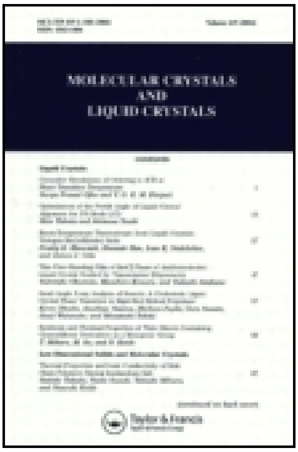

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The Two-Component Host Lattice Based on Hydrogen Bonds and Face-To-Face and Edge-To-Face π-π Interactions

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THE TWO-COMPONENT HOST LATTICE BASED ON HYDROGEN BONDS AND FACE-TO-FACE AND EDGE-TO-FACE π–π INTERACTIONS

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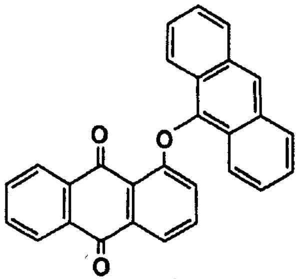
Abstract 1-(9-Anthryloxy)anthraquinone (**1**) was found to form a stable three-component crystalline complex, $(\mathbf{1})_2$(hydroquinone)(benzene). The crystal structure shows the rigid two-component host lattice constituted of **1** and hydroquinone, in which benzene is enclathrated. The two host components are linked by the hydrogen bonds as well as the unique orthogonal C-H---π---H-C and face-to-face π–π interactions. Benzene is retained within the host lattice up to 173 °C.

INTRODUCTION

Organic supramolecular crystals have recently become an important subject of research, since they exhibit particular solid-state properties and behaviors which cannot be achieved in single-component crystals. For example, studied extensively are hydrogen-bonded molecular complexes for molecular recognition,[1] clathrate crystals for enantio-differentiation,[2] charge-transfer complexes for molecular conductors.[3] Most of these crystalline molecular complexes are composed of two components. On the other hand, three-component crystalline solids are rarely encountered.[4]

With the intention to explore three-component cocrystalline solids, we designed a conformationally flexible compound, 1-(9-anthryloxy)anthraquinone (**1**), as a host species for clathrate crystals. The design of this host compound is rather against the general requirement that the host molecules should have a rigid basic framework and bulky substituents.[5] However, we assumed that molecular flexibility could allow possible intermolecular interactions, which have been incorporated in the molecule of **1**, such as hydrogen bonds, charge-transfer interactions, and/or π–π interactions: on complexation of **1**, the lattice control is not the principal factor in molecular packing and therefore it might be possible to assemble distinct compounds leading to cocrystallization. In this report we demonstrate a unique occurrence of a stable three-heteromolecular crystalline complex derived from **1**, hydroquinone (**2**), and benzene.



1

2

INCLUSION PROPERTIES

When compound **1** was recrystallized with **2** from benzene, the crystalline complex with a stoichiometric ratio 2 : 1 : 1 of (**1**) : (**2**) : (benzene) was isolated as orange prisms. The DSC analysis of the complex exhibited the sharp endotherm peak at 173 °C corresponding to the desolvation of benzene (Figure 1). The desolvation temperature is remarkably high in comparison to the boiling point of pure guest liquid, indicating that the host lattice is quite rigid to hold benzene within. With the guest loss, the crystals collapse to melt at 209 °C, as seen in Figure 1. The melting point is lower than that of pure **1** (240-242 °C). The observation that the elimination of the guest molecules is associated with melting of the crystals seems to be characteristics for three-component clathrates. The melt sample, after cooled down, exhibited the phase rationalized by a simple mixture of **1** and hydroquinone, which was identified by an X-ray powder diffraction study.

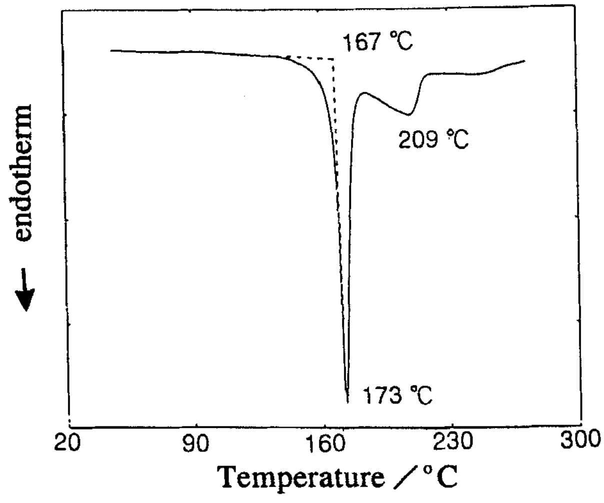


FIGURE 1 DSC profile of $(\mathbf{1})_2$(hydroquinone)(benzene)

CRYSTAL STRUCTURE

Unit cell packing of $(\mathbf{1})_2$(hydroquinone)(benzene) is shown in Figure 2. Crystal Data: triclinic, space group P1, a = 11.779(3), b = 12.747(2), c = 8.818(1) Å, α = 107.14(1), β = 92.59(3), γ = 101.86(3)°, V = 1230.3(5) Å^3, Z = 1, Dc = 1.335 gcm^{-3}, Mo-Kα radiation, λ= 0.710690 Å, 4.0° < 2θ < 55.0°, 5656 reflections were collected, of which 2896 unique reflections [$|Fo| > 2.5\,\sigma\,(|Fo|)$] were used for refinement (862 parameters), converging to R = 0.047 and Rw = 0.052. Space group P1 was ascertained by S. H. G. (second harmonic generation) activity.

