The Structure of Hexabenzotriphenylene and the Problem of Overcrowded "D_{3h}" Polycyclic Aromatic Compounds

Lisa Barnett,[†] Douglas M. Ho,[†] Kim K. Baldridge,[‡] and Robert A. Pascal Jr.*[,†]

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08544, and San Diego Supercomputer Center, La Jolla, California 92137

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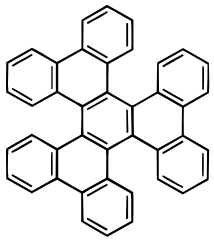
Abstract: Hexabenzotriphenylene (**1**, dibenzo[*f,j*]phenanthro[9,10-*s*]picene) has been prepared in 5% yield by vacuum pyrolysis of phenanthrene-9,10-dicarboxylic anhydride, and its X-ray structure has been determined. Compound **1** is a strongly twisted, D_3-symmetric molecular propeller, in contrast to other highly substituted triphenylenes (perfluoro- and perchlorotriphenylene) which adopt C_2-symmetric conformations. Computational studies of these and other overcrowded, nominally D_{3h}-symmetric, polycyclic aromatic compounds are reported, and the origins of their conformational preferences and the adequacy of various computational methods for treating these compounds are discussed.

Highly symmetric polycyclic aromatic hydrocarbons (PAHs) have commanded increasing attention since the discovery of the fullerenes. Much effort has been spent in the synthesis of convex, bowl-shaped PAHs akin to the fullerenes,[1] but other shapes, such as saddles and twists, have been constructed.[1,2] Among members of the latter class, hexabenzotriphenylene (**1**, dibenzo[*f,j*]phenanthro[9,10-*s*]picene) has a rather checkered



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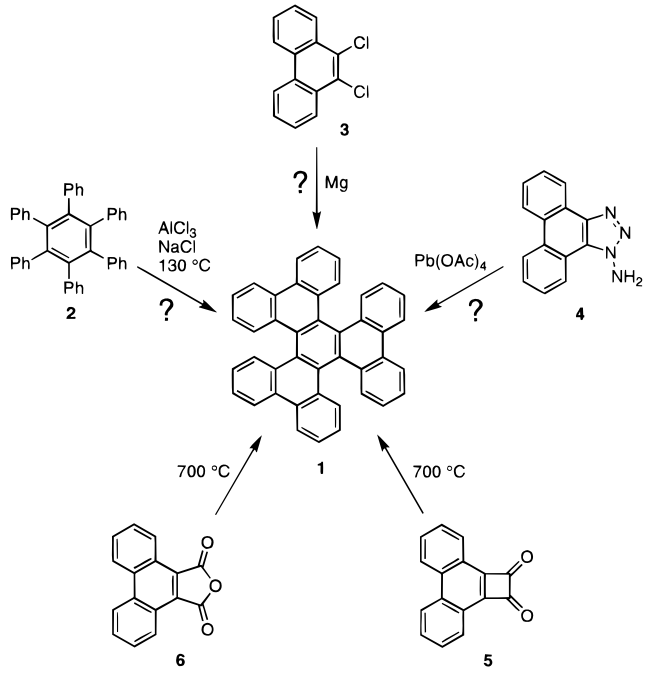
history. At least four different syntheses of **1** have been reported (Scheme 1),[3−6] but the characterization of the products has not always been of the highest standard, and it is clear that at least some of the reports are incorrect. There is still no X-ray structure of this sterically very crowded hydrocarbon, but molecular mechanics calculations indicate that **1** should be a strongly twisted three-bladed molecular propeller. We report herein a new, two-step synthesis of hexabenzotriphenylene from commercial starting materials and its unambiguous characterization as a highly twisted, D_3-symmetric molecular propeller by X-ray crystallography. In addition, we report computational studies of the conformational preferences of this and other overcrowded, nominally D_{3h}-symmetric polycyclic aromatics, which are observed to display an unusual structural dichotomy.

Scheme 1



Results and Discussion

Synthesis and Structure of Hexabenzotriphenylene. The first report of hexabenzotriphenylene is a patent application filed in 1958, in which Halleux claimed to have formed **1** by cyclodehydrogenation of hexaphenylbenzene (**2**) in an $AlCl_3$−NaCl mixture at 120−130 °C (Scheme 1), but no characterization was offered.[3] Shortly thereafter, Carey and Millar reported the synthesis of **1** in 60% yield by treatment of 9,10-dichlorophenanthrene (**3**) with Mg in boiling tetrahydrofuran.[4] This material was characterized by its melting point, UV

[†] Princeton University.
[‡] San Diego Supercomputer Center.

(1) (a) Siegel, J. S.; Sieders, T. J. *Chem. Br.* **1995**, *31*, 313−316. (b) Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235−242.
(2) (a) Pascal, R. A., Jr. *Pure Appl. Chem.* **1993**, *65*, 105−110. (b) Qiao, X.; Ho, D. M.; Pascal, R. A., Jr., *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1531−1532.
(3) Halleux, A. L., Br. Patent 852,981 1960.
(4) Carey, J. G.; Millar, I. T. *J. Chem. Soc.* **1959**, 3144−3146.
(5) Barton, J. W.; Grinham, A. R. *J. Chem. Soc., Perkin Trans. 1* **1972**, 634−637.
(6) Hacker, N. P.; McOmie, J. F. W.; Meunier-Piret, J.; Van Meerssche, M. *J. Chem. Soc., Perkin Trans. 1* **1982**, 19−23.

