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A new supramolecular system of racemic-bis-β-naphthol, benzoquinone and aromatic hydrocarbon, which shows high molecular recognition ability

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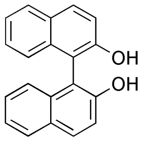
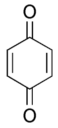
Racemic-bis-β-naphthol, benzoquinone and aromatic hydrocarbons formed a new three component supramolecular system as black crystals. X-ray analysis of the crystals shows that (+)- and (−)-bis-β-naphthol and benzoquinone form a quinhydrone-type crystalline lattice with aromatic stacking and hydrogen bonding in which the third aromatic hydrocarbon component is accommodated. As the cavity created has a definite shape and size, only hydrocarbons which fit the cavity are selectively included.

Light coloured organic compounds sometimes form strongly coloured charge-transfer complexes, as exemplified by greenish grey quinhydrone which is formed from benzoquinone and hydroquinone by recrystallization from solvent or just by mixing both components in the solid state.[1] Here we report the formation of black organic inclusion complex crystals from (±)-bis-β-naphthol (**1a**), benzoquinone (**2**) and aromatic hydrocarbons. By the same recrystallization method from various aromatic hydrocarbons of group A, similar black inclusion complex crystals containing toluene (**4**), *i*-propylbenzene (**5**), 1-methylstyrene (**6**), phenylacetylene (**7**), *o*-xylene (**8**) and *m*-xylene (**9**) as guests were obtained. None of these black inclusion complexes showed clear mp because **2** sublimes easily from the complexes before melting. Hydrocarbon guests of group A in parentheses, such as *tert*-butylbenzene (**11**) and mesitylene (**12**), did not form inclusion complexes, probably due to steric reasons.



1

a: (±)-form
b: (+)-form
c: (−)-form

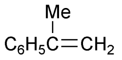


2

These inclusion crystals are the first examples of a new supramolecular system consisting of protic and non-protic aromatic hydrocarbons. Although various supramolecular systems have been described,[2] we are aware of only one example of a supramolecular system consisting of protic and non-protic components.[3]

hydrocarbon guests of group A

C_6H_6 **3**
C_6H_5Me **4**
$C_6H_5CHMe_2$ **5**



$C_6H_5C(Me){=}CH_2$ **6**
$C_6H_5C{\equiv}CH$ **7**
o-$C_6H_4Me_2$ **8**
m-$C_6H_4Me_2$ **9**
p-$C_6H_4Me_2$ **10**
($C_6H_5CMe_3$ **11**
1,3,5-$C_6H_3Me_3$ **12**)

These black inclusion crystals turned to white crystals by loss of **2** and the volatile hydrocarbon guest on standing, but they were stable enough for X-ray analysis when sealed in a capillary glass tube. Crystal data for inclusion compounds with **3**–**9** as guests suggest that they are all isostructural to each other. The inclusion complex with *p*-xylene (**10**) has a different stoichiometry and cell parameters suggesting a different structure. X-Ray analysis of a 2 : 1 : 2 complex (**I**) of **1a**, **2** and **4** shows that **2** is sandwiched almost in parallel by two naphthol rings of **1b** and **1c**, and the triplet structures are stacked along the *c* axis. There is a hydrogen-bond network between **1a** and **2** as shown schematically in Fig. 2: one OH of **1** forms a hydrogen bond with O of **2** within the triplet, and the other OH with O of **2** of

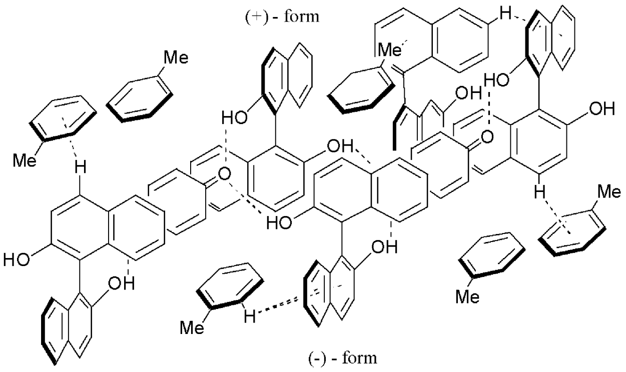


Fig. 2 Schematic illustration of crystal **I**.