An X-ray crystallographical analysis revealed that a molecule of hydroquinone **2** is hydrogen bonded with two molecules of **1** at the carbonyl groups to make a trimeric unit (**1**)---(**2**)---(**1**) (Figure 3). The hydroquinone ring adopts nearly perpendicular to the anthraquinone ring of **1** and, therefore, no direct charge-transfer interactions due to π–π overlap is observed. The trimeric units are further connected with the neighboring trimeric units by the face-to-face π–π interactions of the anthracene rings of **1** with an interplanar distance of 3.4 Å (Figure 4a). Thus the infinite chain of a ---(**1**)--(**2**)---(**1**)---(**1**)---(**2**)---(**1**)--- sequence is lined up along the a axis. Benzene molecules are enclathrated only by van der Waals force in the cavities given by this chain structure (Figure 5).

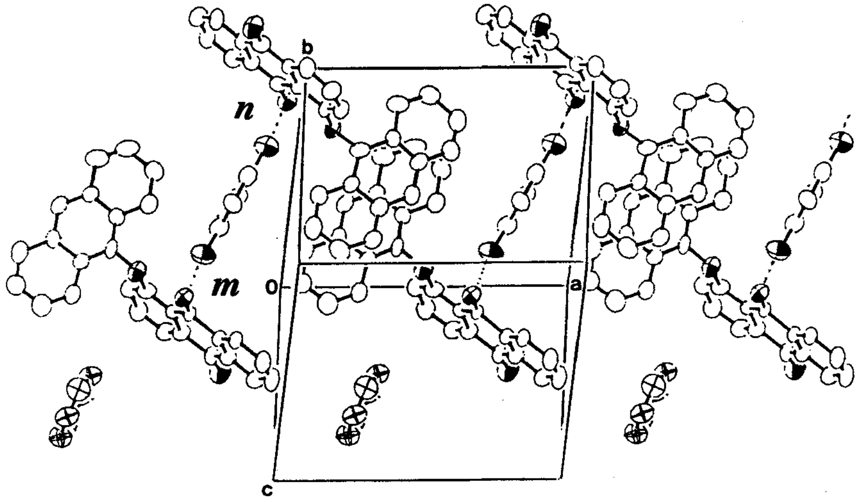


FIGURE 2 Unit cell packing of $(\mathbf{1})_2$(hydroquinone)(benzene). Dotted lines indicate hydrogen bonds. m: 2.908(7) Å, n: 2.912(7) Å.

π–π INTERACTIONS

The orientation associated with the π–π interactions is thought to be electrostatic in origin and, thereby, the most intense π–π interactions occur in offset stacked and edge-to-face orientations.[6] The arrangement of the π–π orientation observed in the anthracene rings of **1** is the offset parallel stack as seen in graphite (Figure 2). Furthermore, another extreme case of the π–π interactions, *i. e.* edge-to-face orientation,[7] is observed for the π plane of hydroquinone and the anthracene ring of **1**, as illustrated in Figure 4b. A pair of **1** molecules, which are nearly centrosymmetrically related, are positioned with their C4-H bonds on the anthracene ring directed orthogonally towards the center of the hydroquinone ring. The distance between the C4 carbon of the anthracene ring and the mean plane of the hydroquinone ring is as short as 3.2 Å, which corresponds approximately to 2.1 Å for a (C)H--π separation. This arrangement is evidently indicative of the edge-to-face π–π interaction. Such an interaction would be much more

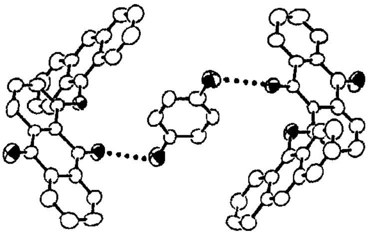


FIGURE 3 The host molecules with the relation linked by the hydrogen bond.

