting point for analogous elaborations. A complete description of this expanding mini-universe is not possible, but we might mention here just two of the many synthetically accessible examples.

Elaboration of **3** with one 9,10-anthradiyl moiety can give only the already mentioned **6** or **8**. But fusion of two anthradiyl moieties can give not only the five noniptycenes already mentioned (**10**, **12**, **14**–**16**), but ten others, two of the more symmetric of which are **27** and **28**, derived by fusion at *syn* or *anti* b-type bonds. Note that **27** completes five of the six sides in **26**. Some progress toward compounds of this type will be described (*vide infra*). Finally, all of the iptycenes mentioned so far contain only benzenoid rings; but numerous iptycenes with fused rings (naphthalenoid, etc.) can be envisioned. We will mention here only two types of such iptycenes.†



27



28

A few fused-ring triptycenes are known.[7,22] Since our

---

† The iptycene nomenclature is easily extended to fused-ring examples (see Ref. 12, footnote 12). Thus, **29** is [3(b)^{b}.1.1]triptycene.

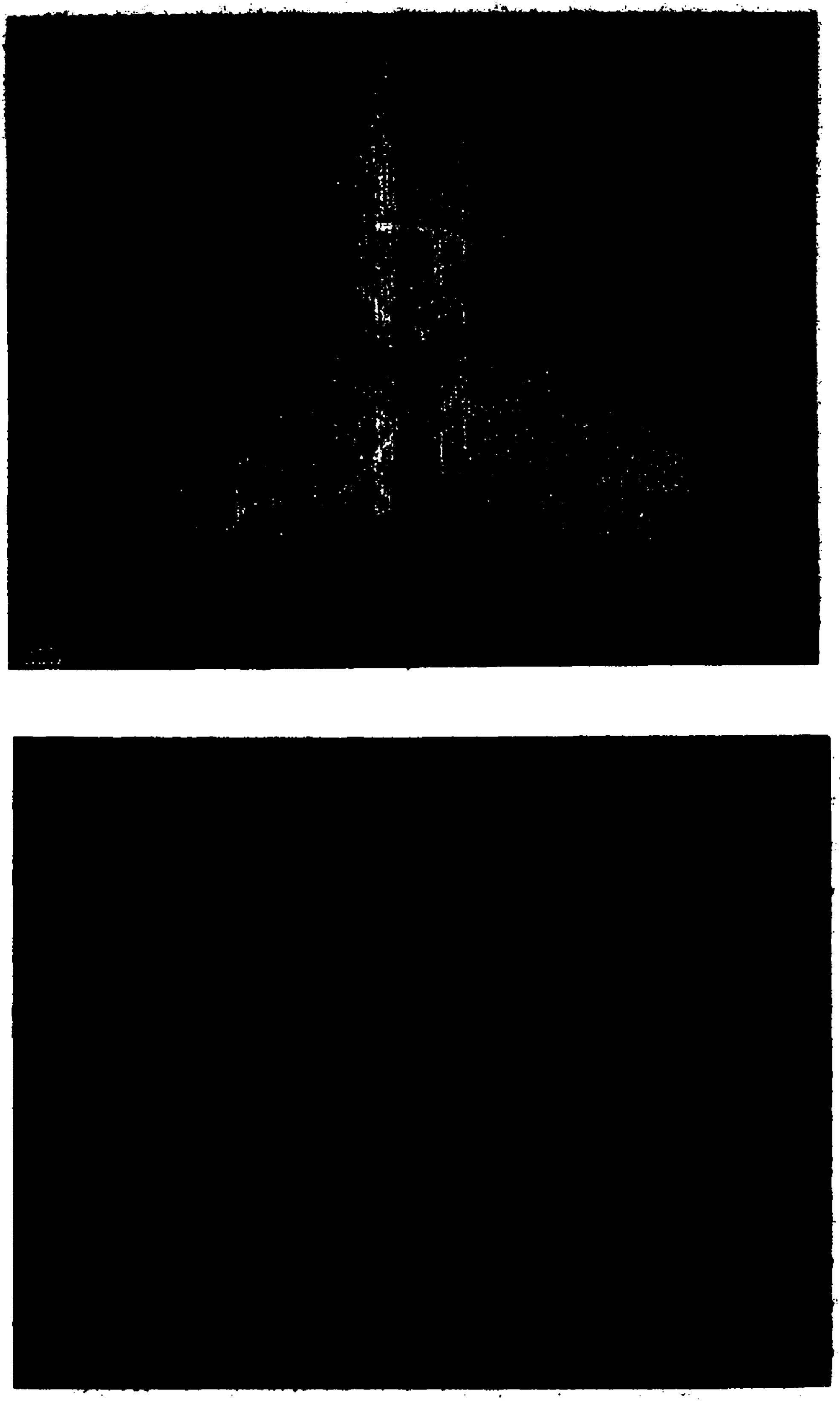


Fig. 1. Model of **24**: (a) view down the C_3 axis; (b) same, with three equivalent cavities filled by balloons; (c) view down a C_2 axis.

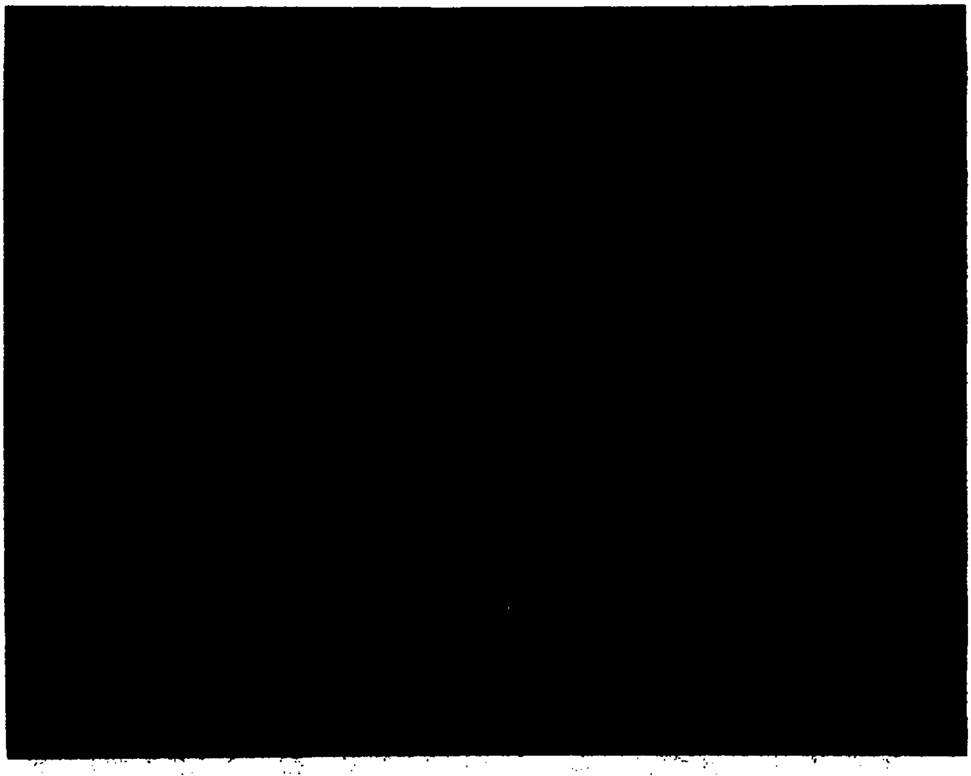
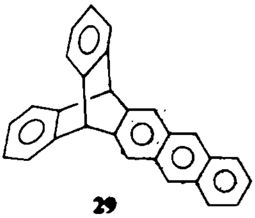


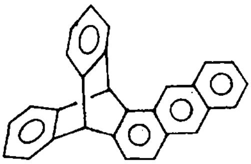
Fig. 2. Model of **15**; helicity results from fusing 9,10-anthradiyl moieties to the a,b′,c″ bonds of the central triptycene unit.

synthetic routes often involve cycloadditions to an anthracene moiety in an iptycene, it is useful to consider triptycenes that contain the anthracene ring system. There are only two possibilities for replacing one benzene moiety by anthracene, **29** and **30**. Of these, only **29** is known.[22] The published route to **29** is multi-step and gives a low overall yield. We will describe here several short, excellent routes to **29**.

