

Hexagonal crystalline inclusion complexes of 4-iodophenoxy trimesoate†

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Bifurcated $I \cdots \pi$ and $I \cdots O=C$ halogen bonding interactions assist in formation of unique iodo–arene trimers leading to nanoscale channels in inclusion complexes of trimesic acid iodophenolate.

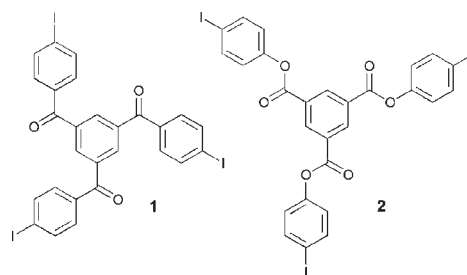
Crystalline inclusion complexes continue to provide inspiration for the design of new organic and metal–organic solids. Particularly intriguing from a functional materials standpoint are inclusion complexes possessing sizable channels or pores extending through the crystalline lattice. Such structures are interesting as it is envisioned that crystal engineering of robust tailor-made porous organic and metal–organic solids from relatively simple molecular building blocks will afford valuable new catalysts and molecular storage/separation devices.¹ Not surprisingly, the *de novo* synthesis of porous crystalline solids (especially those comprised of purely organic components) has proven to be non-trivial.²

Progress in this area, however, has been reported in recent years. In particular, the tecton approach has been successfully applied in the construction of organic inclusion complexes in which large percentages (> 50%) of the crystal lattices are solvent accessible.³ This strategy entails incorporation of hydrogen bonding functionality along the periphery of relatively rigid organic scaffolds. Strong hydrogen bonding interactions may then become the dominant supramolecular interaction in the crystal, sometimes at the expense of close packing.

Non-covalent interactions between organic halogens and nucleophiles (halogen bonding interactions) offer an alternative to hydrogen bonding as a structurally defining supramolecular motif, and halogen bonding is emerging as an important tool in crystal engineering.^{4,5} Halogen bonding interactions between amines, nitrogen heterocycles, carbonyl groups, and other organic halides (so-called type II halogen bonding) is now well-documented and the strength of these interactions can sometimes rival that of conventional hydrogen bonds.^{4,6} Porous organic crystalline networks mediated through halogen bonding interactions, however, are rare,⁷ although notable exceptions are encountered in crystal structures of 4-chloro- and 4-bromophenoxy triazines.⁸ Halogen-

bonded trimers are commonly observed motifs in these structures and, in combination with symmetry elements inherent to the phenoxy triazine framework, give rise to hexagonal packing arrangements with large (~ 12 Å diameter) channels.

We recently reported results of a study examining the influence of halogen bonding interactions on the solid state structures of 4-halo-substituted triarylbenzenes (*e.g.*, **1**).⁹ In continuing research, we sought to probe the interplay between symmetry and electronic factors upon halogen bonding by characterizing analogues of triarylbenzenes in which haloaryl moieties were substituted with electron donating or electron withdrawing groups. As part of this work 1,3,5-tris(4-iodophenoxy carbonyl)benzene (**2**) was prepared,¹⁰ and we wish to disclose the results of preliminary crystallographic investigations. In particular, crystallization of **2** from $CHCl_3$, pyridine, and benzene produced hexagonal inclusion complexes possessing nanometre-sized channels. Significantly, these porous inclusion complexes appear to be mediated in part by unprecedented $I \cdots \pi$ trimer motifs supported in a bifurcated fashion by $I \cdots O=C$ interactions.



Crystals of **2** obtained from $CHCl_3$ exhibited a hexagonal morphology, and the structure was found to be an inclusion complex of stoichiometry $2 \cdot 3CHCl_3$ solved in the non-centrosymmetric space group $P6_5$.† The triester **2** assembles in layers stacked parallel to the *c* axis. Molecules of **2** adopt an approximately symmetrical conformation, but slight differences in the angles of each iodophenoxy ring with respect to the carbonyl linkages result in deviation from perfect C_3 symmetry. The most striking feature of the structure is the manner in which three iodophenoxy ester moieties from three independent molecules come together in a triangular array seemingly facilitated by the roughly trigonal symmetry of **2**, templating effects of the included solvent, and bifurcated $I \cdots \pi$ and $I \cdots O=C$ interactions (Fig. 1). The metrics of the three sets of halogen bonding interactions are not identical (reflecting the absence of C_3 symmetry in the molecular units) and all $I \cdots \pi$ and $I \cdots O$ distances slightly exceed the sums of the relevant van der Waals radii (see Fig. 1 caption).¹¹ Despite