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spectrum, and combustion analysis,[4] but in 1980 Biermann and Schmidt demonstrated that this substance was not hexabenzotriphenylene (without, however, establishing its true composition).[7] In 1972 Barton and Grinham found that oxidation of 1-amino-1*H*-phenanthro[9,10-*d*]triazole (**4**), a process known to yield 9,10-phenanthryne, in the absence of an aryne trap gave a small amount of a high-melting substance which exhibited a parent ion at *m*/*z* 528 in its mass spectrum.[5] More conservative than their predecessors, they concluded that this material was "possibly hexabenzotriphenylene" formed by trimerization of the aryne.[5] Most recently, Hacker et al. reported the formation of **1** in 13% yield by pyrolysis of cyclobuta[*l*]phenanthrene-1,2-dione (**5**).[6] This product was characterized by melting point and ^{1}H NMR, IR, UV, and mass spectra,[6] and these data gave every reason to believe that the elusive **1** had been prepared.

Having recently reported the preparation of perchlorotriphenylene by the pyrolysis of tetrachlorophthalic anhydride,[8] we conjectured that similar treatment of phenanthrene-9,10-dicarboxylic anhydride (**6**) would provide a simple, if perhaps low-yielding, synthesis of **1**, since **6** may be obtained by photolysis of commercial diphenylmaleic anhydride.[9] In the event, pyrolysis of **6** under vacuum in a quartz tube at 550−700 °C gave compound **1** in 5% yield after purification by preparative TLC. The ^{1}H NMR, UV, and mass spectra of this material were essentially the same as those of Hacker et al.,[6] and, if only a small amount of **1** is required, our synthesis is quite convenient. Indeed, the limiting factor is the preparation of the anhydride **6**, which is difficult to perform on large scale since the photolysis is conducted on a dilute suspension in water.

Unlike many PAHs, compound **1** is quite soluble in common organic solvents, but it proved very difficult to grow single crystals suitable for X-ray studies. Finally, an orange plate, obtained by the slow cooling of a very concentrated solution of **1** in nitrobenzene, gave satisfactory diffraction. Compound **1** crystallized in the common space group $P2_1/c$, and the structure was solved and refined without difficulty. The original determination was carried out at 298 K, but to obtain better atomic coordinates for a detailed comparison with computationally derived geometries, the structure was redetermined at 110 K. The molecular structures obtained from both determinations are illustrated in Figure 1, and a stereoview of the molecule appears in Figure 2. The two structures are extremely similar, but all subsequent discussions of the experimental geometry of **1** refer to data from the 110 K determination.

Compound **1** is a steeply pitched molecular propeller with approximate D_3 symmetry. The molecule may be thought of as three biphenyls, each of them joined at positions 2 and 2′ to a central benzene ring. The mean planes of the three peripheral biphenyls, C(7)−C(18), C(19)−C(30), and C(31)−C(42), make dihedral angles of 28.5, 30.0, and 29.7°, respectively, with the mean plane of the central ring, C(1)−C(6) (see Figure 1). Obviously the propeller distortion of **1** results from the steric conflict between adjacent biphenyl subunits, where the C(8)−C(41), C(17)−C(20), and C(29)−C(32) contacts average only 3.006 Å, well within the sum of the van der Waals radii of the carbon atoms.

The central ring of **1** (ring A, see Table 1) adopts a shallow chair conformation, and it exhibits significant bond alternation, with the three *endo* bonds averaging 1.397 Å and the *exo* bonds

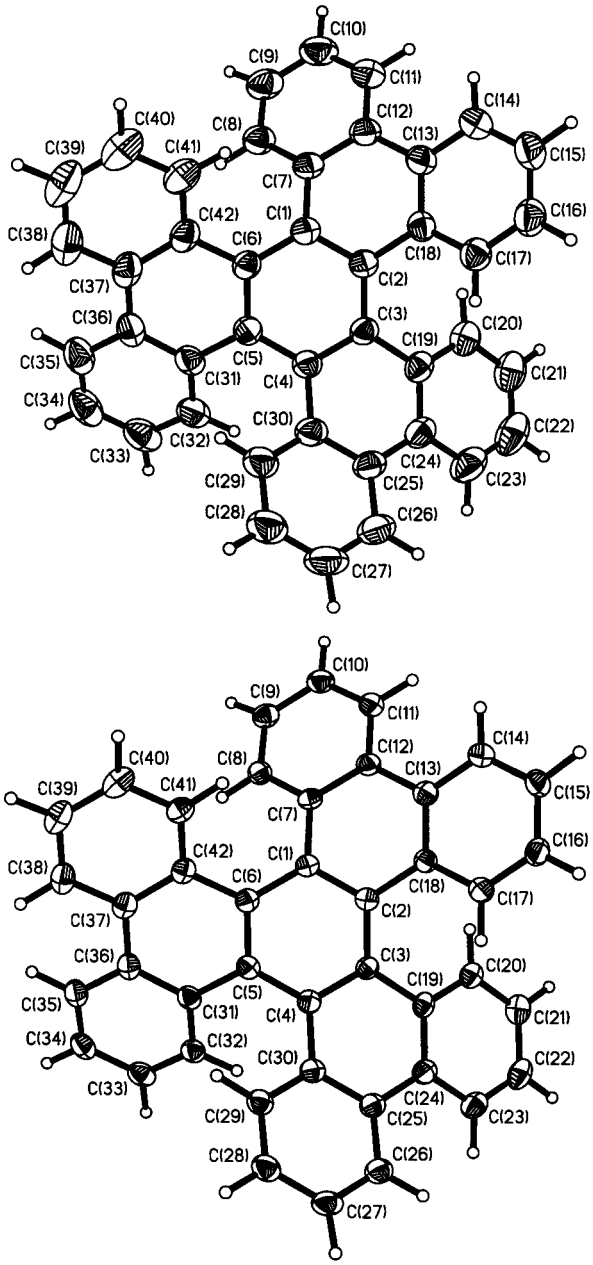


Figure 1. Molecular structure of hexabenzotriphenylene (**1**) at 298 K (above) and 110 K (below). Thermal ellipsoids have been drawn at the 50% probability level.

