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Synthesis and Structure of a Polyphenylene Macrocycle Related to "Cubic Graphite"

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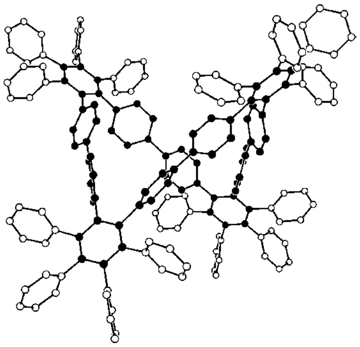
ABSTRACT



Palladium-catalyzed coupling of 1,2-bis(4-bromophenyl)-3,4,5,6-tetraphenylbenzene and the corresponding hexaphenylbenzene bis(boronic acid) gave a mixture of linear and cyclic oligomers of hexaphenylbenzene. An X-ray crystal structure of the tetrameric oligomer showed it to be the polyphenylene macrocycle 4 ($C_{168}H_{112}$). The roughly D_2 symmetric macrocycle contains a large central cavity, and it is one of the channel substructures of "phenylogous cubic graphite".

The carbon framework that has come to be known as "cubic graphite" (**1**, Scheme 1) was first proposed by Gibson et al. in 1946.[1] The structure is composed entirely of benzene rings. Each benzene ring is attached to six other, different benzene rings, and the magnitude of the dihedral angle between all pairs of attached benzene rings is 109.5°. In addition, the benzene rings may be divided into two groups, here illustrated with plain and bold rings; every bold benzene is bound to six plain benzenes, and vice versa. Cubic graphite is the ultimate polyphenylene structure,[2] but it is doubtful that the substance itself will ever be made. It is not the thermodynamically preferred form of carbon (various calculations[3] place it 4.8 to 6.0 kcal/mol above graphite), and so a synthesis under kinetic control is required. However, such a synthesis—which would presumably utilize hexasubstituted benzenes as precursors—will likely fail because there is insufficient space in the carbon lattice to accommodate the reagents needed to form the new C−C bonds.

Now consider a homolog, or phenylog, of cubic graphite (**2**, Scheme 1). The structure is composed of hexaphenylbenzene subunits linked in the same fashion as the benzenes in cubic graphite, but unlike cubic graphite, this structure contains enormous cavities, which would allow the easy passage of solvent and reagents. Given the current interest in polyphenylene nanostructures,[2,4] phenylogous cubic graphite and its substructures are inviting targets for synthesis, and the macrocyclic substructures **3** and **4**, in particular, are especially attractive. Large polyphenyl and polyphenylene macrocycles have shown a propensity to form crystals with large channels,[5,6] and thus are candidates for making hydrophobic, ordered, porous materials,[7] and these particular

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[1] Gibson, J.; Holohan, M.; Riley, H. L. *J. Chem. Soc.* **1946**, 456−461.

[2] Berresheim, A. J.; Müller, M.; Müllen, K. *Chem. Rev.* **1999**, *99*, 1747−1785.

[3] (a) O'Keeffe, M.; Adams, G. B.; Sankey, O. F. *Phys. Rev. Lett.* **1992**, *68*, 2325−2328. (b) Baughman, R. H.; Cui, C. *Synth. Met.* **1993**, *55*, 315−320.

[4] Watson, M. D.; Fechtenkötter, A.; Müllen, K. *Chem. Rev.* **2001**, 101, 1267−1300.

[5] Pascal, R. A., Jr.; Barnett, L.; Qiao, X.; Ho, D. M. *J. Org. Chem.* **2000**, *65*, 7711−7717.

[6] Müller, P.; Uson, I.; Hensel, V.; Schlüter, A. D.; Sheldrick, G. M. *Helv. Chim. Acta* **2001**, *84*, 778−784.

