

The Albatrossenes: Large, Cleft-Containing, Polyphenyl Polycyclic Aromatic Hydrocarbons

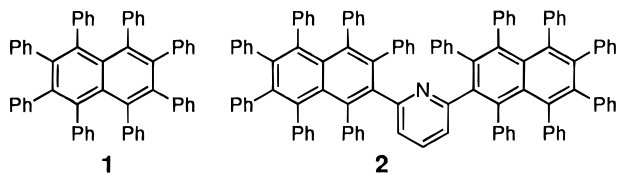
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Abstract: The syntheses and X-ray structures of very large polycyclic aromatic compounds containing clefts defined by polyphenylaryl groups are described. The C_2 -symmetric “albatrossenes” 1,3-bis(heptaphenyl-2-naphthyl)benzene (**7a**) and 1,3-bis(heptaphenyl-1-naphthyl)benzene (**12a**), as well as brominated derivatives, were synthesized by the addition of tetraphenylbenzene to the appropriate polyphenyl biscyclopentadienones. The 2-naphthyl isomers have wide, shallow clefts, and the 1-naphthyl isomers have deep, narrow clefts which were observed to change size dramatically in different crystal environments. In a similar way, 1,3,5-tris(pentaphenylphenyl)benzene (**19**), a D_3 -symmetric molecular propeller with a diameter of 21 Å, and 1,3,5-tris(heptaphenyl-2-naphthyl)benzene (**22**) were prepared by the addition of diphenylacetylene and tetraphenylbenzene, respectively, to a triscyclopentadienone.

Our persistent interest in highly substituted polycyclic aromatic compounds has been focused chiefly on molecules with great strain and unusual geometries, and as a result, the syntheses of these compounds often employ extreme conditions and proceed in low yield.¹ A notable exception is octaphenyl-naphthalene (**1**), which may be prepared in 26% yield in three simple steps from commercially available starting materials.² Octaphenyl-naphthalene is a relatively large molecule ($C_{58}H_{40}$), and for many purposes it may be thought of as a rectangular hydrocarbon slab with approximate dimensions of $14 \text{ \AA} \times 12 \text{ \AA} \times 6 \text{ \AA}$. Compound **1** is extremely stable, and unlike many large polycyclic aromatic compounds, it has good solubility properties. Most significantly, the eight phenyl groups are derived from benzil and 1,3-diphenylacetone, and so numerous modifications of **1** are accessible from the many readily available derivatives of its two simple precursors.



The easy synthesis of **1** and its derivatives permits the construction of large organic compounds containing clefts or cavities defined by more than one octaaryl-naphthalene. We recently reported the synthesis and structure of one such compound, bis(heptaphenyl-2-naphthyl)pyridine (**2**, “albatrossidine”), in which a pyridine nitrogen lies at the bottom of a large shallow cleft formed by the two heptaphenyl-naphthyl “wings”.³ We now report the syntheses and structures of the “albatrossenes”, polycyclic aromatic hydrocarbons containing clefts defined by two polyphenylaryl groups attached to a central benzene ring, as well as several three-winged analogs, which are giant molecular propellers.

[⊗] Abstract published in *Advance ACS Abstracts*, July 15, 1997.

(1) Both extreme geometries and reaction conditions are found in these two examples: (a) Pascal, R. A., Jr.; McMillan, W. D.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 5652–5653. (b) Shibata, K.; Kulkarni, A. A.; Ho, D. M.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 5983–5984.

(2) Qiao, X.; Padula, M. A.; Ho, D. M.; Vogelaar, N. J.; Schutt, C. E.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **1996**, *118*, 741–745.

(3) Tong, L.; Ho, D. M.; Vogelaar, N. J.; Schutt, C. E.; Pascal, R. A., Jr. *Tetrahedron Lett.* **1997**, *38*, 7–10.

Results and Discussion

Syntheses of the Albatrossenes. The syntheses of two-winged, C_2 -symmetric albatrossenes are outlined in Scheme 1. At the outset of this study, the prime targets were the isomeric 1,3-bis(heptaphenyl-2-naphthyl)benzene (**7a**) and 1,3-bis(heptaphenyl-1-naphthyl)benzene (**12a**). These compounds are superficially similar in planar drawings, but molecular mechanics calculations^{4,5} indicated that their shapes would be quite different. Compound **7a** was predicted to have a wide, shallow cleft, while that in **12a** was expected to be deep and narrow, with much greater crowding of the phenyl rings near the center of the molecule.

The key intermediates in the albatrossene syntheses are compounds in which two tetraphenylcyclopentadienone moieties share a common phenyl group. The 3-phenyl group is common in biscyclopentadienone **5a**, the precursor of **7a**. Compound **5a** is a large molecule ($C_{52}H_{34}O_2$), but its preparation requires only the simplest reactions. 1,3-Benzenediacetic acid (**3a**) is converted to the acid chloride and then treated with benzene and aluminum chloride to give crude 1,3-bis(benzoylmethyl)benzene. Without purification, this diketone is oxidized to the highly crystalline, bright yellow tetraketone **4a**, and a double aldol condensation with 2 equiv of 1,3-diphenylacetone gives the biscyclopentadienone **5a**.

We were surprised to find that compound **5a** was unknown. The chemistry of biscyclopentadienones was studied in the 1960s by Ogliaruso et al.,⁶ but for some reason their research focused on the preparation of *para*-linked bistetracyclones such as **13** but not the *meta*-linked **5a**. These authors went on to synthesize 1,4-bis(pentaphenylphenyl)benzene^{6,7} (**14**, the first albatrossene!) by heating **13** with diphenylacetylene, and they

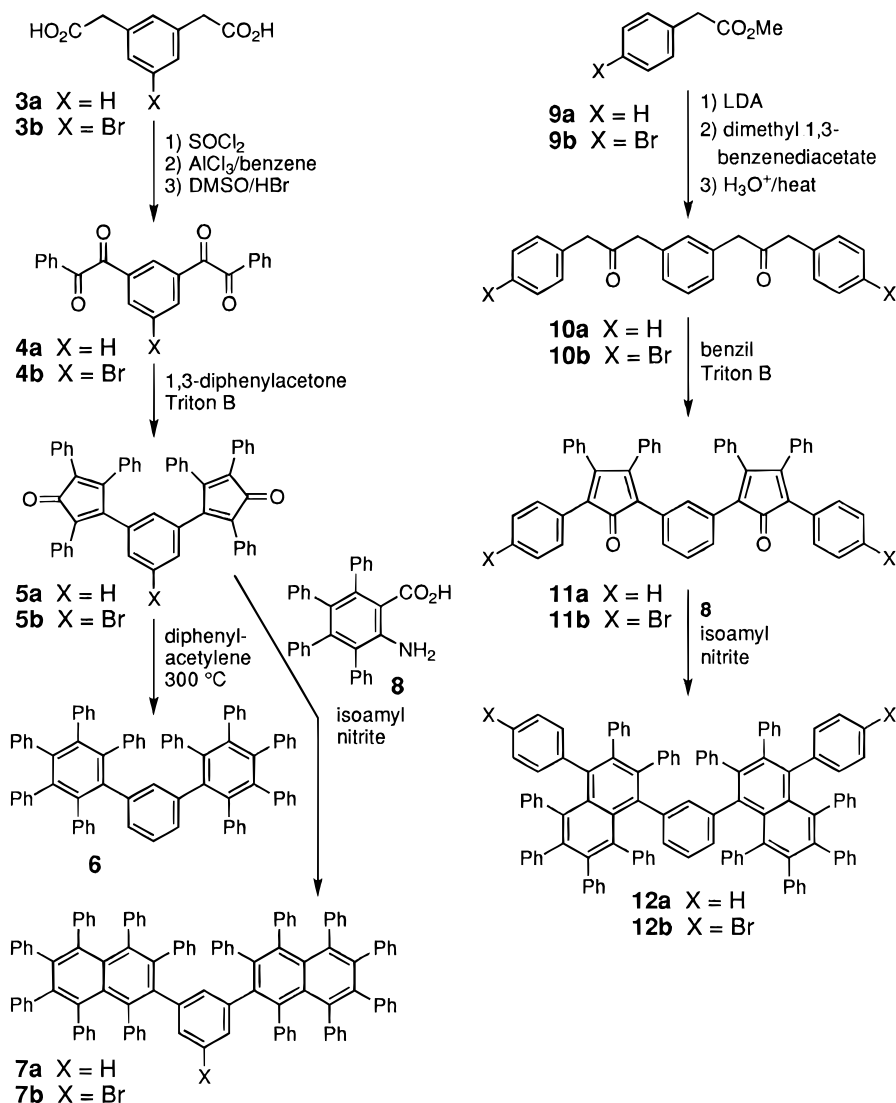
(4) Molecular mechanics calculations were performed by using the SYBYL⁵ force field implemented in the SPARTAN program package (versions 3.0 and 4.1; Wavefunction, Inc., Irvine, CA).

(5) Clark, M.; Cramer, R. D., III; Van Opdenbosch, N. *J. Comput. Chem.* **1989**, *10*, 982–1012.

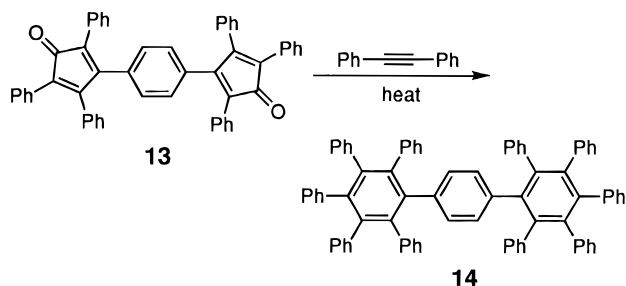
(6) (a) Ogliaruso, M. A.; Shadoff, L. A.; Becker, E. I. *J. Org. Chem.* **1963**, *28*, 2725–2728. (b) Ogliaruso, M. A.; Becker, E. I. *J. Org. Chem.* **1965**, *30*, 3354–3360.

(7) The standard systematic name for compound **14** is 2',3',5',6',2''',3''',5''',6'''-octaphenyl-1,1':4',1''':4''',1''''-quinquephenyl, but this is neither shorter nor more illuminating than “1,4-bis-(pentaphenylphenyl)benzene”, so the latter style of nomenclature will be employed in this paper.

Scheme 1



also prepared a variety of molecules containing two *para*-linked hexaphenylbenzene groups. However, compound **14** and all of their other bis-hexaphenylbenzenes are extended structures without clefts.



In any event, following the lead of Ogliaruso et al., compound **5a** was heated with diphenylacetylene at 300 °C to yield 1,3-bis(pentaphenylphenyl)benzene (**6**) in 86% yield, thus demonstrating **5a**'s suitability as a double Diels–Alder diene. We then diazotized tetraphenylanthranilic acid² (**8**) in the presence of **5a** to yield 1,3-bis(heptaphenyl-2-naphthyl)benzene (**7a**) in a more modest yield of 12%. However, monoaddition products are also isolated from this reaction, as well as unreacted **5a**, and these may be treated again with **8** to give substantially more of the albatrossene **7a**. Finally, in order to facilitate an X-ray

structure determination, compound **7b**, which differs from **7a** only in the presence of a bromine atom on the central ring, was prepared from 5-bromo-1,3-benzenedicarboxylic acid (**3b**) by an essentially identical sequence of reactions. All three polyphenyl aromatics are very stable, crystalline compounds. However, **7a** and **7b** are much more soluble in common organic solvents than **6** (we were unable to record the ¹³C NMR spectrum of **6**), and in general we have found the heptaphenyl-naphthyl-substituted compounds to be more soluble than their pentaphenylphenyl-substituted counterparts, a desirable characteristic of the former.

