

A Hydrogen-Bonded Molecular Ladder. The Crystal Structure and Guest-Binding Properties of a Bishydroquinone Derivative of Anthracene

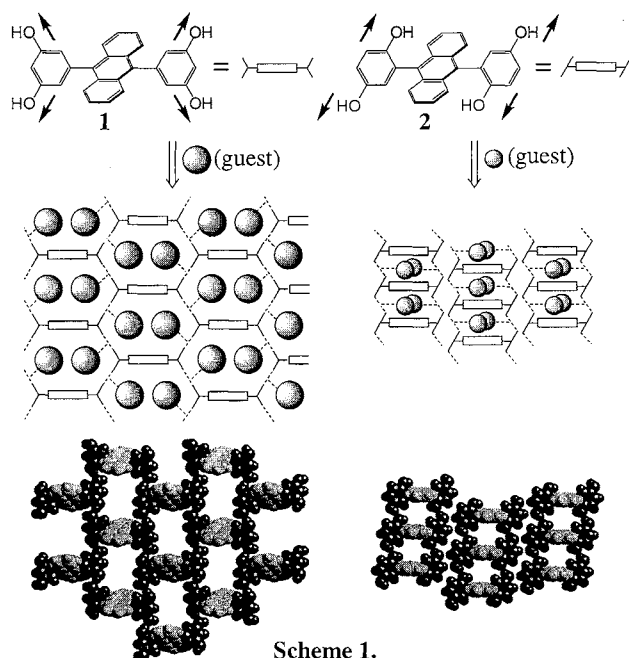
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9,10-Bis(2,5-dihydroxy-1-phenyl)anthracene, an H-shaped tetraphenol, forms a doubly hydrogen-bonded ladder-like polymeric chain in the crystal. The small in-ladder cavities incorporate tiny guests such as acetone selectively.

Crystal engineering relies mostly on intended intermolecular network formation in crystals, which, chemists hope, is predictable and hence designable on the basis of molecular geometry and interaction topology.¹ A variety of topologically interesting networks have been designed.² A problem associated with designing host materials is that 3-dimensional networks often undergo interpenetration to give dense packing with no guest incorporation.³ We have been working on an orthogonal bisresorcinol derivative of anthracene (**1**), which forms a hydrogen-bonded (O-H...O-H) 2D net free of interpenetration (Scheme 1). The resulting huge cavities are capable of binding two guest molecules via host-guest hydrogen bonding (O-H...O-H...O=C).⁴ The present work is concerned about alteration of network structure and cavity size. We report here that an analogous hydroquinone derivative **2** forms a novel ladder-like 1D chains⁵ with much smaller cavities (Scheme 1).



Scheme 1.

Tetraol **2** was prepared by Suzuki coupling of 9,10-dibromoanthracene with propanediol-boronate **4** derived from 2,5-dimethoxyphenylboronic acid (**3**), followed by subsequent demethylation of the resulting tetramethoxy derivative **5**⁶ (Scheme

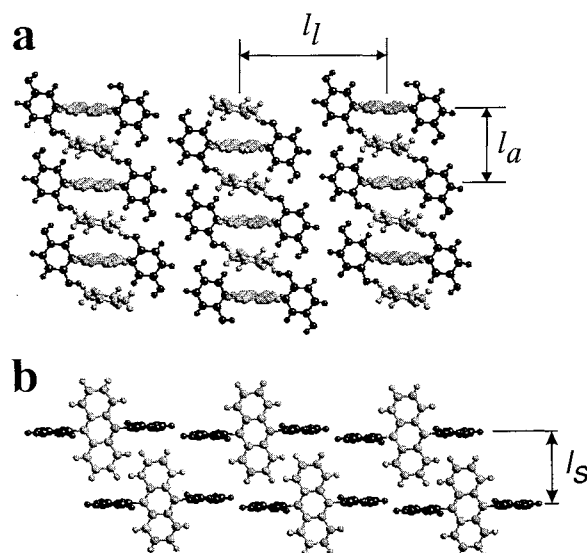
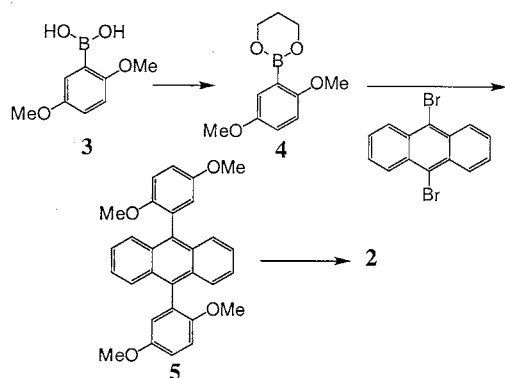


Figure 1. Crystal structure of adduct **2** - acetone in stereo; side view of a molecular sheet (a), top view of two neighboring sheets, which included guest molecules are omitted for clarity (b). l_a , l_l and l_s are inter-ring, inter-ladder and inter-sheet distances, respectively.

