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Polar host–guest assembly mediated by halogen···π interaction: inclusion complexes of 2,4,6-tris(4-halophenoxy)-1,3,5-triazine (halo = chloro, bromo) with trihalobenzene (halo = bromo, iodo)

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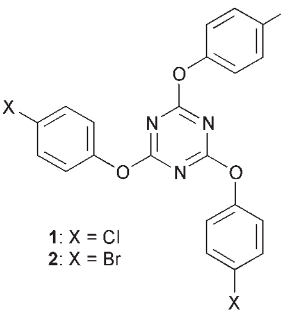
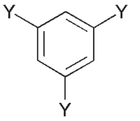
Received (in Columbia, MO, USA) 15th February 2001, Accepted 5th April 2001
First published as an Advance Article on the web 1st May 2001

Crystallization of four isomorphous host–guest complexes in the polar space group $P6_3$ is ascribed to the recurring halogen(guest)···π(host) interaction.

Self-assembly of chiral crystals from achiral components[1] is a current endeavor in crystal engineering with applications in asymmetric synthesis and materials science. Crystallization of achiral or racemic molecules in acentric space groups is relevant not only for the design of functional solids, such as host–guest,[2] nonlinear optics,[3] but also has implications in our fundamental understanding of spontaneous resolution during crystallization.[4] In this context, it was recently noted by some of us[5] that co-crystallization of 2,4,6-tris(4-chlorophenoxy)-1,3,5-triazine **1** and 1,3,5-tribromobenzene (TBB) from an equimolar mixture of benzene and ethyl acetate afforded a 1:1 complex, **1**·TBB, that belongs to the non-centrosymmetric space group $P6_3$. In **1**·TBB, the triazine molecules form a hexagonal network *via* the robust Cl···Cl trimer synthon. Tribromobenzene guest molecules located in the channels are bonded *via* C–Br···π and C–H···π interactions[6] to the C=C bond mid-point of the host phenyl ring rather than to the ring centroid, as ascertained by neutron diffraction.[5] In this paper we demonstrate the structural significance of halogen···π interactions[7] in inducing polar aggregation of molecules in the solid state. The description of space groups using terms such as (non)centrosymmetric, acentric, chiral and polar has been clarified in the crystallographic literature.[8]



1: X = Cl
2: X = Br



TBB: Y = Br
TIB: Y = I

Crystallization of chlorotriazine **1** and 1,3,5-triiodobenzene (TIB) from PhH–EtOAc afforded crystals of **1**·TIB (1:1) in space group $P6_3$.† The TIB guest species are accommodated in an open hexagonal network formed by a triangulo halogen synthon (Cl···Cl 3.56 Å, 107.0°, 167.0°) of triazine host molecules (Fig. 1). The hexahost framework of **1** and **2** with trihalobenzene guests is virtually identical to the intermolecular interaction network observed in their channel inclusion complexes with other guest species: benzene, hexamethylbenzene (HMB), hexachlorobenzene (HCB), trinitromesitylene (TNM), 1,3,5-trinitrobenzene (TNB), mesitylene (MES), 2,4,6-collidine (CLN) and hexamethylphosphoramide (HMPA).[9] However, the latter host–guest structures are centrosymmetric (space group $P6_3/m$) with the triazine core lying on a crystallographic mirror plane. Thus inclusion of trihalobenzene guests in the hexagonal nanotubes induces significant structural changes in the mutual orientation of host phenyl rings. Yet there is minimal change in the lattice parameters of **1**·TBB and **1**·TIB compared to the centrosymmetric structures (Table 1). Adjacent phenoxy rings are parallel in the $P6_3/m$ structures while they are twisted by an angle (τ) of 51.3° and 54.3° to each other in **1**·TBB and **1**·TIB. As a result of phenyl group tilting, away from the halogen and closer to the hydrogen, the guest molecules form short C–I···π

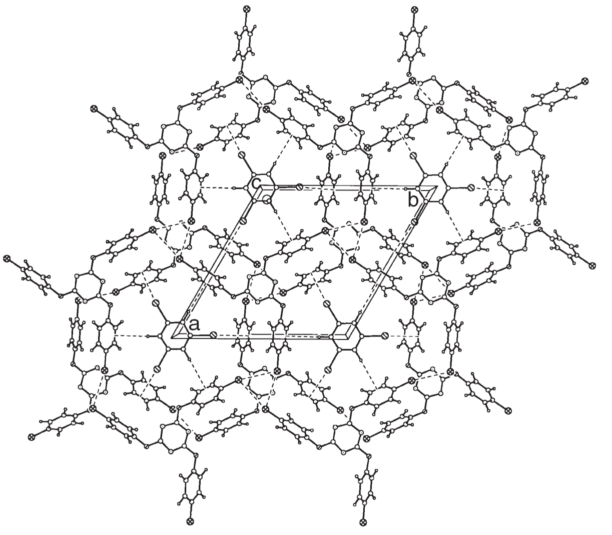


Fig. 1 Hexa-host network in **1**·TIB assembled through Cl···Cl triangulo synthon. TIB guest molecules are bonded *via* C–I···π and C–H···π interactions. Notice the herringbone motif between host phenoxy rings of adjacent channels.