The synthesis of albatrossene **12a**, in which the naphthyl wings are attached at C-1 (rather than at C-2 as in **7a**), requires a bistetracyclone in which the 2-phenyl group is shared—compound **11a**. In this sequence (Scheme 1), a mixed double Claisen condensation of methyl phenylacetate and dimethyl 1,3-benzenediacetate gave the diketone **10a**, and aldol condensation with 2 equiv of benzil then produced the desired bicyclopentadienone **11a**. In order to generate the hindered **12a**, compound **11a** was treated twice with a slight excess of isoamyl nitrite and **8**, ultimately giving **12a** in 5% yield. Again, in order to facilitate an X-ray structure determination, compound **12b**, which differs from **12a** by the addition of two bromine atoms, was prepared by essentially the same sequence of reactions from methyl *p*-bromophenyl acetate (**9b**). In this case the yield of the final aryne addition was somewhat higher (14%).

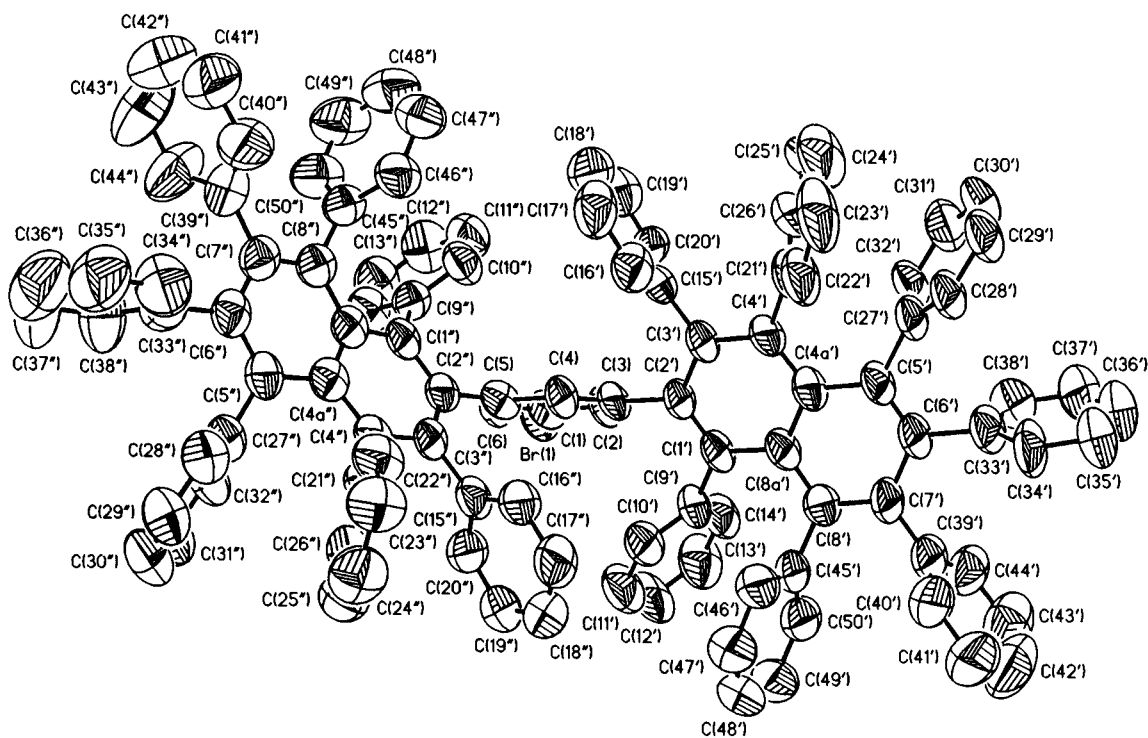


Figure 1. X-ray structure of compound **7b** (from crystal form A). Thermal ellipsoids have been drawn at the 50% probability level, and hydrogens have been omitted for clarity.

The ^1H NMR spectra of the albatrossenes consist entirely of aromatic proton resonances, but it is notable that all but one of these compounds show at least one resonance below δ 6.0, and a few resonances fall at higher field than δ 5.0, suggestive of aryl protons poised above the centers of nearby aromatic rings. In addition, the ^{13}C NMR spectra of the heptaphenylnaphthyl-substituted albatrossenes are exceedingly complex, each with more than 70 badly overlapped resonances. Only 42 lines would be expected for each in the fast exchange limit for all single-bond rotations, so these molecules experience at least some restricted rotation at room temperature and possibly exist as more than one discrete conformation on the NMR time scale. Due to the complexity of the NMR spectra of these molecules, the acquisition of X-ray crystallographic data is essential for confident characterization.

X-ray Structures of the Albatrossenes. Ostensibly single crystals of compounds **7a** and **12a** were easily obtained, and X-ray diffraction data were collected, but neither structure could be solved for several months. For this reason, the brominated compounds **7b** and **12b** were prepared, so that the structures could be solved by heavy atom methods. Two independent structures of **7b** (from two different crystal forms) and one of **12b** were thus determined. At that point, the structure of **12a** was solved, which proved to contain two independent molecules in the asymmetric unit. Thus we have two independent structures of the albatrossenes **7** and three of the albatrossenes **12**, a situation which permits an unusually reliable assessment of the conformations of these complex molecules.

(a) Compound 7b. Single crystals of **7b** were obtained by concentration of a nitrobenzene-toluene solution. Diffraction data were collected on two different crystals from the same crystallization tube. Both crystal A and crystal B were triclinic, space group $P\bar{1}$, but their unit cells had different dimensions and volumes. Each crystal contained one molecule of **7b** in the asymmetric unit, but they differed in the number and types of solvent molecules of crystallization. Because the same tube produced more than one type of crystal, the amount and identity of the included solvent could not be checked by NMR analysis

of a bulk sample. However, the best refinements of the two resulting crystal structures indicated that the composition of crystal A was $(\mathbf{7b})_1(\text{nitrobenzene})_{3.5}(\text{toluene})_1$ and that of crystal B was $(\mathbf{7b})_1(\text{nitrobenzene})_1$.

The structures of **7b** in these two crystals are very similar, so only the molecular structure of **7b** from crystal A, with the crystallographic numbering scheme, is illustrated in Figure 1. The molecules adopt a conformation with approximate C_2 symmetry, and the two heptaphenylnaphthyl wings are oriented *trans* to one another and roughly perpendicular to the central benzene ring. Both of the perphenylnaphthyl groups have substantial end-to-end twists⁸ (crystal A, 23.3° and 19.8°; B, 23.2° and 22.4°). There are many potential rotational degrees of freedom in **7b**, but its conformation is strongly constrained by interactions of the phenyl groups near the center of the molecule. Thus the edges of the C(1')- and C(1'')-phenyls press into the faces of the C(3'')- and C(3')-phenyls, respectively, such that the C(10')- and C(10'')-hydrogens are positioned only 2.74 and 2.80 Å (for crystal A; for crystal B, 2.69 and 2.73 Å) above the mean planes of the C(3'')- and C(3')-phenyl rings. These hydrogen atoms are probably responsible for the most highly upfield resonances in the ^1H NMR spectrum of **7b**.

The packing of the molecules of **7b** in crystals A and B is also remarkably similar. In each case, the molecules pack cleft-to-cleft and back-to-back in layers parallel to the *ac* plane. This packing is illustrated in Figure 2, which also serves to highlight the shallow cleft in compound **7b**. There is scarcely any visible difference in the packing when viewed from this perspective. The principal differences between the structures A and B are in the separation of adjacent *ac* layers and the slippage of these layers relative to one another. The separation of the layers is also illustrated in Figure 2. In crystal A, the centers of the layers are separated by 16.7 Å, while in crystal B, the distance is only 13.3 Å. The net result is that in crystal A the layers of **7b** are

(8) Pascal, R. A., Jr.; McMillan, W. D.; Van Engen, D.; Eason, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4660–4665; see note 17 for the definition of "end-to-end twist".

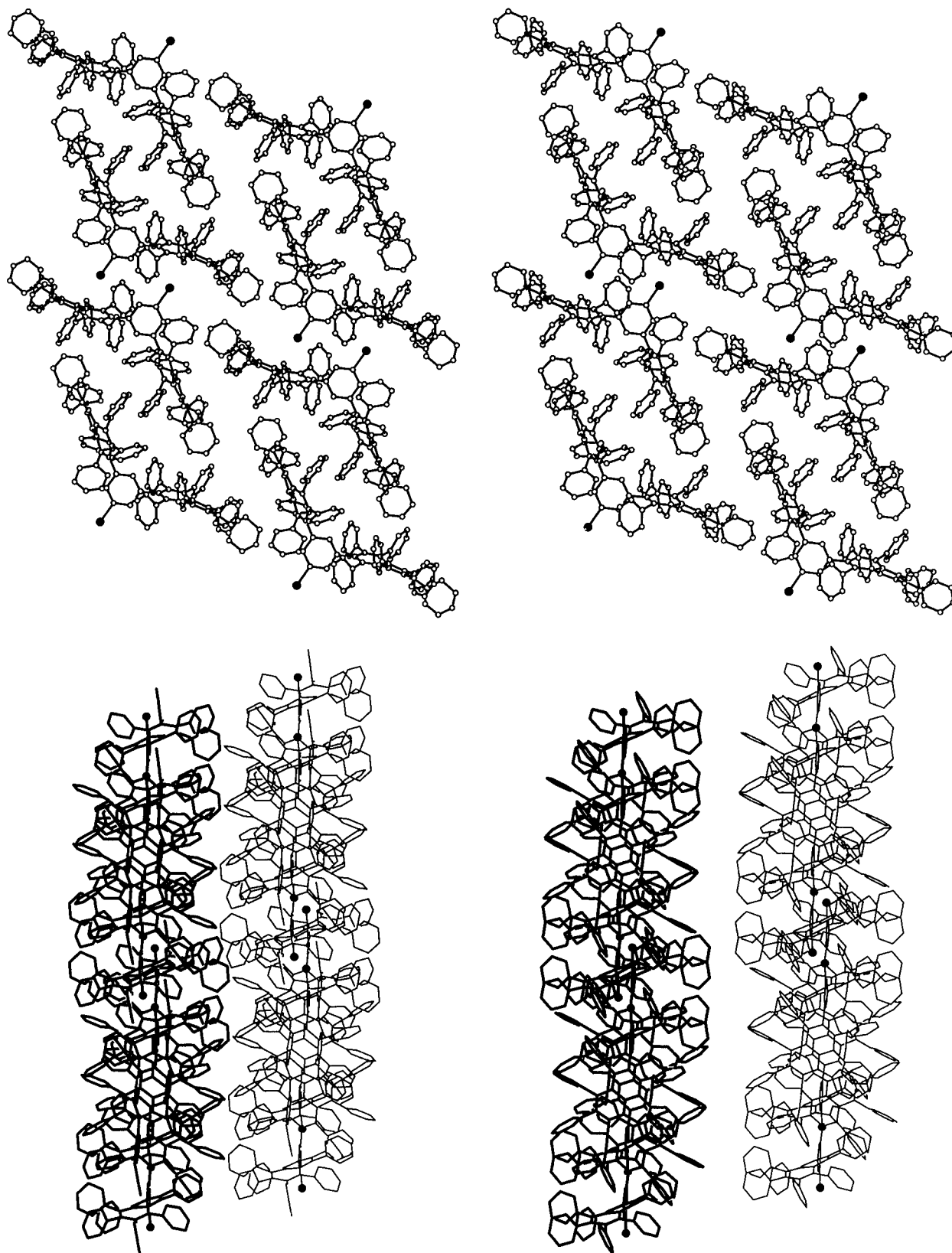


Figure 2. Two views each of the crystal packing of compound **7b** in crystal A (right) and crystal B (left). The top views are perpendicular to the *ac* plane; the bottom views are down the *c* axis. The hydrogen atoms and interstitial solvent molecules have been omitted.

almost entirely separated by solvent molecules, but in crystal B the layers are in van der Waals contact except for a single solvent site. It would seem from these two structures that the nicely interlocked *intralayer* packing of **7b**, which utilizes most of the surface area of these molecules, provides the driving force for crystallization, and that the *interlayer* packing of the edges is almost incidental.

