GLC-pure *trans*-**9** (mp 56–58 °C), and a 2.20-g mixture of the two diastereomers. Anal. Calcd for $C_8H_{18}NO_2PS$: C, 43.04; H, 8.13; P, 13.87. Found (mixture of diastereomers): C, 43.09; H, 8.21; P, 13.77.

***cis*- and *trans*-2-Methoxy-3-phenyl-5-*tert*-butyl-1,3,2-oxazaphosphorinane.** A solution of absolute methanol (2.0 g, 62 mmol) and anhydrous triethylamine (5.0 g, 49 mmol) in anhydrous ethyl ether (50 mL) was added slowly to a cooled (0 °C), rapidly stirred solution of 2-chloro-3-phenyl-5-*tert*-butyl-1,3,2-oxazaphosphorinane[3b] (6.0 g, 22 mmol), in anhydrous ethyl ether (100 mL) under a nitrogen atmosphere. The reaction mixture was allowed to warm to room temperature and stirred for 24 h. The triethylamine hydrochloride was filtered off, the volatile materials were removed by rotary evaporation, and the residue was distilled (bp 140–141 °C/1.5 torr) to give 4.0 g of GLC-pure 2-methoxy-3-phenyl-5-*tert*-butyl-1,3,2-oxazaphosphorinane (68% yield): ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.90 (s, 9 H, $C(CH_3)_3$), 1.69–2.10 (m, 1 H, methine H), 3.42 (d, J_{PH} = 12 Hz, 3 H, OCH_3), 3.29–3.82 (m, 2 H, NCH_2), 3.82–4.33 (m, 2 H, OCH_2), 6.78–7.40 (m, 5 H, aromatic); ^{31}P NMR ($CDCl_3$) δ 133.90 and 130.15 (intensity ratio 15:85).

***cis*- and *trans*-2-Methoxy-2-oxo-3-phenyl-5-*tert*-butyl-1,3,2-oxazaphosphorinane, 10.** A solution of N_2O_4/dichloromethane (9 mL of 3.2% wv) was slowly added to a cooled (−70 °C) solution of *cis*- and *trans*-2-methoxy-3-phenyl-5-*tert*-butyl-1,3,2-oxazaphosphorinane (2.7 g, 10 mmol) in anhydrous dichloromethane (80 mL). The reaction mixture was warmed to room temperature, and the solvent was removed in vacuo to give 2.7 g of a yellow oil. A 0.5-g sample of the crude product was chromatographed on silica gel using a gravity column, eluting with ethyl ether to give 150 mg of GLC-pure *cis*-**10** as a colorless oil [^{31}P NMR ($CDCl_3$) δ 1.21; mass spectrum, *m/e* (relative intensity) 283 (33%, M^+), 201 (13%), 200 (100%), 106 (58%), 77 (10%), 42 (13%)] and 150 mg of GLC-pure *trans*-**10** as a colorless oil [^{31}P NMR ($CDCl_3$) δ 2.47; mass spectrum, *m/e* (relative intensity) 283 (31%, M^+), 201 (11%), 200 (100%), 106 (39%), 105 (10%), 77 (11%), 42 (13%).

Similarly, the $POCD_3$ compound was prepared, and the trans isomer was isolated for ^{1}H NMR analysis.

***cis*- and *trans*-2-Methoxy-2-thio-3-phenyl-5-*tert*-butyl-1,3,2-oxazaphosphorinane, 11.** Sulfur (120 mg, 3.7 mmol) was added to a stirred solution of *cis*- and *trans*-2-methoxy-3-phenyl-5-*tert*-butyl-1,3,2-oxazaphosphorinane (1.0 g, 3.7 mmol) in benzene (40 mL). The reaction mixture was stirred at room temperature for 2 h, heated to 40 °C, and stirred for an additional 2 h. The benzene was removed by rotary evaporation to leave 1.09 g of crude product. A small amount of the crude product was distilled (160 °C/0.4 torr) to give an analytically pure mixture (46:54 by GLC analysis) of *cis*- and *trans*-**11**. Anal. Calcd for $C_{14}H_{22}NO_2PS$: C, 56.17; H, 7.41; P, 10.35. Found: C, 56.32; H, 7.73; P, 10.35. A 1.0-g sample of the crude product was chromatograted on a gravity column of silica gel, eluted with ethyl acetate/hexane (1:20), to give 200 mg of GLC-pure *cis*-**11** and 500 mg of GLC-pure *trans*-**11**.

X-ray Single-Crystal Structure Study of 7. Clear, colorless crystals of **7**, suitable for X-ray, diffraction, were obtained by vapor diffusion of a solution of the compound in diethyl ether with *n*-pentane. A well-formed crystal was mounted on a Syntex P$\bar{1}$ auto diffractometer equipped with a scintillation counter and graphite monochromated Mo Kα radiation. The automatic centering, indexing, and least-squares routines were carried out on 15 reflections in the 2θ range 20–25° to obtain the cell dimensions which are given in Table IV. The data were reduced to F_o and $\sigma(F_o)$. Lorentz and polarization factors were applied to all reflections. The θ–2θ scan mode over the range $3.5 \leq 2\theta \leq 50°$ was used to collect the data, all of which were used in the calculations.

