Crystalline inclusion compounds of 1-(9-anthryloxy)anthraquinone as a host compound: X-ray structural characterization and π–π interaction modes in the crystal enclathrating benzene as a guest

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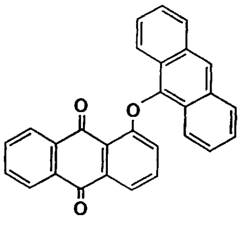
Kazunori Ochiai,[a] Yasuhiro Mazaki,[a] Shin-ichi Nishikiori,[a] Keiji Kobayashi *,[a] and Shigenobu Hayashi[b]

[a] *Department of Chemistry, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153, Japan*
[b] *National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305, Japan*

Inclusion properties of the clathrate crystals, (1)(C_6H_6) and (1)$_2$(hydroquinone)(C_6H_6), derived from a conformationally flexible host compound 1-(9-anthryloxy)anthraquinone (1), have been investigated by means of X-ray crystallography, DSC analysis and ^{2}H NMR spectroscopy. Complex (1)(C_6H_6) is a true clathrate: benzene is embedded in a host lattice constituted of the intermolecular face-to-face π–π overlap (π–π; 3.54 Å) of the anthraquinone rings of 1. Crystal data: $P2_1/c$, $a = 16.882(2)$, $b = 8.970(1)$, $c = 16.405(2)$ Å, $\beta = 91.53(2)°$, $Z = 4$, $D_c = 1.280$ g cm^{-3}. The crystal structure of a three-component clathrate (1)$_2$(hydroquinone)(C_6H_6) shows the rigid two-component host lattice composed of 1 and hydroquinone. Crystal data: $P\bar{1}$, $a = 11.779(3)$, $b = 12.747(2)$, $c = 8.818(1)$ Å, $\alpha = 107.14(1)$, $\beta = 92.59(3)$, $\gamma = 101.86(3)°$, $Z = 1$, $D_c = 1.335$ g cm^{-3}. The two host components are linked by the hydrogen bonds (O–O; 2.908, 2.912 Å) as well as the unique orthogonal C–H–π–H–C (C–π; 3.2 Å) and face-to-face π–π interactions (π–π; 3.43 Å). Benzene is retained within the host lattice up to 173 °C. The crystal structure of guest-free host 1 has also been determined. Crystal data: $P\bar{1}$, $a = 15.566(5)$, $b = 15.625(5)$, $c = 11.571(2)$ Å, $\alpha = 98.21(2)$, $\beta = 94.20(2)$, $\gamma = 132.74(2)°$, $Z = 4$, $D_c = 1.337$ g cm^{-3}. ^{2}H NMR spectroscopy has been used to study the molecular motion of [$^2H_6$]benzene in the clathrates. Quadrapole echo line shapes, measured as a function of temperature, could be accounted for in terms of an in-plane 60° jump about the major symmetry axis. The activation parameters for a 60° jump are 9.4 and 19 kJ mol^{-1} for (1)(C_6D_6) and (1)$_2$(hydroquinone)(C_6D_6), respectively.

Crystalline inclusion compounds, designated as clathrates,[1] have recently become an important subject of research, not only due to their practical uses such as molecular recognition,[2] but also due to a deepening understanding of crystal engineering and dynamic behaviour in the solid state.[3] Most clathrate crystals are composed of two components, whereas three-component crystalline solids are rarely encountered except for organic ionic crystals or radical salts, which sometimes incorporate solvent molecules to give multicomponent crystals.[4] With the intention of exploring three-component cocrystalline solids, we designed a conformationally flexible compound, 1-(9-anthryloxy)anthraquinone (1), as a host species of clathrate crystals.[5] 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 as seen in the hexadiynediol host and the thienothiophene host.[6–8] However, we assumed that molecular flexibility could allow possible intermolecular interactions incorporated in the molecule of 1, such as hydrogen bonds, charge-transfer interactions, electrostatic 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 different compounds leading to cocrystallization under the influence of intermolecular interactions. Thus, compound 1 was recrystallized from various single and mixed solvents. Compound 1 has so far afforded only three clathrates including an expected three-component crystal. In this report we demonstrate the solid-state characterization of two crystals enclathrating benzene as a guest species, in particular, focusing on a three-component clathrate.



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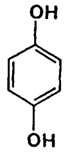

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Results and discussion

Inclusion properties

Compound 1 afforded no clathrates with polar guest compounds having hydrogen bond donor/acceptor sites such as amines, alcohols and carboxylic acids. The clathrates isolated up to now are (1)(C_6H_6), (1)$_3$(anthracene) and (1)$_2$(hydroquinone)(C_6H_6). The host : guest ratios were evaluated by ^{1}H NMR spectral integration. Although there are only three examples, 1 seems to have a trend to enclathrate planar aromatic compounds. This observation suggests that the π–π intermolecular interaction is playing a role in cocrystallization. A remarkably stable three-component crystalline complex, (1)$_2$(hydroquinone)(C_6H_6), was isolated as orange prisms, when compound 1 was recrystallized with hydroquinone (2) from benzene.