(b) Compounds 12. Crystals of compound **12b** were obtained by concentration of a CH_2Cl_2 – CH_3OH solution. The crystals were trigonal, space group $P3_221$, $Z = 3$; thus each molecule lies on a special position and possesses crystallographic C_2 symmetry. In addition, several solvent molecules are included in the asymmetric unit. The structure of **12b**, with the crystallographic numbering scheme, is illustrated in Figure

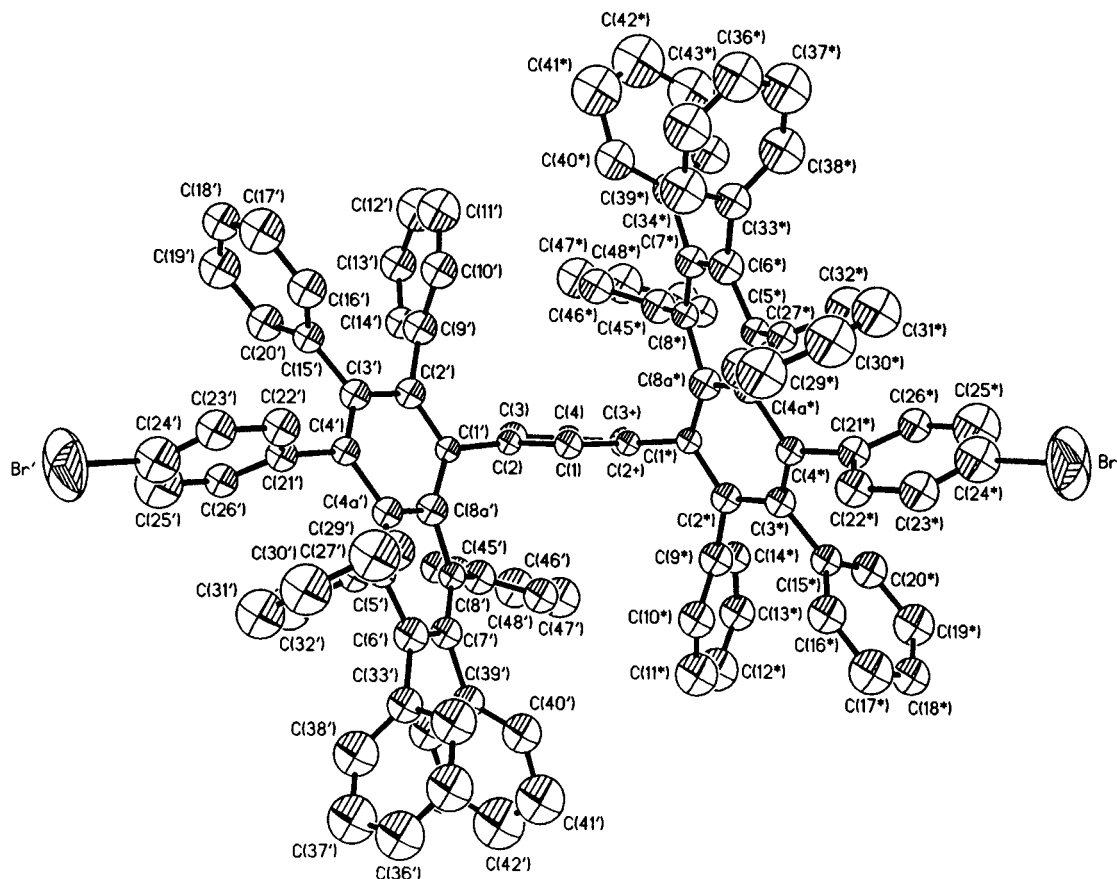


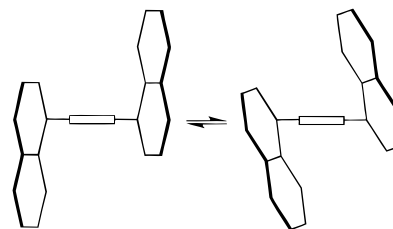
Figure 3. X-ray structure of compound **12b**. Thermal ellipsoids have been drawn at the 50% probability level, and hydrogens have been omitted for clarity.

3 and the cleft is more clearly shown in Figure 5. Once again, the heptaphenyl naphthyl groups are oriented *trans* to one another and roughly perpendicular to the central benzene ring, and the naphthalenes have an end-to-end twist of 20.1° . The cleft in compound **12b** is much more distinctive than in **7b**, and its shape is a direct result of the stacking of the central benzene ring with the two flanking, *peri* phenyl groups on the “bottom” of the molecule. The centroids of these C(8′)-phenyls are forced to within 3.2 \AA of the mean plane of the central ring, and this steric conflict forces the two naphthyl groups to bend toward each other, narrowing and deepening the central cleft. In addition, the edges of the C(8′)-phenyls are forced into the faces of the C(2′)-phenyls of the opposite wing, which also promotes the bending and twisting of the naphthyl groups toward each other.

The cleft of compound **12b** has rough dimensions of $3 \text{ \AA} \times 6 \text{ \AA} \times 11 \text{ \AA}$, and not surprisingly it contains a molecule of solvent in the crystal, in this case a badly disordered methanol. The molecules of **12b** are packed around the crystallographic 3_2 screw axes so that successive clefts form a solvent channel parallel to the *c* axis, and the included solvent is disordered along this channel. Interestingly, $P3_221$ is a chiral space group, so each crystal contains a single enantiomer of **12b**.

Crystals of the parent albatrossene **12a** were obtained by concentration of a $\text{CHCl}_3\text{--CH}_3\text{OH}$ solution, but unlike **12b**, this material contained no solvent of crystallization. The crystals were triclinic, space group $P\bar{1}$, $Z = 4$; thus there are two independent molecules of **12a** in the asymmetric unit. This is a very large structure—220 carbons—so large that conventional direct methods failed to solve it. However, the structure eventually yielded to the X-ray structure solution program CRUNCH,⁹ and once solved, it refined without difficulty.

The structure of one of the two similar molecules of **12a** is illustrated in Figure 4. The most dramatic difference between the structures of **12a** and **12b** is the collapse of the central cleft of the molecule (Figure 5), even though this requires additional distortion of the heptaphenyl naphthyl groups. For example, the four independent naphthyl groups in the structure of **12a** have end-to-end twists of 29.6° , 26.2° , 20.6° , and 35.1° , all of which are greater than the 20.1° twist seen in **12b**. A “Venetian blind” effect due to rotation of the naphthyl substituents relative to the central benzene ring (illustrated below) also narrows the cleft. Thus the dihedral angle between the mean planes of the naphthyl wings in **12b** and the central benzene is 73.0° , which permits a relatively open cleft [$\text{C}(4a')\text{--C}(4a^*) = 7.51 \text{ \AA}$], but the corresponding dihedral angles in **12a** are 58.2° , 58.4° , 58.7° , and 52.9° , which closes the cleft considerably [$\text{C}(4a')\text{--C}(4a^*) = 6.35 \text{ \AA}$].



Interestingly, these large differences in geometry do not reflect great differences in energy. Molecular mechanics calculations⁴

(9) (a) de Gelder, R.; de Graaff, R. A. G.; Schenk, H. *Acta Crystallogr., Sect. A* **1993**, *49*, 287–293. (b) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. The DIRDIF-94 program system. Crystallography Laboratory, University of Nijmegen, The Netherlands, 1994.

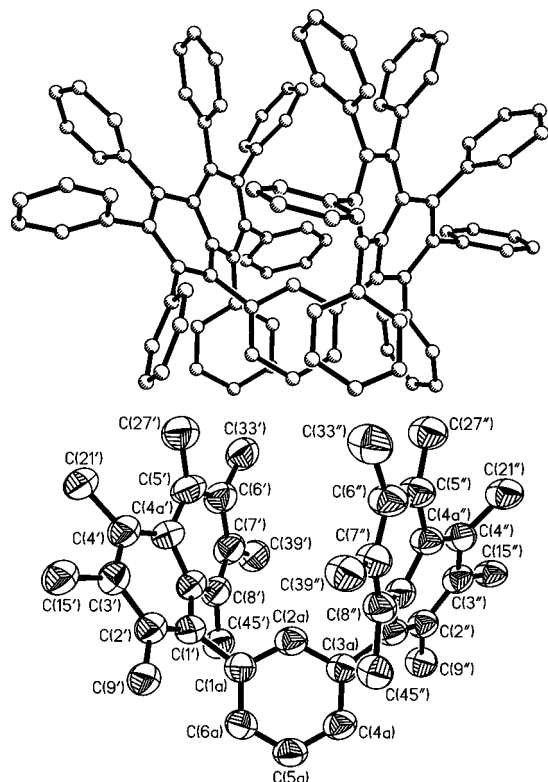


Figure 4. X-ray structure of compound **12a**. In the lower figure, thermal ellipsoids have been drawn at the 50% probability level, and for clarity only the *ipso* carbons of the phenyl substituents have been included.

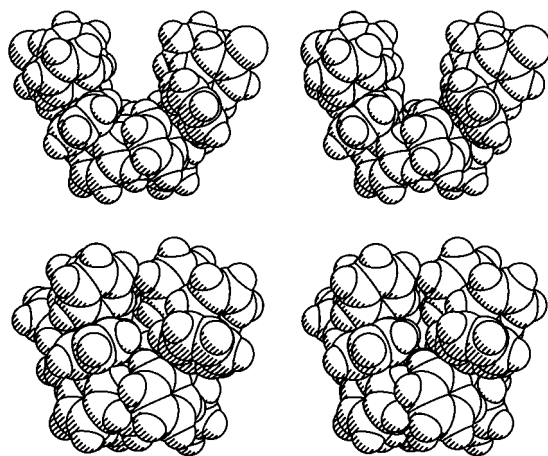


Figure 5. Stereoview of the structures of compounds **12b** (above) and **12a** (below) which illustrates the collapse of the cleft in compound **12a**.

indicate that the “closed-cleft” structure **12a** is less than 1.5 kcal/mol higher in energy than the “open-cleft” **12b**, so the clefts in the compounds **12** can easily “breathe” in order to accommodate guests of various sizes, or none at all.

