

Use of Halogen Sensor Groups for Specific Trapping of Polyhaloalkanes

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Multiple halogen...halogen interactions between the bromine atoms of **3** and polyhaloalkanes result in the formation of stable inclusion compounds, as illustrated here for the X-ray structure of **3**·CHCl₃, while other molecules of comparable size are excluded.

The design of molecules capable of specific recognition of other chemical species is a major area of current interest and importance.¹ We are interested in the use of crystal engineering principles² to obtain simple molecules which will exhibit such properties by means of intermolecular host-guest forces. Such materials would have potential application in areas such as sensing devices, selective and chiral separations, and chemical sequestration.³

For example, we have reported previously⁴ the novel behaviour of keto alcohol **1** where the *endo*-hydroxy group is poorly hydrogen-bonded, partly because of the V-shaped concavity of the molecule and partly because of the *exo*-methyl substituent. Alternatively, the -OH functions as a sensor group capable of complexing with dimethylsulfoxide (DMSO) and producing a coordination clathrate.⁵ More significantly, however, **1** will sequester DMSO from solution in the form of a crystalline precipitate.^{3,4}

Here we demonstrate that the combination of a V-shaped molecular framework and *exo*-halogen substituents can lead to specific entrapment of small polyhaloalkane guests. Friedländer reaction⁶ of bicyclo[3.3.1]nonane-2,6-dione⁷ with *o*-amino-benzaldehyde⁸ afforded the diquinoline derivative **2** in 74% yield, and then bromination with *N*-bromosuccinimide yielded specifically (71%) the anticipated *exo,exo*-dibromide **3**.

Diquinoline **2** exhibited no inclusion properties, but crystallisation of **3** from chloroform gave a 1 : 1 inclusion compound. Inclusion was also noted using carbon tetrachloride, bromo-trichloromethane, and 1,1,1-trichloroethane. However, use of a wide range of other solvents (*e.g.* acetone, acetonitrile, benzene, dichloromethane, methanol, ethyl acetate, DMSO) resulted in no inclusion and amorphous samples of pure **3**.

Examination of the crystal structure of **3**·CHCl₃[†] allows these inclusion properties to be rationalised. Aromatic molecules frequently pack maximising face-face and edge-face interactions^{2a} and both modes operate here. The closest face-face separation is 3.46 Å, while the T-shaped edge-face interaction involves three C(13)-H...Ar close contacts of 2.67, 2.82 and 2.87 Å, respectively, as shown in Fig. 1. Although the angle between normals to the aromatic rings of **3** is 84.3° and this packing could potentially result in formation of an extended network throughout the solid, this is prevented

by the bulky *exo*-bromine atoms, all of which are oriented outwards. Hence, **3** packs poorly by itself but efficiently with an appropriate guest.

Neighbouring bromines interact through a particularly short (3.46 Å) and a rather longer (4.10 Å) Br...Br intermolecular attraction, providing a crystal structure capable of accommodating chloroform guests within small lattice cavities. The chloroform H is hydrogen-bonded to one of the quinoline nitrogens, providing a partial anchor between host and guest (distances N...HCCl₃ 2.40, N...CCl₃ 3.37 Å, respectively). However, the other nitrogen atom has no intermolecular contacts under 3.50 Å.

Each chloroform molecule is also positioned to give Cl...Br interactions with the bromine sensor groups of four different molecules of **3**. Intermolecular halogen...halogen attractions are recognised as being widely involved in structural chemistry.^{2b} Here, the three chlorines exhibit short interactions

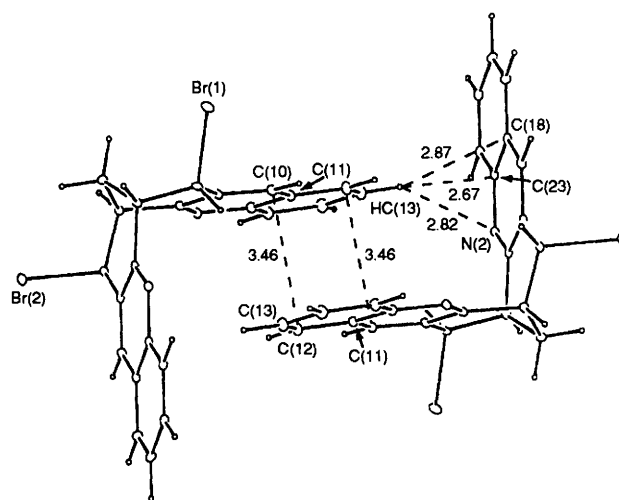


Fig. 1 Pair of molecules of **3** in the inclusion compound **3**·CHCl₃ showing the aromatic face-face and edge-face interactions. The close contacts (Å) are represented as dashed lines.

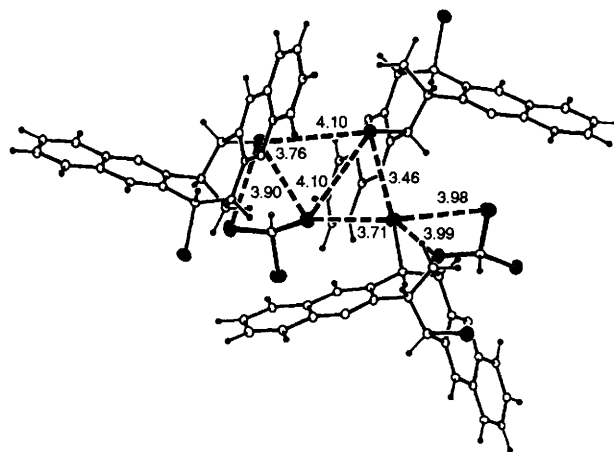
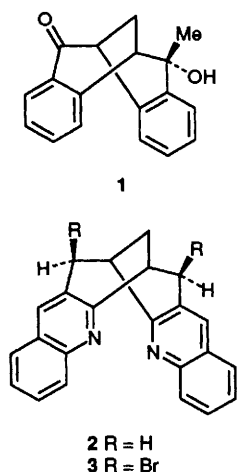


Fig. 2 The intermolecular halogen...halogen attractions (Å), represented as dashed lines, present in the inclusion compound **3**·CHCl₃. Both bromo and chloro atoms are drawn as large filled circles, and hydrogen atoms as small filled circles.

with one (3.98 Å), two (3.90, 3.99 Å) and three (3.71, 3.76 and 4.10 Å) bromine atoms respectively (Fig. 2).

It is the generation of this network of halogen interactions which finally stabilises the host-guest combination and which results in trapping of chloroform (and other polyhaloalkanes) but excludes other potential guest molecules.

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Footnote

† Crystal data for: $C_{23}H_{16}N_2Br_2 \cdot CHCl_3$, $M = 599.6$, monoclinic, $P2_1/c$, $a = 9.865(3)$, $b = 15.307(3)$, $c = 17.946(5)$ Å, $\beta = 122.12(1)^\circ$, $V = 2295(1)$ Å³, $Z = 4$, $D_c = 1.73$ g cm⁻³, λ (Mo-K α) = 0.7107 Å, $\mu = 38.6$ cm⁻¹. Anisotropic thermal parameters were refined for all the non-hydrogen atoms, final $R = 0.031$ for 2571 independent reflections [$I > 3\sigma(I)$] and 280 variables. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at

the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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