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Carbon Nanorings

All-Hydrocarbon Inclusion Complexes of Carbon Nanorings: Cyclic [6]- and [8]Paraphenyleneacetylenes**

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The discovery and large-scale synthesis of fullerenes[1] has aroused renewed interest in π-conjugated systems on curved surfaces. The subsequent discovery of layered carbon nanotubes,[2,3] bucky onions,[4] and the "fullerene peapod"[5] has raised questions about the nature of the attractive force involved in the layering of curved π-conjugated systems. However, the poor solubility of these substances has prohibited detailed studies that might answer such questions. Suitable model compounds would be needed—in this context, fullerenes, corannulene,[6] and related compounds,[7,8] as well as belt-shaped molecules[9] have been studied both experimentally and theoretically—however, the question has remained to be answered clearly. We have recently reported the synthesis and spectroscopic characterization of cyclic paraphenyleneacetylenes, [6]CPPA (**1**) and [8]CPPA (**2**), as strained but isolable compounds.[10] Semi-empirical calcula-

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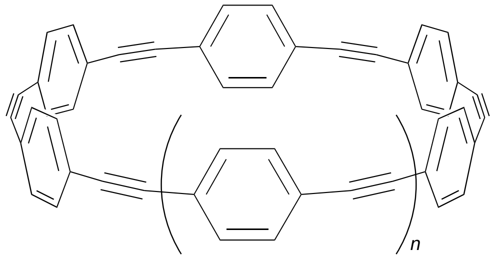
tions (AM1 and PM3) predict that they have cylindrical structures with diameters of 1.31 and 1.74 nm, respectively, and thus may be termed "carbon nanorings", which would serve as good model compounds for carbon nanotubes. Here we report the X-ray crystallographic characterization of inclusion complexes of **1** with hexamethylbenzene (HMB) and **2** with four toluene (Tol) molecules, which are the first all-hydrocarbon inclusion complexes of cylindrical conjugated systems.



1 ($n = 1$); **2** ($n = 3$)

Crystallization from a solution of [6]CPPA (**1**) in dichloromethane/hexane containing a stoichiometric excess of HMB (approximately 5 equiv) afforded the 1:1 inclusion complex **1**·HMB as distorted hexagonal prisms (decomp. 156 °C).[11] Similarly, a solution of [8]CPPA (**2**) in toluene furnished the 1:4 inclusion complex **2**·4 Tol as prismatic single crystals.[12] In contrast to HMB, hexachlorobenzene, the molecular size of which (van der Waals diameter, $D = 9.7$ Å) is almost the same as that of HMB ($D = 9.8$ Å), failed to yield a crystalline complex with **1**. While the fine needlelike crystals of **1** obtained from benzene or carbon tetrachloride are sensitive to air (oxygen) even at low temperatures,[10] it is notable that the crystals of **1**·HMB are fairly stable in air at room temperature. On the other hand, crystals of **2**·4 Tol tend to effloresce with the loss of the toluene molecules at around room temperature. Crystals were, therefore, loaded in sealed capillaries for X-ray analysis.

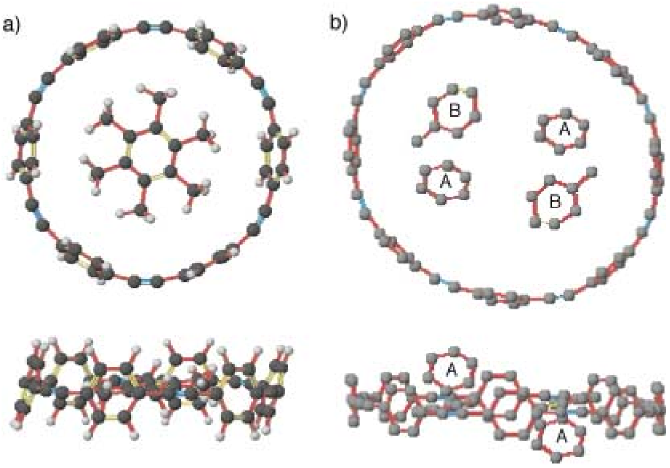


Figure 1. Molecular structures of: a) **1**·HMB and b) **2**·4 Tol. The protons as well as the methyl carbon atoms of toluene molecules A in the **2**·4 Tol complex have been removed for clarity. A and B indicate toluene molecules with different spatial geometries.

Table 1: Structural parameters of host molecules of the reported inclusion complexes.