1.434 Å. However, this is much less pronounced than the bond alternation in the three adjoining rings (B, C, and D), which are quite twisted. There, the six *radial* bonds average 1.471 Å, and the three *outer* bonds 1.454 Å, but the six *benzo* bonds average only 1.407 Å, and the *endo* bonds 1.397 Å (Table 1). Thus, in compound **1** there are six ordinary peripheral benzene rings linked to each other and to a somewhat distorted central benzene ring by single bonds or bonds of only slightly higher order.

Computational Studies of Hexabenzotriphenylene. How well do modern computational methods reproduce the experimental geometry of **1**? Although most methods might be expected to give structures with a "reasonable" appearance, a truly excellent geometry is much more difficult to obtain, since **1** contains (a) strong nonbonded interactions and (b) a highly delocalized π-system, both of which are often poorly handled by low levels of theory. A series of molecular mechanics

(7) Biermann, D.; Schmidt, W. *J. Am. Chem. Soc.* **1980**, *102*, 3173−3181.

(8) (a) Shibata, K.; Kulkarni, A. A.; Ho, D. M.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 5983−5984. (b) Shibata, K.; Kulkarni, A. A.; Ho, D. M.; Pascal, R. A., Jr. *J. Org. Chem.* **1995**, *60*, 428−434.

(9) Sargent, M. V.; Timmons, C. J. *J. Chem. Soc., Suppl. 1* **1964**, 5544.

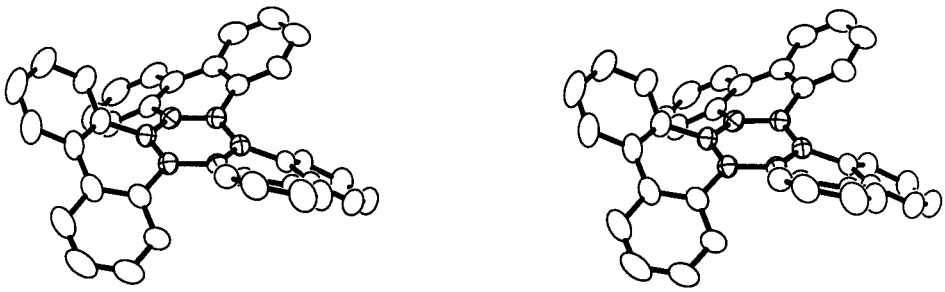
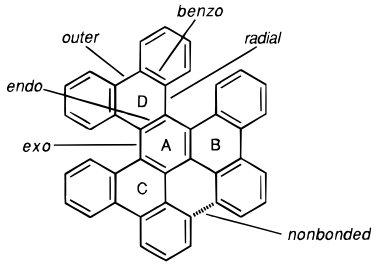


Figure 2. Stereoview of the structure of hexabenzotriphenylene (298 K structure). Thermal ellipsoids have been drawn at the 50% probability level.

Table 1. Comparison of Experimental and Calculated Geometries for Hexabenzotriphenylene



geometry type: metric[a]	exptl		mechanics	semiempirical			ab initio			HDFT	
	298 K	110 K	MMX	MNDO	AM1	PM3	STO-3G	3-21G	6-31G*	B3LYP/ cc-pVDZ	B3PW91/ cc-pVDZ
rms deviation[b]			0.102	0.163	0.083	0.094	0.070	0.059	0.060	0.065	0.061
maximum dev.[b]			0.229	0.318	0.203	0.247	0.171	0.111	0.116	0.144	0.138
distances[c]											
endo	1.396	1.397	1.405	1.421	1.408	1.401	1.386	1.386	1.387	1.412	1.409
exo	1.433	1.434	1.430	1.445	1.426	1.428	1.444	1.428	1.434	1.441	1.437
radial	1.471	1.471	1.466	1.476	1.454	1.459	1.491	1.480	1.480	1.474	1.469
benzo	1.406	1.407	1.416	1.432	1.414	1.405	1.399	1.397	1.399	1.422	1.419
outer	1.453	1.454	1.468	1.473	1.450	1.451	1.478	1.464	1.464	1.460	1.457
nonbonded	3.017	3.006	3.085	3.326	2.899	2.962	2.979	3.009	3.053	3.044	3.024

[a] All distances are given in angstroms. [b] Deviations are given with respect to the 110 K structure. [c] For the experimental structures, the average values for the three or six equivalent distances are given.

(MMX[10]), semiempirical molecular orbital (MNDO,[11] AM1,[12] and PM3[13]), ab initio molecular orbital (HF/STO-3G, HF/3-21G(*), HF/6-31G*[14]), and hybrid density functional (HDFT) calculations (B3LYP/cc-pVDZ and B3PW91/cc-pVDZ[15]) were performed to give fully optimized geometries for **1**, and as expected, all yielded D_3-symmetric propeller conformations generally similar to the X-ray structure. A closer examination of the results is found in Table 1, which gives the rms and maximum deviations of the experimental atomic positions from those of the best fit[16] of each of the computed structures, as well as selected experimental and computational C−C bond distances.

All of the tested methods indicate that the B, C, and D rings should show strong bond alternation, with lesser but significant alternation of the central ring. Even the PM3 calculation was able to match closely the experimental bond lengths, but the AM1 calculation yielded the best overall fit among the semiempirical methods. However, the *nonbonded* C−C contact distances were poorly handled by these (and molecular mechanics) calculations, and for this reason all of the ab initio and HDFT methods gave significantly better geometries than the lower levels. The HF/3-21G(*) calculation most closely agreed with the X-ray structure, with the HF/6-31G* and HDFT geometries only very marginally worse. Interestingly, both HDFT methods appeared to overestimate systematically the bond distances by a small amount. For example, *all* of the C−C bond distances given by the B3LYP/cc-pVDZ calculation (including those not listed in Table 1) were greater than the experimental values, by 0.003 to 0.015 Å. The reason for this overestimation is the relatively small basis set employed (cc-pVDZ), and such a systematic error has been noted previously.[18] The magnitudes of the deviations of the Hartree−Fock-calculated bond lengths from the experimental values were no smaller than those from the HDFT geometries, but the former were scattered on either side of the experimental values, and the resulting cancellation of errors led to better overall geometries.