Thermal behaviour

Fig. 1 shows the differential scanning calorimetry (DSC)

Table 1 Crystal data and experimental and refinement parameters for the structure analysis

	(1)(C_6H_6)	(1)$_2$(Hydroquinone)(C_6H_6)	Guest-free 1
Molecular formula	($C_{28}H_{16}O_3$)(C_6H_6)	($C_{28}H_{16}O_3$)$_2$($C_6H_6O_2$)(C_6H_6)	($C_{28}H_{16}O_3$)
Formula weight, g mol^{-1}	478.52	989.03	400.41
Space group	$P2_1/c$	$P1$	$P1$
a/Å	16.882(2)	11.779(3)	15.566(5)
b/Å	8.970(1)	12.747(2)	15.625(5)
c/Å	16.405(2)	8.818(1)	11.571(2)
α (deg.)	90.00	107.14(1)	98.21(2)
β (deg.)	91.53(2)	92.59(3)	94.20(2)
γ (deg.)	90.00	101.86(3)	132.74(2)
V/Å^3	2483.4(6)	1230.3(5)	1989.1(12)
Z	4	1	4
F(000)	1000	516	832
λ/Å	0.710 69	0.710 69	0.710 69
Crystal dimensions/mm	0.5 × 0.4 × 0.1	0.4 × 0.2 × 0.1	0.5 × 0.2 × 0.1
D_c/g cm^{-3}	1.280	1.335	1.337
Range scanned, 2θ (deg.)	4–55	4–55	4–55
No. of reflns. collected	5697	5656	9024
No. of reflns. obs.	1725	2896	5324
No. of reflns. used	1597 ($4 < 2\theta < 50$)	2896	5324
Criterion for obs. reflns.	$F_o > 2.5\sigma F_o$	$F_o > 2.5\sigma F_o$	$F_o > 2.5\sigma F_o$
No. of parameters	423	862	688
R factor	0.089	0.047	0.064
R_w	0.064	0.052	0.075

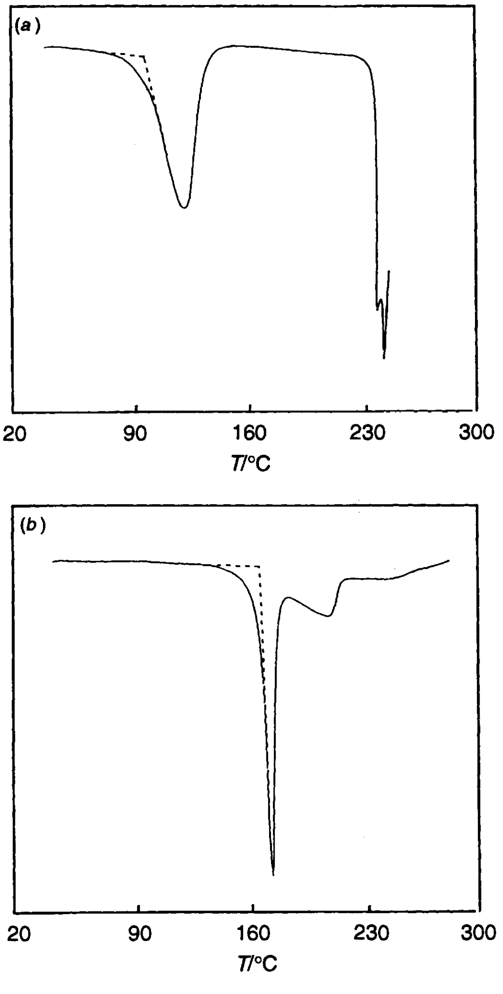


Fig. 1 DSC profiles of the clathrates including benzene: (*a*) (1)(benzene); (*b*) (1)$_2$(hydroquinone)(benzene)

traces for complexes (1)(C_6H_6) and (1)$_2$(hydroquinone)(C_6H_6). Complex (1)(C_6H_6) releases the guest molecules over a wide temperature range 80–140 °C with the peak temperature at 125 °C. After the loss of the benzene the crystals revert to the phase identical to that of the guest-free **1**, as revealed by the X-ray powder diffraction pattern. On the other hand, (1)$_2$(hydroquinone)(C_6H_6) exhibits a sharp endothermic peak at 173 °C corresponding to the desolvation of benzene. The desolvation temperature is remarkably high in comparison to the boiling point of pure guest liquid, indicating that the guest molecules are strongly held within the host lattice. With the release of the guest species, the crystals start to melt, giving the endotherm peak at 209 °C. This melting temperature is lower than that of pure **1** (240–242 °C) but higher than that of hydroquinone (170–171 °C). The melt sample, after being cooled down, exhibited the X-ray powder patterns rationalized by a simple mixture of **1** and hydroquinone. Thus, **1** and hydroquinone cannot retain the two-component host lattices and split into individual phases without mixing in the solid state. In fact, no crystalline complexes were formed by recrystallization of quinone **1** and hydroquinone from solvents other than benzene. This seems to indicate that the formation of the three-component crystal (1)$_2$(hydroquinone)(C_6H_6) is not principally ascribed to charge-transfer interactions in contrast to the formation of the well known quinhydrone complex (benzoquinone)(hydroquinone).

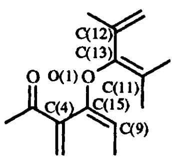
Crystal structure of (1)(benzene)

Crystal data are summarized in Table 1 together with those of (1)$_2$(hydroquinone)(C_6H_6) and guest free **1**. A perspective view of the molecular packing is shown in Fig. 2. All the host and guest molecules are crystallographically equivalent. The anthracene and anthraquinone rings are arranged nearly orthogonally to each other: the plane formed by the C–O–C bonds is almost coplanar with that of the anthraquinone ring and perpendicular to that of the anthracene ring, as can be seen in Fig. 2. Such a structure is interpreted in terms of the preferential conformation to avoid the steric repulsion between the peri-hydrogen atoms of the anthracene rings and the anthraquinone ring. The torsional angles defined by the C–O–C bonds are listed in Table 2.