Conformational Preferences of the Albatrossenes. In each of the albatrossene structures the molecule adopts a conformation of approximate or exact C_2 symmetry where the two polyphenylnaphthyl groups are *trans* to one another. We have no direct evidence for the existence of a second, *cis* conformation of either **7** or **12**, but the *cis* conformation of **7** is calculated to be only about 1 kcal/mol higher in energy than the *trans*-**7** and is very likely to be present in solution. On the other hand, *cis*-**12** is much higher in energy than *trans*-**12**, and it is probably inaccessible. Each of the two observed structures of the compounds **12** represents a distortion of an ideal ground state

conformation produced by relatively modest perturbations of critical bond angles and torsional angles. Because of the large size of the molecule, these distortions translate into very substantial changes in the size and shape of the cleft. We have previously observed a similar phenomenon in the crystal structures of Rebek’s acridine diacid with various guests.¹⁰ With diamine guests (pyrazine and quinoxaline) the cleft in the diacid opened to as much as 8.36 Å, but with chloride ion bound, the cleft narrowed to 6.21 Å, in what had previously been thought to be a relatively rigid molecule.

In the four X-ray structures reported above, there are nine independent octaphenylnaphthalene substructures. Every one of these is twisted, with end-to-end twists ranging from 19.8° to 35.1°, in contrast to the structure of octaphenylnaphthalene (**1**) itself, which adopts a C_i symmetric conformation.² Twisted naphthyl groups were also observed in the structure of albatrossidine **2**,³ so it is tempting to speculate that it is the octaphenylnaphthalene structure which is anomalous! This suggestion is supported by AM1 calculations¹¹ which indicate that the twisted, C_2 symmetric conformation of **1** is 2.6 kcal/mol lower in energy than the crystallographically observed C_i conformation.² However, the octaphenylnaphthalene groups in the albatrossenes are interacting with each other, and this may bias their conformations. A simple derivative of **1** should be prepared (e.g., with one methyl group added) and its structure determined, in order to resolve this issue.

Syntheses of Giant Molecular Propellers. It is apparent from the structures of the albatrossenes described above that it should be possible to place at least three polyphenylaryl groups on a single benzene ring, as in compound **19** (Scheme 2). Conversion of 1,3,5-benzenetriacetic acid¹² (**15**) to the acid chloride followed by Friedel–Crafts acylation with benzene gave triketone **16**, and this was oxidized to the highly crystalline hexaketone **17** with DMSO/HBr. No problem was encountered in the condensation of **17** with diphenylacetone, which afforded triscyclopentadienone **18** in 77% yield, despite the apparent steric hindrance in the product. When **18** was heated with diphenylacetylene at 300 °C, 1,3,5-tris(pentaphenylphenyl)benzene (**19**) was isolated in 35% yield, the high temperature overcoming any steric barrier to this Diels–Alder reaction. In addition, a suitably desymmetrized derivative of **19** was required for dynamic NMR studies, so the hexamethoxy derivative **21** was prepared in 46% yield by heating **18** with bis(4-methoxyphenyl)acetylene (**20**).

Given the synthesis of **19**, it seemed likely that a triple addition of tetraphenylbenzynes to **18** would succeed. Indeed, diazotization of tetraphenylanthranilic acid (**8**) in the presence of **18** gave 1,3,5-tris(heptaphenyl-2-naphthyl)benzene (**22**) in 15% yield. Thus this enormous hydrocarbon ($C_{162}H_{108}$) is prepared in only four steps from **15**, which is itself only one step removed from inexpensive commercial starting materials.¹² Interestingly, our search of the literature indicates that compound **22** is the largest hydrocarbon composed entirely of aromatic rings to have been prepared in pure form.

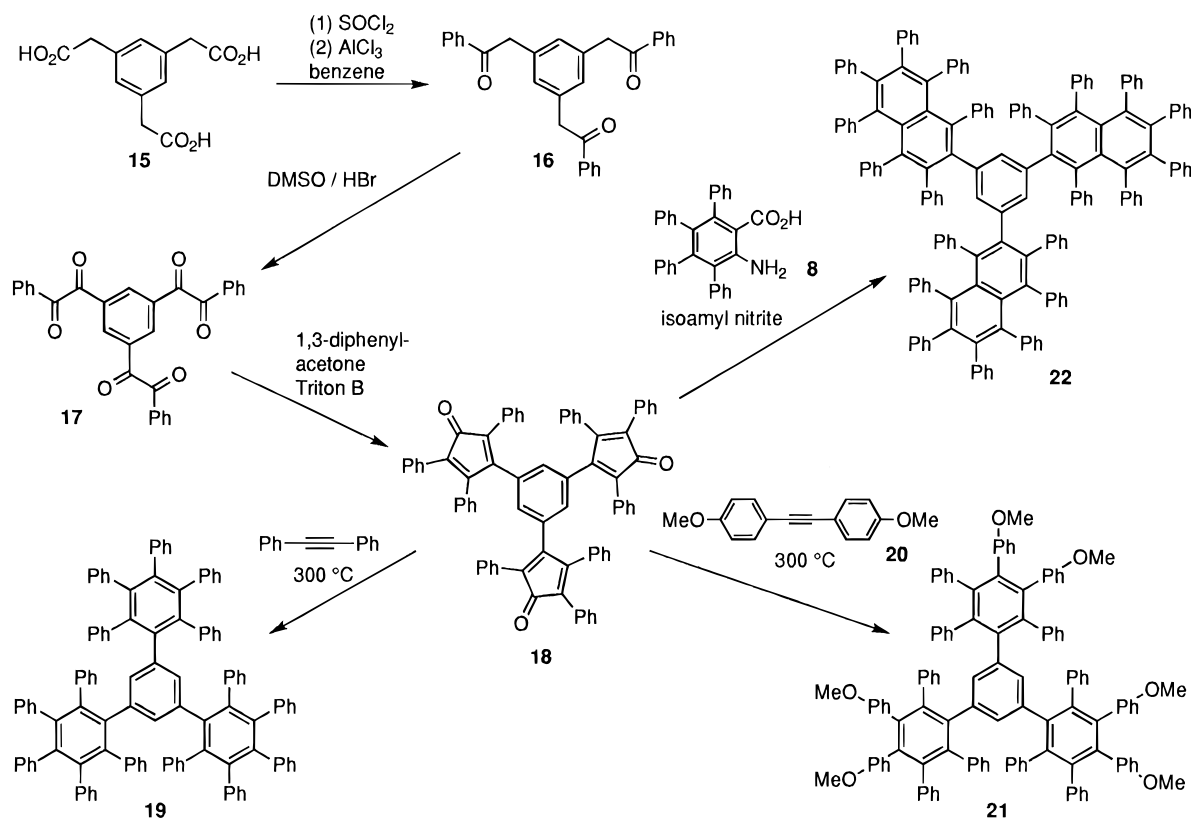
X-ray Structure of Compound 19. Single crystals of **19** were obtained from a $CHCl_3$ – CH_3OH solution, and the initial X-ray measurements indicated that the crystals were monoclinic, space group $P2_1/c$, with either $Z = 8$ or $Z = 12$, that is, either two or three crystallographically independent molecules of **19** in the asymmetric unit. With at least 228 independent carbons

(10) (a) Pascal, R. A., Jr.; Ho, D. M. *J. Am. Chem. Soc.* **1993**, *115*, 8507–8508. (b) Pascal, R. A., Jr.; Ho, D. M. *Tetrahedron* **1994**, *50*, 8559–8568.

(11) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909.

(12) Newman, M. S.; Lowrie, H. S. *J. Am. Chem. Soc.* **1954**, *76*, 6196–6197.

Scheme 2



and some solvent of crystallization (the crystals decomposed upon drying), the structure solution was, similar to that of **12a**, well beyond the scope of conventional direct methods. After a great many trials, the structure was solved by molecular replacement using the SYBYL geometry. The crystal proved to contain two very similar molecules of **19** in the asymmetric unit as well as numerous badly disordered chloroform molecules. Compound **19** ($\text{C}_{114}\text{H}_{78}$) is larger than all but one hydrocarbon listed in the Cambridge Structural Database,¹³ hexakis(2,6-*tert*-butyl-4-biphenyl)ethane ($\text{C}_{122}\text{H}_{150}$),¹⁴ but there are no coordinates deposited for this structure, and its accuracy has been challenged.¹⁵

The structure of one of the molecules of **19** is illustrated in Figures 6 and 7. Compound **19** is a three-bladed propeller 21 Å in diameter, and it adopts a conformation of approximate D_3 symmetry. The blades are tilted with respect to the central benzene ring with dihedral angles ranging from 55.5° to 60.2° , and these blades define three broad, chiral clefts on the sides of the molecule. The faces of the central benzene ring are completely shielded from the external environment by two "tents" formed from the interlocking *o*-phenyl groups on the blades. The tents enclose two cavities, with a volume of approximately 15 \AA^3 each.

Compound **19** is probably the largest D_3 -symmetric molecular propeller to have been prepared. Numerous smaller molecular propellers are known,¹⁶ but the vast majority of these compounds have the structure $(\text{Aryl})_3\text{X}$, where X is a single atom. The static and dynamic stereochemistry of these compounds has been

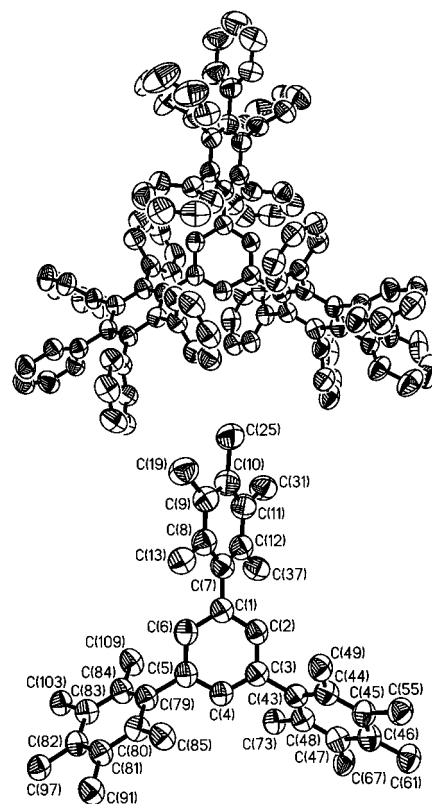


Figure 6. X-ray structure of compound **19**. Thermal ellipsoids have been drawn at the 30% probability level, and hydrogens have been omitted for clarity. In the lower drawing all but the *ipso* carbons of the peripheral phenyl groups have been omitted.

extensively investigated,¹⁷ and some, such as perchlorotriphenylamine,¹⁸ have very high barriers to enantiomerization due

(17) For a thorough discussion of the stereochemistry of molecular propellers, see: Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26–33.

(13) Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 146–153.

(14) Stein, M.; Winter, W.; Rieker, A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 692–694.

(15) Kahr, B.; Van Engen, D.; Mislow, K. *J. Am. Chem. Soc.* **1986**, *108*, 8305–8307.

(16) For a review of helical organic molecules, including molecular propellers, see: Meurer, K. P.; Vögtle, F. *Top. Curr. Chem.* **1985**, *127*, 3–75.