(10) The MMX force field in PCMODEL Version 5.0 was employed.
(11) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899−4907.
(12) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902−3909.
(13) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209−220.
(14) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986; pp 63−100.
(15) See the Experimental Section for a description of these methods.
(16) The function OFIT in Siemens SHELXTL[17] was used to determine the best fit of the experimental and calculated geometries and the deviations of the atomic positions; all of the non-hydrogen atoms were employed for the fitting.
(17) Sheldrick, G. M. *SHELXTL* Version 5. Siemens Analytical X-ray Instruments, Madison, Wisconsin, 1996.
(18) (a) Martin, J. M. L.; El-Yazal, J.; Francois, J.-P. *Mol. Phys.* **1995**, *86*, 1437−1450. (b) Baldridge, K. K.; Siegel, J. S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 745−748.

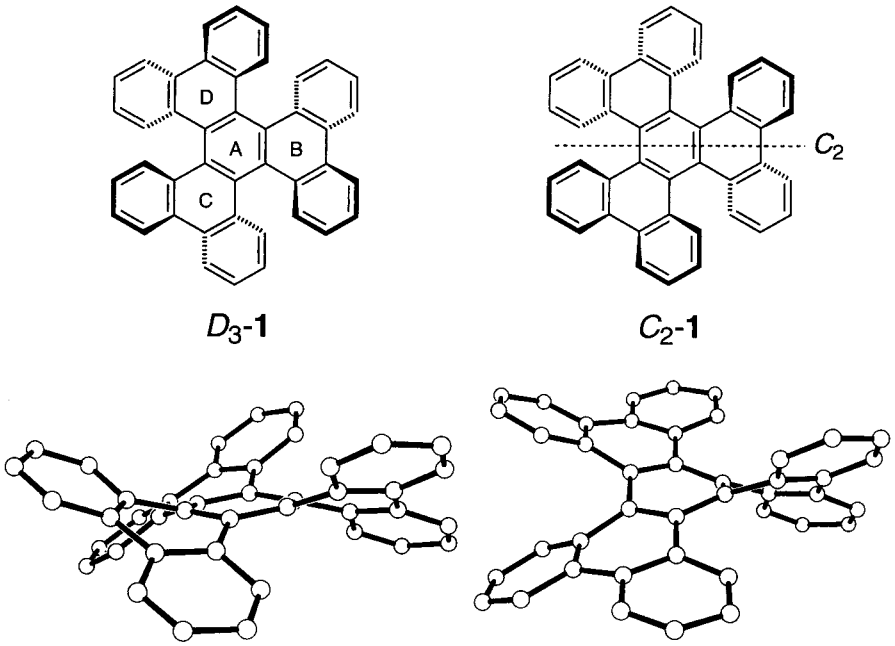
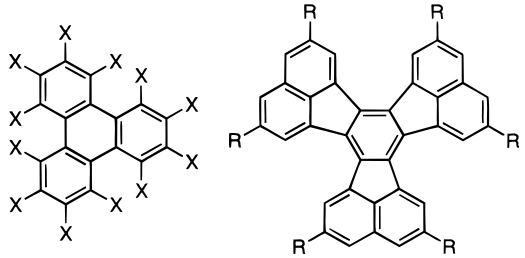


Figure 3. Schematic and perspective drawings of the D_3 and C_2 conformations of hexabenzotriphenylene. The HF/3-21G(*) geometries have been used.

The C_2/D_3 Dichotomy. The experimentally determined conformation of hexabenzotriphenylene provides an important check of the principles thought to govern the shapes of similar molecules. Consider polycyclic aromatic compounds with "ideal" D_{3h} symmetry (that is, when drawn flat on paper). Simple examples such as triphenylene (**7**) may realize this symmetry (at least approximately),[19] but with increasing substitution such molecules must adopt conformations of lower symmetry to relieve steric congestion. Intuitively one might expect these compounds to distort into D_3-symmetric molecular propellers, as observed for **1**, but recent X-ray structures of several similar molecules show this to be more the exception than the rule! Both perfluorotriphenylene (**8**) and perchlorotriphenylene (**9**) adopt C_2-symmetric conformations which are not propellers at all.[8,20] Decacyclene (**10**) is a D_3 propeller,[21] but, in contrast, 2,5,8,11,14,17-hexa(*tert*-butyl)-decacyclene (**11**, where the *tert*-butyl groups are not in conflict) adopts an approximate C_2 conformation in the crystal.[22] Why should these seemingly similar structures fall into two distinct classes?



The two conformations of hexabenzotriphenylene are depicted in Figure 3, and they serve to illustrate the conformational possibilities that exist for the nominally D_{3h} polycyclic aromatic compounds **7**−**11** as well. Note that in the D_3 structure of **1**, the interleaving of the outer benzo groups yields an alternating "up−down−up−down−up−down" pattern, but in the C_2 conformation the pattern is "up−down−up−up−down−down". In the D_3 geometry, the greatest distortion is in rings B, C, and D, which are twist-boats, whereas the A ring is a much less distorted, shallow chair. By contrast, in the C_2 geometry, the A ring is most highly distorted (twist-boat), and the B, C, and D rings are shallow boats.