Table 1 Crystal data of some isomorphous complexes of **1** and **2** with various guests in $P6_3/m$ and $P6_3$ space groups

	Host/ guest	Space group	Z	$a = b$ (Å)	c (Å)
2·CLN[a]	1:1	$P6_3/m$	2	15.468(2)	7.087(1)
1·$\frac{1}{2}$HCB[b]	2:1	$P6_3/m$	2	15.435(2)	6.876(1)
1·$\frac{1}{2}$HMB[b]	2:1	$P6_3/m$	2	15.411(2)	6.867(1)
2·$\frac{1}{2}$HMB[b]	2:1	$P6_3/m$	2	15.554(4)	6.951(3)
1·$\frac{1}{2}$TNB[b]	2:1	$P6_3/m$	2	15.255(2)	7.005(2)
2·$\frac{1}{2}$TNM[b]	2:1	$P6_3/m$	2	15.719(2)	7.034(1)
1·$\frac{1}{2}$HMPA[b]	2:1	$P6_3/m$	2	15.234(2)	6.880(1)
1·TBB[c]	1:1	$P6_3$	2	15.166(6)	6.743(2)
1·TIB[d]	1:1	$P6_3$	2	15.482(1)	7.011(1)
2·TBB[d]	1:1	$P6_3$	2	15.442(1)	6.991(1)
2·TIB[d]	1:1	$P6_3$	2	15.627(2)	7.046(1)

[a] Ref. 9*a*. [b] Ref. 9*b*. [c] Ref. 5 (neutron data). [d] This paper.

DOI: 10.1039/b102150h

(3.43 Å, 158.3°; Σ vdW radii = 2.0 + 1.7 = 3.7 Å) and long C–H$\cdots\pi$ (3.00 Å, 177.4°) interactions with different C=C bonds of the host phenyl ring.‡ Three such sinusoidal motifs stabilize the polar host–guest architecture (Fig. 2). The C–I$\cdots\pi$ interaction is polarization-induced, such that the C–I$^{\delta(+)}$ vector points towards the mid-point of a $\pi^{\delta(-)}$ bond, and is reminiscent of the type II halogen$\cdots$halogen interaction[9] between host molecules. In effect, a slice of the host–guest layer in **1**·TIB is stabilized by Cl$\cdots$Cl, C–I$\cdots\pi$ and C–H$\cdots\pi$ interactions (Table 2). The halogen$\cdots\pi$ radial motif in **1**·TIB channel resembles the Cl$\cdots\pi$ interaction observed recently in the pseudo-threefold cavity of calix[6]pyrrole with 2,2,2-trichloroethanol guest.[10] The interplay of numerous weak interactions, aryl–aryl, C–H$\cdots$N, aryl–halogen and inter-halogen, resulting in microcavities that are tailored to the guest structure has been noted in a halogenated tweezer host molecule.[11]

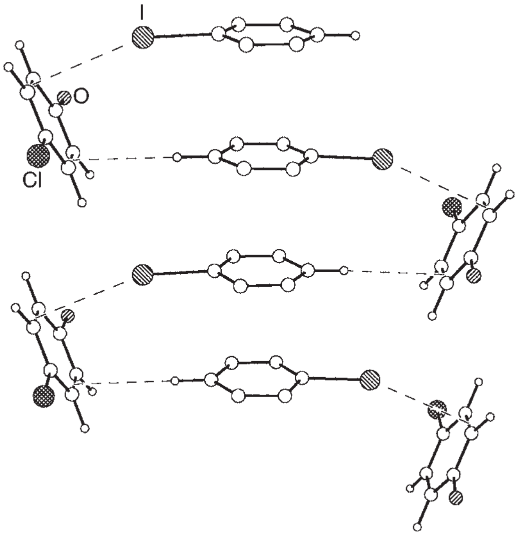


Fig. 2 Sinusoidal chain of C–I$\cdots\pi$ and C–H$\cdots\pi$ interactions in **1**·TIB that result in polar crystallization. Three such motifs rotated by 120° stabilize the host–guest channel architecture. Molecular fragments are truncated for clarity.