The structure was solved by direct methods and refined by full-matrix least-squares techniques.[17] Hydrogen atoms were added to the model in geometrically ideal positions and refined isotropically. Refinement converged at $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.0614$ and $R_w = \sum w^{1/2}|F_o - F_c|/\sum w^{1/2}|F_o| = 0.0634$.

Acknowledgment. This work was supported by a grant (CA11045) from the National Cancer Institute of the Public Health Service.

Registry No. 6, 103752-08-5; **7**, 103752-09-6; *cis*-**8**, 103752-10-9; *trans*-**8**, 103752-04-1; *cis*-**9**, 103752-11-0; *trans*-**9**, 103752-05-2; *cis*-**10**, 103752-12-1; *trans*-**10**, 103752-06-3; *cis*-**11**, 103752-13-2; *trans*-**11**, 103752-07-4; 2-(hydroxymethyl)-2-methylpropylamine, 26734-09-8; 2-chloro-3-phenyl-5,5-dimethyl-1,3,2-oxazaphosphorinane, 103752-14-3; *N*-phenyl-2-(hydroxymethyl)-2-methylpropylamine, 94844-02-7; 2-methoxy-3-phenyl-5,5-dimethyl-1,3,2-oxazaphosphorinane, 103752-15-4; phosphorous oxychloride, 10025-87-3; 2-(hydroxymethyl)-3,3-dimethylbutylamine, 15521-17-2; thiophosphoryl chloride, 3982-91-0; *cis*-2-methoxy-5-*tert*-butyl-1,3,2-oxazaphosphorinane, 103752-16-5; *trans*-2-methoxy-2-phenyl-5-*tert*-butyl-1,3,2-oxazaphosphorinane, 103752-17-6; 2-chloro-3-phenyl-5-*tert*-butyl-1,3,2-phosphorinane, 83096-42-8; methyl phosphorodichloridate, 677-24-7; phosphorous trichloride, 7719-12-2.

Supplementary Material Available: Tables of fractional atomic coordinates and thermal parameters, and hydrogen atom fractional coordinates for **7** (2); tables of structure factor amplitudes for **7** (10 pages). Ordering information is given on any current masthead page.

(17) All calculations were performed with the Shelxtl program system written by G. M. Sheldrick.

Tritriptycene: A D_{3h} C_{62} Hydrocarbon with Three U-Shaped Cavities†

Abdollah Bashir-Hashemi, Harold Hart,* and Donald L. Ward‡

Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48824. *Received January 27, 1986*

Abstract: The first synthesis of tritriptycene **6** (5,7,9,14,16,18,28,33-octahydro-28,33[1′,2′]-benzeno-7,16[2′,3′]-anthraceno-5,18[1′,2′]:9,14[1″,2″]-dibenzenoheptacene) from the readily available pentiptycene **9** in six steps and 11% overall yield is described. Tritriptycene forms a 1:1 crystalline complex with acetone, whose X-ray structure is described. The parallel benzene moieties in **6** are 9.0 Å apart (or 5.5 Å, allowing for the thickness of the π clouds). The carbonyl carbon of the acetone lies near the center of the U-shaped cavity, approximately equidistant (4.5 Å) from the centers of the faces of the four benzene moieties that make up the cavity.

Triptycene (**1**) was first synthesized over 40 years ago by P. D. Bartlett,[1] who prepared it in seven steps and low yield from anthracene and *p*-benzoquinone. Some years later, a one-step synthesis from benzyne and anthracene was developed by Wittig,[2] a discovery that opened up the area of triptycene chemistry.[3]

Despite this substantial history, the considerable potential for extending the rigid triptycene framework to construct larger

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‡ Author to whom inquiries regarding the X-ray structure should be directed.

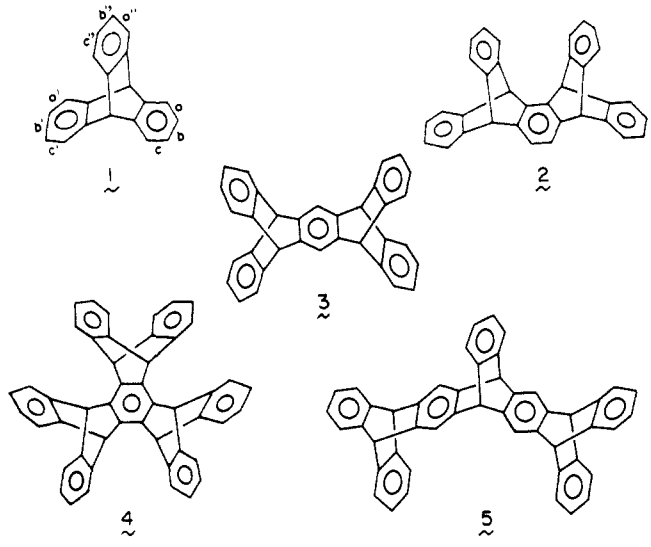
(1) Bartlett, P. D.; Ryan, M. J.; Cohen, S. G. *J. Am. Chem. Soc.* **1942**, *64*, 2649.

(2) Wittig, G.; Ludwig, R. *Angew. Chem.* **1956**, *68*, 40.