The anthraquinone rings of the molecule **1** are overlapped in a face-to-face manner with the neighbouring anthraquinone ring with an interplanar distance of 3.54 Å to make a dimeric unit. This short contact is associated with the π–π interaction. The mode of overlapping deviates from total overlap by small shift along the short anthraquinone axis to locate one carbonyl oxygen atom close to the carbonyl carbon atom of the neighbouring molecule, as shown in Fig. 3. Such an offset geometry could allow electrostatic attractive interactions of the

Table 2 Conformation of the ether bonds: torsional angles (deg.) for (**1**)(C_6H_6), (**1**)$_2$(hydroquinone)(C_6H_6) and guest-free **1**

Atom				(**1**)(C_6H_6)	(**1**)$_2$(hydroquinone)(C_6H_6) A	(**1**)$_2$(hydroquinone)(C_6H_6) B	Guest-free **1** A	Guest-free **1** B
C9	C15	O1	C13	9.5(11)	7.2(9)	2.0(9)	−4.5(6)	13.0(7)
C4	C15	O1	C13	−178.1(7)	−176.1(5)	−178.1(5)	174.4(4)	−169.4(4)
C15	O1	C13	C12	−95.3(8)	103.2(6)	88.7(7)	−83.2(5)	95.7(5)
C15	O1	C13	C11	89.5(9)	−83.1(7)	−96.5(7)	98.5(5)	−90.3(5)



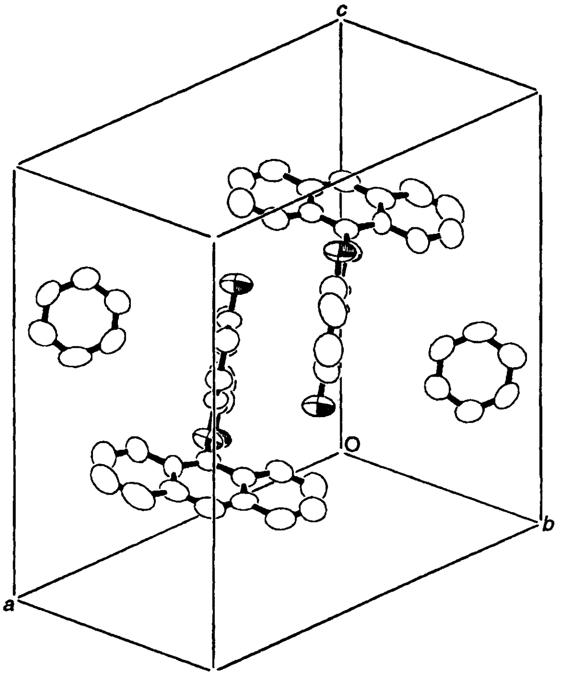


Fig. 2 Unit cell packing of (**1**)(benzene): the interplanar distance of the face-to-face anthraquinone rings is 3.54 Å

carbonyl groups between the stacked molecules of **1**. There are no distinct intermolecular interactions between the guest and host molecules. Thus (**1**)(C_6H_6) is regarded as a true clathrate.

Crystal structure of (1)$_2$(hydroquinone)(benzene)

A perspective view of the molecular packing is shown in Fig. 4. There are two crystallographically independent molecules of **1**. The conformation of the anthraquinone and anthracene rings is again almost perpendicular with respect to each other. The torsional angles are summarized in Table 2.

A molecule of hydroquinone **2** is hydrogen-bonded with two molecules of **1** at one of the two carbonyl groups of **1** to make a trimeric unit **1**–**2**–**1**. The other carbonyl group of **1** that is located far from the anthracene substituent is not involved in hydrogen bonding. The hydroquinone ring adopts a nearly perpendicular geometry to the anthraquinone ring of **1** and, therefore, no direct charge-transfer interactions due to π–π overlap are observed. The trimeric units are further connected with the neighbouring trimeric units by the face-to-face π–π interactions of the anthracene rings of **1** with an interplanar distance of 3.43 Å (Fig. 5). Thus the infinite chain of a –**1**–**2**–**1**–**1**–**2**–**1**–sequence is lined up along the *a* axis.

The anthraquinone moieties of the adjacent **1** molecules are also arranged to make parallel overlap (Fig. 6). The interplanar separation of the π-systems is 3.56 Å, being longer than that observed between the anthracene rings. Benzene molecules are enclathrated only by a van der Waals force in the cavities given by the two-component host lattices.

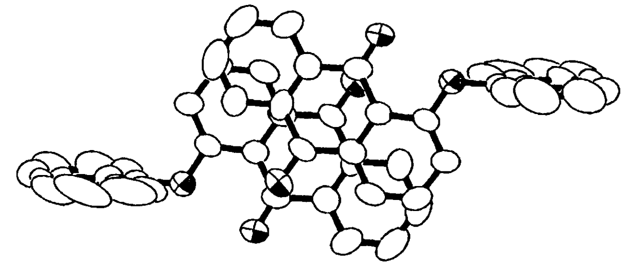


Fig. 3 Overlap diagrams showing π–π stacking in the anthraquinone–anthraquinone rings in (**1**)(benzene)

