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Hydrogen-Bonded Network Formation in Organic Crystals As Effected by Perpendicular and Divergent Hydroxyl Groups: The Crystal Structure of a Bisresorcinol Derivative of Anthracene

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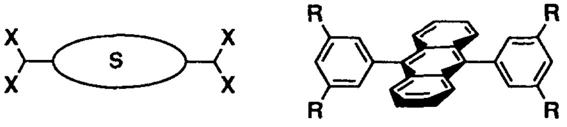
Abstract *An anthracene derivative 1a having two nearly perpendicular resorcinol moieties forms an extensive hydrogen-bonded network that results in enforced formation of anthracene columns. The crystal structure of 1a $(C_6H_6)_2(CH_3CO_2CH_2CH_3)_2$ contains molecular sheets composed of hydrogen-bonded polyresorcinol chains and face-to-face anthracene columns, together with large cavities which are filled with two benzene and two ethyl acetate molecules*

A potential area related to *molecular recognition* is organic crystal structure control based on manipulated intermolecular forces such as hydrogen bonding[3-7] A simple and general strategy for switching from restricted host-guest complexation to extensive intermolecular interaction would be to use divergent (exo[3c] or outwardly-directed[4c]) functional groups rather than convergent[8] (endo or inwardly-directed) ones. In a particular case where the divergent functional groups (X) are perpendicularly directed with respect to an appropriate aromatic spacer (S) (Chart 1), an extensive hydrogen-bonded network formation involving Xs would result in an ordered arrangement of S in the perpendicular direction. We wish to report here that a bisresorcinol derivative of anthracene forms hydrogen-bonded molecular sheets with enforced anthracene columns.

The nickel(0)-catalyzed reaction of 9,10-dibromoanthracene and 3,5-dimethoxyphenylmagnesium chloride,[9] followed by demethylation with BBr_3 of the resulting tetramethoxy derivative,[10] afforded an anthracene compound **1a** having two divergent resorcinol moieties (Chart 1).[11] Slow penetration of benzene vapor into an ethyl acetate solution of **1a** afforded crystals of **1a**$\cdot(C_6H_6)_2\cdot(CH_3CO_2CH_2CH_3)_2$, single crystal X-ray diffraction of which at room temperature revealed the following aspects.[12]

(1) The dihedral angles of the two resorcinol rings (A and B) with respect to the anthracene ring in compound **1a** are not identical, 77.5 and 82.0°, respectively. (2) The OH groups form an extensive hydrogen-

Chart 1



1a R = OH
1b R = CH_3

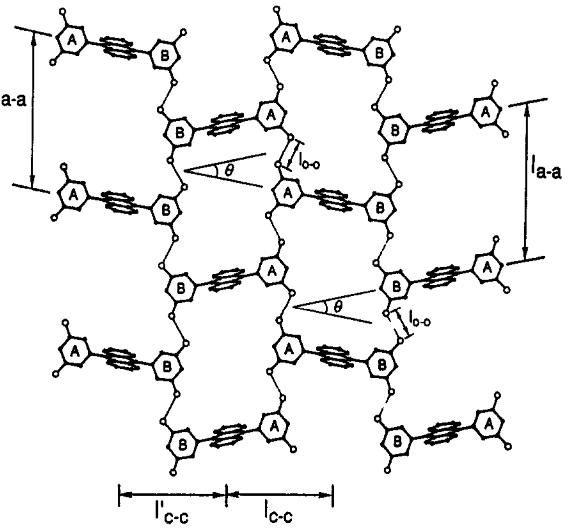


Fig 1 Hydrogen-bonded network in a molecular sheet of the crystal of compound **1a**.

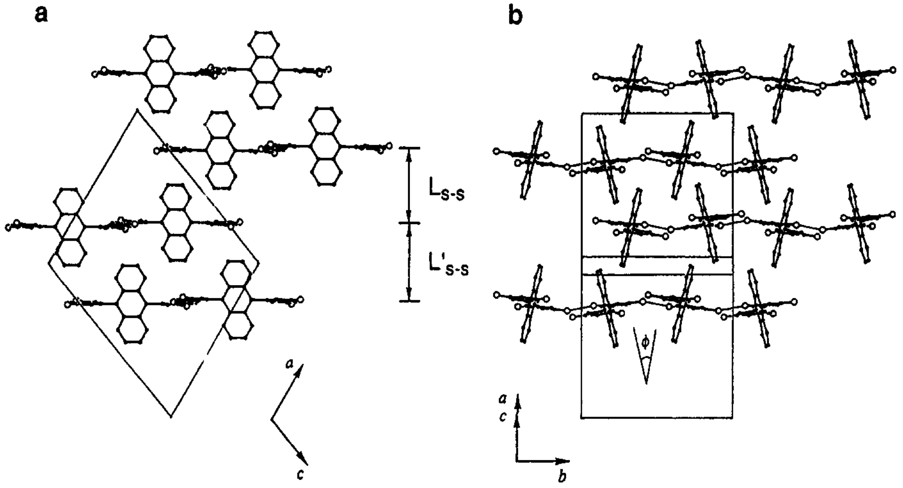


Fig 2. Arrangement of molecular sheets in the crystal of compound **1a**; top view (a) and side view (b)