We have previously rationalized the C_2 structures of the perhalotriphenylenes by noting that most of the distortion in the C_2 conformation is forced on the central, "nonaromatic" ring (that is, it shows a high degree of bond alternation),[23] whereas a D_3 conformation would minimize distortion in the central ring at the expense of increased distortion in the peripheral, more highly delocalized, "aromatic" rings.[8b] If this interpretation is correct, then hexabenzotriphenylene (where the bond distances in the X-ray structure show that the central ring is more highly delocalized than in triphenylene but, in contrast, that the B, C, and D rings have strong bond alternation) should indeed adopt a D_3 conformation to minimize distortion of its fully aromatic central ring, despite intramolecular steric interactions closely akin to those in the perhalotriphenylenes. The magnitude of the out-of-plane distortions in each ring of **1** are fully consonant with this idea. The rms deviation of the carbon atoms of ring A from the mean plane of the ring is only 0.058 Å, but the rms deviations of the carbons in the highly twisted rings B, C, and D average 0.119 Å. The six peripheral benzo groups are nearly planar, with rms deviations averaging only 0.010 Å.

We thus have a simple rule-of-thumb for predicting the conformations of overcrowded "D_{3h}" polycyclic aromatics: if the central ring is expected to be aromatic (possessing shorter, benzene-like bonds), then a D_3 conformation should be pre-

(19) (a)Ahmed, F. R.; Trotter, J. *Acta Crystallogr.* **1963**, *16*, 503−508. (b) Filippini, G. *J. Mol. Struct.* **1985**, *130*, 117−124.

(20) Hursthouse, M. B.; Smith, V. B.; Massey, A. G. *J. Fluorine Chem.* **1977**, *10*, 145−155.

(21) Ho, D. M.; Pascal, R. A., Jr. *Chem. Mater.* **1993**, *5*, 1358−1361.

(22) Zimmermann, K.; Goddard, R.; Kruger, C.; Haenel, M. W. *Tetrahedron Lett.* **1996**, *37*, 8371−8374.

(23) Triphenylene is known from both experimental[19] and computational[24] studies to exhibit a great deal of bond alternation in the central ring, and it is best regarded as three fully delocalized benzene rings linked by bonds of low order. In triphenylene the *endo* bonds average 1.411 Å, the *exo* bonds average 1.470 Å,[19b] and similar, or even greater, bond alternation is seen in **2** and **3**.[8,19]

Table 2. Calculated Energies for C_2 and D_3 Conformations of Overcrowded "D_{3h}" Polycyclic Aromatic Compounds

	mechanics ΔH_f (kcal/mol)	semiempirical ΔH_f (kcal/mol)			ab initio E (HF, au[a])	
compd	MMX	MNDO	AM1	PM3	STO-3G	3-21G(*)
C_2 hexabenzotriphenylene (**1**)	183.70	217.70	215.47	201.06	−1584.99208	−1595.52644[h]
D_3 hexabenzotriphenylene	174.66	211.50	209.97	196.31	−1585.00454	−1595.53933[h]
difference[b]	9.0	6.2	5.5	4.8	7.8	8.1[h]
experimental geometry[c] $\sim D_3$						
C_2 perfluorotriphenylene (**8**)	−396.90	−430.39	−409.85	−415.96	−1849.72326	−1864.56011
D_3 perfluorotriphenylene	−400.14	−428.70	−408.24	−414.31	−1849.71697	−1864.54950
difference[b]	3.2	−1.7	−1.6	−1.7	−3.9	−6.7
experimental geometry[d] C_2						
C_2 perchlorotriphenylene (**9**)	60.32	61.57	55.29	38.88	−6128.13901	−6166.48582
D_3 perchlorotriphenylene	52.47	61.22	56.25	40.72	−6128.13071	−6166.47428
difference[b]	7.8	0.4	−1.0	−1.8	−5.2	−7.2
experimental geometry[e] $\sim C_2$						
C_2 decacyclene (**10**)	191.35	193.41	228.83	195.90	−1357.10042	−1366.10211
D_3 decacyclene	188.89	191.93	233.61	195.62	−1357.10135	−1366.10327
difference[b]	2.5	1.5	−4.8	0.3	0.6	0.7
experimental geometry[f] $\sim D_3$						
C_2 2,5,8,11,14,17-(t-Bu)$_6$decacyclene (**11**)	34.19	171.62	123.79	52.79	−2283.00430	−2297.76787
D_3 2,5,8,11,14,17-(t-Bu)$_6$decacyclene (**11**)	31.92	176.73	123.71	53.39	−2283.00482	−2297.76856
difference[b]	2.3	−5.1	0.1	−0.6	0.3	0.4
experimental geometry[g] $\sim C_2$						
C_2 1,4,5,8,9,12-Me$_6$triphenylene (**12**)		79.13	69.42	56.40	−911.69406	−917.65401
D_3 1,4,5,8,9,12-Me$_6$triphenylene (**12**)		78.83	70.83	59.43	−911.68179	−917.64261
difference[b]		0.3	−1.4	−3.0	−7.7	−7.2
predicted geometry: C_2						
C_2 1,6,7,12,13,18-Me$_6$decacyclene (**13**)		189.05	214.42	175.78	−1588.53257	−1598.96346
D_3 1,6,7,12,13,18-Me$_6$decacyclene (**13**)		179.38	214.41	173.72	−1588.54424	−1598.97534
difference[b]		9.7	0.0	2.1	7.3	7.5
predicted geometry: D_3						
C_2 hexafurotriphenylene **14**		−3.31	98.93	31.01	−1572.23281	−1583.19941
D_3 hexafurotriphenylene **14**		−4.99	98.14	31.11	−1572.23163	−1583.19716
difference[b]		1.7	0.8	−0.1	−0.7	−1.4
predicted geometry: C_2						
C_2 hexafurotriphenylene **15**		−2.14	89.88	36.14	−1572.16569	−1583.12209
D_3 hexafurotriphenylene **15**		−7.00	86.67	33.34	−1572.17430	−1583.13164
difference[b]		4.9	3.2	2.8	5.4	6.0
predicted geometry: D_3						
C_2 hexaphenanthrotriphenylene **16**[i]				459.52		
D_3 hexaphenanthrotriphenylene **16**				457.52		
difference[b]				2.0		
predicted geometry: D_3						