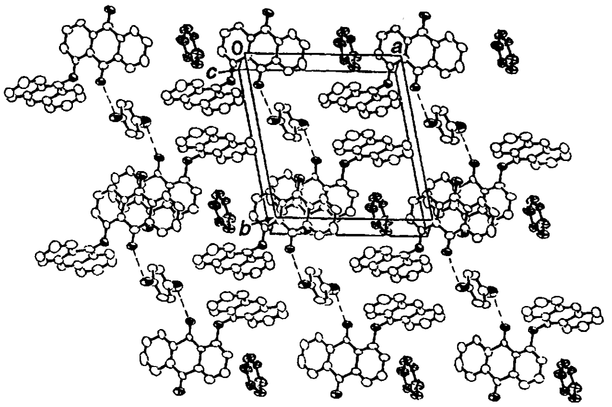


Fig. 4 X-Ray crystal structure of (**1**)$_2$(hydroquinone)(benzene). Dashed lines indicate the oxygen atoms linked by hydrogen bonds. O–O distances: 2.908(7) and 2.912(7) Å.

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.[9] The arrangement of the π–π orientation observed in the anthracene rings of **1**, and in those in (**1**)(C_6H_6) as well, is the offset parallel stack (Fig. 5). Furthermore, another extreme case of the π–π interactions, *i.e.* edge-to-face orientation,[9–10] is observed for the π-plane of hydroquinone and the anthracene ring of **1** in (**1**)$_2$(hydroquinone)(C_6H_6), as illustrated in Fig. 7. A pair of molecules of **1**, which are nearly centrosymmetrically related, are positioned with their C(4)–H bonds on the anthracene ring directed orthogonally towards the centre 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 appropriate to be designated as a C–H–π interaction,[11] or in this particular case as a C–H–π–H–C

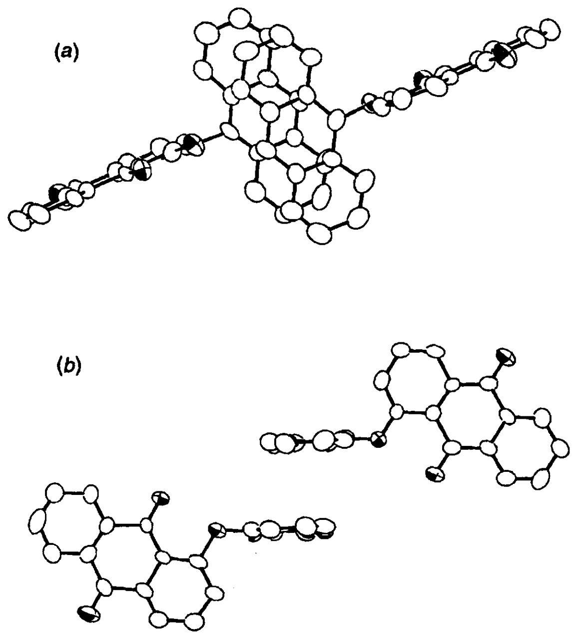


Fig. 5 Overlap diagrams showing π–π stacking in the anthracene–anthracene rings in $(\mathbf{1})_2$(hydroquinone)(benzene): (*a*) projection perpendicular to the anthracene rings: (*b*) side view of the anthracene rings

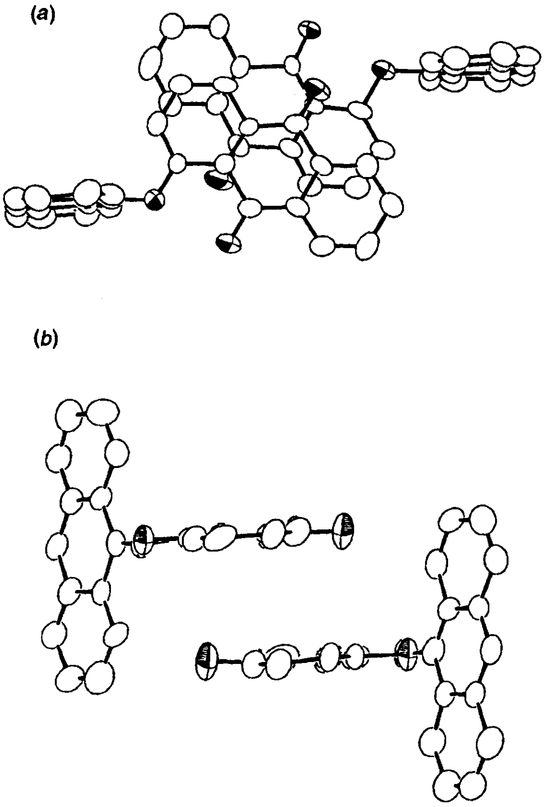


Fig. 6 Overlap diagrams showing π–π stacking in the anthraquinone–anthraquinone rings in $(\mathbf{1})_2$(hydroquinone)(benzene): (*a*) projection perpendicular to the anthraquinone rings; (*b*) side view of the anthraquinone rings

interaction. It seems reasonable that the hydroquinone ring facilitates the C–H–π–H–C attractive interactions because of its π excessive nature due to the electron-donating substituents. This type of C–H–π–H–C interaction has recently been found between the guest and host molecules in a cyanoborate clathrate[12] and also for the π-system of the C≡C bond.[13]

Both in $(\mathbf{1})(C_6H_6)$ and $(\mathbf{1})_2(\text{hydroquinone})(C_6H_6)$ crystals, the anthraquinone rings, rather than the anthracene rings, are parallel stacked. This is in line with the concept that π–π interactions are stabilized in the π-deficient rings; the anthraquinone rings experience much less electron-electron repulsive interactions than the π-rich anthracene rings do. For $(\mathbf{1})_2(\text{hydroquinone})(C_6H_6)$, the π–π stacking of the anthracene rings are also observed.