	1	**2**
long axis [Å]	13.3	18.4
short axis [Å]	13.0	16.3
average bond angles of sp carbon atoms [°]	162.5, ≈165.6 (164.4)	164.3, ≈171.4 (168.6)
twist angles of benzene rings [°][a]	1, −9, 17	1, 2, 2, 5
bend angles of benzene rings [°][b]	151.9, 149.2, 149.5	160.5, 157.6, 156.6, 154.0

[a] Evaluated from dihedral angles between least-square planes. [b] The angles between the two *para*-benzyl bonds of each boat-form benzene ring.

Figure 1 shows the structures of the inclusion complexes. There are a number of notable features in the results: First, the host molecules **1** and **2** have fairly smooth cylindrical structures, as predicted by theoretical calculations, with bent triple bonds and shallow benzene rings in a boat conformation (Table 1). The average bond angle of the sp carbon atoms of **1** (164.3°) and **2** (168.6°) are similar to those found in the strained but fairly stable cyclooctyne (165°)[13] and [2.2.2.2]metacyclophanetetrayne (168.8°);[14] the high stability of the **1**·HMB complex seems reasonable from the above results. Second, while the cyclic paraphenyleneacetylene moiety of **1**·HMB is almost circular when viewed from above and slightly oblique from a side-on view, its counterpart in **2**·4 Tol is rather elliptical, with a more upright geometry. Since the ring sizes of **1** and **2** are very large relative to their constituent carbon–carbon bonds, the carbon nanorings would be expected to be considerably flexible and, hence, susceptible to deformation by the packing forces within the crystals. Therefore, the relatively high reactivity of **1** and **2** after efflorescence would result from the flexibility as well as the ring strain of these compounds. Third, the cavity size of **1** is comparable to that of (10,10) carbon nanotubes (13.8 Å),[15] and that of **2** is larger than that of well-known tubular host molecules, such as [8]calixarenes,[16] cyclic oligosaccharides (cyclodextrins),[17] and cyclic peptides.[18] Fourth, the crystal structures (Figure 2) can be classified as possessing a γ structure, similar to those of coronene and kekulene,[19] in which the host molecules overlap each other in a parallel-displaced manner. In both complexes, diphenyleneacetylene units

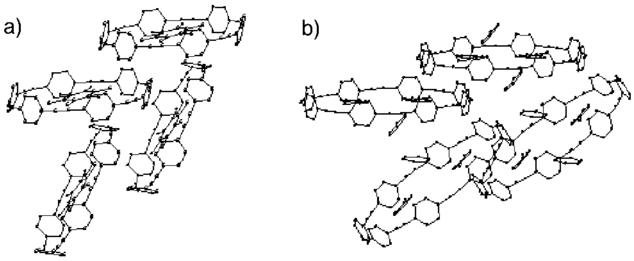


Figure 2. Crystal packing of: a) **1**·HMB and b) **2**·4 Tol. The protons of both complexes have been omitted for clarity as have the methyl carbon atoms of the toluene molecules A in the **2**·4 Tol compound.

interlock each other, rather like gear wheels. Therefore, these crystals do not possess any open channels that result from the arrangement of the host molecules.

In complex **1**·HMB, the guest HMB molecule is situated at the center of the cavity of **1**, tilted at 9° from the horizontal plane of the host ring. Although no particularly short contacts are seen, there are contacts close to the van der Waals distance between the carbon framework of **1** and the methyl groups of the HMB moiety (3.7–3.8 Å).

In contrast, there are two pairs of toluene molecules with differing spatial geometry in complex **2**·4Tol: One pair of toluene molecules (A; see Figure 1) is situated at the severely bent sites of the elliptical cylinder and the molecules are only moderately tilted (12°), while those of the other pair (B) are somewhat disordered and are tilted to a greater extent. The A-type toluene molecules appear to act as an adhesive between the neighboring host molecules through multiple edge-to-face interactions (Figure 3); the π face of a guest molecule is in contact with the edge of an aromatic ring of a neighboring host molecule (the closest C···H contact is 3.0 Å), and the edge of the guest is also in contact with the inner surface of the host (the closest C···H contact of this variety is 2.9 Å). The rapid efflorescence of the crystal may be a result of the higher mobility of the disordered B-type toluene molecules.

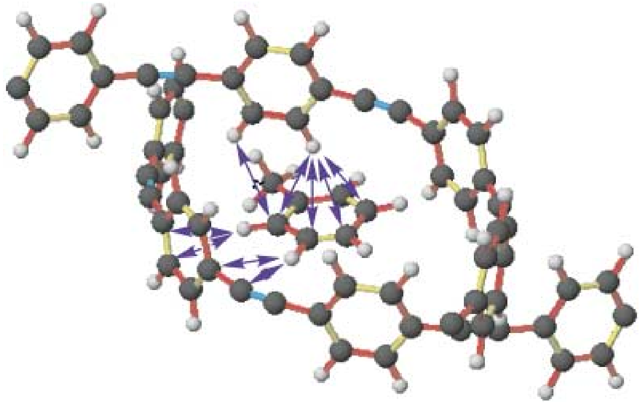


Figure 3. A partial molecular structure of **2**·4Tol. Short contacts (less than 3.2 Å) between **2** and the toluene molecule A are indicated with blue arrows.