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

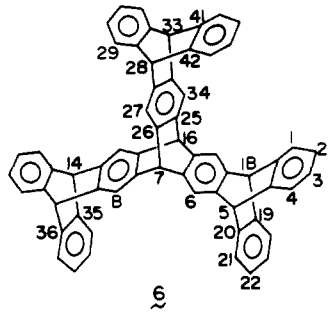
0002-7863/86/1508-6675$01.50/0

theoretically interesting and useful compounds has only recently been realized.[4,5] Triptycene is the parent of a large class of compounds for which we have suggested the generic term "iptycenes".[4] Examples tht have recently been synthesized are the pentiptycenes **2**[6] and **3**[4a,7] and the heptiptycenes **4**[4a,8] and **5**.[4b]

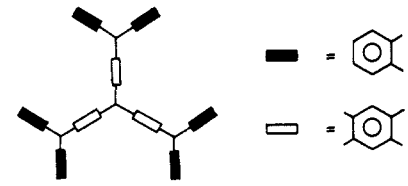


Iptycenes **2** and **3** can be considered as derived from triptycene by fusing a 9,10-anthradiyl moiety to an a or b bond of **1**. Similarly, **4** and **5** are structurally related to **1** by fusing on two such moieties, either at the ac bonds or the bb′ bonds, respectively. A rather large group of first-generation iptycenes (24 structural isomers, or 30 if enantiomers are counted separately) can be developed by fusing up to six 9,10-anthradiyl moieties to the benzenoid bonds of triptycene.[5]

Among the more interesting of these possibilities is the noniptycene **6**, for which we suggest the trivial name *tritriptycene*.[9]

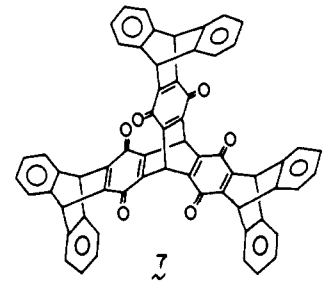


Like triptycene itself, **6** has D_{3h} symmetry, Tritriptycene has three U-shaped cavities symmetric about the three C_2 axes, with parallel face-to-face arene rings at each end of the cavity. These cavities might be expected to accommodate small guest molecules or metallic moieties that could be complexed to the arene rings. A schematic end-on view emphasizes these possibilities. For these reasons, **6** was an attractive synthetic target.



6 (end on view)

The molecular framework of **6** has been constructed.[10] Triptycene tris(quinone)[11] was converted, through reaction with anthracene, to the trisquinone **7**, which was further elaborated to tris-hydroquinone ethers with six side chains extending from the ether oxygens. These products could bind ions in the three molecular cavities. Trisquinone **7** could not, however, be converted

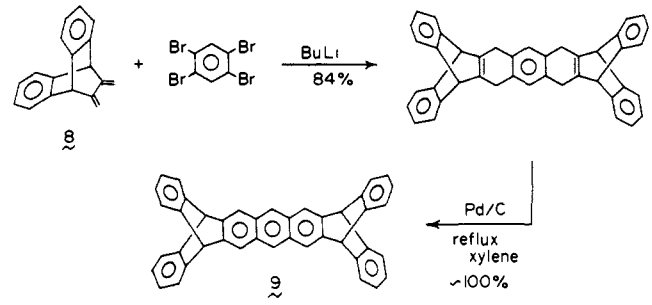


to the parent hydrocarbon **6** which, until now, was unknown.[10]

We describe here the first synthesis of **6** and the X-ray structure of its molecular complex with acetone.

Results and Discussion

We began with pentiptycene **9**,[4b] which already possesses a substantial part of the required framework. An improved two-step synthesis of **9** from diene **8** and 1,2,4,5-tetrabromobenzene in >80% yield was recently described.[5]



In principle, **6** could be prepared directly from **9** in one step by the addition of 2,3-triptycyne. Several attempts to carry out this or analogous model reactions, however, either failed or gave low yields. For example, the reaction of **9** with 2,3-dibromotriptycene[5] and butyllithium at room temperature failed to give **6**. With the thought of proceeding stepwise, **9** was treated with 1,2,4,5-tetrabromobenzene and **1** equiv of butyllithium, but without success. Solubility difficulties may be a factor in these failures. An adduct of **9** was obtained in low yield by using the diazonium carboxylate derived from 4,5-dibromoanthranilic acid,[12] but because of the lengthy route to this 4,5-dibromobenzyne precursor and the low yield, this route was dropped.

We decided to convert **9** to a diene analogous to **8**, with the hope that such a diene could be further elaborated to **6**. Reaction of pentiptycene **9** with 1,4-dichloro-2-butene (sealed tube, 200 °C, 4 days), followed by base-catalyzed elimination, gave the dimethylene compound **11** in 50% overall yield. The structure of **11** was clear from its ^{1}H NMR spectrum. In particular, the downfield aromatic singlets (δ 8.06, 7.81) due to the anthracene

(4) (a) Hart, H.; Shamouilian, S.; Takehira, Y. *J. Org. Chem.* **1981**, *46*, 4427. (b) Hart, H.; Raju, N.; Meador, M. A.; Ward, D. L. *Ibid.* **1983**, *48*, 4357.

(5) Hart, H.; Bashir-Hashemi, A.; Luo, J.; Meador, M. A. *Tetrahedron* **1986**, *42*, 1641.

(6) The ring system has been described,[4a] and we have recently prepared the parent compound: unpublished results with Khalil Shahlai.