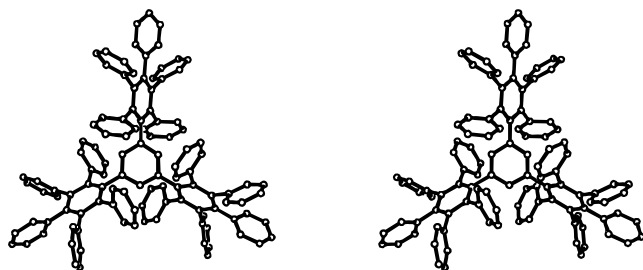


Figure 7. Stereoview of the X-ray structure of compound **19**.

to the high degree of distortion that must accompany the rotation of the propeller blades about the aryl–X bond.^{16–18} The X-ray structure of **19** shows that its central *o*-phenyl groups are tightly packed, but their geometries are not unusual. However, substantial distortions would be required to permit the interconversion of enantiomers of **19**, even though the blades are much further apart in an (aryl)₃benzene propeller than in the classical (aryl)₃X propellers. Resolved enantiomers might show exceptional optical activity, so we investigated the barriers to rotation in compound **19** and its derivatives.

Dynamic NMR Studies. The ¹³C NMR spectrum of **19** contains only 18 sharp resonances (for 114 carbons). So simple a spectrum can result only if **19** has time-averaged *D*_{3h} symmetry or *D*₃ symmetry with rapid rotation of the peripheral phenyl groups. A large barrier might exist for rotation about the central benzene–pentaarylphenyl bonds in **19**, but because of the high symmetry of **19**, it would not be evident in the NMR spectrum. In order to provide an unambiguous NMR “handle” for this rotation in **19** the hexamethoxy derivative **21** was prepared. Four conformers of compound **21** are likely: two enantiomeric pairs of *C*₃ and *C*₁ diastereomers. The enantiomers may interconvert by three 60° rotations about the central benzene–pentaarylphenyl bonds, but interconversion of the *C*₃ and *C*₁ diastereomers requires a full 180° rotation about one of these bonds.¹⁷ If all conformers are of approximately equal energy, then statistical considerations ensure that there will be a 1:3 ratio of *C*₃ and *C*₁ conformers.

The 600 MHz ¹H NMR spectrum of **21** at room temperature shows five methyl resonances: an upfield group of three very close resonances in a 1:2:1 ratio and a downfield group of two resonances, separated by 1.6 Hz, in a 2:2 ratio. One of the latter pair is slightly broader and is probably due to the superposition of two separate resonances. This is the expected pattern if the 60° rotations are fast at room temperature, so the resolution of compound **19** into pure enantiomers will be impossible at normal temperatures. A variable temperature NMR experiment conducted at 500 MHz in toluene-*d*₈ showed coalescence of the downfield resonances at 60 °C, corresponding to a ΔG_c^\ddagger of 18.9 kcal/mol for the 180° rotation of the pentaarylphenyl groups.^{19,20} Thus all possible single-bond rotations appear to be accessible for compound **19** and **21** on the laboratory time scale at room temperature.

In contrast to that of **19**, the ¹³C NMR spectrum of **22** contains more than 70 badly overlapping lines; 40 resonances would be expected in the fast exchange limit of all single bond rotations, so there is also restricted rotation in this compound. It is probable that **22** exists as a mixture of *C*₃ (all *cis* naphthyls)

and *C*₁ (one *trans* naphthyl) conformers, and their interconversion is slow. When the ¹³C NMR spectrum of **22** was recorded at 140 °C in 1,1,2,2-tetrachloroethane-*d*₂, some resonances coalesced, particularly in a region near δ 130, but the spectrum still contained at least 60 sharp lines. This indicates that rotation of the heptaphenyl-naphthyl groups remains slow at 140 °C and that the barrier to rotation is above 20 kcal/mol; however, we have been unable to achieve a chromatographic separation of the diastereomeric *C*₃ and *C*₁ isomers, so the barrier is likely to be below 26 kcal/mol.

Conclusions

The results presented herein show that very large aromatic hydrocarbons with well-defined conformations need not be difficult to prepare. Polyphenyl polycyclic aromatic compounds have excellent solubility properties, and they are very stable. Moreover, the polyphenylaryl groups have large surface areas which can be used to create molecular clefts, and it is not necessary to restrict these structures to simple hydrocarbons. Their highly modular syntheses use only simple reactions that are tolerant of many functional groups and permit the introduction of a wide variety of substituents on the peripheral phenyls.

The albatrossenes are akin to several polycyclic aromatic systems of current interest. Most closely related are the *C*₂-symmetric 2,6-dinaphthylbenzoic acids that Siegel and co-workers have proposed for use as chiral complexing agents or catalysts.²¹ Compound **12** also calls to mind Zimmerman’s “molecular tweezers”,²² which are forged from anthracene subunits. The albatrossenes share the merits of these smaller compounds but have a much greater surface area for interaction with various guests. The three-bladed propellers **19** and **22**, in addition to their kinship with many smaller propeller structures,^{16,17} are reminiscent of aromatic dendrimers,^{23,24} but the propellers are more densely substituted. The present chemistry is simple enough that true dendrimers might be prepared with similar reactions. For example, the triscyclopentadienone **18** could be treated with 3 equiv of a bisalkyne, and the remaining alkynes in the product could be treated with more **18**, etc., to create an ever-branching structure. Since only Diels–Alder reactions would be used in such a dendrimer synthesis, a great variety of functional groups might be easily incorporated.

Thus the chemistry of polyphenyl polycyclic aromatic compounds should be rich, and the preparation of highly functionalized versions of these molecules is now in progress.

Experimental Section

An “aqueous workup” is the washing of an organic extract with aqueous Na₂CO₃ or NaHCO₃, and then water, followed by drying over Na₂SO₄.

5-Bromo-1,3-benzenediactic acid (3b). A solution of 1,3-bis-(bromomethyl)-5-bromobenzene²⁵ (11.0 g, 32 mmol) and KCN (7.6 g, 117 mmol) in methanol (73 mL) and H₂O (22 mL) was heated to reflux for 5 h. After cooling, ether was added, and after an aqueous workup,

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(19) For $\Delta\nu = 1.3$ Hz in the absence of exchange at 500 MHz, the Gutowsky–Holm approximation¹⁶ gives $k_c = 2.9$ s⁻¹ for coalescence at 60 °C (333 K); if a transmission coefficient of 1 is assumed for the Eyring equation, $\Delta G_c^\ddagger = 18.9$ kcal/mol.¹⁶

(20) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic: New York, 1982; pp 77–123.

concentration gave a brown solid. This solid (the dicyano derivative) was heated in a solution of concentrated H₂SO₄ (60 mL), water (60 mL), and acetic acid (50 mL) at reflux overnight. The reaction mixture was concentrated on a rotary evaporator and extracted with ether, and after an aqueous workup, concentration gave the crude solid diacid, which was recrystallized once from benzene–methanol to give pure **3b** (3.4 g, 12.5 mmol, 39%), mp 176–177 °C: ¹H NMR (DMSO-*d*₆) δ 3.58 (s, 4 H), 7.15 (s, 1 H), 7.37 (s, 2 H), 12.45 (br s, 1 H); ¹³C NMR (DMSO-*d*₆) δ 39.9, 121.1, 129.7, 130.5, 137.5, 172.2 (6 of 6 expected resonances observed); MS, *m/z* 272 (M⁺ [⁷⁹Br], 40), 227 (M – CO₂H, 44), 199 (54), 182 (100); exact mass 271.9661, calcd for C₁₀H₉⁷⁹BrO₄ 271.9685.

1,3-Bis(phenylglyoxalyl)benzene (4a). A mixture of 1,3-benzene-diacetic acid (2.0 g, 10 mmol), thionyl chloride (7 mL), and benzene (27 mL) was heated at reflux for 1 h. The excess thionyl chloride and benzene were distilled away, and then benzene (40 mL) was added. While cooling in an ice bath, AlCl₃ (3.4 g, 25 mmol) was added slowly. The ice bath was then removed and the temperature was maintained at 50 °C overnight. The resulting mixture was poured onto a mixture of ice (15 g) and concentrated HCl (5 mL), and after an aqueous workup, concentration gave crude 1,3-bis(benzoylmethyl)benzene (1.5 g). This material was heated at reflux overnight with a mixture of 48% HBr (5 mL) and DMSO (80 mL). Concentrated HCl (20 mL) and water (200 mL) were added, and the mixture was heated for another 1.5 h. After cooling to room temperature, the mixture was extracted three times with ether, and the combined organics were then washed four times with water in order to remove residual DMSO. After drying over Na₂SO₄, concentration gave tetraketone **4a** as a light yellow solid (1.47 g, 4.3 mmol, 43%), mp 84–86 °C (lit.²⁶ mp 98–99.5 °C): ¹H NMR (CDCl₃) δ 7.54 (t, *J* = 8 Hz, 4 H), 7.69 (m, 3 H), 7.99 (dd, *J* = 8 Hz, 1.5 Hz, 4 H), 8.25 (dd, *J* = 8 Hz, 1.5 Hz, 2 H), 8.60 (t, *J* = 1.5 Hz, 1 H); ¹³C NMR (CDCl₃) δ 129.3, 130.0, 130.2, 130.9, 132.7, 133.9, 135.4, 135.7, 192.8, 193.5 (10 of 10 expected resonances observed); MS, *m/z* 342 (M⁺, 2), 324 (M – H₂O, 4), 237 (M – C₆H₅CO, 20), 105 (C₆H₅CO⁺, 100).

5-Bromo-1,3-bis(phenylglyoxalyl)benzene (4b). Diacid **3b** (1.5 g, 5.5 mmol) was carried through the procedure described for the preparation of **4a**, to give compound **4b** (1.73 g, 4.1 mmol, 75%). An analytical sample was obtained by recrystallization from CHCl₃–ethanol, mp 128–129.5 °C: ¹H NMR (CDCl₃) δ 7.55 (t, *J* = 8 Hz, 4 H), 7.71 (t, *J* = 8 Hz, 2 H), 7.98 (dd, *J* = 8 Hz, 1.5 Hz, 4 H), 8.37 (d, *J* = 1.5 Hz, 2 H), 8.50 (t, *J* = 1.5 Hz, 1 H); ¹³C NMR (CDCl₃) δ 124.0, 129.1, 130.1, 132.2, 135.2, 135.4, 137.9, 190.9, 192.3 (9 of 10 expected resonances observed); MS, *m/z* 422 (M⁺ [⁸¹Br], 0.1), 420 (M⁺ [⁷⁹Br], 0.1), 317 (M – C₆H₅CO, 4), 315 (M – C₆H₅CO, 4), 105 (C₆H₅CO⁺, 100); exact mass 419.9988 (calcd for C₂₂H₁₃⁷⁹BrO₄ 419.9998).

1,3-Bis(3-oxo-2,4,5-triphenylcyclopenta-1,4-dienyl)benzene (5a). A 40% solution of Triton B in methanol (0.23 mL, 0.5 mmol) was added to a solution of 1,3-diphenylacetone (0.55 g, 2.5 mmol) and compound **4a** (0.35 g, 1.0 mmol) in refluxing butanol (20 mL), and the heating was continued for 1 h. At this time another equal portion of 40% Triton B solution was added, and heating was continued for an additional 2.5 h. After cooling in an ice bath, a dark solid was collected by filtration and washed with cold ethanol, to leave deep purple **5a** (0.40 g, 0.58 mmol, 58%), mp 308–311 °C: ¹H NMR (CDCl₃) δ 6.63 (s, 1 H), 6.81 (t, *J* = 7.5 Hz, 6 H), 7.02–7.27 (m, 27 H); ¹³C NMR (CDCl₃) δ 125.2, 125.8, 127.7, 127.9, 128.1, 128.2, 128.4, 128.8, 129.1, 129.2, 129.3, 129.4, 130.2, 130.4, 130.5, 130.7, 133.0, 134.2, 154.0, 154.3, 200.3 (21 of 21 expected resonances observed); MS, *m/z* 690 (M⁺, 70), 662 (M – CO, 30), 456 (33), 278 (100); exact mass 690.2567, calcd for C₅₂H₃₄O₂ 690.2559.