There are four possible isomeric triptycenes that can



29

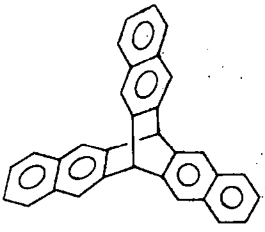


30

be obtained by replacing two benzene moieties by anthracene (two are chiral) and six possible isomers with three anthracene moieties (one is chiral). None of these is known, and all are potentially useful synthons for higher iptycenes.

As to higher iptycenes containing fused rings, there is some interest in the naphthalenes, especially if one is seeking high-melting materials. We note, for example, an over 100° increase in melting point on going from **1** (m.p. 256°) to **31** (m.p. 387–389°).[22]

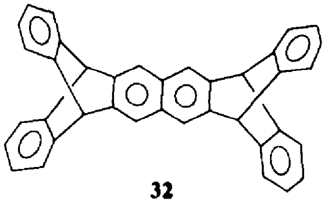
One can regard iptycenes **1**, **2**+**3**, and **4** as having been derived from benzene by fusing on one, two or three 9,10-anthradiyl moieties. One can enter one group of fused-ring iptycenes in a similar manner by fusing one to four 9,10-anthradiyl moieties to a naphthalene, anthracene, tetracene, etc. nucleus. The number of possible isomers are:



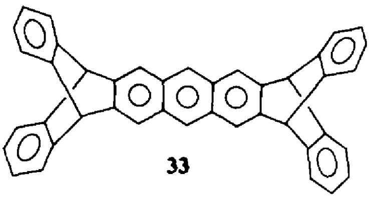
31

No. of fusions	No. of isomers
1	2
2	5
3	2
4	1

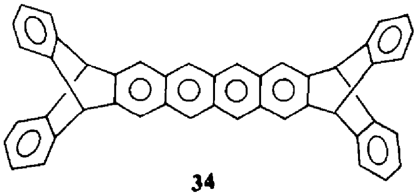
Examples include **32**–**34**, which have two such fusions at the bb′ bonds of the central fused-ring system. Compound **33** has already been prepared[15] as the immediate precursor of **8**. We will describe here a substantially improved route to **33**, as well as routes to its lower and higher homologs **32** and **34**. The synthesis of other fused-ring iptycenes is in progress, especially those which contain an anthracene moiety suitably located so that the molecule can serve as an effective precursor for oligoiptycenes such as those in Table 1.



32



33



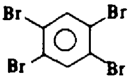
34

We will first describe several useful synthons for iptycenes, then show how these can be applied to: (a) improved syntheses of **29**, **3** and **33**; (b) the synthesis of other iptycenes containing an anthracene moiety; and finally (c) the synthesis of **32** and **34**.

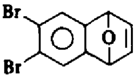
RESULTS AND DISCUSSION

Useful synthons. Triptycenes are usually prepared by aryne addition to an anthracene (or by modification of another triptycene). Cycloadditions will also be important in the construction of higher iptycenes. Rather than tackle each particular iptycene as a unique synthetic challenge, it is useful to have available a number of building blocks which can then be employed in various sequences to construct certain ring systems.

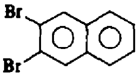
Among the synthons we have found useful are the following.



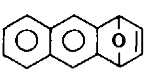
35



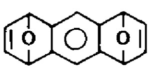
36



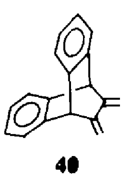
37



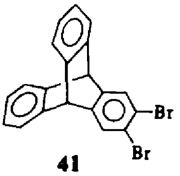
38



39

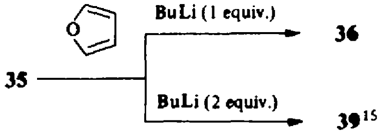


40



41

1,2,4,5-Tetrabromobenzene[23] is useful as the synthetic equivalent of either 4,5-dibromobenzyne or 1,4-benzadiyne and is readily prepared in good yield by bromination of 1,4-dibromobenzene. Treatment of **35** with either one or two equivalents of butyllithium and furan then gives synthons **36** or **39**. Since the double bonds in **36** and **39** are effective dienophiles, these synthons can be used to build fused-ring iptycenes.

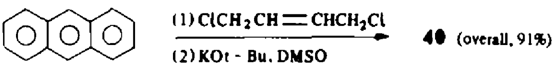


2,3-Dibromonaphthalene **37** is a useful 2,3-naphthyne equivalent. It has been prepared by several methods,[24,25] the best involving bromination of the commercially available naphthalene–hexachlorocyclopentadiene bis-Diels–Alder adduct followed by pyrolysis of the bromination product at 220° (overall yield of **37** in two steps, 46%). As an alternative, we describe here the metal-catalyzed deoxygenation of **36** using $TiCl_4$ and zinc, which proceeds in excellent yield.

$$\mathbf{36} \xrightarrow[\text{THF}]{\text{TiCl}_4,\ \text{Zn}} 37\ (86\%)$$

The 2,3-anthryne equivalent **38**[26] is readily prepared from **37**, furan and phenyllithium.[25b]

Bis-methylene **40** is a useful diene for iptycene synthesis. Literature syntheses[27] require four steps from anthracene, except for one[28] which requires only two steps. Experimental details† have not appeared so we describe here the conditions we used. The successful use of 1,4-dichloro-2-butene as a dienophile in this reaction is noteworthy, particularly in view of the report that 2-butyne-1,4-diol does not give an adduct with anthracene.[27]

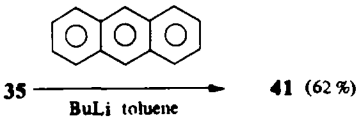


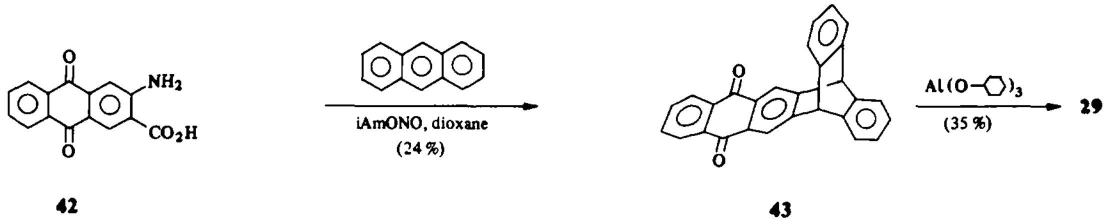
2,3-Dibromotriptycene **41** is a useful 2,3-triptycyne equivalent. It has been prepared previously from 2-aminotriptycene (2 steps)[12] and from anthracene and 4,5-dibromoanthranilic acid.[29] We have found that **41** can be obtained in one step and in much better yield from **35** and anthracene.

Improved syntheses of **29**. The triptycene **29** was previously synthesized by the route shown.[22] The overall yield was only 8.4% from **42** which itself requires

---

† Credited to Dr David Eaton, E. I. duPont de Nemours and Company.





five steps from toluene[30] or is obtained in a low-yield, multi-step route from phthalic anhydride.[31] Since **29** is potentially a very useful synthon for iptycenes through cycloadditions to the anthracene moiety, we sought a good short route to it. Three methods will be presented because they illustrate different uses for the above synthons and also because two intermediates in the longest synthesis can themselves be useful synthons.