(7) Skvarchenko, V. R.; Shalaev, V. K. *Dokl. Akad. Nauk SSSR, Ser. Khim. (Engl. Transl.)* **1974**, *216*, 307.

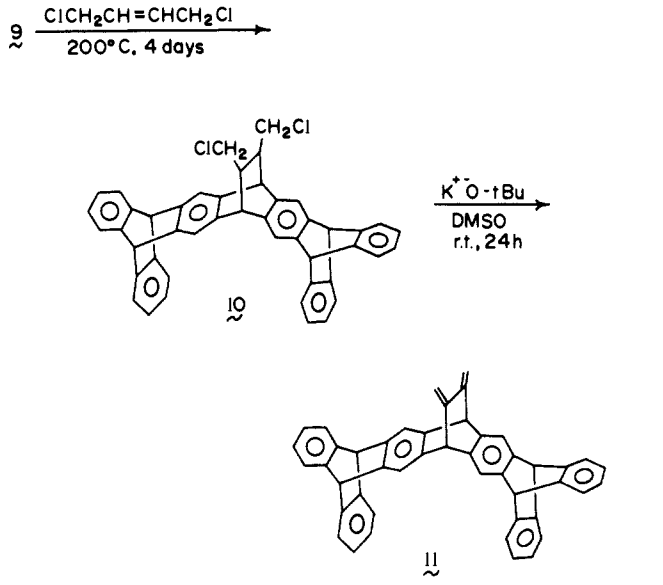
(8) Huebner, C. F.; Puckett, R. T.; Brzechfta, M.; Schwartz, S. L. *Tetrahedron Lett.* **1970**, 359. Huebner, C. F. U.S. Patent 3641179, Feb 8, 1972.

(9) The IUPAC preferred name for **6** is 5,7,9,14,16,18,28,33-octahydro-28,33-*o*-benzeno-7,16[2′,3′]-anthraceno-5,18:9,14-di-*o*-benzenoheptacene, and the current *Chemical Abstracts* name is given in the Abstract. We thank Dr. Loening of Chemical Abstracts Service for these names. When additional tritriptycenes are prepared (there are seven additional isomers possible, not counting enantiomers), it may be useful to refer to **6** as b,b′,b″-tritriptycene.

(10) Webster, O. W., Seminar, Michigan State University, Oct 25, 1984.

(11) Russell, G. A.; Suleman, N. K.; Iwamura, H.; Webster, O. W. *J. Am. Chem. Soc.* **1981**, *103*, 1560.

(12) Wittig, G.; Harle, H.; Knauss, E.; Niethammer, K. *Chem. Ber.* **1960**, *93*, 951.

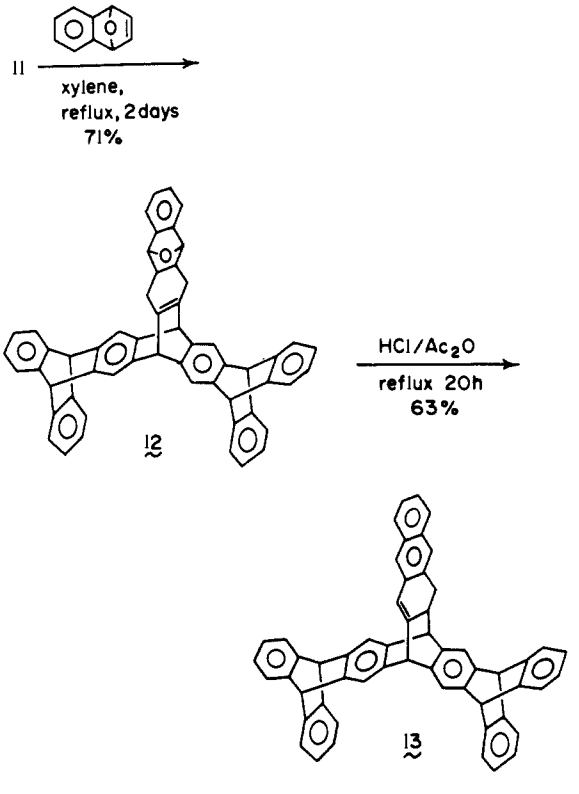


moiety in **9** had disappeared. Instead, the aromatic region in **11** showed a four-proton singlet at δ 7.22 for the protons on the "inner" aromatic rings and four-proton doublets of doublets for the four sets of aromatic protons in the "outer" rings (δ 7.28, 7.20, 6.93, 6.81). Also present was a four-proton singlet at δ 5.28 for the "outer" bridgehead protons and three two-proton singlets at δ 5.11, 4.97, and 4.65 for the remaining bridgehead protons and two sets of vinyl protons.

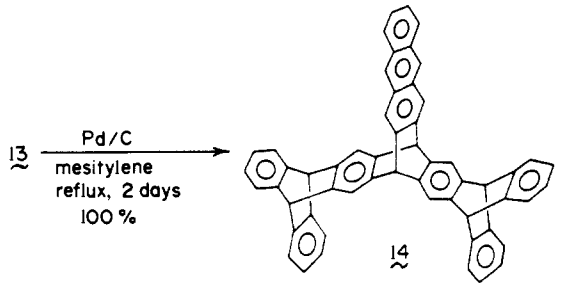
We intended to add the remaining 9,10-anthradiyl moiety to **11** directly. However, model cycloaddition experiments with **8** and either 9,10-dihydro-9,10-ethenoanthracene (dibenzobarrelene) or its 11-chloro derivative failed, and this direct approach was also dropped.