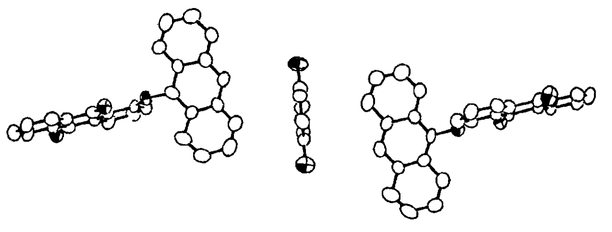


Fig. 7 Face-to-edge C–H–π–H–C interaction constituting the two-heteromolecular host lattice of $(\mathbf{1})_2$(hydroquinone)(benzene): the C–π distance is as short as 3.2 Å

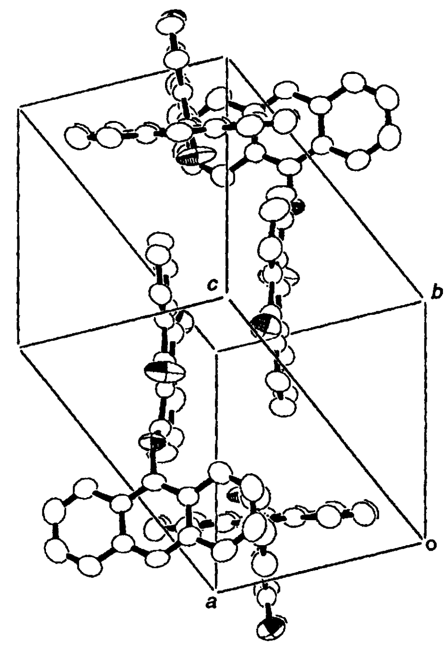


Fig. 8 Unit cell packing of guest-free **1**

It is interesting to note that one carbonyl group of **1** is free from hydrogen bonding despite its strong ability as a hydrogen bond acceptor. Instead, much weaker C–H–π interactions, using the poor hydrogen bond acceptor π moiety, participate in molecular packing. This provides a rather unusual example of hydrogen bond rules that all good proton donor and acceptors are used in hydrogen bonding.[14,15]

Crystal structure of guest-free 1

The crystal structure of the guest-free **1** is shown in Fig. 8. The conformation remains essentially constant when we compare the guest free host compound with the benzene inclusion compounds (Table 2). Thus, the intermolecular interactions exerted on the complexation does not force the host molecule into a different conformation. We have recently described the fact that the strong hydrogen bonding between the host and guest components alters the conformational preference of the host species in the crystal.[7]

There are two independent molecules of **1**, **A** and **B**, in a unit cell. Two **A** and **B** molecules are aligned respectively centrosymmetrically (Fig. 8). All the anthraquinone rings are aligned almost parallel along the *b* axis. However, those are not face-to-face stacked. There are no specific intermolecular interactions between the molecules.

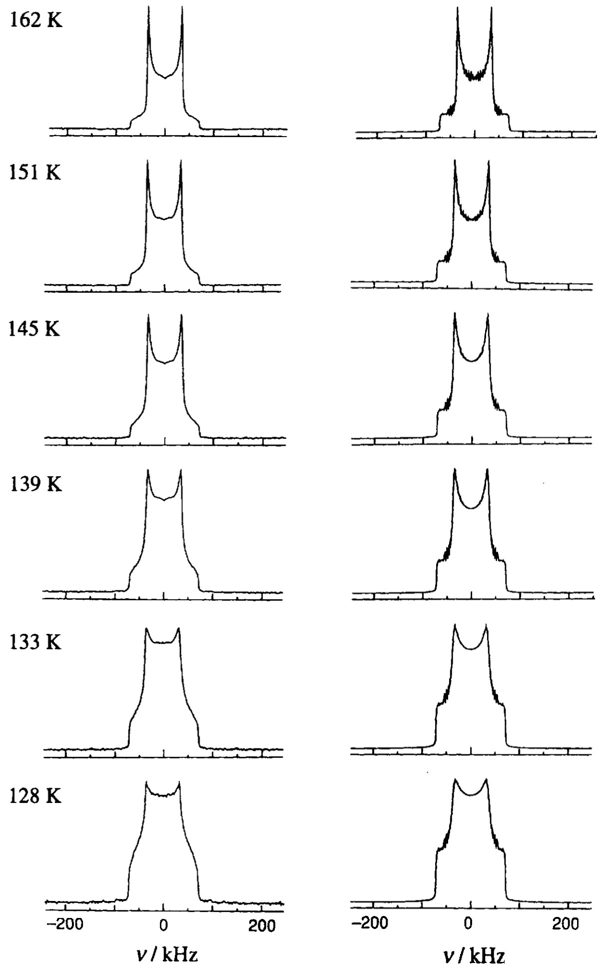


Fig. 9 Solid-state ^2H NMR spectra (left-side) recorded for (**1**)(C_6D_6) and simulated ^2H NMR spectra (right-side) calculated assuming the two-site 60° jump motion. The pulse spacing is 15 μs.