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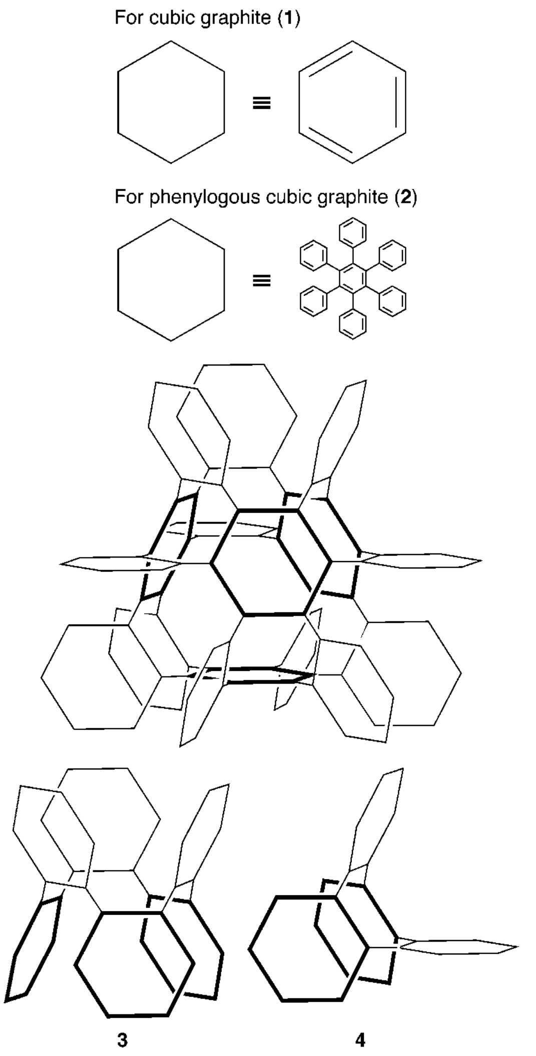
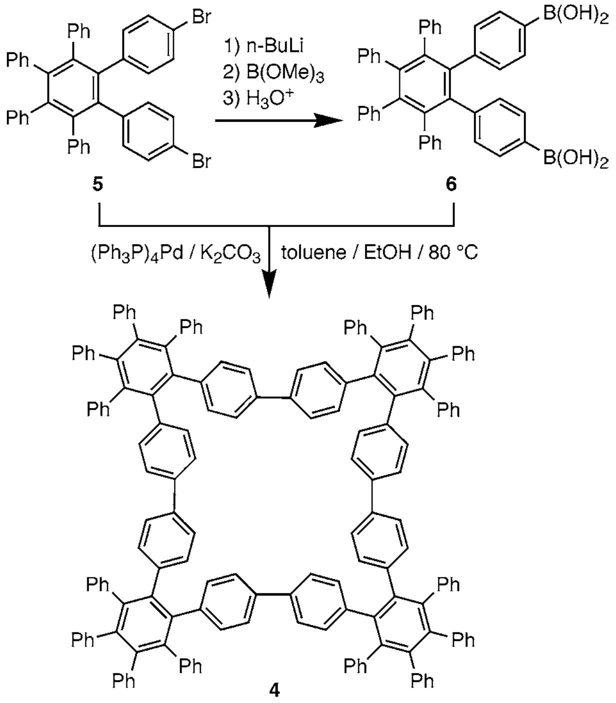
Scheme 1



macrocycles ($C_{252}H_{168}$ and $C_{168}H_{112}$) might be produced in very short syntheses.

The alternating plain and bold rings in **3** and **4** suggest that they can be prepared by coupling two complementary hexaphenylbenzene derivatives. Accordingly, the dibromohexaphenylbenzene **5** (Scheme 2) was converted to the bis(boronic acid) **6**, and equimolar quantities of the two were employed in a Suzuki coupling reaction.[8] This procedure gave a 35% yield of nonpolar oligomers of hexaphenylbenzene as well as a considerable amount of polar material (possibly unreacted boronic acids). The nonpolar material was fractionated into five components, and FAB MS analysis indicated that these five fractions contained two, three, four, five, and six hexaphenylbenzene units, respectively. The most abundant product was the trimeric fraction (17% yield), but the base peak in its mass spectrum was *m/z* 1758, which corresponds to the molecular ion of a nonmacrocyclic trimer retaining two bromine atoms ($C_{126}H_{84}Br_2$). The same was true of the pentamer (4% yield, *m/z* 2824 ($C_{210}H_{140}Br_2$)). In contrast, the tetramer (5% yield) showed predominantly *m/z* 2130, possibly the macrocycle **4** ($C_{168}H_{112}$), and the hexameric fraction (1.5% yield) showed prominent ions for both macrocyclic and acyclic (bromine-containing) molecules. However, the structures of these compounds could not be assigned with complete confidence on the basis of their MS, ^1H NMR, and ^{13}C NMR spectra, so we focused our attention on the crystallization of the hexamer and tetramer.

Scheme 2



Both compounds are freely soluble in common organic solvents, but after many trials only compound **4**[9] gave satisfactory crystals; its hepta(nitrobenzene) solvate was obtained from nitrobenzene−ethylene glycol, a highly unusual solvent combination. The X-ray structure[10] of **4** is illustrated in Figure 1. It is one of only about a dozen X-ray structures of hydrocarbon molecules containing more than

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(7) Davis, M. E. *Nature* **2002**, *417*, 813−821.

(8) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457−2483.

(9) From 0.32 mmol each of **5** and **6** were obtained 16 mg of **4** (0.0075 mmol, 4.7% yield); TLC R_f 0.38 (1:1 hexanes−benzene); ^1H NMR ($CDCl_3$) δ 6.68−6.97 (m); ^{13}C NMR ($CDCl_3$) δ 124.5, 125.1, 125.3, 125.4, 125.5, 125.6, 126.7, 126.8, 126.9, 127.0, 130.1, 131.5, 131.6, 131.7, 131.8, 133.2, 137.3, 137.5, 137.8, 139.0, 139.2, 139.3, 139.5, 139.9, 140.0, 140.1, 140.5, 140.61, 140.67, 140.73, 140.8, 141.0; FAB MS, *m/z* 2130 ($^{12}C_{166}{}^{13}C_2H_{112}$, M^+, 91) and 1598 ($^{12}C_{124}{}^{13}C_2H_{84}$, M − $C_{42}H_{28}$, 100).