5-Bromo-1,3-bis(3-oxo-2,4,5-triphenylcyclopenta-1,4-dienyl)benzene (5b). Tetraketone **4b** (0.52 g, 1.24 mmol) was carried through the procedure described for the preparation of **5a**, to give deep purple **5b** (0.14 g, 0.18 mmol 15%), mp 125.5–128 °C: ¹H NMR (CDCl₃) δ 6.5–7.5 (m); MS, *m/z* 770 (M⁺ [⁸¹Br], 100) 742 (M – CO, 33), 178 (75).

1,3-Bis(pentaphenylphenyl)benzene (6). Compound **5a** (63 mg, 0.09 mmol) and diphenylacetylene (380 mg, 2.1 mmol) were mixed in a screw-capped Pyrex tube and heated to 300 °C in a metal bath for 2

h. After cooling, the mixture was slurried with acetone, and the resulting crystalline solid was collected to give pure compound **6** (76 mg, 0.077 mmol, 86%) which exhibited a single component upon TLC analysis (*R_f* 0.46, silica gel GF, 9:1 hexanes–ethyl acetate), mp > 350 °C: ¹H NMR (CDCl₃) δ 6.15 (d, *J* = 7 Hz, 4 H), 6.26 (m, 3 H), 6.67–7.00 (m, 47 H); FAB MS, *m/z* 991 (M⁺ [¹³C], 100), 938 (6), 926 (10), 914 (6), 898 (8), 854 (13), 837 (9), 807 (20).

1,3-Bis(heptaphenyl-2-naphthyl)benzene (7a). Biscyclopentadienone **5a** (0.15 g, 0.22 mmol) in 1,2-dichloroethane (5 mL) was heated to reflux under argon. A solution of isoamyl nitrite (0.1 mL) in 1,2-dichloroethane (7 mL) was added, followed by the addition of 3,4,5,6-tetraphenylanthranilic acid² (0.20 g, 0.45 mmol) in 1,2-dichloroethane (7 mL) over 0.5 h. Heating was continued for 3 h; then ethanol (4 mL) and 1 N NaOH (6 mL) were added to terminate the reaction. Chloroform was added, and after an aqueous workup, the resulting material was chromatographed on a column of silica gel (solvent, 98:2 hexanes–ethyl acetate), and the fractions containing **7a**, which exhibited *R_f* 0.12 upon TLC analysis (silica gel GF, same solvent), were combined and concentrated to give pure **7a** as a colorless solid (37 mg, 0.026 mmol, 12%), mp 237–239 °C: ¹H NMR (CDCl₃) δ 4.99 (d, *J* = 7 Hz, 1 H), 5.82 (m, 2 H), 5.91 (m, 3 H), 6.15 (d, *J* = 7 Hz, 2 H), 6.23 (m, 3 H), 6.32–6.92 (m, 63 H); ¹³C NMR (CDCl₃) >70 resonances observed; 42 are expected in the fast exchange limit of all single-bond rotations; FAB MS, *m/z* 1395 (M⁺ [¹³C], 100), 1318 (M – C₆H₅, 10).

5-Bromo-1,3-bis(heptaphenyl-2-naphthyl)benzene (7b). Biscyclopentadienone **5b** (0.13 g, 0.17 mmol) was carried through the procedure described for the preparation of **7a**, to give compound **7b** as a colorless solid (25 mg, 0.017 mmol, 10%), mp 170–173 °C: ¹H NMR (CDCl₃) δ 5.02 (br s, 1 H), 5.83 (br s, 1 H), 5.86 (br s, 1 H), 5.96 (d, *J* = 1.5 Hz, 1 H), 6.01 (d, *J* = 1.5 Hz, 1 H), 6.13–6.98 (m, 68 H); ¹³C NMR (CDCl₃) >80 resonances observed; 42 are expected in the fast exchange limit; FAB MS, *m/z* 1475 (M⁺ [¹³C]⁸¹Br], 88), 1396 (19), 1126 (24), 917 (31), 776 (63), 307 (100).

1,3-Bis(3-phenyl-2-oxopropyl)benzene (10a). Ether (40 mL) and *n*-butyllithium (8.0 mL, 2.5 M solution in hexanes) were added under argon to a 3-necked round-bottomed flask and cooled in an ice bath. Diisopropylamine (2.1 mL) was added, and the solution was stirred for 30 min. At this time, methyl phenylacetate (2.0 mL) was added dropwise, and the mixture was stirred for 15 min. Dimethyl 1,3-benzenediacetate (1.47 g, 6.6 mmol) was added dropwise, and precipitation was immediately observed. The ice bath was removed, and the mixture was stirred overnight. The reaction mixture was poured into 1 N HCl (100 mL), and the layers were separated. The aqueous layer was extracted twice with ether, and the combined organic layers were washed with water and dried over Na₂SO₄. The solvent was removed, and the residue was heated with 6 N HCl (15 mL) and acetic acid (100 mL) at reflux for 7 h. The solvent was removed again and the residue extracted with ether, and after an aqueous workup, the material was chromatographed on silica gel (solvent, 9:1 hexanes–ethyl acetate). The fractions containing the desired product, which exhibits *R_f* 0.11 upon TLC analysis (same solvent), were combined and concentrated to give pure **10a** (285 mg, 0.83 mmol, 13% yield), mp 54–55 °C: ¹H NMR (CDCl₃) δ 3.55 (s, 4 H), 3.57 (s, 4 H), 6.78 (t, *J* = 1.5 Hz, 1 H), 6.91 (dd, *J* = 7.5 Hz, 1.5 Hz, 2 H), 7.01 (dd, *J* = 7.5 Hz, 2 Hz, 4 H), 7.08–7.21 (m, 7 H); ¹³C NMR (CDCl₃) δ 48.8, 49.2, 127.0, 128.2, 128.7, 128.9, 129.5, 130.7, 133.9, 134.4, 205.4 (11 of 11 expected resonances observed); MS, *m/z* 342 (M⁺, 19), 223 (M – C₆H₅CH₂O, 24), 91 (C₆H₅CH₂⁺, 100); exact mass 342.1621, calcd for C₂₄H₂₂O₂ 342.1620.

1,3-Bis[3-(4-bromophenyl)-2-oxopropyl]benzene (10b). Methyl *p*-bromophenylacetate (**9b**, 2.5 g, 11 mmol) was carried through the same procedure described for the preparation of **10a** to give compound **10b** (527 mg, 1.05 mmol, 9%), mp 129.5–131 °C: ¹H NMR (CDCl₃) δ 3.67 (s, 4 H), 3.69 (s, 4 H), 6.90 (s, 1 H), 6.99 (d, *J* = 8 Hz, 4 H), 7.05 (d, *J* = 8 Hz, 2 H), 7.25 (t, *J* = 8 Hz, 1 H), 7.42 (d, *J* = 8 Hz, 4 H); ¹³C NMR (CDCl₃) δ 48.6, 49.3, 48.6, 121.4, 129.4, 130.9, 131.4, 132.0, 133.0, 134.4, 204.8 (11 of 11 expected peaks observed); MS, *m/z* 500 (M⁺ [⁷⁹Br⁸¹Br], 19), 303 and 301 (M – BrC₆H₄CH₂CO, 95), 169 (100); exact mass 499.9817, calcd for C₂₄H₂₀⁷⁹Br⁸¹BrO₂ 499.9810.

1,3-Bis(2-oxo-3,4,5-triphenylcyclopenta-1,4-dienyl)benzene (11a). A 40% solution of Triton B in methanol (0.4 mL, 0.8 mmol) was added

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to a solution of compound **10a** (0.35 g, 1.0 mmol) and benzil (0.53 g, 2.5 mmol) in boiling butanol (15 mL), and the solution was heated at reflux for 1 h. At this time another equal portion of 40% Triton B was added, and heating was continued for an additional 2.5 h. The reaction mixture was then concentrated to leave a purple residue. This material was chromatographed on silica gel (solvent, 95:5 hexanes–ethyl acetate) to give a purple solid which proved to be the monocyclopentadienone. This material (125 mg) was heated with benzil (41 mg, 0.2 mmol) in ethanol (10 mL) at reflux. A solution of 10% KOH in ethanol (0.25 mL) was added, and the solution was heated at reflux for 3 h. After cooling in the freezer, compound **11a** precipitated as deep purple crystals (92 mg, 0.13 mmol 13% yield), mp 284–286 °C: $^1\text{H NMR}$ (CDCl_3) δ 6.80 (m, 7 H), 6.94–7.12 (m, 27 H); $^{13}\text{C NMR}$ (CDCl_3) δ 125.40, 125.43, 127.5, 128.1, 128.6, 129.4, 129.5, 130.3, 130.86, 130.93, 133.1, 133.3, 154.5, 154.7, 200.2 (15 of 21 expected peaks observed); FAB MS, m/z 690 (M^+ , 28), 307 (100).

1,3-Bis[2-oxo-3-(4-bromophenyl)-4,5-diphenylcyclopenta-1,4-dienyl]benzene (11b). A 40% solution of Triton B in methanol (0.3 mL, 0.6 mmol) was added to a solution of compound **10b** (0.30 g, 0.6 mmol) and benzil (0.31 g, 1.5 mmol) in boiling butanol (10 mL), and the solution was heated at reflux for 1 h. At this time another equal portion of 40% Triton B was added, and heating was continued for an additional 2 h. After cooling in an ice bath, a dark solid was collected by filtration and washed with cold ethanol, leaving deep purple compound **11b** (0.35 g, 0.41 mmol, 69%), mp 273.0–276.5 °C: $^1\text{H NMR}$ (CDCl_3) δ 6.87 (t, $J = 7$ Hz, 8 H), 7.01–7.35 (m, 24 H); $^{13}\text{C NMR}$ (CDCl_3) δ 122.0, 124.3, 125.6, 128.0, 128.2, 128.4, 128.8, 128.9, 129.0, 129.3, 129.5, 130.0, 130.8, 131.4, 131.9, 132.2, 132.9, 133.1, 154.8, 155.2, 199.8 (21 of 21 expected peaks observed); MS, m/z 848 (M^+ [$^{79}\text{Br}^{81}\text{Br}$], 97), 820 ($\text{M} - \text{CO}$, 15), 358 (20), 356 (21), 278 (54), 98 (100).