^2H NMR

Analysis of ^2H NMR powder line shapes has been used to study molecular motion in a wide range of solids including host–guest clathrate crystals.[16] The line shapes are highly characteristic of the jump motion, in which molecules or fragments of molecules undergo instantaneous exchange between two or more discrete sites.[16,17] We have prepared the clathrate crystals, (**1**)(C_6D_6) and (**1**)$_2$(hydroquinone)(C_6D_6) including deuteriated benzene as guest species, and measured deuterium NMR powder line shapes. Typical spectra for (**1**)(C_6D_6) measured in the temperature range 130–160 K are shown in Fig. 9. Similar spectra were also obtained for (**1**)$_2$(hydroquinone)(C_6D_6) at 170–200 K.

The guest benzene is embedded only by the lattice control and, therefore, the guest motion should be associated with the void space around the guest molecules. The structures of the cavity trapping the guest benzene molecules are illustrated in Fig. 10. Based on these cavity structures in-plane reorientation among six sites separated by a 60° azimuth angle around the six-fold axis is considered to be most reasonable for molecular motion of the trapped benzene molecules. The powder pattern at room temperature of both (**1**)(C_6D_6) and (**1**)$_2$(hydroquinone)(C_6D_6) showed an axial pattern with a 90 kHz effective quadrupole coupling constant (QCC_{eff}). This axial pattern suggests the benzene molecules undergo reorientation about the six-fold axis. The value for QCC_{eff} calculated based on the six-site reorientation model is 92.25 kHz, and is in good agreement with the observed value. As the temperature is decreased, hence the jump rate is decreased, the shape of the powder pattern is distorted from the axial shape and its intensity is decreased, as seen in the spectra of (**1**)(C_6D_6) (Fig. 9). Also shown in Fig. 9 are simulated ^2H line shapes based on the six-site reorientation model. Each spectrum has been normalized to unit intensity. The agreement between the observed and simulated spectral patterns is quite satisfactory. From an Arrhenius plot in this temperature range, the activation energy for the six-site reorientational motion in the (**1**)(C_6D_6) crystal was derived to be 9.4 kJ mol^{-1}. Similarly, for (**1**)$_2$(hydroquinone)(C_6D_6), the activation energy of 19 kJ mol^{-1} was deduced.

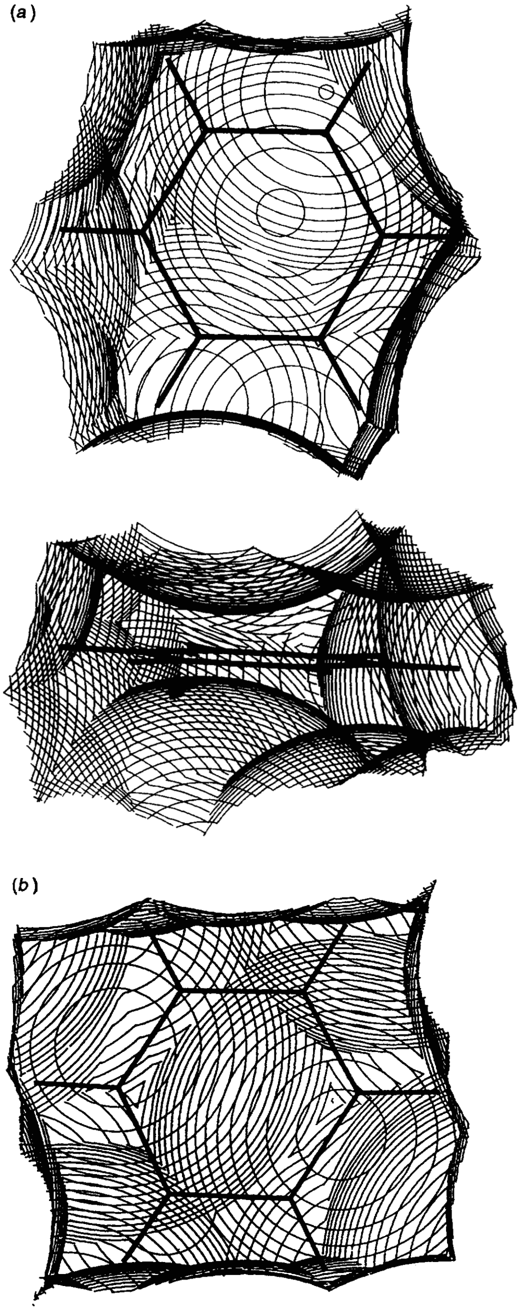


Fig. 10 Composite diagram of the cavity drawn by the program CAVITY. The contours are drawn in sections separated by 0.1 Å. (*a*) (**1**)(benzene); (*b*) (**1**)$_2$(hydroquinone)(benzene).

A higher activation energy obtained for (**1**)$_2$(hydroquinone)(C_6D_6) is consistent with the results of the DSC analysis indicating that (**1**)$_2$(hydroquinone)(C_6H_6) is more tightly packed than (**1**)(C_6H_6). Furthermore, this is in line with the density of the crystals; (**1**)$_2$(hydroquinone)(C_6H_6) has a higher density (1.33 g cm^{-3}) than (**1**)(C_6H_6) (1.28 g cm^{-3}). The cavity is regarded as an important factor for the dynamic behaviour in the crystalline state.[18,19] Fig. 10 illustrates the inclusion cavity as composite diagrams of the cavity limited by a concave surface of the sphere from the surrounding atoms.[19] The radius of each sphere is taken to be 1.2 Å greater than the van der Waals radius of the corresponding atom. Fig. 10 appears to indicate qualitatively that the encapsulating cavity in (**1**)$_2$(hydroquinone)(C_6H_6) is narrower than that of (**1**)(C_6H_6) and that the shape of the cavity of (**1**)$_2$(hydroquinone)(C_6H_6) is less suited for an in-plane 60° jump than that of (**1**)(C_6H_6).