The first synthesis requires four steps from **36**. Treatment of **36** with anthracene in refluxing xylene gave a single adduct **44** in 96% yield. The stereochemistry was not determined but is probably *exo*. The oxygen bridge was removed by acid to give **45** (65%). The last ring was added by cycloaddition of the corresponding aryne to furan followed by deoxygenation of the resulting adduct **46** with low valent titanium. The overall yield of **29** in four steps from **36** is 35%. Both **45** and **46** are potentially useful iptycene synthons.

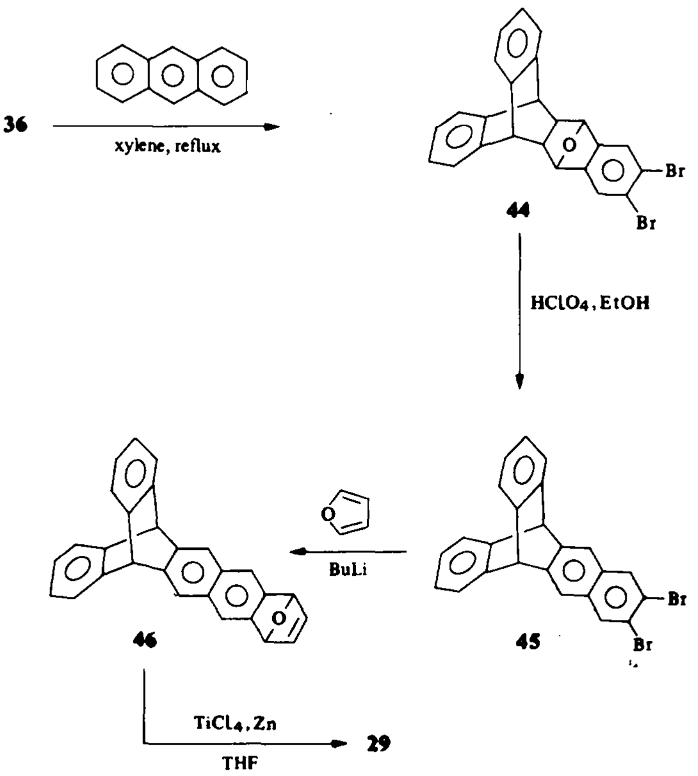
By starting with the three-ring precursor **38**, the synthesis could be shortened to two steps and an overall yield of 62%. Cycloaddition of **38** to anthracene gave adduct **47** in 93% yield and acid-catalyzed dehydration removed the oxygen bridge to give **29** (67%).

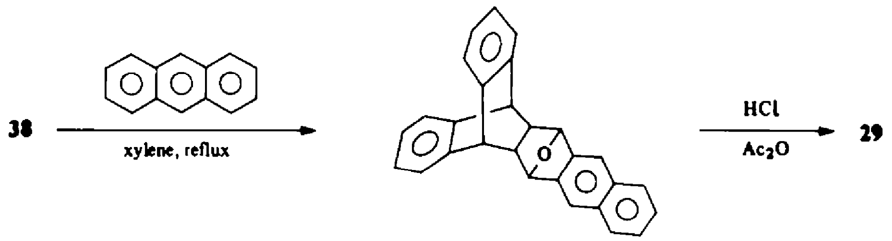
Finally, **29** could be prepared in two steps from **37** and **40**. The crude dihydroadduct **48** was dehydrogenated directly to give **29** in 73% overall yield.

All three methods presented here are good and represent very substantial improvements over the literature method.[22] 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.

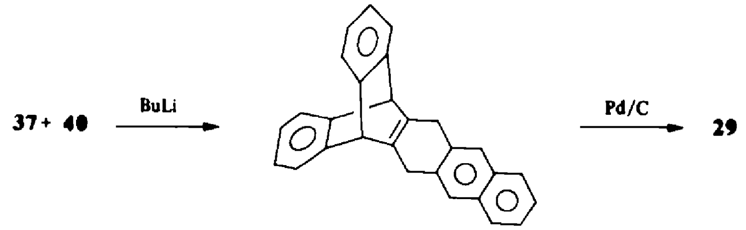
Improved syntheses of 3 *and* 33

Our previous synthesis of 3[11] from **35**, anthracene and butyllithium proceeds in one step and 94% yield based on consumed anthracene. On the face of it, this would seem an excellent method, but there are, in fact, some technical difficulties with the method. The yield, based on **35**, is only 26%, and there is a substantial





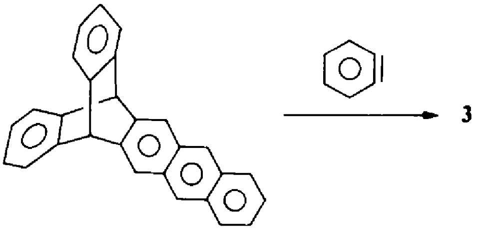
47



48

amount of anthracene remaining which must be separated from the desired 3 by chromatography and/or sublimation. Hence, a better route seemed desirable.

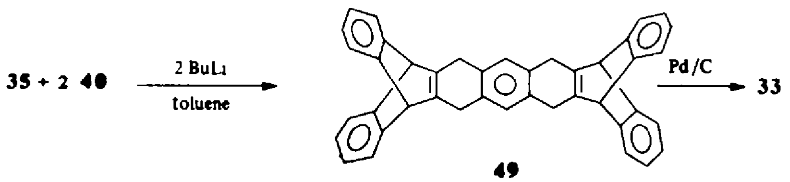
With 29 now readily available by several good methods (*vide supra*), it could be treated with benzyne (via benzenediazonium-2-carboxylate hydrochloride) to give 3. The yield was 65%. We anticipate that use of an appropriate benza-1,4-diyne equivalent with 29 will lead analogously to 27 and 28.†



29

Pentiptycene 33 was previously prepared from a bis-Diels–Alder addition of 39 to anthracene, followed by acid-catalyzed dehydration to remove both oxygen bridges.[15] The overall yield was 24–32%, the dehydration yield being only 41%.

We now find that 33 can be more easily prepared from the reaction of 35 with two equivalents of 40 and butyllithium. The bis-adduct 49 was formed in 84% yield and was nearly quantitatively dehydrogenated to 33.



49

Other iptycenes with anthracene moieties

Pentiptycene 33 has a central anthracene moiety. It was also desirable to have available the regioisomer 52 with an "outer" anthracene moiety.‡ This target was achieved in two steps from synthons 29 and 38. The cycloaddition gave the regioisomeric adducts 50 and 51 in 91% yield and approximately 59:41 ratio (NMR). The structures are assigned on the grounds that endo addition to 38 would give crowded structures and that 50 is less crowded than 51. The mixture was not separated but dehydrated directly to give 52 in 41% yield.

The heptiptycene 54 was synthesized from 29 and 46 by an analogous route. In this case, mainly one cycloadduct, thought to be 53, was formed in 88% yield. Dehydration gave the desired 54 in 70% yield.

Cycloadditions to the anthracene moieties of 52 and 54 are in progress.

