

Synthesis, structure and inclusion properties of 1,4,15,18-tetrahydro-1,4,15,18-tetraoxodibenzo[*b,h*]tetraphenylene†

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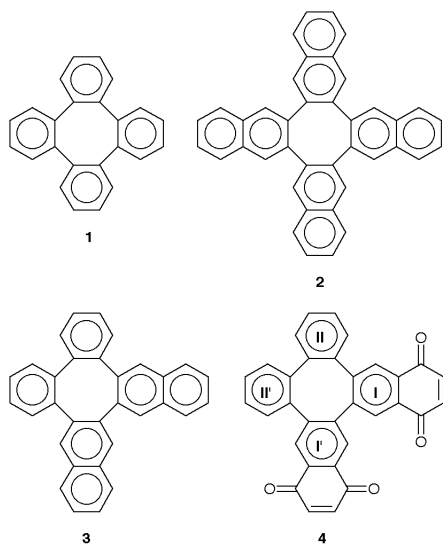
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Received (in Cambridge, UK) 24th May 1999, Accepted 24th June 1999

The new host molecule 1,4,15,18-tetrahydro-1,4,15,18-tetraoxodibenzo[*b,h*]tetraphenylene forms inclusion complexes with specific guest molecules, exhibiting two distinctly different types of host lattices whose construction is dictated by intermolecular, face-to-face $\pi\cdots\pi$ interactions between benzoquinone rings across inversions centres.

Recent advances in crystal engineering¹ have generated a large variety of fascinating supramolecular frameworks which rely on non-covalent bonding interactions^{2,3} for their self-organization. The geometry of the π -stacking motif is of particular interest since Burley and Petsko⁴ have identified two important orientations for aromatic–aromatic interactions, namely face-to-face and edge-to-face interactions, in their survey of protein crystal structures.⁵

Our investigation of the host–guest chemistry of tetraphenylene **1**⁶ and its benzo-fused derivatives, *e.g.* **2**^{6d} and **3**,^{6c} revealed that a secondary molecular C_2 axis passing through the



centres of a pair of opposite carbon–carbon single bonds, which gives tetraphenylenes their twisted shapes, would be a prerequisite component of inclusion behaviour.^{6a,b,7} In order to substantiate this presumption and to enhance the inclusion capacity of the otherwise non-polar tetraphenylenes, namely **1**, **2** and **3**, we decided to undertake the design of a functionalized oxo derivative of **3**. Here we report the synthesis and “guest-specific” clathrate inclusion property of 1,4,15,18-tetrahydro-1,4,15,18-tetraoxodibenzo[*b,h*]tetraphenylene (**4**).

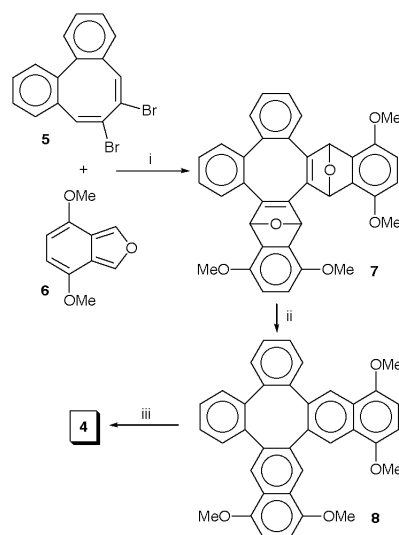
As can be seen in Scheme 1, the synthesis of bis-quinone **4** began with dehydrobromination of the known dibromide **5**⁸

with Bu^tOK in the presence of freshly generated 4,7-dimethoxyisobenzofuran (**6**).⁹ This reaction presumably proceeded through a cyclodienediene intermediate⁸ which underwent intermolecular Diels–Alder reaction with the reactive isobenzofuran **6**. In this way, **7** was obtained in 53% yield as the major product after careful chromatographic separation. Low-valent titanium deoxygenation¹⁰ of **7** then produced the tetramethoxy compound **8** in 79% yield. On oxidation with silver(II) oxide and nitric acid in dioxane, **8** was smoothly converted to the desired product **4** in 60% yield.

A mixture of toluene–xylene–mesitylene (1:1:1 v/v/v) was added to a solution of **4** in CH₂Cl₂, and the resulting solution allowed to stand at room temperature for several days, after which crystals of **4**·C₆H₃Me₃ appeared in the form of yellow prisms. Slow evaporation of a solution of **4** in hexane–EtOAc (1:1 v/v) yielded yellow plate-like crystals of **4**·C₆H₁₄. Recrystallisation of **4** in EtOAc–AcOH (1:1 v/v) gave yellow prismatic crystals of **4**·AcOH. Yellow crystals of **4**·C₆H₁₂ in the form of prisms were obtained from evaporation of a solution of **4** in cyclohexane–EtOAc (1:1 v/v).