[a] 1 au = 627.503 kcal/mol. [b] $C_2 - D_3$; all differences are given in kcal/mol; positive values favor the D_3 conformation. [c] This work. [d] Reference 20. [e] Reference 8. [f] Reference 21. [g] Reference 22. [h] At higher levels the following results were obtained: HF/6-31G*: C_2 - 1604.49522, D_3 - 1604.50826, difference 8.2 kcal/mol; B3LYP/cc-pVDZ: C_2 - 1615.07248, D_3 - 1615.08045, difference 5.0 kcal/mol. [i] The ΔH_f of the most stable C_2 conformation is given.

ferred, but if the central ring is nonaromatic (possessing some very long "single" bonds and great bond alternation), then a C_2 conformation will be observed. How well do the available experimental data agree with this simple concept and with the results of computational studies?

Table 2 lists the results of molecular mechanics, semiempirical molecular orbital, and ab initio molecular orbital calculations of the energies of the fully optimized C_2 and D_3 conformations of the five overcrowded D_{3h} polycyclic aromatic compounds for which there are experimental geometries, as well as calculations for five as-yet-unknown polycyclic aromatic compounds. In addition, Table 3 compares some of the experimental and calculated structures[16] and provides some selected geometric data. The known compounds are discussed first.

All of the computational methods correctly yield a strong preference (by 5−9 kcal/mol) for the D_3 geometry of hexabenzotriphenylene (**1**), with the highest level employed, B3LYP/cc-pVDZ, favoring the D_3 conformation by 5.0 kcal/mol. For the perhalotriphenylenes **8** and **9**, however, the results are mixed: at all ab initio levels, the experimentally observed C_2 geometries are strongly preferred (by 4−7 kcal/mol), the semiempirical methods show a weaker C_2 preference (1−2 kcal/mol), but the MMX force field favors the incorrect D_3 geometries. The decacyclenes **10** and **11** are a more difficult test, since the steric conflict in these molecules is not so great. All of the methods but AM1 predict that decacyclene should prefer the experimentally observed D_3 conformation by a small margin (0.3−2.5 kcal/mol), but the results for hexa(*tert*-butyl)-decacyclene **11** are rather scattered. However, the higher levels of theory indicate that the C_2 and D_3 conformations of **11** differ in energy by at most a few tenths of a kcal/mol; thus, crystal packing forces may have a significant influence on the preferred conformation in the solid state.[25] In any event, such small differences in energy lie within the errors inherent in the computational methods (especially the semiempirical calculations) and indicate no more than that both conformations are accessible. Of special concern is the fact that the MMX force field invariably prefers the D_3 conformations, an apparent error shared by the SYBYL[26] and MMFF[27] force fields (data not shown).

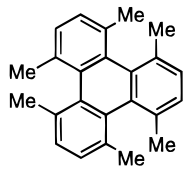
(24) (a) Glidewell, C.; Lloyd, D. *Tetrahedron* **1984**, *40*, 4455−4472. (b) Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 9583−9587.

Table 3. Comparison of Experimental and Calculated Geometries for Overcrowded "D_{3h}" Polycyclic Aromatics

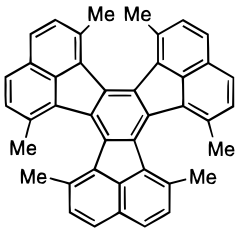
metric[a]	**1**-D_3	**8**-C_2	**9**-C_2	**10**-D_3	**11**-C_2	**12**-C_2	**13**-D_3	**14**-C_2	**15**-D_3
Experimental vs Calculated[b] Geometries									
rms deviation	0.059	0.041	0.058	0.067	0.203[d]				
maximum dev.	0.111	0.067	0.137	0.167	0.612				
Experimental Central Ring Dimensions									
endo[c]	1.397[e]	1.399[f]	1.414[g]	1.444[h]	1.439[i]				
exo[c]	1.434	1.495	1.478	1.384	1.393				
circumference[j]	8.49	8.68	8.68	8.48	8.50				
Calculated Central Ring Dimensions									
endo[c]	1.386	1.407	1.406	1.440	1.444	1.417	1.448	1.400	1.405
exo[c]	1.428	1.470	1.486	1.369	1.370	1.491	1.369	1.464	1.405
circumference[j]	8.44	8.63	8.68	8.43	8.44	8.72	8.45	8.59	8.43
circumference for other conformer	8.48 (C_2)	8.62 (D_3)	8.58 (D_3)	8.43 (C_2)	8.44 (D_3)	8.67 (D_3)	8.46 (C_2)	8.55 (D_3)	8.44 (C_2)

[a] All distances are given in angstroms. [b] The HF/3-21G(*) geometries have been employed for the comparisons. [c] As defined in Table 1. [d] Because of the relatively free rotation of the t-butyl groups, their methyl carbons were not included in the fit. [e] This work. [f] Reference 20. [g] Reference 8. [h] Reference 21. [i] Reference 22. [j] (3 × endo) + (3 × exo).