bonded network with an O•••O distance of $l_{\text{o-o}} = 2.82$ Å. This leads to a molecular sheet composed of hydrogen-bonded polyresorcinol chains and *enforced* anthracene columns (Figure 1). The face-to-face anthracene-anthracene distance is $l_{\text{a-a}} = 13.7$ Å and the column-to-column distances are $l_{\text{c-c}} = 9.88$ and $l'_{\text{c-c}} = 9.95$ Å. The phenyl-anthracene-phenyl axes of the two hydrogen-bonded molecules are coplanar with a cross angle of $\theta = 19.7°$. The two hydrogen-bonded resorcinol moieties are nearly coplanar (Figure 2), the deviation from coplanarity being ~11°. The angle ϕ (Figure 2, side view b) between two anthracene rings is $\phi = 25.6°$. (3) Two neighboring sheets slide from each other so as to give a *staggered* arrangement of the anthracene moieties (Figure 2, top view a and side view b).[13] The sheet-to-sheet distances are $L_{\text{s-s}} = 7.07$ and $L'_{\text{s-s}} = 7.25$ Å. (4) The sheet structure involving an extensive hydrogen-bonded network leaves large cavities, which are filled with two benzene and two ethyl acetate molecules as shown in Figure 3. The ester molecules are stacked with an anthracene ring and are hydrogen bonded to an OH group, the O•••O=C distance being 2.68 or 2.69Å. (5) The hydrogen bonding is essential for the characteristic structure described above. The X-ray crystal structure of otherwise closely related tetramethyl derivative **1b** (Chart 1) is quite different,[14] where the major intermolecular interaction is methyl-anthracene stacking. There is neither anthracene column nor cavity enough to incorporate solvent molecules.

The present work demonstrates that symmetrically-arranged, divergent OH groups lead to an extensive hydrogen-bonded network in organic crystals, with concomitant formation of spacer columns and cavities therein. Further work is now under way to modify function (S) and interaction-responsible (X) moieties (Chart 1) in various ways and to control molecular alignment in organic crystals based on the present strategy.

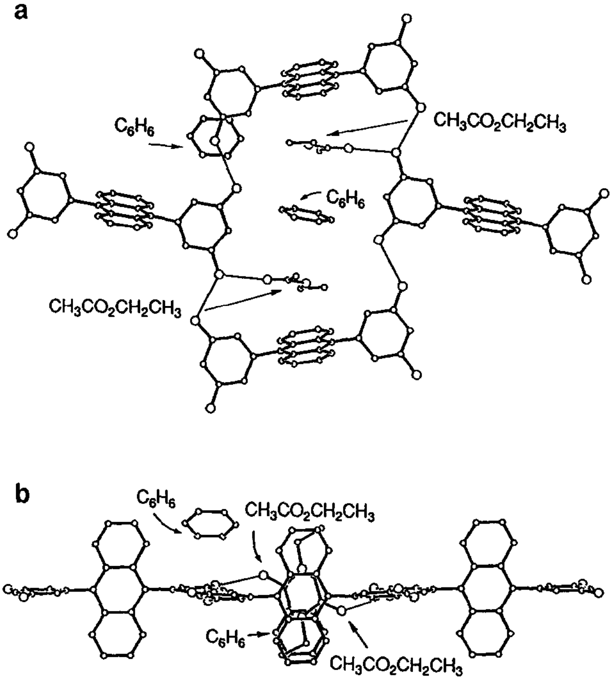


Fig. 3 Packing geometry for two benzene and two ethyl acetate molecules incorporated in the cavity (a) and its top view (b)

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12. Monoclinic $P2_1/c$, a = 16.579(4), b = 14 272(2), c = 18 391(2) Å, β = 111.15(1)°; V = 4058.6 Å^3; Z = 4; R = 0.059 and R_w = 0 047; number of reflections used, 3489. The crystals are not so stable under prolonged X-ray irradiation
13. Compound **1a** in crystal is chiral since the two resorcinol-anthracene dihedral angles are different. One sheet of the crystal is composed of one enantiomer, while the neighboring one is of the other enantiomer.
14. Monoclinic $P2_1/n$, a = 9.184(5), b = 8 159(2), c = 15 284(8) Å, β = 100.14(2)°, V = 1127 3 Å^3; R = 0 049 and R_w = 0.076, number of reflections used, 2266

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