Host **4** exhibits selective inclusion behaviour toward aromatic solvents: it does not form any crystalline adduct with either pyridine or benzene, and it selectively includes mesitylene from an equivolume mixture of toluene–*p*-xylene–mesitylene, forming a 1:1 crystalline complex. Among potential guests of the aliphatic type, only *n*-hexane and AcOH (as a hydrogen-bonded cyclic dimer) have been found to form 1:1 crystalline inclusion compounds with **4**. In the case of saturated ring systems, cyclohexane readily forms a 1:1 complex with **4**, but THF does not.

X-Ray analysis** has shown that the 1,4,15,18-tetrahydro-1,4,15,18-tetraoxodibenzo[*b,h*]tetraphenylene host molecule (**4**) has normal molecular dimensions and exhibits structural features common to the four inclusion compounds: a crystallographic C_2 axis†† passes through the midpoints of two opposite



Scheme 1 Reagents and conditions: i, Bu^tOK, THF (53%); ii, TiCl₄, LiAlH₄, Et₃N, THF, reflux (79%); iii, AgO, HNO₃, dioxane (60%).

† Dedicated to Professor Peter J. Garratt on the occasion of his retirement.

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Table 1 Selected structural parameters of inclusion complexes of 1,4,15,18-tetrahydro-1,4,15,18-tetraoxodibenzo[*b,h*]tetraphenylene (**4**)

Inclusion complex	Dihedral angle between rings (°) in host molecule		Intermolecular $\pi\cdots\pi$ interaction between pair of adjacent benzoquinone rings	
	I-I'	II-II'	<i>d</i> , interplanar spacing/Å	<i>D</i> , centroid-to-centroid distance/Å
4 ·Mesitylene	56.1	62.7	3.476	3.728
4 ·Hexane	67.1	63.3	3.581	3.909
4 ·Acetic acid	73.2	65.0	3.426	3.926
			3.508	3.825
4 ·Cyclohexane	69.7	65.3	3.441	3.883

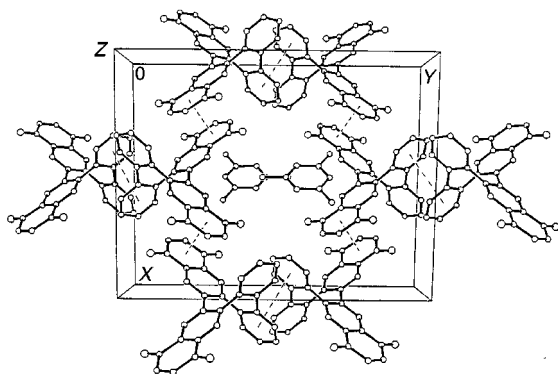


Fig. 1 Crystal structure of **4**·mesitylene (1:1) showing the packing of mesitylene guest molecules arranged in a zigzag column along an open channel running parallel to the *c* axis. The centroid-to-centroid distances between pairs of $\pi\cdots\pi$ interacting rings are represented by broken lines.

carbon-carbon single bonds in the central cyclooctatetraene ring, which is tub-shaped with C-C and C=C bonds alternating around it. The naphthoquinone rings I and I' and the benzene rings II and II' are disposed alternately above and below the mean plane of the molecule, and the dihedral angles between pairs of rings of the same kind are listed in Table 1. The resulting molecular configuration of **4** enables it to function as an efficient host for a wide range of guest molecules.

Complexes **4**·C₆H₃Me₃ and **4**·C₆H₁₄ are isostructural with the same host framework and differ only in regard to the enclosed guest molecules. As shown in Fig. 1, the host molecules are connected by intermolecular face-to-face $\pi\cdots\pi$ interactions¹¹ between pairs of centrosymmetrically-related benzoquinone rings to form a zigzag chain running parallel to the [1 0 1] direction. The contact between these rings is described by two geometric parameters, namely the interplanar spacing *d* and the centroid-to-centroid distance *D*, as listed in Table 1. In an analogous manner, similar but much weaker $\pi\cdots\pi$ interactions between benzene rings across inversion centres (*d* = 4.341, *D* = 4.389 Å) give rise to another type of zigzag chain running parallel to the *c* axis. The three-dimensional host lattice resulting from these two systems of inter-connected chains contains open channels running parallel to the *c* axis, which accommodate the mesitylene guest molecules in a zigzag fashion.