The presently available experimental structures are perhaps not the very best examples for an examination of the C_2/D_3 dichotomy. For example, the halogens in **8** and **9** may have unforseen electronic effects, and the steric conflict in the decacyclenes **10** and **11** is very small. For this reason the same set of semiempirical and ab initio calculations were performed on the hexamethyltriphenylene **12** and the hexamethyldecacyclene **13** (Table 2); these molecules have comparable steric



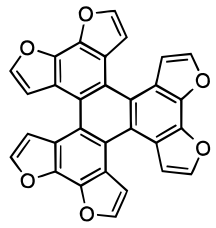
12



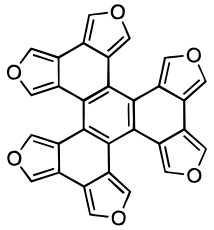
13

conflicts between the methyl substituents and, as hydrocarbons, they should be among the least difficult tests for the computational methods. As expected, the triphenylene **12** is predicted to possess a C_2 conformation, whereas the decacyclene **13** is predicted to be D_3.

We have argued that the choice of the C_2 and D_3 conformation is essentially governed by electronic, not steric, factors. This is best illuminated by the isomeric hexafurotriphenylenes **14** and **15**. For example, is **14** better described as a structure composed of six furans and a central benzene ring (similar to **1**) or as a triphenylene with large peripheral substituents (similar to **8** and **9**)? If the former, it would be expected to adopt a D_3 conformation, if the latter, a C_2. Ab initio calculations favor the latter formulation—there is strong bond alternation of the central ring (see Table 3)—and the C_2 conformation is preferred by a small margin, at least by the higher levels of theory (Table 2). However, reorientation of the peripheral furans to give **15** yields a structure where there are no good "triphenylene" resonance forms. Bond alternation in the central ring is absent,



14



15

and all of the calculations indicate that the D_3 conformation is preferred by 3−6 kcal/mol. Thus, the structures of **14** and **15** are expected to be dramatically different even though the steric conflicts are essentially identical; *the C_2/D_3 dichotomy is a purely electronic effect.*

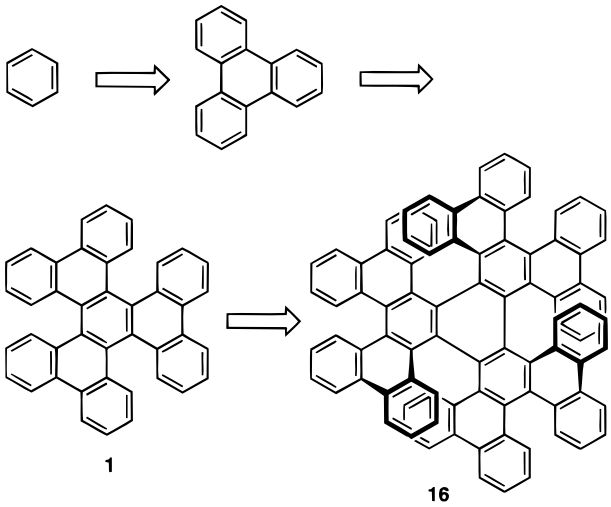
As seen in Table 3, compounds **1** and **8**−**15** exhibit quite a large variation in the degree of bond alternation in their central rings; indeed, the best predictor of their conformational preference appears to be the circumference of their central rings. Those molecules which prefer a D_3 conformation have central ring circumferences that are less than 8.5 Å, while those preferring a C_2 conformation have central ring circumferences that are usually greater than 8.6 Å. It is important to note that both the C_2 and D_3 conformations of the same molecule are calculated to have very similar circumferences of their central ring (Table 3); thus, the central ring geometry is not a product of the conformation, but a determining factor. The lone exception is **11**, for which the circumference is ≤8.5 Å by both experiment and calculation but which is observed to adopt a C_2 structure. However, ab initio calculations indicate that the gas-phase preference is for a D_3 conformation (Table 2), and it is apparent that crystal packing forces have distorted this molecule from an ideal geometry.[25]

Finally, hexabenzotriphenylene may be considered the second-generation "dendrimer" formed by the addition of two benzo groups to the three outer benzene rings of triphenylene, itself formed by the addition of three benzo groups to benzene. Few, if any, other examples of this type of structure are known, and the next member of the triphenylene series would be the compound **16**, which would be exceptionally crowded. Due to its great size ($C_{90}H_{48}$) the conformation of this molecule was explored only at the PM3 level; three separate C_2 conformations and one D_3 conformation were identified which differ in the interleaving of the twelve outer benzene rings. Of these, the D_3 conformation is lowest in energy (see Table 2), a "violation" of our central ring rule-of-thumb; however, this is hardly a simple situation, and any experimental test of the conformation of **16** must await its (very difficult) synthesis.

(25) The experimental structure of compound **11** is an unusually distorted C_2 conformation. The HF/3-21G(*) geometries for **1**, **8**, **9**, and **10** are in excellent agreement with the experimental structures as judged by the rms deviations of their best fits (see Table 3), but the experimental structure for **11** shows a three times greater rms deviation from its calculated geometry. The six *tert*-butyl groups of **11** must be accommodated in the crystal, and it appears that they provide long levers for packing forces to alter the geometry of the molecule from the gas-phase "ideal", for which the higher levels of theory favor a D_3 conformation.

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

(27) Halgren, T. A. *J. Comput. Chem.* **1996**, *17*, 490−519.



Conclusion

Hexabenzotriphenylene has been unambiguously characterized for the first time as a D_3-symmetric molecular propeller, which is unlike the C_2 structures preferred by other crystallographically characterized, crowded, highly symmetric triphenylenes. After evaluation of energies and geometries of this and a variety of similar molecules by a wide range of computational methods, we conclude that to obtain *both* reasonably accurate geometries and relative conformational energies for such compounds, one must go beyond simple molecular mechanics and semiempirical techniques, to, at the very least, low level ab initio calculations.