Our next, and successful, strategy was to convert the diene moiety of **11** to an anthracene ring and then add the final ring required for **6** using benzyne. Models showed that the final cycloaddition would be relatively unhindered.

Treatment of **11** with 1,4-dihydronaphthalene 1,4-endoxide[12] gave adduct **12**, which was then dehydrated with acid to give vinylnaphthalene **13**. The stereochemistry of **12** was not determined. The dehydration of **12** was accompanied by double-bond isomerization, as indicated by loss of the symmetry expected in the ^{1}H NMR spectrum. For example, the spectrum contained a triplet at δ 2.18 for the allylic proton and two doublets of doublets at δ 2.53 and 2.81 for the benzylic protons. Also, the "central" bridgehead protons appeared as two singlets at δ 4.11 and 4.64. The remainder of the spectrum was also consistent with a structure in which the double bond had moved into conjugation with the naphthalene moiety.



Compound **13** was quantitatively dehydrogenated to anthracene **14** by reflux with Pd/C in mesitylene for 2 days. The ^{1}H NMR



spectrum of **14** showed two sets of bridgehead protons, with singlets at δ 5.26 (4 H) and 5.32 (2 H). The protons of the anthracene moiety were easily apparent as two-proton singlets at δ 8.12 and 7.70 and two proton doublets of doublets at δ 7.85 and 7.33. In addition, there was a four-proton singlet at δ 7.41 for the "inner" benzenoid ring protons and two eight-proton multiplets centered at δ 7.22 and 6.83 for the "outer" benzenoid ring protons. The ultraviolet spectrum of **14** possessed a wealth of bands typical of an anthracene, with the longest wavelength absorption at 377 nm.

To complete the synthesis of **6**, it remained simply to add benzyne to the anthracene moiety. The benzyne was generated by thermal decomposition of benzenediazonium 2-carboxylate hydrochloride, using propylene oxide to soak up the hydrogen chloride. The desired **6** was obtained in 51% yield. The structure of **6** was clear from its very simple ^{1}H and ^{13}C NMR spectra, as required by the D_{3h} symmetry. Thus, the bridgehead protons appeared as singlets at δ 5.09 and 5.17 in a 2:6 area ratio. The aromatic protons consisted of a six-proton singlet at δ 7.25 for the "inner" benzenoid ring protons and two sets of doublets of doublets centered at δ 6.80 and 7.18, each for one set of 12 "outer" ring protons.

Although **6** possesses 62 carbon atoms, its D_{3h} symmetry requires only eight carbon peaks in the ^{13}C spectrum. In fact, only seven peaks were observed. The bridgehead carbons were apparently overlapped at δ 53.8. In addition, there were six signals for the aromatic carbons as expected.

To summarize, tritriptycene **6** has been synthesized from the readily available **9** in six steps and overall 11% yield. We are currently working on improvements to shorten the synthesis and increase the overall yield.

Tritriptycene shows extraordinary thermal stability. It does not melt or decompose rapidly below 550 °C. It is moderately soluble in chlorinated hydrocarbons such as methylene chloride or 1,2-dichloroethane.

X-ray Structure of Tritriptycene. Tritriptycene **6** crystallized from acetone (1:1 complex) in space group $P6_3/m$ which takes full advantage of the molecular symmetry. This is in contrast with triptycene itself which, although it possesses the same molecular symmetry as **6** (D_{3h}), crystallizes in a space group (P_{222}) in which every atom is unique.[13]

(13) Anzenhofer, K.; deBoer, J. J. *Z. Kristallogr.* **1970**, *131*, 103. Hazell, R. G.; Paweley, G. S.; Lund-Peterson, C. E. *J. Cryst. Mol. Struct.* **1971**, *1*, 319. Neuman, M. A. *Trans. Am. Crystallogr. Assoc.* **1970**, *6*, 111.

(14) The numbering system is shown on structure **6** with the following changes. Because of the mirror plane, only 11 carbon atoms are unique (3, 4, 4a, 5, 5a, 6, 6a, 7, 20, 21, and 22). Reflection atoms are analogously numbered, but primed (for example, C2 on structure **6** becomes C3′, C19 becomes C20′, and so on). The acetone is arbitrarily numbered as O40, C41 for the carbonyl carbon, and C42 and C43 for the methyl carbons. Different orientations for the acetone methyls are designated by a or b.

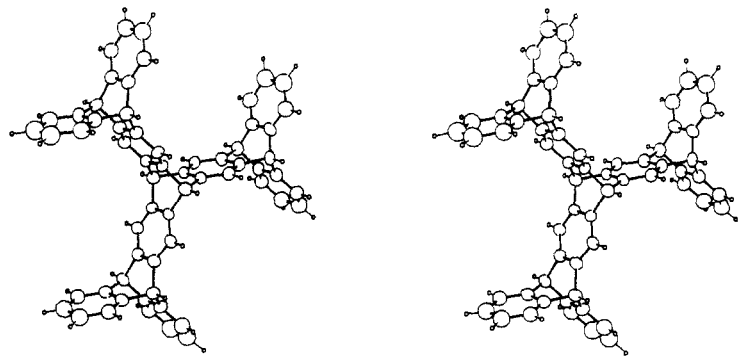


Figure 1. Stereoview of **6** (30% probability ellipsoids).