Compounds **4**·AcOH and **4**·C₆H₁₂ have essentially the same type of sandwich-like crystal structure although they belong to different space groups. In each case the host molecules are linked by $\pi\cdots\pi$ interactions between benzoquinone rings across centres of symmetry to form an infinite chain. Such chains are aligned side by side to constitute a layer, but there is no significant interaction between them. The chains are orientated in different directions, [0 1 $\bar{1}$] in **4**·AcOH and [1 0 $\bar{1}$] in **4**·C₆H₁₂, and the separations between adjacent chains are almost equal, being 8.19 and 8.13 Å, respectively.

In **4**·AcOH, two centrosymmetrically-related guest molecules are linked by a pair of O-H \cdots O hydrogen bonds to form a cyclic dimer, in which all non-hydrogen atoms are almost coplanar (mean deviation 0.026 Å). These dimers are accommodated in voids and sandwiched between layers of host molecules whose mean planes correspond to the (100) series of planes. In a similar manner, the disordered cyclohexane guest molecules in **4**·C₆H₁₂ are sandwiched between pairs of host layers that match the (010) planes. The difference in size of the guest molecules is reflected in the interplanar spacings of the host layers, which are 8.83 and 9.65 Å, respectively.

This work was fully supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project Ref. No. CUHK 456/95P). D.M.D. and X.P.Y. acknowledge with thanks the award of Croucher Foundation Visitorships by the Croucher Foundation (Hong Kong).

Notes and references

** Crystal data for **4**·mesitylene: C₃₂H₁₆O₄·C₉H₁₂, *M* = 584.6, monoclinic, space group *C2/c*, (No. 15), *a* = 15.359(1), *b* = 19.181(2), *c* = 10.616(1) Å, β = 101.12(1)°, *V* = 3068.8(4) Å³, *Z* = 4, *F*(000) = 1224, *D_c* = 1.265 Mg m⁻³, μ (Mo-K α) = 0.081 mm⁻¹, 2450 unique data, final *R*₁ = 0.081, *wR*₂ = 0.229 for 2304 observed data [*I* > 2 σ (*I*)]. For **4**·hexane: C₃₂H₁₆O₄·C₆H₁₄, *M* = 550.6, monoclinic, space group *C2/c* (No. 15), *a* = 15.807(2), *b* = 18.590(3), *c* = 10.590(2) Å, β = 100.55(1)°, *V* = 3059.3(8) Å³, *Z* = 4, *F*(000) = 1160, *D_c* = 1.195 Mg m⁻³, μ (Mo-K α) = 0.077 mm⁻¹, 2386 unique data, final *R*₁ = 0.063, *wR*₂ = 0.191 for 2109 observed data [*I* > 2 σ (*I*)]. For **4**·AcOH: C₃₂H₁₆O₄·C₂H₄O₂, *M* = 524.5, triclinic space group *P1* (No. 2), *a* = 9.345(2), *b* = 10.121(3), *c* = 14.498(2) Å, α = 98.65(1), β = 101.23(1), γ = 101.23(1)°, *V* = 1293.7(5) Å³, *Z* = 2, *F*(000) = 544, *D_c* = 1.346 Mg m⁻³, μ (Mo-K α) = 0.093 mm⁻¹, 3480 unique data, final *R*₁ = 0.069, *wR*₂ = 0.186 for 2906 observed data [*I* > 2 σ (*I*)]. For **4**·cyclohexane: C₃₂H₁₆O₄·C₆H₁₂, *M* = 548.6, monoclinic, space group *P2/n* (No. 13), *a* = 10.498(3), *b* = 9.646(2), *c* = 14.687(3) Å, β = 101.08(1)°, *V* = 1459.6(5) Å³, *Z* = 2, *F*(000) = 576, *D_c* = 1.248 Mg m⁻³, μ (Mo-K α) = 0.080 mm⁻¹, 2415 unique data, final *R*₁ = 0.072, *wR*₂ = 0.219 for 2411 observed data [*I* > 2 σ (*I*)]. Both host and guest molecules in **4**·C₆H₃Me₃, **4**·C₆H₁₄ and **4**·C₆H₁₂ occupy sites of symmetry 2. The cyclohexane guest molecule in **4**·C₆H₁₂ was found to be two-fold disordered with a *C*₂ axis passing through a pair of carbon atoms. CCDC 182/1304. †† The *C*₂ axis is non-crystallographic in the case of **4**·AcOH. See <http://www.rsc.org/suppdata/cc/1999/1607> for crystallographic data in .cif format.

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Communication 9/04144C