(10) Crystal data for **4**: $C_{168}H_{112}\cdot 7C_6H_5NO_2$; monoclinic, space group *Cc* (No. 9); $a = 31.708$ (1) Å, $b = 20.3142$ (8) Å, $c = 26.611$ (1) Å, $\alpha = 90°$, $\beta = 109.871$ (2)°, $\gamma = 90°$, $V = 16\,120$ (1) Å^3, $Z = 4$. A colorless prism (0.06 mm × 0.10 mm × 0.11 mm) was used for data collection, using Mo Kα radiation on a Nonius KappaCCD diffractometer at 200 K. A total of 38 421 reflections ($\theta_{max} = 18.81°$) were reduced to 12 328 unique reflections by using the program DENZO-SMN.[11] The structure was solved by molecular replacement (PATSEE[12]) and it was refined by using Siemens SHELXTL.[13] The disordered solvent electron density was treated by using the SQUEEZE/BYPASS procedure[14] implemented in PLATON,[15] and due to the low number of data for such a large molecule, the benzene rings were modeled as ideal hexagons. $R(F) = 0.0845$, $wR(F^2) = 0.1834$, and $S = 1.214$ for 5344 reflections with $I > 2\sigma(I)$, and $R(F) = 0.1589$, $wR(F^2) = 0.2173$, and $S = 0.922$ for 12 328 unique reflections, 1177 parameters, and 1178 restraints. Full details are given in the Supporting Information.

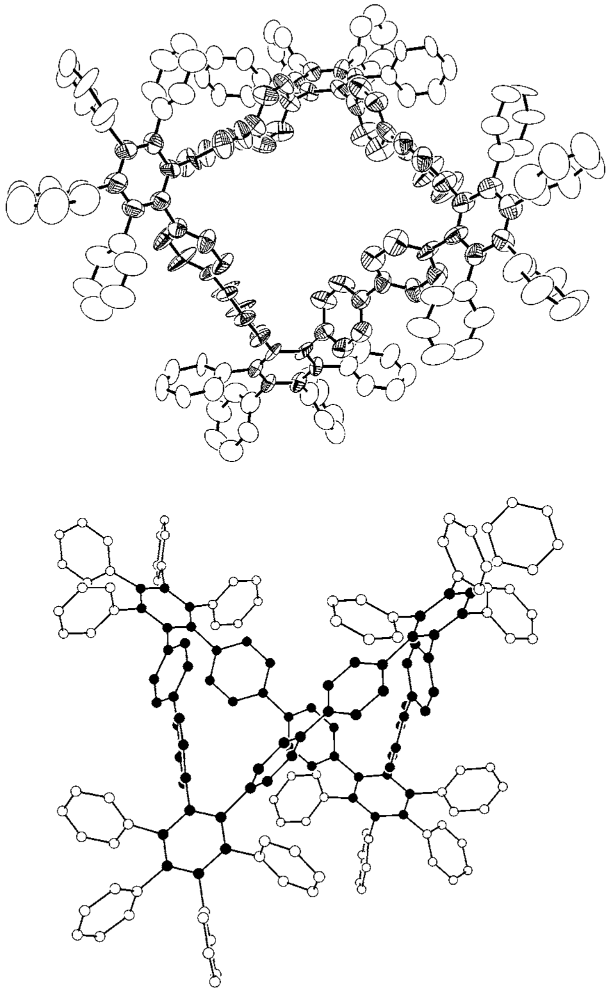

Figure 1. Two views of the molecular structure of compound **4**. Hydrogen atoms have been omitted for clarity, and, in the upper drawing, thermal ellipsoids have been drawn at the 50% probability level.

100 carbons,[6,16] and one of only two structures of large polyphenylene macrocycles.[6]

In the crystal, **4** lies on a general position and thus possesses C_1 symmetry, but its conformation is approximately C_2 or (less closely) D_2 symmetric. The compound contains two large, V-shaped clefts and a central channel between them. The width of the channel is approximately 6 Å, and from it the clefts open to a width of 15 Å. These spaces are occupied by disordered nitrobenzene molecules in the crystal. The ^{13}C NMR spectrum of **4** is consistent with a D_2 symmetric structure in solution as well; 32 resonances were observed; 34 resonances would be expected for a D_2 symmetric structure with fast rotation of the peripheral phenyl groups. However, this apparent high symmetry may reflect only a time-averaged structure. An AM1[17] geometry optimization of **4** under the constraint of D_2 symmetry led to a structure that is 3 kcal/mol higher in energy than the C_1 structure obtained by optimizing the X-ray conformation.

The overall yield of **4** from this cyclization reaction is at present low, despite the use of various catalysts for the reaction, but if it can be improved, then larger macrocyclic substructures of phenylogous cubic graphite will be within reach.

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Supporting Information Available: Full experimental procedures for the preparation of **4** and **6**, the full procedure for the solution and refinement of the X-ray structure of **4**, and a crystallographic information file (CIF) containing the X-ray structural information. This material is available free of charge via the Internet at http://pubs.acs.org.

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