Experimental Section

Hexabenzotriphenylene (1). Phenanthrene-9,10-dicarboxylic anhydride[9] (**6**, 60 mg, 0.24 mmol) was placed in the sealed end of a quartz tube (1 cm × 60 cm), and the tube was attached to a vacuum pump and evacuated (∼0.2 Torr). The center section of the tube (∼20 cm) was placed in a tube furnace, and the furnace was heated to 700 °C. A Bunsen burner was used to heat and sublime the anhydride (with some decomposition and gas evolution) into the center section of the tube. During the next few minutes, a yellow-brown material condensed on the distal, unheated portion of the quartz tube. This material was extracted with chloroform, and the extract was filtered, concentrated, and fractionated by preparative silica gel TLC (solvent, 4:1 hexanes−benzene). There were three major bands with R_f 0.57, 0.32, and 0.26. The fraction at R_f 0.57 was shown by ^{1}H NMR analysis to be phenanthrene. The material collected at R_f 0.32 proved to be pure compound **1** (2.2 mg, 5% yield). Slow cooling of a solution of **1** in nitrobenzene yielded yellow crystals suitable for X-ray analysis. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.22 (t, 6 H, J = 7.5 Hz), 7.55 (t, 6 H, J = 7.5 Hz), 8.16 (d, 6 H, J = 7.5 Hz), 8.54 (d, 6 H, J = 7.5 Hz); MS, m/z 528 (M^+, 30), 352 ($M - C_{14}H_8$, 100), 176 ($M - C_{28}H_{16}$, 22); UV (heptane) λ_{max} 212, 236, 250, 298 (sh), 348 (sh), 362, 382 (sh) nm.

X-ray Crystallographic Analyses of Hexbenzotriphenylene (1). Formula $C_{42}H_{24}$; monoclinic, space group $P2_1/c$, a = 19.9721 (5) Å, b = 7.0005 (1) Å, c = 19.5456 (5) Å, β = 104.013 (1)°, V = 2651.4 (1) Å^3, Z = 4, D_{calcd} = 1.324 g/cm^3. An orange plate with dimensions 0.04 mm × 0.25 mm × 0.28 mm was used for intensity measurements at 298 K with a Nonius KappaCCD diffractometer and Mo Kα radiation (λ = 0.710 74 Å). A total of 45 305 reflections (θ_{max} = 27.4°) were indexed, integrated, and corrected for Lorentz and polarization effects (using the program DENZO[28]), the data were scaled and merged (SCALEPACK[28]) to give 6512 unique reflections (R_{int} = 0.066), and 456 extinctions were discarded to give 6016 unique reflections in the final data set. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 (SHELXTL[17]). All atomic coordinates were refined; carbon atoms were refined anisotropically, and hydrogens isotropically. The refinement converged to $R(F)$ = 0.0512, $wR(F^2)$ = 0.1091, and S = 1.095 for 3652 reflections with $I > 2\sigma(I)$, and $R(F)$ = 0.1007, $wR(F^2)$ = 0.1327, and S = 1.013 for 6016 unique reflections, 475 parameters, and 0 restraints. A second determination was performed at 110 K using the same crystal: a = 19.8971 (8) Å, b = 6.9274 (2) Å, c = 19.4153 (8) Å, β = 103.846 (1)°, V = 2598.3 (2) Å^3, D_{calcd} = 1.351 g/cm^3; 57 890 reflections (θ_{max} = 27.5°), 5952 unique reflections; $R(F)$ = 0.0563, $wR(F^2)$ = 0.1417, and S = 1.176 for 3809 reflections with $I > 2\sigma(I)$, and $R(F)$ = 0.0962, $wR(F^2)$ = 0.1621, and S = 1.054 for 5952 unique reflections, 475 parameters, and 0 restraints. Full details are provided in the Supporting Information.

Computational Studies. The MMX force field implemented in PCMODEL (Version 5.0; Serena Software, Bloomington, Indiana) was employed for molecular mechanics calculations. All semiempirical molecular orbital calculations (MNDO, AM1, PM3) and most conventional ab initio calculations at the HF/STO-3G and HF/3-21G(*) levels were performed by using the SPARTAN program package (Version 5.0; Wavefunction, Inc., Irvine, California), and its built-in default thresholds for wave function and gradient convergence were employed. Frequency calculations were performed on the AM1- and PM3-optimized equilibrium geometries to verify that these were true potential minima. GAUSSIAN 94 (Gaussian, Inc., Pittsburgh, Pennsylvania) was employed for several of the larger ab initio calculations, again employing the default convergence criteria. In addition to the conventional Hartree−Fock techniques, hybrid density functional calculations (HDFT; an improvement over DFT methods obtained by inclusion of the exact Hartree−Fock exchange based on Kohn−Sham orbitals) were performed for comparison in this study. The HDFT methods employed two different exchange-correlation functionals, Becke's three-parameter functional[29] in combination (a) with nonlocal correlation provided by the Lee−Yang−Parr expression[30,31] which contains both local and nonlocal terms, B3LYP, and (b) with the nonlocal correlation provided by the Perdew 91 expression,[32] B3PW91. Dunning's correlation consistent basis set, cc-pVDZ,[33] was used with the HDFT methods. This basis set is a [3s2p1d] contraction of a [9s4p1d] primitive set. Finally, the HF/3-21G(*) calculations for compound **11** were performed by using the parallel version of GAMESS[34] and its analytically determined gradients and search algorithms.

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Supporting Information Available: Crystal structure reports for compound **1** (including full experimental details, tables of atomic coordinates, bond distances, bond angles, thermal parameters, and selected figures), and an X-ray crystallographic file, in CIF format (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA983471I

(28) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307−326.
(29) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.
(30) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.
(31) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200−206.
(32) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244−13249.
(33) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358−1371.
(34) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Elbert, S. T. *J. Comput. Chem.* **1993**, *14*, 1347−1363.