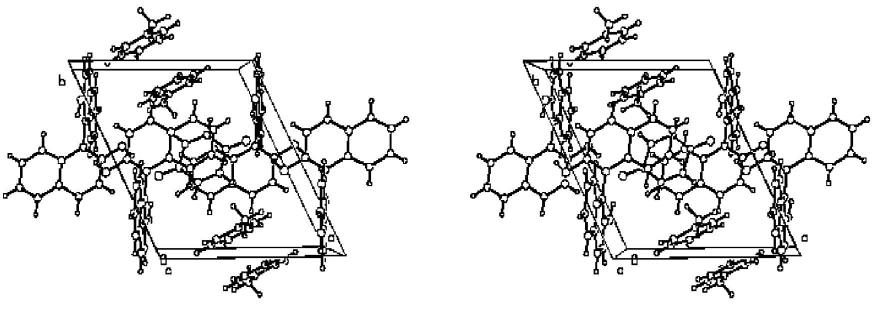


Fig. 1 Stereoview of crystal **I** along the *c* axis.

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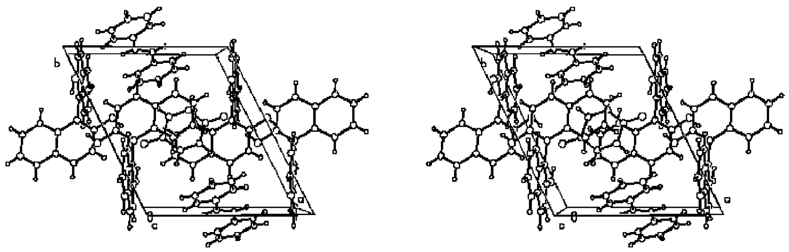
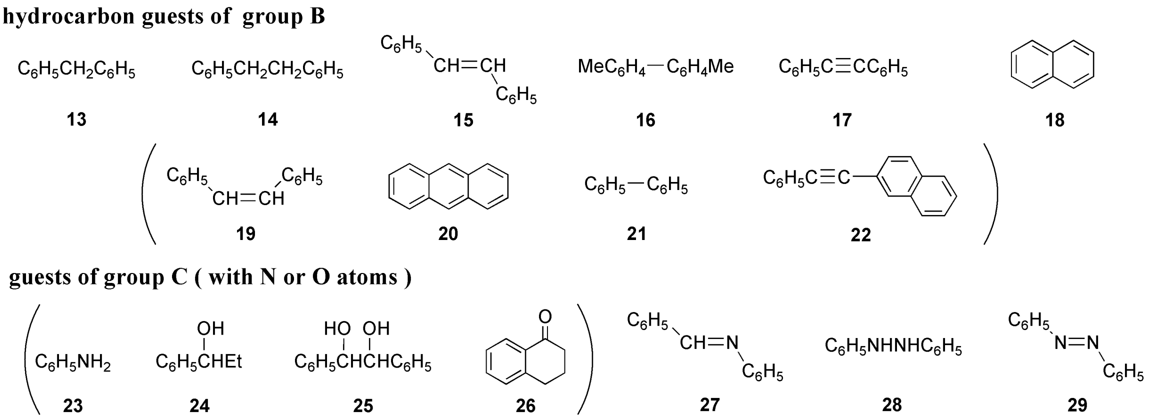


Fig. 3 Stereoview of crystal **II** along the *c* axis.



the neighbouring triplet. In the cavity thus created, the aromatic hydrocarbon guest is accommodated (Fig. 1 and Fig. 2). **2** resides on the center of inversion.