It is noteworthy that although CPPAs **1** and **2** form the complexes **1**·HMB and **2**·4Tol as crystalline substances, spectroscopic studies (electronic absorption and ^{1}H NMR) have provided little evidence for the complexation between the host and guest molecules in nonpolar solvents such as benzene and chloroform. Therefore the attractive force between the host and guest molecules or their association constants must be weak or small, respectively. Nevertheless, the formation of such crystalline complexes indicates the existence of an attractive force between the hosts and guests.

Theoretical studies predict that curved aromatic hydrocarbons would be polarized owing to the unsymmetrical nature of their π orbitals.[7c,20–22] It has been reported, however, that a semi-empirical calculation (AM1) and a density functional calculation (BP/DN**) gave inconsistent predictions for the electrostatic potential on the inside surface of corannulene.[7c]

In view of the higher electronegativity of an sp^2 carbon atom, as compared to its sp^3 counterpart, and the hyperconjugative property of a methyl group, the methyl protons of HMB and toluene and the aromatic protons of toluene should be positively charged, though only very slightly.[23] On the contrary, hexachlorobenzene, which failed to form a crystalline complex, should take on partial negative charge on the outer chlorine atoms. Thus, the attractive force in the complexes **1**·HMB and **2**·4Tol, although weak, would be best understood when assuming that the concave surfaces of the carbon nanorings **1** and **2** have an electrostatically negative potential. Polarization of the π-conjugated systems of **1** and **2** is further supported by the formation of significantly stable complexes between **1** and fullerenes, which are reported in the accompanying paper.[24]

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[11] Crystal data for **1**·HMB ($C_{60}H_{42}$): yellow prism, crystal dimensions 0.3 × 0.1 × 0.1 mm, $M_r = 762.97$: monoclinic, space group $P2_1/a$ (No. 14), $a = 14.343(2)$, $b = 10.227(1)$, $c = 15.487(2)$ Å, $\beta = 106.76(2)°$, $V = 2277.6(51)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.164$ g cm^{-3}, $Mo_{K\alpha}$ ($\lambda = 0.71069$ Å), $2\theta_{max} = 55°$. Intensity data were collected on a

Rigaku RAXIS-RAPID Imaging Plate diffractometer at 296 K. The structure was solved with direct methods on F^2 with SHELXS-86. A total of 8006 reflections were collected, 4892 unique reflections were measured and used in the refinement, 271 parameters, $R1 = 0.082$, w$R2$(Rw) = 0.165 (0.168) for 853 reflections with $I > 2\sigma(I)$, GOF = 0.67, max. peak in final difference map = 0.78 e Å^{-3}. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically and refined by using a rigid model. The high $R1$ value is a result of the disorder of an included molecule.

[12] a) Crystal data for **2**·4 Tol ($C_{92}H_{64}$): Crystal dimensions 0.2 × 0.2 × 0.3 mm, $M_r = 1159.49$, monoclinic, space group $C2/c$ (No. 15), $a = 20.320(9)$, $b = 12.892(5)$, $c = 29.131(2)$ Å, $\beta = 105.02(2)°$, $V = 7370.6(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.263$ g cm^{-3}, $Mo_{K\alpha}$ ($\lambda = 0.71069$ Å), $\theta_{max} = 23.86°$. Intensity data were collected on a KappaCCD diffractometer at 298 K. A total of 6643 reflections were collected, 6639 independent reflections were measured and used in the refinement, 431 parameters, $R1 = 0.062$, $wR2 = 0.093$ for 2217 reflections, GOF = 2.61, max. peak in final difference map = 0.78 e Å^{-3}. The structure was solved with direct methods on $F > 3\sigma$ with maXus (MacScience Japan). All non-hydrogen atoms, except for the methyl carbon atoms of the disordered toluene molecules, were refined anisotropically. Hydrogen atoms associated with **2** and the fixed toluene molecules were refined isotropically, and the other hydrogen atoms were placed geometrically and refined by using a rigid model. The high GOF value results from the disordered toluene molecules. b) CCDC-153427 (**1**·HMB) and CCDC-153428 (**2**·4 Tol) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdccam.ac.uk).

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