Synthesis of fused-ring pentiptycenes 32 and 34

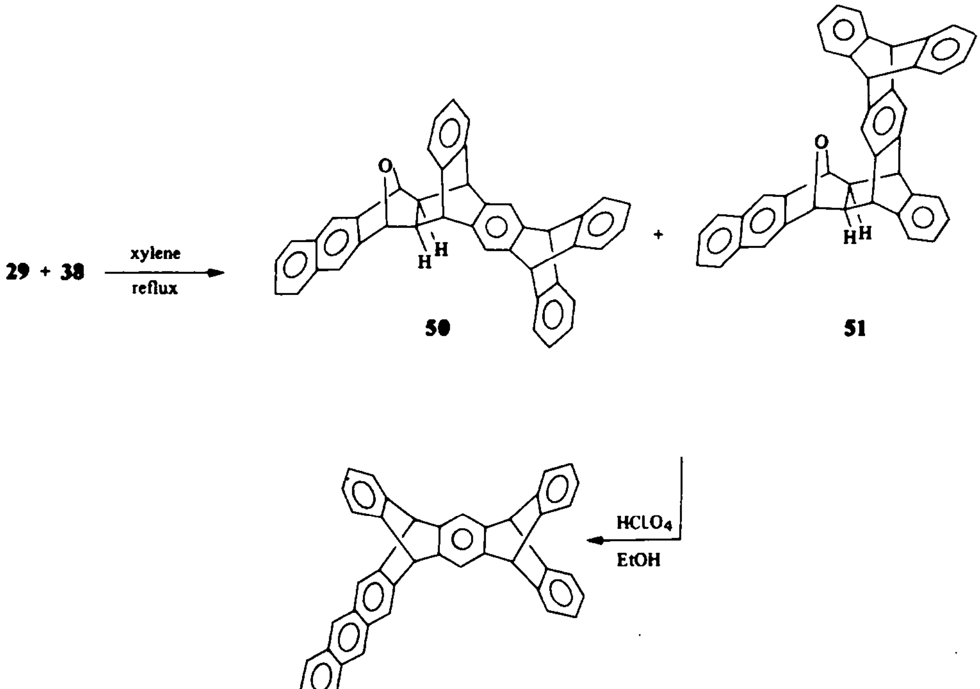
The available synthons can also be used for these syntheses. Treatment of 41 with butyllithium and furan gave adduct 55 in 75% yield. Cycloaddition to anthracene gave 56 (72%) which was dehydrated (66%) to 32. Alternatively, 41 and 40 gave adduct 57 (70%) which could be dehydrogenated quantitatively to 32.

The tetracene analog 34 was prepared starting with synthons 36 and 40. The thermal cycloaddition gave a single adduct 58 (85%). Dehydration was accompanied by double-bond isomerization to give 59 (71%) which was used with 40 again to add the second bicyclo[2.2.2]octane moiety. Compound 60 was formed in 87% yield and dehydrogenated quantitatively giving 34 in four steps and 52% overall yield from 36 and 40.

---

† Work in progress with J. Luo.

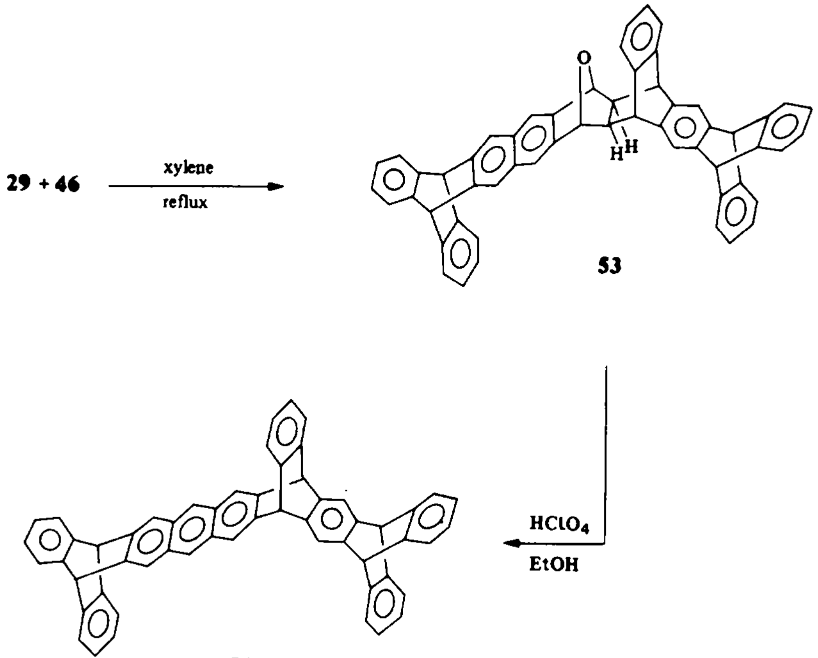
‡ The iptycene nomenclature[11] readily distinguishes between 33 and 52; the former is [1.1.3(b)^{6}.1.1]pentiptycene, whereas the latter is [3(b)^{6}.1.1^{6}.1.1]pentiptycene.



50

51

52



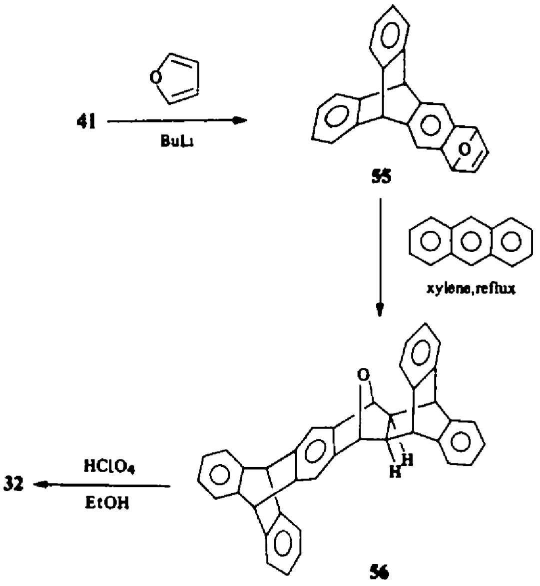
53

54

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, often with very pleasing symmetry features. They also form a useful framework for studying various phenomena in chemistry such as factors which contribute to high melting points and thermal stability, host–guest phenomena, restricted rotation, charge transfer and many others.

In this paper, we have described just a few possible "unnatural" products of this type that are worthy and challenging synthetic targets. The discussion was limited mainly to unsubstituted carbocyclic frameworks, but further elaboration, including heterocycles, etc., is clearly possible. We have described seven synthons (35–41) useful for iptycene synthesis and



illustrated their utility in new syntheses of **29** (three routes), **3**, **32**, **33**, and **34**. We have also demonstrated the versatility of **29** as a synthon in the preparation of higher iptycenes **52** and **54**. All of these compounds originate in just a few steps from readily available materials, i.e. 1,2,4,5-tetrabromobenzene, furan, anthracene, 1,4-dichloro-2-butene, and butyllithium.

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

EXPERIMENTAL

General procedures. NMR spectra (^1H 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 Cary 219 spectrometer. Mass spectra were measured at 70 eV using a Finnigan 4000 spectrometer with the INCOS data system. Very high melting materials were measured on a Hitachi M-80A spectrometer with a direct inlet temp of 300–400° at Ube Industries, Japan. M.ps (Fisher electrothermal or MEL TEMP, modified when necessary for high temp) are uncorrected Anhyd $MgSO_4$ was the drying agent throughout, silica gel for chromatography was 230–400 mesh, and microanalyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, Michigan.

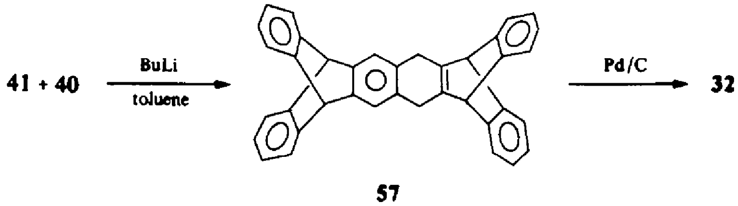
1,2,4,5-Tetrabromobenzene (**35**)

Since this compound is the starting point for several synthons and iptycenes and because we found 1,4-dibromobenzene a better precursor than benzene[23] for large-scale preparation, we give the details here.