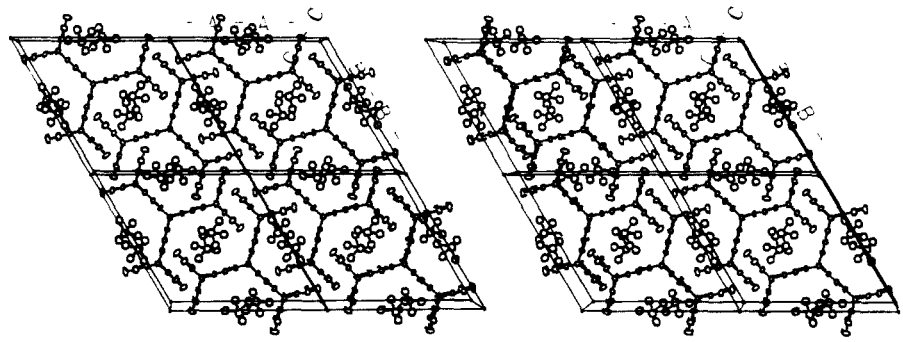


Figure 2. Stereoview of the packing pattern (four unit cells) of the 1:1 **6**/acetone complex (20% probability ellipsoids).

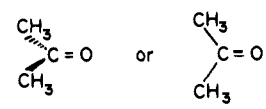
The bond lengths and bond angles observed for **6** agreed closely with the corresponding values reported for triptycene.[13]

Figure 1 shows a stereodrawing of the structure of **6** with the acetone molecules removed. Due to reflection across a mirror plane perpendicular to the *C* axis, the benzene ring planes are all parallel to the *C* axis. The angles between the benzene ring plane normals are very close to the ideal values of 0, 60, and 120°. The distance between nearly parallel benzene rings (for example, the rings containing C20 and C36 in structure **6**) is 9.0 Å (or 5.5 Å if one allows 3.5 Å for the thickness of the π clouds) The point midway between the centers of these two rings lies almost perpendicular to and at almost the same distance from (i.e., 4.5 Å) the other two benzene rings that form the U-shaped cavity (i.e., the rings containing C6 and C8 on structure **6**). Each tritriptycene molecule contains three equivalent cavities of this type. An atom (such as a metal) with orbitals directed toward these rings could interact with all four rings.

The packing diagram, including the acetone guest molecules, is shown in Figure 2. This structure has several interesting features. Each unit cell contains two tritriptycene molecules. One is situated with its central atom (C7) lying on the inversion hexad axis (at $^2/_3$, $^1/_3$, z) and with the molecule bisected by the mirror plane at $z = 0.25$. The other molecule is bisected by the mirror plane at $z = 0.75$, with C7 lying on the other inversion hexad axis (at $^1/_3$, $^2/_3$, z).

The acetone molecules are disordered as regards occupancy. The figure shows acetone molecules in each of the three host cavities, but the 1:1 host:guest ratio requires that there be, on a statistical average, only $^1/_3$ of an acetone at each guest site (or, put another way, on statistical average, only one of the three host cavities is occupied by a guest molecule; of course, some host molecules may not be affiliated with any guests, and others may accommodate two or even three guests).

The acetone molecules are also disordered as regards position. The carbonyl carbon lies in the mirror plane at $z = 0.25$ (or $z = 0.75$) and is essentially at the "center" of the host cavity (i.e., approximately equidistant from the centers of the four benzene rings that define the U-shaped cavity). The positional disorder for the acetone refined to two molecules whose planes are orthogonal to one another but have common positions for the carbonyl carbon and oxygen atoms:



The oxygen and the methyl carbons do *not*, however, lie in the mirror plane but are reflected through that plane. The total model of the acetone contains, therefore, at each guest site (2) $^1/_6$ oxygen, (1) $^1/_3$ carbon, and (8) $^1/_{12}$ methyl carbon atoms. Because of this disorder, with its consequent diminished scattering, the acetones were refined as a rigid group centered on the carbonyl carbon, and hydrogens were not included in the model.

There are no apparent strong binding forces between the tritriptycene and acetone molecules, but the channel nature of the complex is clear from the figure. It remains to be seen whether other complexes can be found in which all three cavities of each host molecule are occupied.

Experimental Section

Dimethylene Compound 11. A mixture of pentiptycene **9**[4b,5] (0.53 g, 1 mmol) and 1,4-dichloro-2-butene (20 mL, cis–trans mixture from Aldrich Chemical Co.) was heated in a sealed tube at 190–200 °C for 4 days. The black reaction mixture was passed over neutral alumina with methylene chloride as eluent and then chromatographed over silica gel using methylene chloride–hexane (2:1) as eluent to give 0.4 g (61%) of crude bis(chloromethyl) adduct **10**. ^{1}H NMR (areas correspond to the sum of the cis and trans products): δ 1.55 (m, 2 H), 2.22 (m, 2 H), 2.71 (t, 2 H), 2.86 (t, 2 H), 3.15 (dd, 2 H), 3.35 (dd, 2 H), 4.18 (s, 2 H), 4.32 (s, 2 H), 5.25 (s, 8 H), 6.85 (m, 8 H), 7.08 (m, 8 H), 7.20 (m, 8 H), 7.26 (s, 8 H), 7.46 (m, 8 H).