Conclusions

A conformationally flexible host compound, **1**, which has been designed by incorporating the versatile possible intermolecular interactions–not only lattice control, but also hydrogen bond and π–π interactions, electrostatic interactions, and charge-transfer interactions–acts as a host species for a few planar aromatic compounds. It has been revealed by X-ray crystal structural analyses that the preferential conformation of the ether bond in **1** holds the anthracene and anthraquinone rings perpendicular to each other, providing inclusion voids in the crystal lattices. We have encountered a novel type of three-component clathrate. The complex can be regarded as a unique clathrate crystal in which the host lattice is constituted of two different components by using the hydrogen bonds and two typical π–π interactions. The guest benzene molecules are enclathrated only by van der Waals interactions through the lattice control in this two-component host cavity. Nevertheless, the guest molecules are retained up to 173 °C, indicating that the host compounds are tightly connected by the above-noted intermolecular interactions. Furthermore, the inclusion cavity of the benzene molecules provides a small void for their 60° jump motion in the cavity.

Among the possible intermolecular interactions, charge-transfer seems to be only a little involved, as judged from the colour change on complexation and the crystal structure. Thus, the charge-transfer interaction is not regarded as a principal factor for the formation of the three-component complex.

Experimental

1-(9-Anthryloxy)anthraquinone (1)

A suspension of anthrone (2.32 g, 11.94 mmol) and LAH (60% in mineral oil; 0.50 g, 12.50 mmol) in dry THF (60 ml) was refluxed for 1 h under argon. To the solution 1-fluoroanthraquinone[20] (1.00 g, 4.42 mmol) in dry THF (100 ml) was added in portions over a period of 30 min and then refluxed with stirring for 24 h. Water (25 ml) was slowly added to the resulting mixture to yield a yellow precipitate which was isolated by filtration. The filtrate was extracted three times with dichloromethane (300, 100 and 100 ml each). The extracts and a solution of the precipitate in dichloromethane were combined, dried by magnesium sulfate, and evaporated to give the crude **1**. Purification by column chromatography on silica gel with hexane/dichloromethane as eluent yielded the pure ether **1** as orange prisms of mp 240–242 °C in 77% yield: δ_H(500 MHz, $CDCl_3$) 6.58 (dd, J = 8.4, 1.1 Hz, 1 H), 7.37 (dd, 8.4, 7.7 Hz, 1 H), 7.43 (dd, J = 7.4, 6.6 Hz, 2 H), 7.50 (dd, J = 8.8, 6.6 Hz, 2 H), 7.82 (td, J = 7.5, 1.5 Hz, 1 H), 7.88 (td, J = 7.5, 1.5 Hz, 1 H), 8.02 (dd, J = 7.7, 1.1 Hz, 1 H), 8.08 (dd, J = 8.8, 7.4 Hz, 4 H), 8.34 (dd, J = 7.7, 1.5 Hz, 1 H) and 8.44 (dd, J = 7.7, 1.5 Hz, 1 H), 8.44 (s, 1 H).

X-Ray crystallographic analysis†

Diffraction data of all three crystals were recorded on a RIGAKU AFC-5 four-circular diffractometer at T = 298 K by using graphite-monochromated Mo-Kα radiation with the ω-$2\theta/\omega$ scan technique. For (**1**)(C_6H_6), in order to avoid guest release during the data collection, the sample was coated with adhesive. The space group $P1$ of the crystal (**1**)$_2$(hydroquinone)(C_6H_6) was ascertained by SHG (second harmonic generation) activity. The structures were solved by a direct method using the SHELXS-86 program. Hydrogen atoms were located by calculations for (**1**)(C_6H_6), and by difference Fourier synthesis for the other two. Block diagonal least-squares refinement was performed with anisotropic temperature factors for all non-hydrogen atoms and isotropic temperature factors for hydrogen atoms. The crystal data, experimental and refinement parameters are summarized in Table 1.

NMR experiments

^2H NMR powder patterns of (**1**)(C_6D_6) and (**1**)$_2$(hydroquinone)(C_6D_6) were measured at 61.42 MHz on a Bruker MSL 400 NMR spectrometer attached with a variable temperature N_2-gas-flow probe controlled with a Bruker B-VT-1000 temperature controller. A phase alternated quadrupole echo pulse sequence with 3.5 μs 90° pulse width, 15–95 μs pulse spacing time and 2–30 s recycle delay time was employed for the measurement. The powder patterns were simulated using a FORTRAN program written based on the calculation method developed by A. J. Vega and Z. Luz[21] and using values of quadrupole coupling constant QCC_{eff} = 183 kHz and asymmetry factor η_{eff} = 0.041 for the static state.[17] The activation energy for molecular motion was derived from a plot of jump rate *vs.* temperature and Arrhenius equation.

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References

1 (*a*) E. Weber and M. Czugler, in *Molecular Inclusion and Molecular Recognition-Clathrates I and II*, ed. E. Weber, in *Top. Curr. Chem.*, 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.

2 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; (*d*) G. Kaupp, *Angew. Chem., Int. Ed., Engl.*, 1994, **33**, 728; (*e*) F. Toda, K. Tanaka, Z. Stein and I. Goldberg, *J. Org. Chem.*, 1994, **59**, 5748 and refs. cited therein.