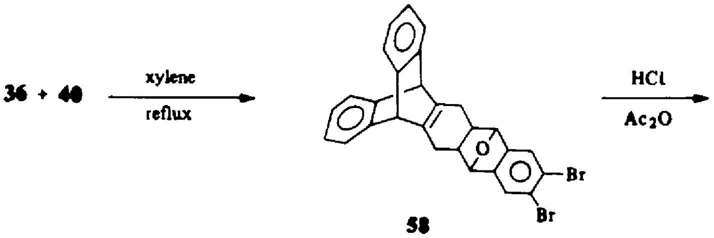
To a soln of 1,4-dibromobenzene (100 g, 0.42 mol) in 400 ml CCl_4 was added 100 ml (2 mol) Br_2, and the mixture was heated at 40° overnight, then at reflux for 12 hr. The cooled mixture was slowly added to stirred, cold 20% Na_2SO_3 (1000 ml). The resulting ppt was filtered, washed with water (100 ml), then MeOH (100 ml) and saved. The combined filtrates were extracted with CH_2Cl_2, and the extracts were washed with water, dried, and evaporated. The residue was combined with the above ppt and recrystallized from toluene (with Norit) to give 138 g (83%) of **35**, m.p. 180–182° (lit.[23] 181°); ^1H-NMR: δ 7.87 (s).

6,7-Dibromo-1,4-dihydronaphthalene-1,4-epoxide (**36**)

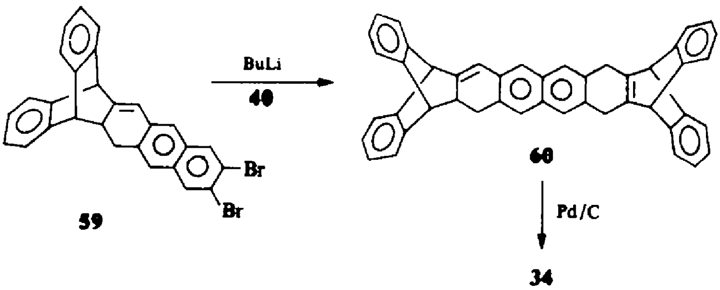
To a stirred soln of **35** (8 g, 20 mmol) and furan (10 ml) in dry toluene (200 ml) at −23° under argon was added n-BuLi (22 mmol in 200 ml hexane) dropwise over 3 hr. After the mixture



57



58



59

slowly came to room temp, MeOH (1 ml) was added, and the mixture was washed with water, dried, and the solvent removed (rotavap). The resulting yellow oily solid was triturated with hexane to give 4.1 g (70%) of **36**, recrystallized from MeOH, 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* (rel. intensity) 302 (9), 276 (19), 193 (100), 113 (46), 87 (21), 63 (25). (Found: C, 39.86; H, 2.07. Calc for $C_{10}H_6Br_2O$: C, 39.78; H, 2.00%.)

2,3-*Dibromonaphthalene from* 36

To an ice-cold suspension of Zn dust (2.0 g) in 50 ml THF under argon was carefully added 2 ml of $TiCl_4$, and the mixture was heated to reflux for 5 min, then cooled to 0° and a soln of **36** (1.0 g, 3.3 mmol) in 20 ml THF was added dropwise. The mixture was refluxed overnight, cooled and poured into 100 ml of cold 10% HCl. The mixture was extracted with CH_2Cl_2 and the extract was washed with water, dried and evaporated. The residue was chromatographed over silica gel using CH_2Cl_2–hexane (1:1) as eluent to give 810 mg (86%) of **37**, m.p. 138–140° (lit.^{25} 139–140°).

11,12 - *Dimethylene* - 9,10 - *dihydro* - 9,10 - *ethanoanthracene* (40)

A mixture of anthracene (5.34 g, 30 mmol) and 1,4-dichloro-2-butene (20 ml, *cis/trans* mixture) was heated in a sealed tube at 190° for 48 hr. The black product was first passed through alumina using CCl_4 as eluent, then chromatographed over silica gel using CH_2Cl_2–hexane (2:1) as eluent to give 8.4 g (96%) of 11,12 - bis - chloromethyl - 9,10 - dihydro - 9,10 - ethanoanthracene **65**, m.p. 145–146° (hexane); ^{1}H-NMR: δ 1.86 (m, 2H), 2.95 (m, 2H), 3.32 (m, 2H), 4.45 (s, 2H), 7.15 (m, 4H), 7.35 (m, 4H); mass spectrum, *m/e* (rel. intensity) 302 (M^+, 13), 229 (3), 215 (14), 202 (19), 189 (7), 178 (100), 165 (5).

To a soln of **65** (3.03 g, 10 mmol) in DMSO (40 ml) and THF (10 ml) was added t-BuOK (3.3 g, 30 mmol) and the dark green soln was stirred overnight, then poured into ice–water (400 ml) and extracted with ether. The organic layer was washed with brine, dried, and the solvents removed. The resulting white solid was recrystallized from hexane to give 2.2 g (95%) of diene **40**, m.p. 156–157° (lit.^{27} 157–157.5°).

2,3-*Dibromotriptycene* (41)

To a stirred soln of **35** (4.0 g, 10 mmol) and anthracene (4.0 g, 22 mmol) in dry toluene (300 ml) at room temp, Ar atmosphere, was slowly added (4 hr) a soln of BuLi (10 mmol in 203.7 ml hexane). The mixture was stirred overnight, quenched with water, extracted with ether, dried and the solvent removed. The residue was dissolved in hot acetone, cooled and filtered to remove the unreacted anthracene. The acetone was removed from the filtrate and the residue was chromatographed over silica gel with cyclohexane as eluent to give 2.6 g (62%) of **41**, m.p. 191–192° (lit.^{12} 188–190°).

5,14[1′,2′]*Benzeno* - 5,14 - *dihydropentacene* (29)

Method A. A soln of **36** (18.12 g, 60 mmol) and anthracene (10.9 g, 61.2 mmol) in xylene (700 ml) was heated at reflux for 4 days. The solvent was evaporated and the residue was recrystallized (THF–MeOH) to give **44** (27.65 g, 96%) as fine off-white crystals, m.p. 265–266°; ^{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, 48.45, 80.82, 123.61, 123.81, 124.17, 125.31, 125.90, 126.17, 128.17, 141.10, 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 **44** (19.2 g, 40 mmol) in EtOH (400 ml) was added dropwise 72% perchloric acid (45 ml) and the soln was heated at reflux (5 hr). The cooled mixture was poured into ice–water (1200 ml). The solid was filtered, washed with MeOH and dried. Recrystallization (THF–MeOH) gave a tan solid which was recrystallized from toluene to give **45** (12.01 g, 65%) as colorless needles, 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, 120.58, 123.84, 125.78, 131.64, 144.02, 155.16 (two peaks absent).

To a stirred soln of **45** (6.93 g, 15 mmol) and furan (60 ml) in dry THF (1200 ml) at −78° under argon was added n-BuLi (17.25 mmol in 300 ml hexane) dropwise over 5 hr. The mixture was allowed to come slowly to room temp, MeOH (2 ml) was added. The mixture was washed with water, dried and evaporated. The residue was recrystallized from MeOH to give **46** (3.89 g, 70%) as light yellow crystals, m.p. 188–190°; ^{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 to reflux and a soln of **46** (4.44 g, 12 mmol) in 100 ml THF was added dropwise (30 min). After 8 hr at reflux, the cooled mixture was poured into dil HCl. The purple mixture was extracted with CH_2Cl_2 and the extract was washed with water and dried. Solvent removal gave a solid which was recrystallized from $CHCl_3$–hexane to give **29** (3.44 g, 81%), m.p. 221–222°;† ^{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). (Found: C, 94.81, H, 5.15. Calc for $C_{28}H_{18}$: C, 94.88; H, 5.12%.)