To a solution of crude **10** (0.4 g, 0.6 mmol) in 20 mL of dimethyl sulfoxide and 5 mL of tetrahydrofuran was added potassium *tert*-butoxide (400 mg, 3.5 mmol) and the resulting dark green solution was stirred for 24 h, then poured into ice–water, and extracted with ethyl acetate. The organic layer was washed with brine and dried, and the solvents were removed. The residue was chromatographed over silica gel with methylene chloride–hexane (1:1) as eluent to give 310 mg (89%) of pure diene **11**, mp 382–384 °C dec. ^{1}H NMR δ 4.65 (s, 2 H), 4.97 (s, 2 H), 5.11 (s, 2 H), 5.28 (s, 4 H), 6.81 (dd, 4 H), 6.93 (dd, 4 H), 7.20 (dd, 4 H), 7.22 (s, 4 H), 7.28 (dd, 4 H); mass spectrum, *m/e* (relative

intensity) 582 (M^+, 2), 530 (5), 356 (10), 292 (2), 265 (4), 179 (14), 178 (86), 43 (100).

Adduct 12. A mixture of dimethylene compound **11** (140 mg, 0.24 mmol) and 1,4-dihydronaphthalene 1,4-endoxide[12] (35 mg, 0.24 mmol) in 20 mL of xylene was heated at reflux for 2 days. The clear solution was cooled and the resulting precipitate was filtered and washed with hexane (20 mL) to give 125 mg (71%) of **12**, mp >500 °C. ^{1}H NMR δ 1.70 (m, 2 H), 2.10 (m, 2 H), 2.59 (m, 2 H), 4.52 (s, 2 H), 4.81 (s, 2 H), 5.16 (s, 2 H), 5.20 (s, 2 H), 6.75–7.45 (m, 24 H).

Dehydration Product 13. A solution of endoxide **12** (726 mg, 1 mmol) in acetic anhydride (30 mL) and concentrated hydrochloric acid (6 mL) was heated at reflux for 20 h. The clear solution was concentrated (rotavap) and the organic materials were extracted with methylene chloride. The extract was washed with 20% aqueous sodium carbonate (50 mL), then dried, and concentrated and the residue chromatographed over silica gel with methylene chloride–hexane (1:1) as eluent to give 446 mg (63%) of pure **13**, mp >500 °C. ^{1}H NMR δ 2.18 (t, 1 H), 2.53 (dd, 1 H), 2.81 (dd, 1 H), 4.11 (s, 1 H), 4.64 (s, 1 H), 5.27 (s, 2H), 5.29 (s, 2 H), 6.38 (d, 1 H), 6.83 (m, 4 H), 6.90 (m, 4 H), 7.20–7.35 (m, 16 H), 7.38 (m, 2 H).

Heptiptycene 14. A solution of **13** (260 mg, 0.37 mmol) in 20 mL of mesitylene containing 50 mg of 10% Pd/C was heated at reflux for 48 h. The mixture was filtered and the catalyst was washed with methylene chloride (3 × 20 mL). The combined organic layers were concentrated, and the residue was chromatographed over silica gel with methylene chloride–hexane (1:2) as eluent to give 210 mg (83%) of pure **14**, mp 354–356 °C dec. ^{1}H NMR δ 5.26 (s, 4 H), 5.32 (s, 2 H), 6.83 (m, 8 H), 7.22 (m, 8 H), 7.33 (dd, 2 H), 7.41 (s, 4 H), 7.70 (s, 2 H), 7.85 (dd, 2 H), 8.12 (s, 2 H); mass spectraum, *m/e* (relative intensity) 408 (2), 392 (4), 382 (20), 302 (3), 285 (2), 274 (5), 252 (4), 235 (2), 225 (8), 202 (3), 44 (100); UV (CH_2Cl_2) λ_{max} 377 nm (ϵ 7200), 357 (10450), 340 (81000), 324 (4800), 293 (480000).

Tritriptycene 6. A mixture of heptiptycene **14** (176 mg, 0.25 mmol), benzenediazonium 2-carboxylate hydrochloride (185 mg, 1 mmol), and propylene oxide (2 mL) in 20 mL of 1,2-dichloroethane was heated at 40 °C for 4 h and then at reflux for 12 h. The clear solution was cooled and the organic product was extracted with methylene chloride. The combined organic layers were washed with water, dried, and concentrated and the resulting residue was chromatographed over silica gel with hexane–ether (2:1) as eluent to give 96 mg (51%) of **6**, mp >550 °C. ^{1}H NMR δ 5.09 (s, 2 H), 5.17 (s, 6 H), 6.80 (dd, 12 H), 7.18 (dd, 12 H), 7.25 (s, 6 H); ^{13}C NMR δ 53.8, 119.3, 123.2, 124.8, 142.3, 142.7, 145.2; mass spectrum, *m/e* (relative intensity) 782 (M^+, 100), 783 (76), 784 (26); obtained on a JEOL HX-110HF instrument by field desorption from an activated tungsten emitter, acquired for 10 min while ramping the emitter current from 20 to 30 mA at 0.5 mA/s; UV (CH_2Cl_2) λ_{max} 297 nm (ϵ 40000), 289 (31000), 279 (26000), 273 (22500). Anal. Calcd for $C_{62}H_{38}$: C, 95.11; H, 4.89. Found: C, 93.80; H, 5.18.[15]

Attempted Reaction of 9 with 2,3-Triptycyne. To a suspension of **9** (212 mg, 0.4 mmol) and 2,3-dibromotriptycene[5] (200 mg, 0.49 mmol) in 30 mL of toluene and 20 mL of THF at room temperature was slowly added a solution of *n*-butyllithium (0.5 mL, 0.5 mmol) in 5 mL of hexane. The mixture was stirred overnight and then quenched with water (1 mL). Extraction with ether and the usual workup did not afford a product with the expected NMR spectrum (no new bridgehead protons).