1,3-Bis(heptaphenyl-1-naphthyl)benzene (12a). Biscyclopentadienone **11a** (92 mg, 0.13 mmol) in 1,2-dichloroethane (5 mL) was heated to reflux under argon. A solution of isoamyl nitrite (0.07 mL) in 1,2-dichloroethane (5 mL) was added, followed by the slow addition of 3,4,5,6-tetraphenylanthranilic acid (**8**, 132 mg, 0.30 mmol) in 1,2-dichloroethane (5 mL) over 0.5 h, and heating was continued for 8 h. The treatment with isoamyl nitrite and **8** was then repeated, and heating was continued overnight. Ethanol (4 mL) and 1 N NaOH (6 mL) were added to terminate the reaction. CHCl_3 was then added, and after an aqueous workup, the resulting material was chromatographed on a column of silica gel (solvent, 95:5 hexanes–ethyl acetate). The fractions containing the desired product, which exhibited R_f 0.14 upon TLC analysis (silica gel GF, 2.5% ethyl acetate in hexanes), were combined and concentrated to give pure **12a** as a pale yellow solid (9 mg, 0.006 mmol, 5%); mp >350 °C (darkens at 293 °C). $^1\text{H NMR}$ (CDCl_3) δ 4.97 (br s, 1 H), 5.28 (br s, 1 H), 5.38 (t, $J = 8$ Hz, 1 H), 5.80 (d, $J = 8$ Hz, 2 H), 6.11 (br s, 2 H), 6.22 (s, 1 H), 6.32 (m, 4 H), 6.41 (br s, 1 H), 6.51–7.25 (m, 62 H). FAB MS, m/z 1395 (M^+ [$^{13}\text{C}_1$], 100), 1318 ($\text{M} + \text{H} - \text{C}_6\text{H}_5$, 10), 659 ($[\text{M} + \text{H} - \text{C}_6\text{H}_5]^{2+}$, 27).

1,3-Bis[2,3,5,6,7,8-hexaphenyl-4-(4-bromophenyl)-1-naphthyl]benzene (12b). Biscyclopentadienone **11b** (250 mg, 0.29 mmol) was carried through the same procedure used for the preparation of **12a**, to give compound **12b** as a pale yellow solid (63 mg, 0.041 mmol, 14%), mp >350 °C: $^1\text{H NMR}$ (CDCl_3) δ 4.91 (br s, 1 H), 5.27 (br s, 1 H), 5.37 (t, $J = 8$ Hz, 1 H), 5.80 (dd, $J = 8$ Hz, 1 Hz, 2 H), 6.09 (br d, $J = 6$ Hz, 2 H), 6.19 (s, 1 H), 6.21–7.17 (m, 64 H); $^{13}\text{C NMR}$ (CDCl_3) δ 119.1, 125.0–134.5 (broad, overlapping resonances), 135.8, 137.0, 137.4, 138.0, 139.1, 139.2, 139.91, 139.98, 140.03, 141.2, 140.4, 140.6, 140.7, 140.8, 141.3, 141.9, 142.0; FAB MS, m/z 1553 (M^+ [$^{13}\text{C}_1^{81}\text{Br}^{79}\text{Br}$], 100).

1,3,5-Tris(benzoylmethyl)benzene (16). 1,3,5-Benzenetriacetic acid¹² (**15**, 1.5 g, 5.95 mmol), thionyl chloride (5 mL), and benzene (15 mL) were heated to reflux for 1.5 h. The excess thionyl chloride and benzene were distilled away, and then benzene (40 mL) was added. While cooling in an ice bath, AlCl_3 (3.4 g, 25 mmol) was added slowly. The ice bath was then removed, and the temperature was maintained at 50 °C overnight. The resulting mixture was poured onto a mixture of ice (20 g) and concentrated HCl (5 mL), and after an aqueous workup, concentration to dryness and recrystallization of the residue from CHCl_3 gave light yellow crystals of **16** (2.14 g, 4.95 mmol, 83%),

mp 101–103 °C: $^1\text{H NMR}$ (CDCl_3) δ 4.23 (s, 6 H), 7.08 (s, 3 H), 7.34–7.44 (m, 6 H), 7.53 (m, 3 H), 7.95 (d, $J = 8$ Hz, 1.5 Hz, 6 H); $^{13}\text{C NMR}$ (CDCl_3) δ 45.5, 128.7, 128.8, 129.5, 133.3, 135.4, 136.7, 197.5 (8 of 8 expected resonances observed); MS, m/z 432 (M^+ , 11), 313 ($\text{M} - \text{C}_6\text{H}_5\text{COCH}_2$, 3), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100); exact mass 432.1716, calcd for $\text{C}_{30}\text{H}_{24}\text{O}_3$ 432.1725.

1,3,5-Tris(phenylglyoxalyl)benzene (17). Compound **16** (2.0 g, 4.6 mmol) was mixed with 48% HBr (7 mL) and DMSO (120 mL) and heat overnight at reflux. Concentrated HCl (36 mL) and water (200 mL) were added, and the mixture was heated for another 1.5 h. After cooling to room temperature, the mixture was extracted with CHCl_3 three times, and the combined organics were then washed four times with water in order to remove residual DMSO. After drying over Na_2SO_4 , concentration gave crude hexaketone **17** as a brown solid (1.74 g), but one recrystallization from CHCl_3 –benzene gave pure **17** (1.25 g, 2.64 mmol, 57%), mp 188–190 °C: $^1\text{H NMR}$ (CDCl_3) δ 7.55 (t, $J = 8$ Hz, 6 H), 7.71 (tt, $J = 8$ Hz, 1 Hz, 3 H), 8.00 (dd, $J = 8$ Hz, 1 Hz, 6 H), 8.84 (s, 3 H); $^{13}\text{C NMR}$ (CDCl_3) δ 129.4, 130.4, 132.4, 134.8, 135.7, 191.2, 192.4 (7 of 8 expected resonances observed); MS, m/z 474 (M^+ , 4), 456 ($\text{M} - \text{CO}$, 5), 369 ($\text{M} - \text{C}_6\text{H}_5\text{CO}$, 100); exact mass 474.1105, calcd for $\text{C}_{30}\text{H}_{18}\text{O}_6$ 474.1103.

1,3,5-Tris(3-oxo-2,4,5-triphenylcyclopenta-1,4-dienyl)benzene (18). A 40% solution of Triton B in methanol (0.4 mL, 0.8 mmol) was added to a solution of 1,3-diphenylacetone (0.92 g, 4.0 mmol) and compound **17** (0.50 g, 1.05 mmol) in boiling butanol (20 mL), and the solution was heated at reflux for 1 h. At this time another equal portion of 40% Triton B was added, and heating was continued for an additional 2 h. After cooling in an ice bath, a dark solid was collected by filtration and washed with cold ethanol, leaving deep purple compound **18** (0.81 g, 0.81 mmol, 77%), mp 300–303 °C: $^1\text{H NMR}$ (CDCl_3) δ 6.46 (s, 3 H), 6.72 (m, 6 H), 7.03–7.38 (m, 39 H); $^{13}\text{C NMR}$ (CDCl_3) δ 125.3, 126.2, 127.8, 128.09, 128.15, 128.18, 128.4, 128.9, 129.1, 129.3, 130.2, 130.3, 130.5, 130.6, 133.0, 134.8, 153.0, 154.0, 199.9 (19 of 19 expected resonances observed); FAB MS, m/z 998 (M^+ [$^{13}\text{C}_1$], 100), 575 (36).

1,3,5-Tris(pentaphenylphenyl)benzene (19). Compound **18** (100 mg, 0.10 mmol) and diphenylacetylene (636 mg, 3.57 mmol) were mixed in a screw-capped Pyrex tube and heated to 300 °C in a metal bath for 2 h. After cooling, the mixture was taken up in acetone, and crude **19** precipitated as light green crystals (67 mg). This material was subjected to preparative TLC (silica gel GF, 9:1 hexanes–ethyl acetate) to give pure compound **19** (51 mg, 0.035 mmol, 35% yield) as a pale yellow solid, mp 242–244 °C: $^1\text{H NMR}$ (CDCl_3) δ 5.68 (d, $J = 7$ Hz, 6 H), 6.25 (s, 3 H), 6.43 (m, 6 H), 6.63–6.76 (m, 45 H), 6.88 (m, 6 H), 7.01–7.09 (m, 12 H); $^{13}\text{C NMR}$ (CDCl_3) δ 124.6, 124.7, 124.8, 126.1, 126.2, 127.3, 131.1, 131.2, 131.5, 131.8, 134.2, 136.6, 137.5, 139.3, 139.9, 140.5, 140.7, 140.9 (18 of 18 expected resonances observed); FAB MS, m/z 1448 (M^+ [$^{13}\text{C}_2$], 45), 1314 (20), 896 (22), 850 (32).

Bis(4-methoxyphenyl)acetylene (20). 4,4'-Dimethoxybenzil (513 mg, 1.9 mmol) and trimethyl phosphite were placed in a screw-capped Pyrex tube, and this material was heated at 215 °C overnight under argon. After cooling to room temperature, a light yellow precipitate formed which was collected by suction filtration. Recrystallization of this material from ethanol gave pure **20** as light yellow needles (202 mg, 0.85 mmol, 45% yield), mp 133–135 °C (lit.²⁷ mp 140–146 °C); $^1\text{H NMR}$ (CDCl_3) δ 3.82 (s, 6 H), 6.87 and 7.45 (AA'BB' system, 8 H); $^{13}\text{C NMR}$ (CDCl_3) δ 55.8, 88.1, 114.1, 115.8, 133.0, 159.5 (6 of 6 expected resonances observed).

1,3,5-Tris{[3,4-bis(4-methoxyphenyl)-2,5,6-triphenyl]phenyl}benzene (21). Triscyclopentadienone **18** (90 mg, 0.090 mmol) and compound **20** were mixed in a screw-capped Pyrex tube and heated to 300 °C in a metal bath for 2 h. After cooling, the mixture was subjected to silica gel column chromatography (4:1 hexanes–ethyl acetate, then 2:1 hexanes–ethyl acetate), and the fractions containing compound **21** were combined and crystallized from CHCl_3 –methanol to give pure **21** (67 mg, 0.041 mmol, 46% yield), mp 224.5–227.5 °C: $^1\text{H NMR}$ (CDCl_3) δ 3.56 (3 close s's, 9 H), 3.59 (2 close s's, 9 H), 5.67 (m, 5 H), 6.20 (m, 3 H), 6.30 (m, 13 H), 6.40 (m, 3 H), 6.55 (m, 9 H), 6.70 (m, 19 H), 6.88 (m, 7 H), 7.03 (m, 13 H); FAB MS, m/z 1630 ($\text{M} + 2\text{H}$ [$^{13}\text{C}_2$], 100).

1,3,5-Tris(heptaphenyl-2-naphthyl)benzene (22). Triscyclopentadienone **18** (0.15 g, 0.15 mmol) in 1,2-dichloroethane (5 mL) was heated to gentle reflux under argon. A solution of isoamyl nitrite (0.12 mL) in 1,2-dichloroethane (7 mL) was added, followed by the slow addition of 3,4,5,6-tetraphenylanthranilic acid (0.22 g, 0.50 mmol) in 1,2-dichloroethane (7 mL) over 0.5 h. Heating was continued for 8 h, and then ethanol (4 mL) and 1 N NaOH (6 mL) were added to terminate the reaction. CHCl_3 was added, and after an aqueous workup, the resulting material was chromatographed on a column of silica gel (solvent, 97:3 hexanes–ethyl acetate). Fractions containing the desired product, which gives R_f 0.45 on TLC (silica gel GF, 9:1 hexanes–ethyl acetate), were combined and concentrated to give pure **22** as a pale yellow solid (46 mg, 0.022 mmol, 15%), mp > 350 °C: $^1\text{H NMR}$ (CDCl_3) δ 4.99 (t, $J = 1$ Hz, 1 H), 5.25 (s, 1 H), 5.27 (t, $J = 1$ Hz, 1 H), 5.49 (m, 4 H), 5.86 (m, 10 H), 6.21–6.97 (m, 91 H); $^{13}\text{C NMR}$ (CDCl_3) > 70 resonances observed; 40 are expected in the fast exchange limit; FAB MS, m/z 2054 (M^+ [$^{13}\text{C}_2$], 100), 1977 ($\text{M} - \text{C}_6\text{H}_5$, 5), 1171 (28).