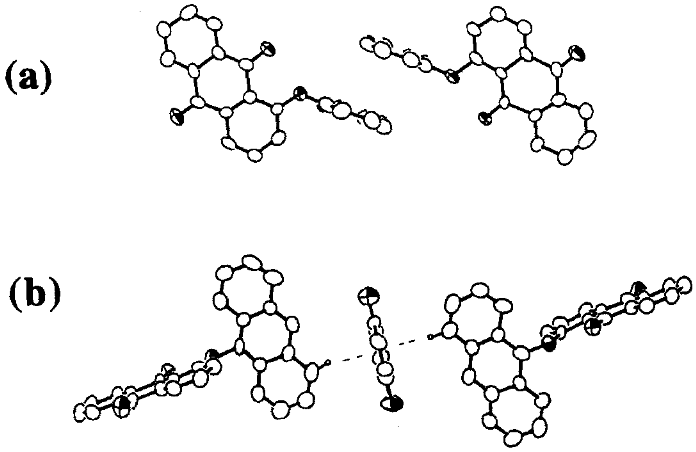


FIGURE 4 The molecular arrangements indicating inter-heteromolecular interactions that constitute the two-heteromolecular host lattice of $(\mathbf{1})_2$(hydroquinone)(benzene). (a) Face-to-face π–π interaction. (b) Face-to-edge C-H---π---H-C interaction.

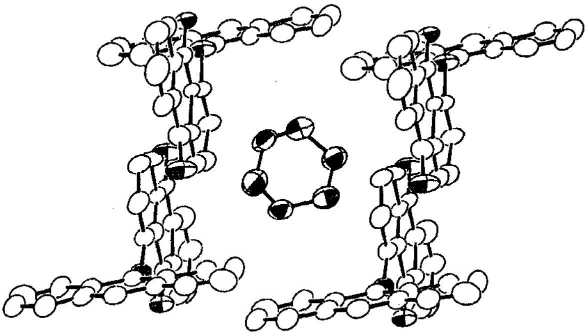


FIGURE 5 The packing arrangement of guest benzene.

appropriate to be designated as a C-H---π interaction or, in this particular case, as a C-H---π---H-C interaction. It seems to be rational that the hydroquinone ring facilitates the C-H---π---H-C attractive interactions because of its π excessive nature. This type of C-H--π---H-C interaction has recently been found between the guest and host molecules in a cyanoborate clathrate[8] and also between the proton of $CHCl_3$ and the π–system of the C ≡C bond.[9]

The complex described herein can be regarded as a novel type of clathrate crystals in which the host lattice is constituted of two distinct components by using the hydrogen-bonding and two typical motives of the π–π interactions. The guest benzene molecules are enclathrated only by the lattice force in this two-component host cavity. Nevertheless the guest molecules are tightly retained up to 173 °C, indicating that the intermolecular interactions connecting the host compounds are strong.

Among the possible intermolecular interactions charge-transfer one seems to be only a little involed, as judged from the color change on complexation and the crystal structure. This is in line with the observation that **1** gave no complex with hydroquinone only; the charge-transfer interaction is not a principal factor for the formation of the three-component complex. Compound **1**, however, formed a 1:1 clathrate crystal with benzene as a guest compound.

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REFERENCES

1. J-M. Lehn, *Angew. Chem. Int. Ed. Engl.*, 1990, **29**, 1304; (b) J. Rebek, Jr.,*Angew. Chem. Int. Ed. Engl.*, 1990, **29**, 245; (c) J. C. MacDonald and G. M.Whitesides, *Chem. Rev.*, 1994, **94**, 2383.
2. G. Kaupp, *Angew. Chem. Int. Ed., Engl.*, 1994, **33**, 728; (b) F. Toda, K. Tanaka, Z. Stein and I. Goldberg, *J. Org. Chem.*, 1994, **59**, 5748, and references cited therein.
3. See for example: J. R. Ferraro and J. M. Williams, *Introduction to Synthetic Electrical Conductors*, Academic Press, San Diego, 1987.
4. Organic ionic crystals or radical salts sometimes incorporate solvent molecules to give multicomponent crystals. However, molecular crystals composed of neutral organic components are quite rare. See for example, D. E. Lynch, G. Smith, K. A. Byriel and C. H. L. Kennard, *J. Chem. Soc., Chem. Commun.*, 1992, 300.
5. Weber and M. Czugler, in *Molecular Inclusion and Molecular Recognition-Clathrates I and II*, ed E. Weber, in *Topics in Current Chemistry*, Springer-Verlag Berlin, 1988, vol. 149, p. 45; (b) E. Weber, in *Inclusion Phenomena and Molecular Recognition*, ed. J. L. Atwood, Plenum Press, New York, 1990, vol. 4, p. 188.
6. C. A. Hunter, *Chem. Soc. Rev.*, 1994, 101; (b) C. A. Hunter, *Angew. Chem. Int. Ed. Engl.*, 1993, **32**, 1584; (c) P. Hobza, H. L. Sezle, E. W. Schlag, *J. Am. Chem. Soc.*, 1994, **116**, 3500.
7. For edge-to-face aromatic interactions, M. C. Grossel, A. K. Cheetham. D. A. O. Hope and S. C. Weston, *J. Org. Chem*, 1993, **58**, 6654, and references cited therein.
8. Hunter, R. H. Haueisen, A. Irving, *Angew. Chem. Int. Ed. Engl.*, 1994, **33**, 566.
9. T. E. Muller, D. M. P. Mingos and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1994, 1787.