Method B. A soln of **38** (786 mg, 4.05 mmol) and anthracene (712 mg, 4.0 mmol) in xylene (20 ml) was heated at reflux for 72 hr. The solvent was evaporated and the residue was recrystallized from $CHCl_3$–hexane to give **47** (1.38 g, 93%) as tan crystals, m.p. 280° (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); 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 **47** (744 mg, 2 mmol) and conc HCl (5 ml) in Ac_2O (20 ml) was heated at reflux for 5 hr. The cooled mixture was poured into 100 ml ice–water, and the resulting solid was filtered, dried and chromatographed over silica gel (eluent cyclohexane, then 1:3 benzene–hexane) to give **29** (474 mg, 67%), m.p. 221–222°.

Method C. To a soln of diene **40** (460 mg, 2 mmol) and **37** (572 mg, 2 mmol) in 50 ml dry toluene under argon was added dropwise (30 min) a soln of n-BuLi (5.4 mmol in 12 ml hexane). The mixture was stirred at room temp overnight, then quenched with 1 ml water and stirred (30 min). The mixture was extracted with 50 ml EtOAc–THF (1:1), and the extract was washed with water, dried (Na_2SO_4) and rotavaped. The residue was recrystallized from CH_2Cl_2–hexane to give **48** (576 mg, 81%). Further purification by chromatography on silica gel with CH_2Cl_2–hexane (1:1) gave 520 mg (73%) of pure **48**, m.p. 298–300°; ^{1}H-NMR: δ 3.80 (s, 4H), 4.92 (s, 2H), 6.96 (dd, 4H), 7.34 (m, 6H), 7.58 (s, 2H), 7.70 (m, 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 **48** (356 mg, 1 mmol) in 20 ml xylene containing 50 mg of 10% Pd/C under argon was heated at reflux for 48 hr. The hot soln was filtered and concentrated under reduced pressure to give colorless crystals of **29** (330 mg, 93%), m.p. 220–222°.

Improved synthesis of 3

A mixture of **29** (354 mg, 1 mmol), benzenediazonium-2-carboxylate hydrochloride (185 mg, 1 mmol) and propylene oxide (2 ml) in 10 ml of 1,2-dichloroethane was heated at reflux for 3 hr. Diethyl carbitol (5 ml) was added and the solvents distilled until a head temperature of 150°. Maleic anhydride (110 mg) was added and the mixture refluxed for 15 min. To the

---

† The literature^{22} m.p. of 287–288° appears to be in error since we get the identical m.p. 221–222° via three independent syntheses of **29**.

cooled mixture was added a soln of 0.4 g of KOH in 6 ml of MeOH–water (2 : 1). The mixture was chilled in ice, and the resulting solid was filtered, washed with MeOH–water (4 : 1) and dried. Recrystallization from CCl_4 gave **3** (280 mg, 65%) as colorless needles, m.p. 465° (dec) (lit.[11] 483°); ^{1}H-NMR : δ 5.30 (s, 4H), 6.92 (dd, 8H), 7.28 (dd, 8H), 7.43 (s, 2H).

Improved synthesis of 33

To a soln of diene **40** (5 g, 21 mmol) and **35** (4 g, 10 mmol) in 300 ml toluene under argon at room temp was added dropwise over 1 hr n-BuLi (27 mmol in 60 ml hexane). The white suspension was stirred overnight, then quenched with 5 ml water. The mixture was stirred for 30 min, then poured into 500 ml of ice–water. The resulting ppt was filtered, washed successively with water (50 ml) and ether (20 ml), and recrystallized from 1,2-dichloroethane to give colorless **49** (4.5 g, 84%), m.p. 342° (dec); ^{1}H-NMR : δ 3.46 (s, 8H), 4.80 (s, 4H), 6.80 (m, 8H), 6.88 (s, 2H), 7.36 (m, 8H); mass spectrum, *m/e* (rel. intensity) 534 (M^+, 38), 356 (21), 339 (4), 258 (7), 228 (5), 178 (100).

A soln of **49** (4.5 g) in 300 ml xylene containing 0.5 g 10% Pd/C was heated at reflux for 48 hr. The hot soln was filtered and concentrated to give 3.6 g of 33. The Pd/C residue was extracted (2 × 50 ml) with CH_2Cl_2 to give an additional 700 mg of 33. The combined products were recrystallized from 1,2-dichloroethane to give 4.0 g (90%) of pure **33**, m.p. > 500°. The NMR spectrum was identical with that of known 33.[15]

[3(b)^b.1.1^b.1.1]*Pentiptycene* (5,18 : 7,16[1′,2′ : 1″,2″]*dibenzeno* - 5,7,16,18 - *tetrahydroheptacene*) (**52**)

A soln of **38** (407.4 mg, 2.1 mmol) and **29** (708 mg, 2 mmol) in xylene (20 ml) was heated at reflux for 4 days. Evaporation of the solvent gave a tan solid which was recrystallized from $CHCl_3$–petroleum ether (30–60°) to yield a mixture of **50** and **51** (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 **50** and **51** (548 mg, 1 mmol) in 20 ml ethanol was added 2 ml of 72% perchloric acid and the mixture was heated at reflux for 5 hr. The cooled mixture was poured into 100 ml ice–water, extracted with CH_2Cl_2 and dried. Evaporation of the solvent and chromatography of the crude product over silica gel with benzene–hexane (1 : 2) as eluent gave **52** (217.3 mg, 41%) as colorless crystals which were recrystallized from 1,2-dichloroethane, m.p. > 430°; ^{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); UV (cyclohexane) λ_{max} 374 nm (ε 3590), 355 (5310), 337 (4770), 320 (3125), 295 (20,080), 286 (21,450), 278 (23,520), 261 (36,950); ^{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, *m/e* (rel. intensity) 530 (M^+, 100), 354 (12), 353 (12), 352 (36), 278 (8), 62 (69), 59 (25), 27 (76). (Found : C, 94.77; H, 5.22. Calc for $C_{42}H_{26}$: C, 95.06; H, 4.94%.)

[1.1.3(b,b)^b.1.1^b.1.1]*Heptiptycene* (5,22 : 7,20 : 11,16[1′,2′ : 1″,2″ : 1‴,2‴] - *tribenzeno* - 5,7,11,16,20,22 - *hexahydrononacene*) (**54**)

A soln of **29** (1.77 g, 5 mmol) and **46** (1.887 g, 5.1 mmol) 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 **53** (3.19 g, 88%) as light yellow crystals, m.p. 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 **53** (2.172 g, 3 mmol) in 70 ml EtOH was added dropwise 6 ml of 72% perchloric acid, and the soln was heated at reflux for 5 hr. The cooled mixture was poured into 200 ml ice–water. The resulting solid was extracted with CH_2Cl_2, dried and evaporated to dryness. The crude product was chromatographed over silica gel with benzene–hexane (1 : 2) as eluent to give **54** (1.48 g, 70%) as colorless crystals from toluene, m.p. 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). (Found : C, 94.81; H, 5.19. Calc for $C_{56}H_{34}$: C, 95.15; H, 4.85%.)