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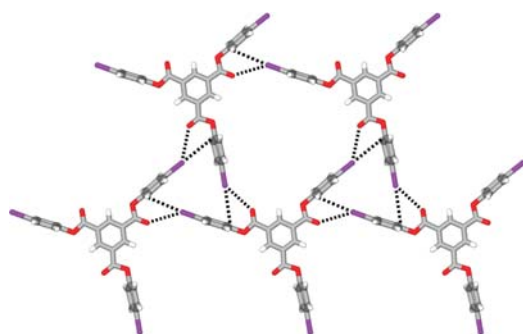


Fig. 1 2D layers in $2\cdot 3\text{CHCl}_3$. Triangular motif mediated by bifurcated $\text{I}\cdots\text{O}$ and $\text{I}\cdots\pi$ interactions (black lines): $d_{\text{I}\cdots\text{O}} = 3.59, 3.60, \text{ and } 3.66 \text{ \AA}$; $d_{\text{I}\cdots\pi} = 3.59, 3.79, \text{ and } 3.87 \text{ \AA}$. CHCl_3 solvates not shown.

the apparent absence of strong non-covalent attractions (at least according to distance criteria), the triangular motif evident in Fig. 1 seems to constitute the dominant supramolecular interaction that serves to position adjacent molecules of **2** laterally to form two-dimensional layers. These interactions differ significantly from halogen bonding exhibited by **1**, perhaps as a consequence of the electron-rich iodophenoxy rings that attenuate the electrophilicity of the iodo groups but increase the nucleophilicity of the arenes. The packing evident in Fig. 1 outwardly resembles the layer structures observed in Nangia and co-workers' triphenoxy triazines, although these latter networks are mediated by well-defined halogen trimer synthons (type II halogen bonding).⁸

The 2D layers stack parallel to the c axis such that the central 1,3,5-tricarbonylbenzene rings are positioned above and below bifurcated halogen bonding trimer moieties and every seventh layer is directly superimposed. This arrangement produces large hexagonal channels that are filled with included CHCl_3 solvates (Fig. 2). The distance across these openings is $\sim 1.3 \text{ nm}$ and the channels extend uninterrupted along the length of the c axis with the included CHCl_3 molecules arrayed in a helical fashion. The porosity of the network was determined to be 37.4%.¹²

We attempted to crystallize **2** under other conditions in the hope of obtaining analogous channel-type inclusion complexes. Slow evaporation of a pyridine solution also deposited large hexagonal crystals and X-ray diffractometry revealed a channel-type inclusion complex of stoichiometry $2\cdot 3\text{C}_5\text{H}_5\text{N}$.[‡] The structure was nearly identical to that of the CHCl_3 solvate

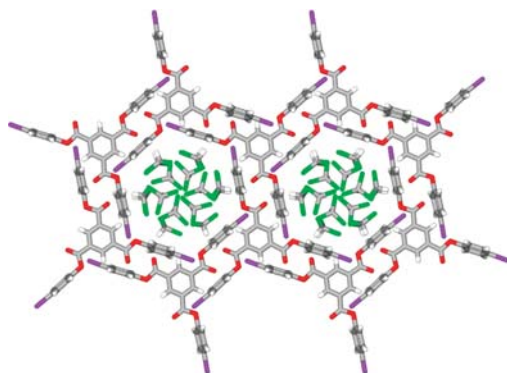


Fig. 2 Extended packing in $2\cdot 3\text{CHCl}_3$ down c . Chloroform solvate molecules reside in hexagonal channels of diameter $\sim 13 \text{ \AA}$.