2). Crystallization of compound **2** as a host from a solution of any ketone listed in Table 1 as a guest afforded a 1:2 (host to guest) adduct. Single crystals were obtained for the acetone adduct, whose X-ray diffraction revealed the following characteristic aspects, referring to Figure 1.⁷ (1) The anthracene and the hydroquinone rings are nearly orthogonal with a dihedral angle of 89.9°. (2) Host molecules **2** in the adduct are parallel-aligned via intermolecular 2-point hydrogen bonding (O-H...O-H). A doubly-linked ladder-like polymeric 1D chain results, whose cavities are filled with two acetone molecules via host-guest hydrogen bonding; the inter-ring distance is $l_r = 7.33$ Å (Scheme 1 for a schematic explanation and Figure 1a for the actual structure). (3) The ladders are aligned laterally to give a pseudo molecular sheet with an inter-ladder distance of $l_l = 14.02$ Å. (4) The sheets are layered in a staggered manner with an inter-sheet distance of $l_s = 8.86$ Å, thereby forming inter-sheet channels (Figure 1b for the top view of two neighboring sheets, where included guest molecules are omitted for clarity). (5) Two guest (acetone) molecules are incorporated in each cavity via host-guest hydrogen bonding (O-H...O-H...O=C).

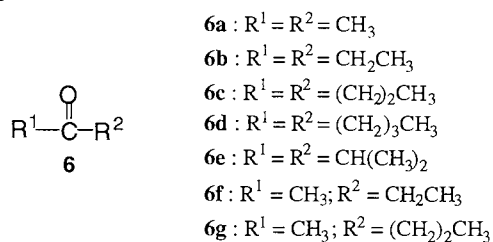
The dimensionality of a network may be predicted on the basis of orientation of the interaction-responsible functional groups in the constituent molecules. This is the case here to the extent that, referring to the arrows in structures in Scheme 1, 2D



Scheme 2.

or X-shaped tetraol **1** forms a 2D network, while 1D or H-shaped tetraol **2** gives a doubly-linked 1D chain. The alteration in network topology results in that of cavity sizes. Each cavity in the ladder is maintained by two molecules of host **2** and is much smaller (thinner although wider) than that in 2D net, which is contributed by four molecules of host **1**. The space-filling models of the cavities with excluded guests are shown in Scheme 1. The size of the cavity is reflected on the selectivity in competitive crystallization using an equimolar mixture of guests A and B. The results are summarized in Table 1, where the guest/host ratios A/2 and B/2 in recovered adducts are listed.

Table 1. Competitive crystallization of host **2** using an equimolar mixture of two ketones **6**



entry	guest A	guest B	A/2	B/2	(A+B)/2	A/B
1	6a	6b	0.9	1.1	2	0.8
2	6a	6f	1.0	1.0	2	1
3	6b	6c	~2	~0	2	vl ^a
4	6b	6d	~2	~0	2	vl ^a
5	6b	6e	~2	~0	2	vl ^a
6	6b	6g	~2	~0	2	vl ^a

^a Very large.

(1) The total guest/host ratios are $(A+B)/2 = 2$ in every case, indicating that the 1:2 (host to guest) stoichiometry holds also for apparently ternary complexes. (2) The C₁ and C₂ alkyl chains are readily accommodable. Thus, 2-propanone (1,1-ketone), 2-butanone (1,2-), and 3-pentanone (2,2-) can be bound with similar affinities (entries 1 and 2), while 4-heptanone (3,3-) and longer ketones are hardly under competitive conditions (entries 3 and 4). 2-Pentanone (1,3-) can not be bound, either, resulting in a striking selectivity among isomeric pentanones (entry 6). (3) Competition between diethyl ketone and diisopropyl ketone results in exclusive incorporation of the former; branched alkyl

group can not be incorporated (entry 5). For comparison, a much bigger cavity provided by host **1** shows the highest affinity for 4,4-ketone (5-nonanone) and branching in the alkyl group is affinity-enhancing.^{4b} When alone, the long-chain and branched ketones **6c**, **6d**, **6e**, and **6g** give 1:2 (host to guest) adducts, in which host **2** may form a network different from that shown above to adjust to the guests. Unfortunately, appropriate single crystals have not been obtained.

In summary, an alteration of the hydrogen-bonding site from X-shaped bisresorcinol to H-shaped bishydroquinone results in a drastic change in network dimensionality and cavity size. The ladder strategy using H-shaped building blocks may allow an easy access to the cyclophane-like supramolecular cavities in the crystals.

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References and Notes

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- 3** → **4** (propanediol in benzene at 20 °C for 12 h; 88%), **4** → **5** (9,10-dibromoanthracene with Pd(PPh₃)₄ + K₃PO₄ in DMF at 100 °C for 12 h; 38%), **5** → **2** (BBr₃ in CH₂Cl₂ at 0 °C for 12 h; 90%). Compound **2**: IR (KBr) 3190 cm⁻¹ (OH); ¹H NMR (DMSO-*d*₆) δ 6.56 (2 H, d, Ar-H), 6.80 (2 H, double d, Ar-H), 6.91 (2 H, d, Ar-H), 7.37 (4 H, AA'BB', Ar-H), 7.61 (4 H, AA'BB', Ar-H), 8.56 (2 H, s, OH), 8.93 (2 H, s, OH). Anal. Found: C, 78.88; H, 4.60%. Calcd for C₂₆H₁₈O₄: C, 79.17; H, 4.60%.
- Crystallographic data for **2**·2(acetone): formula = C₃₂H₃₀O₆, formula weight = 510.59, triclinic, P1, *a* = 8.872(9) Å, *b* = 10.849(2) Å, *c* = 7.332(7) Å, α = 90.81(1)°, β = 105.614(7)°, γ = 92.88(1)°, *V* = 678.5 Å³, *Z* = 1, *d*_{calcd} = 1.25 g/cm³. The final *R* factor was 0.047 (*R*_w = 0.078) for 2078 unique reflections out of 3127 with *I* > 3σ(*I*) and GOF = 1.45.