3 For crystal engineering, see: G. R. Desiraju, *Crystal Engineering*, Elsevier, Amsterdam, 1989. For dynamic behaviours of guest molecules, see recent examples: (*a*) K. D. M. Harris, *Chem. Britain*, 1993, 132; (*b*) A. Mahdyarfar and K. D. M. Harris, *J. Chem. Soc., Chem. Commun.*, 1993, 51; (*c*) M. D. Hollingsworth, *J. Am. Chem. Soc.*, 1993, **115**, 5881; (*d*) A. E. Aliev and K. D. M. Harris, *J. Am. Chem. Soc.*, 1993, **115**, 6369; (*e*) F. Toda *et al.*, *J. Chem. Soc., Chem. Commun.*, 1993, 1139; (*f*) M. D. Hollingsworth, B. D. Santarsiero and K. O. M. Harris, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 649; (*g*) F. Imashiro, *J. Am. Chem. Soc.*, 1993, **115**, 2231; (*h*) M. E. Brown and M. D. Hollingsworth, *Nature*, 1995, **376**, 323. For reactions in clathrate crystals, see: N. Hayashi, Y. Mazaki and K. Kobayashi, *Tetrahedron Lett.*, 1994, **35**, 5883.

4 For a recent non-ionic three-component complex, see: L. J. Barbour, J. W. Steed and J. L. Atwood, *J. Chem. Soc., Perkin Trans. 2*, 1995, 857.

5 K. Ochiai, Y. Mazaki and K. Kobayashi, *Tetrahedron Lett.*, 1995, **36**, 5947.

6 (*a*) F. Toda, *Molecular Inclusion and Molecular Recognition-Clathrates I, in Top. Curr. Chem.*, vol. 140, Springer-Verlag, Berlin, Heidelberg, 1987, p. 43; (*b*) F. Toda, *Molecular Inclusion and*

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† Atomic coordinates, a complete list of bond lengths and angles, thermal parameters and F_o–F_c tables of all the structures have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme see 'Instruction for Authors (1996)', *J. Chem. Soc., Perkin Trans. 2*, 1996, issue 1.

Molecular Recognition-Clathrates II in Top. Curr. Chem., vol. 149, Springer-Verlag, Berlin, Heidelberg, 1988, p. 211.

7 (*a*) Y. Mazaki, N. Hayashi and K. Kobayashi, *J. Chem. Soc., Chem. Commun.*, 1992, 1381; (*b*) Y. Mazaki, K. Awaga and K. Kobayashi, *J. Chem. Soc., Chem. Commun.*, 1992, 1661; (*c*) N. Hayashi, Y. Mazaki and K. Kobayashi, *Adv. Mater.*, 1994, **6**, 654; (*d*) N. Hayashi, Y. Mazaki and K. Kobayashi, *J. Org. Chem.*, 1995, **60**, 6342.

8 N. Hayashi, Y. Mazaki and K. Kobayashi, *J. Chem. Soc., Chem. Commun.*, 1994, 2351.

9 (*a*) 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 and E. W. Schlag, *J. Am. Chem. Soc.*, 1994, **116**, 3500.

10 For edge-to-face aromatic interactions, see: M. C. Grossel, A. K. Cheetham, D. A. O. Hope and S. C. Weston, *J. Org. Chem*, 1993, **58**, 6654, and refs. cited therein.

11 M. Nishio, Y. Umezawa, M. Hirota and Y. Takeuchi, *Tetrahedron*, 1995, **51**, 8665.

12 C. A. Hunter, R. H. Haueisen and A. Irving, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 566.

13 T. E. Muller, D. M. P. Mingos and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1994, 1787.

14 M. Etter, *Acc. Chem. Res.*, 1990, **23**, 120.

15 L. R. Hanton, C. A. Hunter and D. H. Purvis, *J. Chem. Soc., Chem. Commun.*, 1992, 1134.

16 (*a*) A. E. Aliev, S. P. Smart and K. D. Harris, *J. Mater. Chem.*, 1994, **4**, 35; (*b*) N. J. Heaton, R. L. Vold and R. R. Vold, *J. Am. Chem. Soc.*, 1989, **111**, 3211; (*c*) E. Meirovitch and I. Belsky, *J. Phys. Chem.*, 1984, **88**, 6407; (*d*) M. Meirovitch, T. Krant and S. Vega, *J. Phys. Chem.*, 1983, **87**, 1390.

17 J. H. Ok, R. R. Vold, R. L. Vold and M. C. Etter, *J. Phys. Chem.*, 1989, **93**, 7618.

18 (*a*) M. D. Cohen, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 386; (*b*) V. Ramamurthy and K. Venkatesan, *Chem. Rev.*, 1987, **87**, 433.

19 (*a*) Y. Ohashi, A. Uchida, Y. Sasada and Y. Ohgo, *Acta Crystallogr., Sect. B*, 1983, **39**, 54; (*b*) *Reactivity in Molecular Crystals*, Y. Ohashi, ed. VCH-Kodansha, 1993; (*c*) Y. Ohashi, K. Yanagi, T. Kurihara, Y. Sasada and Y. Ogo, *J. Am. Chem. Soc.*, 1981, **103**, 5805.

20 L. Echegoyen, Y. Hafez, R. C. Lawson, J. de Mendoza and T. Torres, *J. Org. Chem.*, 1993, **58**, 2009.

21 J. Vega and Z. Luz, *J. Chem. Phys.*, 86, 1987, **86**, 1803.

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