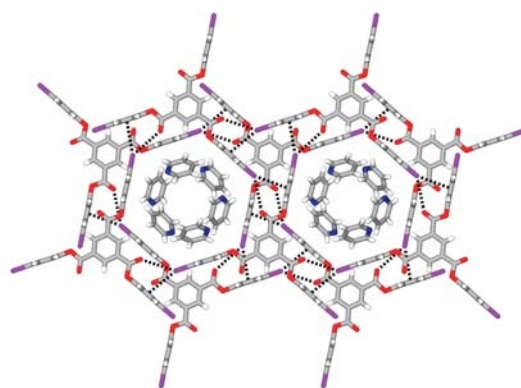


Fig. 3 View (down c) of $2\cdot 3\text{C}_5\text{H}_5\text{N}$. Honeycomb network mediated by $\text{I}\cdots\text{O}$ ($d = 3.77 \text{ \AA}$) and $\text{I}\cdots\pi_{\text{arene centroid}}$ ($d = 3.72 \text{ \AA}$) halogen bonding (black lines). Hexagonal channels possess openings of $\sim 13 \text{ \AA}$ diameter. Disordered pyridine solvates shown with partial occupancy for clarity.

except that the material crystallized in the centrosymmetric space group $P6_3/m$. As shown in Fig. 3, **2** self-assembles to form two-dimensional layers that stack in an ABAB pattern resulting in generation of hexagonal channels parallel to the c axis. As was the case with the CHCl_3 solvate, layers of **2** in $2\cdot 3\text{C}_5\text{H}_5\text{N}$ exhibit bifurcated $\text{I}\cdots\pi$ and $\text{I}\cdots\text{O}=\text{C}$ interactions, although in this instance the metrics of the respective interactions are all identical as a consequence of crystalline symmetry. Additionally, the closest $\text{I}\cdots\pi$ contact is to the centroid of a proximal arene rather than the midpoint of an arene π bond (as is the case in the CHCl_3 solvate). Pyridine molecules line the hexagonal channels and are disordered over two sites. While there is considerable precedent for pyridyl- $\text{N}\cdots\text{I}$ halogen bonds,^{4,6} there are no halogen bonding interactions between the pyridine and aryl iodide groups in $2\cdot 3\text{C}_5\text{H}_5\text{N}$. The theoretical porosity of this structure was calculated to be 39.7%.¹²

Pyridine and chloroform, although disparate compounds, appear to both play vital roles in templating formation of hexagonal structures. Pyridine solvates are arrayed in a C_3 -symmetrical arrangement within individual channels while CHCl_3 solvates are aligned around a six-fold helix. In light of these observations, a series of co-crystallization experiments was performed in which **2** and various three-fold symmetrical co-crystallizing agents were combined in benzene.¹³ Examples of co-crystallizing agents employed include 1,3,5-trihalobenzenes, triazine, mesitylene, trimethylamine- N -oxide, triphenylphosphine, and trimethyl trimesoate. Almost all of these crystallizations initially afforded hexagonal crystals isostructural to the $2\cdot 3\text{C}_5\text{H}_5\text{N}$ inclusion complex with disordered benzene molecules taking the place of pyridine to the exclusion of the co-crystallization additives.^{14‡} Continued contact with the mother liquor, however, invariably resulted in slow disappearance of the large hexagonal blocks concomitant with the appearance of needle-shaped crystals ($t = \text{days to weeks}$). A similar sequence of events was also observed in crystals obtained from pyridine. Determination of unit cell parameters from randomly chosen samples from several crystallization experiments revealed that these needles were isostructural with crystals obtained directly from CH_2Cl_2 . Material obtained in this fashion was found to consist of a close-packed structure of

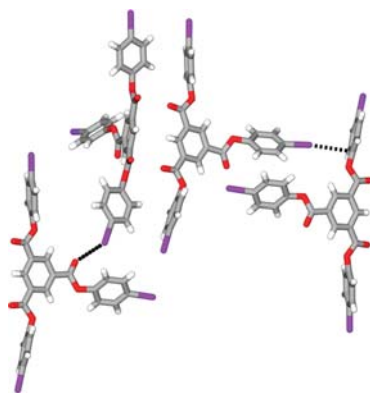


Fig. 4 View of the asymmetric unit in the close-packed structure of **2** and principal halogen bonding interactions: $d_{\text{I} \cdots \pi} = 3.48 \text{ \AA}$, $\text{C-I} \cdots \pi = 174.9^\circ$, $d_{\text{I} \cdots \text{O}} = 3.23 \text{ \AA}$, $\text{C-I} \cdots \text{O} = 142.3^\circ$.