X-ray Crystallographic Analysis of Compound 7b. Crystal A. A colorless needle was cut to 0.08 mm \times 0.09 mm \times 0.18 mm and sealed in a glass capillary for use in X-ray measurements. Crystal data: $\text{C}_{110}\text{H}_{73}\text{Br}\cdot 3.5\text{C}_6\text{H}_5\text{NO}_2\cdot \text{C}_6\text{H}_5\text{CH}_3$; triclinic, space group $P\bar{1}$; $a = 16.95$ (3) Å, $b = 18.22$ (3) Å, $c = 20.32$ (2) Å, $\alpha = 79.39$ (8)°, $\beta = 72.11$ (10)°, $\gamma = 66.73$ (11)°, $V = 5472$ (12) Å³, $Z = 2$, $D_{\text{calcd}} = 1.212$ g/cm³. Intensity data was collected out to $2\theta = 93^\circ$ by using Cu K α radiation ($\lambda = 1.54184$ Å) at 298 K on a Rigaku R-Axis IIC image plate system equipped with a rotating anode and double-focusing mirrors. A total of 175 frames of data were collected with 5° of oscillation per frame. A total of 32 618 reflections were indexed, integrated, and corrected for Lorentz and polarization effects (using the program DENZO^{28,29}), and then the reflections were scaled and merged (SCALEPACK²⁹) to give 9015 unique reflections ($R_{\text{int}} = 0.060$). The structure was solved by heavy atom methods (SHELXTL³⁰) and refined by full-matrix least-squares on F^2 (SHELXL-93³¹). For the molecule of **7b**, all non-H atoms were refined with anisotropic displacement coefficients, and H atoms were included with a riding model [$U(\text{H}) = 1.2U(\text{C})$]. For the solvent molecules (5 sites: 1, 1 NB; 2, 1 NB; 3, 0.5 NB; 4, 0.5/0.5 NB/toluene; 5 0.5/0.5 NB/toluene), all non-H atoms were assigned isotropic displacement coefficients, H atoms were included with a riding model [$U(\text{H}) = 1.2U(\text{C})$ or $1.5U(\text{C}_{\text{methyl}})$], rings were modeled as regular hexagons and refined as rigid groups, and nitro groups were included with restraints but were free to rotate. The refinement converged to $R(F) = 0.115$, $wR(F^2) = 0.308$, and $S = 1.08$ for 7509 reflections with $F > 4\sigma(F)$, and $R(F) = 0.125$, $wR(F^2) = 0.326$, and $S = 1.04$ for 9015 unique reflections, 1135 variables, and 11 restraints. Full details are given in the Supporting Information.

Crystal B. A colorless needle, cut to 0.05 mm \times 0.05 mm \times 0.22 mm and mounted on a glass fiber, was used for X-ray measurements. Crystal data: $\text{C}_{110}\text{H}_{73}\text{Br}\cdot \text{C}_6\text{H}_5\text{NO}_2$; triclinic, space group $P\bar{1}$; $a = 16.922$ (2) Å, $b = 13.627$ (2) Å, $c = 20.291$ (2) Å, $\alpha = 77.741$ (9)°, $\beta = 72.291$ (8)°, $\gamma = 85.612$ (8)°, $V = 4355$ (1) Å³, $Z = 2$, $D_{\text{calcd}} = 1.218$ g/cm³. Intensity measurements were made with $3^\circ \leq 2\theta \leq 45^\circ$ using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 230 K on a Siemens P4 diffractometer. A total of 11 843 reflections were measured, of which 11,266 were unique ($R_{\text{int}} = 0.071$). The structure was solved by heavy atom methods (SHELXTL) and refined by full-matrix least-squares on F^2 (SHELXL-93). The presence of a disordered solvent molecule in the lattice was evident, but this electron density was not well modeled with discrete atoms. Therefore, the SQUEEZE/BYPASS³² procedure implemented in PLATON-96³³ was used to

account for the solvent electron density. A total electron count of 141.6 e in a total volume of 495.8 Å³ was found in a single-potential solvent area, consistent with the presence of two nitrobenzenes (64 e) per unit cell ($141.6 \text{ e}/2 = 70.8 \text{ e}$) and thus a 1:1 **5b**: $\text{C}_6\text{H}_5\text{NO}_2$ ratio. The SQUEEZE-processed data were used for all subsequent cycles of refinement. Due to the weak data, only the bromine atom was refined anisotropically; carbon atoms were refined isotropically and H atoms were included with a riding model [$\text{C}-\text{H} = 0.93$ Å, $U(\text{H}) = 1.2U(\text{C})$]. The refinement converged to $R(F) = 0.079$, $wR(F^2) = 0.133$, and $S = 1.09$ for 2819 reflections with $F > 4\sigma(F)$, and $R(F) = 0.241$, $wR(F^2) = 0.189$, and $S = 0.68$ for 11,263 unique reflections (three reflections were suppressed) and 450 variables. Full details are given in the Supporting Information.

X-ray Crystallographic Analysis of Compound 12a. A colorless prism of **12a**, 0.04 mm \times 0.12 mm \times 0.22 mm in size and mounted on a glass fiber, was used for X-ray measurements. Crystal data: $\text{C}_{110}\text{H}_{74}$; triclinic, space group $P\bar{1}$; $a = 12.43$ (1) Å, $b = 25.51$ (2) Å, $c = 27.74$ (5) Å, $\alpha = 114.89$ (7)°, $\beta = 100.08$ (9)°, $\gamma = 90.61$ (8)°, $V = 7820$ (16) Å³, $Z = 4$, $D_{\text{calcd}} = 1.185$ g/cm³. Intensity data were collected and processed in a manner similar to that described for compound **7b**, crystal A, yielding a total of 11 880 unique reflections. The structure was solved by direct methods (CRUNCH⁹) and refined by full-matrix least-squares on F^2 (SHELXL-93). All non-H atoms were refined with anisotropic displacement coefficients, and H atoms were included with a riding model [$\text{C}-\text{H} = 0.93$ Å, $U(\text{H}) = 1.2U(\text{C})$]. The refinement converged to $R(F) = 0.065$, $wR(F^2) = 0.183$, and $S = 1.08$ for 10 821 reflections with $F > 4\sigma(F)$, and $R(F) = 0.070$, $wR(F^2) = 0.194$, and $S = 1.05$ for 11 875 unique reflections (five reflections were suppressed) and 1981 variables. Full details are given in the Supporting Information.

X-ray Crystallographic Analysis of Compound 12b. A colorless prism of **12b**, 0.18 mm \times 0.22 mm \times 0.25 mm in size, was sealed in a glass capillary for use in X-ray measurements. Crystal data: $\text{C}_{110}\text{H}_{72}\text{Br}_2\cdot 2\text{CH}_2\text{Cl}_2\cdot 4\text{CH}_3\text{OH}$; trigonal, space group $P3_21$; $a = b = 17.493$ (2) Å, $c = 26.676$ (4) Å, $V = 7069$ (2) Å³, $Z = 3$, $D_{\text{calcd}} = 1.305$ g/cm³. Intensity measurements were made with $3^\circ \leq 2\theta \leq 45^\circ$ using Mo K α radiation at 298 K on a Siemens P4 diffractometer. A total of 6594 reflections were measured, of which 6090 were unique ($R_{\text{int}} = 0.067$). The structure was solved by heavy atom methods (SHELXTL) and refined by full-matrix least-squares on F^2 (SHELXL-93). The presence of several disordered solvent molecules was evident, and the refinement of a discrete-atom solvent model converged to $R(F) = 0.077$, but it was abandoned in favor of a solvent-free model due to uncertainty in the identity of the included solvent. The SQUEEZE/BYPASS procedure described above was again employed to account for the solvent electron density, and the SQUEEZE-processed data were used for all subsequent cycles of refinement. Due to the weak data, only the bromine was refined anisotropically; carbon atoms were refined isotropically, and H atoms were included with a riding model [$\text{C}-\text{H} = 0.93$ Å, $U(\text{H}) = 1.2U(\text{C})$]. The refinement converged to $R(F) = 0.055$, $wR(F^2) = 0.092$, and $S = 1.01$ for 1555 reflections with $F > 4\sigma(F)$, and $R(F) = 0.176$, $wR(F^2) = 0.116$, and $S = 0.61$ for 6090 unique reflections and 230 variables. Full details are given in the Supporting Information.

X-ray Structure of Compound 19. A colorless plate of **19**, 0.25 mm \times 0.38 mm \times 0.50 mm in size, was sealed in a glass capillary for use in X-ray measurements. Crystal data: $\text{C}_{114}\text{H}_{78}\cdot 2.5\text{CHCl}_3$; monoclinic, space group $P2_1/c$; $a = 24.80$ (3) Å, $b = 27.15$ (2) Å, $c = 33.26$ (4) Å, $\beta = 98.77$ (11)°, $V = 22,133$ (44) Å³, $Z = 8$, $D_{\text{calcd}} = 1.048$ g/cm³. Intensity data were collected and processed in a manner similar to that described for compound **7b**, crystal A, yielding a total of 18 850 unique reflections ($R_{\text{int}} = 0.092$). The structure was solved by molecular replacement (PATSEE³⁴) and refined by full-matrix least-squares on F^2 (SHELXL-93). In addition to the two independent molecules of **19** eight disordered chloroform sites were identified in the asymmetric unit. Most of these exhibited partial occupancy, and refinement led to a model with an overall formulation for the asymmetric unit of $(\text{19})_2(\text{CHCl}_3)_{5.6}$. However, this model refined to

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only $R(F) = 0.190$, so the SQUEEZE/BYPASS procedure implemented in PLATON-96 was once again employed to account for the solvent electron density. A total electron count of 1041 e in a volume of 7870 Å³ was found for a single large solvent region in the unit cell (35.6% of the cell volume). This electron count corresponds to 18 CHCl₃'s, which would yield a formulation for the asymmetric unit of (19)₂(CHCl₃)_{4.5}. [(19)₂(CHCl₃)₅ = C₁₁₄H₇₈·2.5CHCl₃ has been used for calculation of the density of the crystal.] SQUEEZE-processed data were employed for all subsequent refinements. The carbon atoms were refined anisotropically with hydrogens riding [C–H = 0.93 Å, $U(H) = 1.2U(C)$], and the refinement converged to $R(F) = 0.116$, $wR(F^2) = 0.298$, and $S = 1.10$ for 14,059 reflections with $F > 4\sigma(F)$, and $R(F) = 0.127$, $wR(F^2) = 0.319$, and $S = 1.00$ for 18,850 unique reflections and 2054 parameters. Full details are given in the Supporting Information.

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Supporting Information Available: Crystal structure reports for compounds **7b**, **12a**, **12b**, and **19**, which include full experimental details, tables of atomic coordinates, bond distances, bond angles, and thermal parameters, and selected figures (162 pages). See any current masthead page for ordering and Internet access instructions.

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