The X-ray structure of the toluene complex shows that the aromatic components are arranged to make a dihedral angle of 64–69° between them, which results in CH$\cdots\pi$ interactions between the C–H of toluene and the naphthol ring as well as the C–H of naphthol and the toluene ring (Fig. 2, the distance between C–H and the center of the 6-membered ring varies from 2.736 to 3.233 Å). Non-aromatic cyclohexane did not form an inclusion crystal with **1a** and **2**.

As the cavity is large enough to accommodate two guest molecules, one hydrocarbon guest molecule twice the size of **3** could be fitted in the cavity. Actually, a variety of guest molecules of twice the size of **3**–**9** such as those of group B (**13**–**17**) are accommodated to form stable 2 : 1 : 1 complexes of **1a**, **2** and the hydrocarbon as black crystals. The crystal data suggested that all the complexes are isostructural. Naphthalene (**18**) is included with a different stoichiometry and is not isostructural. These inclusion complexes also lost **2** through sublimation by heating and did not show a clear mp.

The X-ray structure of the 2 : 1 : 1 complex (**II**) of **1a**, **2** and *trans*-stilbene (**15**) is shown in Fig. 3. The arrangement of **1b**, **1c**, **2** and the guest molecules is very similar to that of the toluene complex (**I**)† Instead of two toluene molecules related by a centre of inversion, one *trans*-stilbene molecule resides on a centre of inversion. *cis*-Stilbene (**19**) is not included, probably because **19** has a bent structure and cannot fit in a straight cavity with a centre of inversion symmetry. Anthracene (**20**) might be too big as a fused-ring aromatic hydrocarbon to be accommodated, and biphenyl (**21**) is probably too short to occupy the long cavity. 2-Naphthylphenylacetylene (**22**) would be sterically too bulky to be accommodated in the cavity. Guests of group C in parentheses such as aniline (**23**), 1-phenylpropanol (**24**), 1,2-diphenyl-1,2-ethanediol (**25**) and 1-tetralone (**26**) which contain O and N atoms did not form inclusion crystals with **1a** and **2**, probably because these guests interact with **1a** and **2** and interrupt hydrogen bond formation between them. Guests of group C such as benzylidenaniline (**27**), hydrazobenzene (**28**) and azobenzene (**29**) formed inclusion complexes. This is probably due to the fact that the moieties capable of forming hydrogen bonding are hidden within the guest molecules whose geometries are similar to *trans*-stilbene (**27**–**29**).

Thus, the new series of supramolecular systems displayed high selectivity for inclusion. Detailed characterization and structural analysis of the whole series of crystals will be published elsewhere.

Notes and references

† *Crystal data*: for **I**: triclinic, space group $P\bar{1}$ (#2), a = 10.1524(9), b = 10.8140(10), c = 11.7724(11) Å, α = 98.011(2), β = 97.747(2), γ = 115.41(2)°, U = 1126.98(18) Å^3, D_c = 1.275 g cm^{-3}, Mo-Kα radiation (λ = 0.71069 Å) for Z = 2. Least-squares refinement based on 2727 reflections with $I > 2.0\sigma(I)$ (out of 4925 unique reflections) led to a final R = 0.058. CCDC 17674. For **II**: triclinic, space group $P1$ (#2), a = 10.18428(14), b = 10.8554(14), c = 11.5925(16) Å, α = 99.418(3), β = 98.393(3), γ = 116.126(3)°, U = 1100.1(3) Å^3, D_c = 1.300 g cm^{-3}, Mo-Kα radiation (λ = 0.71069 Å) for Z = 2. Least-squares refinement based on 3720 reflections with $I > 2.0\sigma(I)$ (out of 6120 unique reflections) led to a final R = 0.048. CCDC 176715. See http://www.rsc.org/suppdata/cc/b2/b203998m/ for crystallographic files in .cif or other electronic format.

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2 *Comprehensive Supramolecular Chemistry, Vol. 6*, ed. D. D. MacNicol, F. Toda, R. Bishop, Pergamon, Oxford, 1996.

3 S. A. Bourne, K. L. Gifford and F. Toda, *J. Inclusion Phenom. Mol. Recognit. Chem.*, 1998, **32**, 91.