The 1 : 1 inclusion complexes of tribromobenzene and triiodobenzene with 2,4,6-tris(4-bromophenoxy)-1,3,5-triazine **2**, **2**·TBB and **2**·TIB respectively,† are isostructural with the corresponding inclusion complexes of **1** (Table 1). The mutual orientation of host phenyl rings and metrics of C–Br/I$\cdots\pi$ and C–H$\cdots\pi$ interactions are given in Table 2. Although the exact reasons as to why achiral or racemic molecules adopt non-centrosymmetric crystal packing are difficult to dissect,[1,4] the present case of four isomorphous structures offers a clue. Three polar chains of C–Br/I$\cdots\pi$ and C–H$\cdots\pi$ guest–host interactions rotated by 120° to each other stabilize the hexagonal nanotubes. The crystal structure would be centrosymmetric if such motifs in adjacent chains run anti-parallel and non-centrosymmetric if they are aligned in the same direction. The polarity of one nanotube is transmitted to adjacent channels *via* the edge-to-face[12] herringbone packing between host phenoxy rings related by a two-fold screw axis. Since inclusion complexes of **1** and **2** with many other guests are all centrosymmetric,[9] polar aggregation with TBB and TIB species in space group $P6_3$ appears to be guest-induced. Thus, the halogen- and hydrogen-bonded synthon in Fig. 2 is the minimum ensemble necessary to amplify polarity in the three-dimensional crystal, in other words it is a supramolecular chiron.[13] The mechanism for polar crystallization with flexible hosts **1** and **2** (guest–host X$\cdots\pi$ interaction) is conceptually different from the phenomenon for parallel alignment of D–π–A chromophores in the constrained channel of perhydrotriphenylene (guest–guest D$\cdots$A interaction).[3]

Table 2 Metrics of intermolecular interactions in inclusion complexes of **1** and **2** in space group $P6_3$. See chemical diagram for labels X, Y and text for definition of torsion angle τ

	1·TBB[a]	**1**·TIB[b]	**2**·TBB[b]	**2**·TIB[b]
X$\cdots$X (Å)	3.441(3)	3.56	3.51	3.55
C–X$\cdots$X (°)	164.9, 104.9	167.0, 107.0	164.9, 104.9	165.3, 105.3
τ, π–π (°)	51.3	54.3	51.6	55.9
Y$\cdots\pi$ (Å)	3.353(4)	3.43	3.51	3.49
C–Y$\cdots\pi$ (°)	158.1(2)	158.3	157.1	158.0
H$\cdots\pi$[c] (Å)	2.817(9)	3.00	2.94	3.03
C–H$\cdots\pi$ (°)	174.0(9)	177.4	176.4	175.2

[a] Ref. 5, neutron data. [b] X-ray data, this study. [c] C–H distance neutron-normalised to 1.083 Å.

We thank the Department of Science and Technology, Government of India (SP/S1/G29/98) and the Hong Kong Research Grants Council (CUHK 4206/99P) for research funding. R. K. R. J. thanks the CSIR for fellowship support.

Notes and references

† *Crystal data*: **1**·TIB ($C_{21}H_{12}Cl_3N_3O_3 \cdot C_6H_3I_3$, M = 916.47). Hexagonal, $a = b$ = 15.4817(6), c = 7.0107(4) Å, $\alpha = \beta$ = 90, γ = 120°, V = 1455.22(12) Å^3, D_c = 2.092 Mg m^{-3}, T = 294 K, space group $P6_3$ (no. 173), Z = 2, μ(Mo-K$_a$) = 0.3532 mm^{-1}, 8911 reflections measured, 1979 unique (R_{int} = 0.0253) which were used in all calculations. Final R = 0.0249 (obs.), 0.0335 (all); $wR(F^2)$ = 0.0616 (obs.), 0.0635 (all). **2**·TBB ($C_{21}H_{12}Br_3N_3O_3 \cdot C_6H_3Br_3$, M = 908.88). Hexagonal, $a = b$ = 15.4420(13), c = 6.9909(7) Å, $\alpha = \beta$ = 90, γ = 120°, V = 1443.7(2) Å^3, D_c = 2.091 Mg m^{-3}, T = 294 K, space group $P6_3$ (no. 173), Z = 2, μ(Mo-K$_a$) = 0.8378 mm^{-1}, 4453 reflections measured, 1715 unique, (R_{int} = 0.1359) which were used in all calculations. Final R = 0.0706 (obs.), 0.0771 (all); $wR(F^2)$ = 0.1681 (obs.), 0.1732 (all). **2**·TIB ($C_{21}H_{12}Br_3N_3O_3 \cdot C_6H_3I_3$, M = 1049.85). Hexagonal, $a = b$ = 15.6268(16), c = 7.0464(10) Å, $\alpha = \beta$ = 90, γ = 120°, V = 1490.2(3) Å^3, D_c = 2.340 Mg m^{-3}, T = 294 K, space group $P6_3$ (no. 173), Z = 2, μ(Mo-K$_a$) = 0.7203 mm^{-1}, 10 527 reflections measured, 2406 unique, (R_{int} = 0.0415) which were used in all calculations. Final R = 0.0269 (obs.), 0.0385 (all); $wR(F^2)$ = 0.0602 (obs.), 0.0644 (all). For structure solution and refinement methods, see ref. 8. CCDC reference numbers 161765–161767. See http://www.rsc.org/suppdata/cc/b1/b102150h/ for crystallographic files in .cif format.

‡ C–I$\cdots\pi$ and C–H$\cdots\pi$ geometries are longer and bent when measured to phenyl ring centroid (3.58 Å, 139.0°; 3.67 Å, 163.8°) because the guest molecule lies about 1 Å below the *sym*-triazine host.

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