A similar result was obtained using 1,2,4,5-tetrabromobenzene in place of the 2,3-dibromotriptycene.

Reaction of 9 with 4,5-Dibromobenzyne. A mixture of **9** (53 mg, 0.1 mmol) and 4,5-dibromobenzenediazonium 2-carboxylate hydrochloride[16] (100 mg, 0.3 mmol) and propylene oxide (2 mL) in 50 mL of 1,2-dichloroethane was heated at reflux under argon for 12 h. The clear solution was cooled and concentrated. The residue was chromatographed (preparative TLC) over silica gel by using hexane/methylene chloride (1:2) as eluent to give 20 mg (26%) of an adduct and 30 mg (57%) of recovered **9**. ^{1}H NMR (adduct) δ 5.12 (s, 4 H), 5.35 (s, 2 H), 6.82 (dd, 8 H), 7.20 (dd, 8 H), 7.28 (s, 4 H), 7.62 (s, 2 H).

Attempted Cycloadditions to 8. A solution of **8** (0.5 g, 2.2 mmol) and 11-chloro-9,10-dihydro-9,10-ethenoanthracene[4a,17] (0.5 g, 2.1 mmol) in 20 mL of xylene was heated at reflux under argon for 3 days. The solvent was evaporated and a ^{1}H NMR spectrum of the residue showed only starting materials. Similar results were obtained with dichlorobenzene (190 °C) or diglyme (220 °C) as the solvent. Reaction in xylene using a sealed tube at 190 °C for 3 days gave only polymeric products. Similar results were obtained using dibenzobarrelene as the dienophile.

Preparation of Crystals for X-ray. Tritriptycene **6** (50 mg) was dissolved in 5 mL of CH_2Cl_2, and 2 mL of acetone was added. After 5 days, during which the solvent slowly evaporated, crystals deposited which were filtered, washed with acetone, and dried. An NMR spectrum showed the expected peaks described for **6** plus a peak at δ 2.16 for the acetone; integration showed that the complex was 1:1 **6**/acetone.

Crystallographic Experiment: Nicolet P3F diffractometer, Mo Kα radiation, cell constants a = 16.646 (3) Å, c = 11.553 (4) Å, v = 2772.3 (12) Å^3, space group = $P6_3/m$, Z = 2, density (calcd) 1.15 g/cm^3, 25 (1) °C, $\theta/2\theta$ scans, 4 deg/min, $2\theta_{max}$ = 50°, 1992 obsd reflections R_1 = 0.096, R_2 = 0.121.

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Registry No. 6, 103960-12-9; **6** (acetone complex, 1:1), 103960-13-0; **8**, 36439-82-4; **9**, 87207-48-5; **9** (tetrahydro derivative), 103960-19-6; *trans*-**10**, 103960-11-8; *cis*-**10**, 103960-14-1; **11**, 103960-15-2; **12**, 103960-16-3; **13**, 103960-17-4; **14**, 103960-18-5; 2-$OHCC_6H_4N_2^+$·Cl^-, 96228-90-9; *cis*-$ClCH_2CH{=}CHCH_2Cl$, 1476-11-5; *trans*-$ClCH_2CH{=}CHCH_2Cl$, 110-57-6; 1,2,4,5-$Br_4C_6H_2$, 636-28-2; 1,2-dihydronaphthalene-1,4-endoxide, 573-57-9.

Supplementary Material Available: The supplemental material contains general procedures; Table I, bond distances; Table II, bond angles; Table III, positional parameters; Table IV, torsional angles; Table V, least-squares planes; Table VI, general temperature factor expressions—U's; and Table VII, root-mean-square amplitudes of thermal vibration (9 pages). Order information is given on any current masthead page.

(15) Despite several attempts, the elemental analysis on **6** always seems to be about 1% low in carbon. Since there is no residue after combustion, it is possible that some oxygen-rich impurity (water?) is present in trace amounts (a 10-mg sample containing 0.1 mg of H_2O, for example, would account for the results). At the suggestion of a referee, we tried benzene as the eluent. Using a Chromatotron for chromatography, we obtained **6** with 88.55% C, 5.42% H. This checks fairly well for **6**·3H_2O (calcd: C, 88.97; H, 5.30). The NMR spectra do not indicate an impurity, and in view of the X-ray structure, there is no doubt about the structure of **6**. Its propensity for binding small molecules is apparent from these results.

(16) Hayashi, T. *Kogyo Kagaku Zasshi* **1956**, *59*, 1093; *Chem. Abstr.* **1958**, *52*, 11779f.

(17) Cristol, S. J.; Hause, N. L. *J. Am. Chem. Soc.* **1952**, *74*, 2193.