[1.1.2(b)^b.1.1]*Pentiptycene* (5,16 : 8,13[1′,2′ : 1″,2″]*dibenzeno* - 5,8,13,16 - *tetrahydrohexacene*) (**32**)

Method A. To a stirred soln of **41** (824 mg, 2 mmol) and furan (5 ml) in 100 ml dry toluene at −23° under argon was added n-BuLi (2 mmol in 50.74 ml hexane) over 2 hr. The mixture was stirred overnight at room temp, quenched with water (1 ml), and extracted with ether. The organic layer was washed with water, dried and evaporated to give a solid residue. Chromatography over silica gel with cyclohexane–CH_2Cl_2 (1 : 2) as eluent gave **55** (0.48 g, 75%) as colorless crystals, m.p. 166–168°; ^{1}H-NMR : δ 5.25 (s, 2H), 5.45 (s, 2H), 6.84 (m, 6H), 7.31 (m, 6H); mass spectrum, *m/e* (rel. intensity) 320 (M^+, 100), 302 (17), 291 (68), 265 (20), 215 (10).

A soln of **55** (400 mg, 1.25 mmol) and anthracene (360 mg, 2 mmol) in 20 ml xylene was heated at reflux for 48 hr. The mixture was concentrated and the residue was chromatographed on silica gel using hexane–CH_2Cl_2 (1 : 2) as eluent to give adduct **56** (450 mg, 72%) as colorless crystals, m.p. > 500°; ^{1}H-NMR : δ 1.80 (m, 2H), 4.64 (s, 2H), 4.20 (m, 2H), 5.28 (s, 2H), 6.8–7.4 (m, 18H).

A mixture of **56** (350 mg, 0.7 mmol) and 4 ml of 72% perchloric acid in 12 ml absolute EtOH was heated at reflux for 3 hr. The cooled soln was poured into 200 ml ice–water and extracted with EtOAc. Combined organic layers were washed successively with water, $NaHCO_3$ aq, water and dried. Removal of the solvents and chromatography over silica gel with hexane–CH_2Cl_2 (1 : 2) as eluent gave **32** (220 mg, 65%) as a colorless powder, m.p. > 500° from 1,2-dichloroethane; ^{1}H-NMR : δ 5.44 (s, 4H), 6.96 (m, 8H), 7.36 (m, 8H), 7.61 (s, 4H); ^{13}C-NMR : δ 53.7, 121.34, 123.5, 125.0, 131.1, 142.2, 144.7; UV (CH_3CN) λ_{max} 376 nm (ε 1800), 356 (3200), 340 (3600), 328 (6970), 320 (6100), 313 (12,000), 269 (83,000), 261 (81,100), 248 (161,800). (Found : C, 94.81; H, 5.14. Calc for $C_{38}H_{24}$: C, 95.00; H, 5.00%.)

Method B. To a stirred soln of diene **40** (1.5 g, 6.5 mmol) and triptycene **41** (2.0 g, 4.8 mmol) in dry toluene (250 ml) under argon at room temp was added n-BuLi (13 mmol in 40 ml hexane) over 1 hr, and the mixture was stirred overnight at room temp, then quenched with 1 ml water, extracted with 1 : 1 EtOAc–THF, washed with water and dried. After solvent removal, chromatography over silica gel using hexane–CH_2Cl_2 (1 : 1) as eluent gave **57** (1.6 g, 70%), m.p. 460° (dec); ^{1}H-NMR : δ 3.52 (s, 4H), 4.83 (s, 2H), 5.30 (s, 2H), 6.92 (m, 8H), 7.10 (s, 2H), 7.36 (m, 8H); mass spectrum, *m/e* (rel. intensity) 534 (M^+, 38), 356 (21), 339 (4), 258 (7), 228 (5), 178 (100).

A soln of **57** (1.5 g, 3.1 mmol) in 250 ml mesitylene containing 450 mg 10% Pd/C was heated at reflux for 48 hr, then worked up as for **33** to give 1.38 g (98%) of **32** whose spectra were identical with those described above.

[1.1.4(b,b,b)^b.1.1]*Pentiptycene* (5,20 : 10,15[1′,2′ : 1″,2″]*dibenzeno* - 5,10,15,20 - *tetrahydrooctacene*) (**34**)

A soln of diene **40** (2.30 g, 10 mmol) and epoxide **36** (3.02 g, 10 mmol) in 50 ml xylene was heated at reflux for 48 hr. The mixture was cooled and the resulting ppt was filtered and recrystallized from toluene to give adduct **58** (4.5 g, 85%), m.p. 286–288°; ^{1}H-NMR : δ 1.75 (m, 2H), 2.20 (m, 2H), 2.83 (m, 2H), 4.75 (s, 2H), 4.88 (s, 2H), 6.90 (m, 4H), 7.20 (m, 4H), 7.42 (s, 2H); mass spectrum, *m/e* (rel. intensity) 532 (M^+, 5), 514 (3), 319 (2), 276 (22), 256 (100), 241 (18), 228 (27), 215 (43), 202 (36), 178 (94).

A mixture of **58** (1.06 g, 2 mmol), conc HCl (6 ml) and Ac_2O (30 ml) was heated at reflux overnight. The cooled mixture was poured into ice-water and extracted with ether. The organic layer was washed with water, dried, evaporated and the residue chromatographed over silica gel using hexane–CH_2Cl_2 (1 : 1) as eluent to give **59** (710 mg, 71%) as a colorless solid, m.p. 251–253° from hexane; ^{1}H-NMR: δ 2.34 (t, 1H), 2.74 (m, 1H), 2.94 (dd, 1H), 4.33 (s, 1H), 4.88 (s, 1H), 6.53 (s, 1H), 7.1–7.33 (m, 12H); mass spectrum, *m/e* (rel. intensity) 514 (M^+, 10), 432 (2), 352 (2), 336 (7), 257 (1), 178 (100).

To a soln of **59** (1.03 g, 2 mmol) and diene **40** (460 mg, 2 mmol) in 200 ml toluene under argon was added dropwise at room temp n-BuLi (6 mmol in 32.4 ml hexane). The mixture was stirred for 4 hr, then quenched with 5 ml water and stirred for 30 min. Water (30 ml) was added, and the resulting ppt was filtered, washed successively with water (2 × 20 ml) and ether (20 ml) and then recrystallized from 1,2-dichloroethane to give **60** (840 mg, 72%), m.p. 380–384° (dec); ^{1}H-NMR: δ 2.14 (t, 1H), 2.56 (m, 1H), 2.81 (dd, 1H), 3.60 (s, 4H), 4.16 (s, 1H), 4.70 (s, 1H), 4.74 (s, 1H), 5.14 (s, 1H), 6.37 (s, 1H), 6.80 (m, 4H), 7.00 (m, 4H), 7.12 (m, 10H), 7.90 (s, 1H), 7.92 (s, 1H).

A soln of **60** (800 mg, 1.37 mmol) in 50 ml mesitylene containing 100 mg 10% Pd/C was heated at reflux for 48 hr. The hot soln was filtered and the Pd/C residue was washed with CH_2Cl_2 (2 × 20 ml). Combined organic layers were evaporated and the residue was recrystallized from 1,2-dichloroethane to give **34** (720 mg, 91%), m.p. > 500°; ^{1}H-NMR (CD_2Cl_2): δ 5.52 (s, 4H), 7.05 (dd, 8H), 7.45 (dd, 8H), 7.84 (s, 4H), 8.41 (s, 4H); ^{13}C-NMR (CD_2Cl_2): δ 53.96, 121.45, 124.15, 125.7, 126.21, 130.67, 130.84, 138.73, 144.43; UV (CH_2Cl_2) λ_{max} 466 nm (ε 6750), 450 (6830), 438 (8540), 412 (5620), 404 (6700), 392 (3520), 382 (4110), 364 (3010), 310 (26,250), 298 (13,520), 284 (7100), 276 (7200). (Found: C, 94.80; H, 5.12. Calc for $C_{46}H_{28}$: C, 95.18; H, 4.82%.)

Acknowledgement—We are indebted to the National Science Foundation (CHE83-19578) and the National Institutes of Health (GM-15997) for partial support of initial phases of this research.

REFERENCES

[1] P. D. Bartlett, M. J. Ryan and S. G. Cohen, *J. Am. Chem. Soc.* **64**, 2649 (1942).

[2] P. D. Bartlett and E. S. Lewis, *Ibid.* **72**, 1005 (1950); P. D. Bartlett and F. D. Greene, *Ibid* **76**, 1088 (1954); G. Wittig and W. Tochtermann, *Justus Liebigs Annln Chem.* **660**, 23 (1962); W. Theilacker and K.-H. Beyer, *Chem. Ber.* **94**, 2968 (1961); A. Streitwieser, Jr., R. A. Caldwell and M. Granger, *J. Am. Chem. Soc.* **86**, 3578 (1964).

[3] G. Wittig and R. Ludwig, *Angew. Chem.* **68**, 40 (1956).

[4] M. Stiles and R. G. Miller, *J. Am. Chem. Soc.* **82**, 3802 (1960); M. Stiles, R. G. Miller and U. Burckhardt, *Ibid* **85**, 1792 (1963); L. Friedman and F. M. Logullo, *Ibid.* **85**, 1549 (1963); L. Friedman and F. M. Logullo, *J. Org. Chem.* **34**, 3087 (1969).

[5] For examples, see: R. W. Hoffman, *Dehydrobenzene and Cycloalkynes*, Table 3.5, entries 107–113, p. 225. Academic Press, New York (1967).

[6] L. F. Fieser, *Organic Experiments*, p. 315. Heath, Boston (1964).

[7] For a review, see: V. R. Skvarchenko, V. K. Shalaev and E. I. Klabunovskii, *Russ. Chem. Rev.* (*Engl. Transl.*) **43**, 951 (1974).

[8] T. Nakazawa and I. Murata, *J. Am. Chem. Soc.* **99**, 1996 (1977); H. Iwamura and K. Makino, *J. Chem. Soc. Chem. Commun.* 720 (1978); I. Murata, *Pure Appl. Chem.* **55**, 323 (1983).

[9] M. Oki, *Topics in Stereochemistry* (Edited by N. L. Allinger, E. L. Eliel and S. H. Wilen), Vol. 14, p. 1. Wiley, New York (1983).

[10] A. Guenzi, C. A. Johnson, F. Cozzi and K. Mislow, *J. Am. Chem. Soc.* **105**, 1438 (1983); Y. Kawada and H. Iwamura, *Ibid.* **105**, 1449 (1983); Y. Kawada, H. Iwamura, Y. Okamoto and H. Yuki, *Tetrahedron Lett.* **24**, 791 (1983); N. Koga and H. Iwamura, *J. Am. Chem. Soc.* **107**, 1426 (1985).

[11] H. Hart, S. Shamouilian and Y. Takehira, *J. Org. Chem.* **46**, 4427 (1981).

[12] V. R. Skvarchenko and V. K. Shalaev, *Dokl. Akad. Nauk SSSR, Ser. Khim.* (*Engl. Transl.*) **216**, 307 (1974).

[13] E. Clar, *Chem. Ber.* **64**, 1676 (1931); W. Theilacker, U. Berger-Bose and K.-H. Beyer, *Ibid.* **93**, 1658 (1960); P. Yates and P. Eaton, *J. Am. Chem. Soc.* **82**, 4436 (1960).

[14] C. F. Huebner, R. T. Puckett, M. Brzechfta and S. L. Schwartz, *Tetrahedron Lett.* 359 (1970); C. F. Huebner, U.S. Patent 3,641,179, 8 Feb. (1972).

[15] H. Hart, N. Raju, M. A. Meador and D. L. Ward, *J. Org. Chem.* **48**, 4357 (1983).

[16] E. Lipczynska-Kochany and H. Iwamura, *Chem. Lett.* 1075 (1982).

[17] G. A. Russell, N. K. Suleman, H. Iwamura and O. W. Webster, *J. Am. Chem. Soc.* **103**, 1560 (1981).

[18] H. Hart and A. Bashir-Hashemi, Paper No. 86 presented at the Organic Division, 190th ACS Meeting, Chicago, Illinois, 8–13 September (1985).

[19] X-ray structures of triptycene and some simple derivatives have been determined: K. Anzenhofer and J. J. deBoer, *Z. Krist.* **131**, 103 (1970); R. G. Hazell, G. S. Paweley and C. E. Lund-Peterson, *J. Cryst. Mol. Struct.* **1**, 319 (1971); K. J. Palmer and D. H. Templeton, *Acta Cryst.* **B24**, 1048 (1968); I. L. Karle and J. A. Estlin, *Z. Krist.* **128**, 371 (1969); N. Sakabe, K. Sakabe, K. Ozeki-Minakata and J. Tanaka, *Acta Cryst.* **B28**, 3441 (1972); W. M. MacIntyre and A. H. Tench, *J. Org. Chem.* **38**, 130 (1973).

[20] Conventional triptycene-derived polymers have already been prepared for similar reasons; for a recent example, see: A. K. Mikitaev, V. V. Korshak, Kh. Kh. Gurdaliev, V. N. Pryadko, V. N. Belousov and K. V. Kalmykov, *Dokl. Akad. Nauk SSSR* (*Engl. Transl.*) **269**, 85 (1983).

[21] Some transition metal complexes of triptycene are known; see, for example, R. L. Pohl and B. R. Willeford, *J. Organomet. Chem.* **23**, C45 (1970); G. A. Moser and M. D. Rausch, *Syn. React. Inorg. Met-Org. Chem.* **4**, 37 (1974). But, in general, this is an understudied area with considerable potential.

[22] M. Sugihashi, R. Kawagita, T. Otsubo, Y. Sakata and S. Misumi, *Bull. Chem. Soc. Japan* **45**, 2836 (1972); T. Hayashi, N. Mataga, Y. Sakata and S. Misumi, *Ibid.* **48**, 416 (1975).

[23] A. Scheufelen, *Justus Liebigs Annln Chem.* **231**, 152 (1885); B. Cox, D. G. Kubler and C. A. Wilson, *J. Chem. Educ.* **54**, 379 (1977).

[24] J. Kenner, W. H. Ritchie and R. L. Wain, *J. Chem. Soc.* 1526 (1937); H. H. Hodgson and D. E. Hathaway, *Ibid.* 841 (1945); B. D. Pearson, *Chem. Ind.* 899 (1960).

[25] [a] A. A. Danish, M. Silverman and Y. A. Tajima, *J. Am. Chem. Soc.* **76**, 6144 (1954); [b] C. S. LeHouillier and G. W. Gribble, *J. Org. Chem.* **48**, 2364 (1983).

[26] C. W. Rees and R. C. Storr, *J. Chem. Soc. C* 765 (1969).

[27] J. S. Meek and R. C. Stacy, *J. Org. Chem.* **26**, 300 (1961); D. N. Butler and R. A. Snow, *Can. J. Chem.* **50**, 795 (1972).

[28] G. C. Johnson and R. G. Bergman, *Tetrahedron Lett.* 2093 (1979), footnote 4.

[29] M. G. Gal'pern, V. K. Shalaev, T. A. Shatsskaya, L. S. Shishkanova, V. R. Skvarchenko and E. A. Luk'yanets, *J. Gen. Chem. U.S.S.R.* (*Engl. Transl.*) **53**, 2346 (1983).

[30] Y. Hosoda, *Senryo Kagaku*, p. 556. Gihodo, Tokyo (1957), this reference is unavailable to us.

[31] H. E. Zimmerman and D. R. Amick, *J. Am. Chem. Soc.* **95**, 3977 (1973); see also: P. C. Hayes and L. A. Paquette, *J. Org. Chem.* **48**, 1257 (1983).