2.† A view of the two independent molecules in the asymmetric unit along with their principal halogen bonding interactions is shown in Fig. 4. Molecules in the asymmetric unit are part of helical chains that intertwine to achieve close packing. Needle-shaped crystals of **2** were more robust than their hexagonal counterparts and DSC analysis revealed a single endothermic transition corresponding to the melting point of **2** (see ESI†).¹⁵ Thus, it appears that the hexagonal crystals obtained from pyridine and benzene are metastable products which are eventually supplanted by the thermodynamically favored close-packed form. Evidently, the combination of halogen bonding, symmetry, and solvent inclusion in **2**·3C₅H₅N and **2**·1.5C₆H₆ is insufficient to maintain an open network, at least under the crystallization conditions employed (*i.e.*, room temperature and pressure).

Wuest *et al.* have noted that maximization of both hydrogen bonding and close-packing is mutually exclusive in certain organic solids.³ This feature can lead to open crystalline architectures in systems where hydrogen bonding interactions dominate. Halogen bonding, though generally recognized as weaker than conventional hydrogen bonding, may be capable of exerting a similar influence over the crystallization process. In the system described above, the combination of trigonal host **2** and appropriate solvent guests produced inclusion complexes with nanometre-sized channels mediated by mutually reinforcing halogen bonding and symmetry interactions. Spontaneous conversion of this solid state network into a solvate-free close-packed structure provides evidence that the open porous framework is thermodynamically less stable. One can envision, however, that in the presence of stronger halogen bonding interactions the thermodynamic preference for close packing may be inverted in favor of porous architectures (analogous to hydrogen bonded networks). Consequently, as the phenomenon of halogen bonding becomes better understood, the engineering of strong and directional halogen bonding interactions should emerge as valuable design elements in the fabrication of functional organic materials such as porous solids. Additionally, the complementary nature of hydrogen and halogen bonding has been noted,¹⁶ and the design of robust crystalline materials that exhibit structurally defining and mutually reinforcing hydrogen/halogen bonding interactions is an attractive area for future investigation.

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Notes and references

† Crystallographic data. **2**·3CHCl₃: C₃₀H₁₈Cl₉I₃O₆, $M = 1174.19$, hexagonal, $P6_3$, $a = 16.3917(3)$, $b = 16.3917(3)$, $c = 24.8007(12) \text{ \AA}$, $V = 5770.9(3) \text{ \AA}^3$, $Z = 6$, $D_c = 2.027 \text{ g cm}^{-3}$, $\mu = 3.103 \text{ mm}^{-1}$, $T (\text{K}) = 100(2)$, 178 452 reflections collected, 8874 unique, 7877 observed ($I > 2\sigma(I)$) reflections, 403 refined parameters, $\text{GOF} = 1.061$, $R_1 = 0.0541$, $wR_2 = 0.1637$, Flack $x = 0.48(4)$ —absolute structure could not be determined, CCDC 688117. **2**·3C₅H₅N: C₄₂H₃₀I₃N₃O₆, $M = 1053.39$, hexagonal, $P6_3/m$, $a = 16.5590(18)$, $b = 16.5590(18)$, $c = 8.4752(9) \text{ \AA}$, $V = 2012.6(4) \text{ \AA}^3$, $Z = 2$, $D_c = 1.738 \text{ g cm}^{-3}$, $\mu = 2.380 \text{ mm}^{-1}$, $T (\text{K}) = 190(2)$, 29 038 reflections collected, 1640 unique, 1367 observed ($I > 2\sigma(I)$) reflections, 83 refined parameters, $\text{GOF} = 1.061$, $R_1 = 0.0470$, $wR_2 = 0.1383$, CCDC 688114. **2**·1.5C₆H₆: C₃₆H₂₄I₃O₆, $M = 933.25$, hexagonal, $P6_3/m$, $a = 16.5473(17)$, $b = 16.5473(17)$, $c = 8.4380(9) \text{ \AA}$, $V = 2000.9(4) \text{ \AA}^3$, $Z = 2$, $D_c = 1.549 \text{ g cm}^{-3}$, $\mu = 2.380 \text{ mm}^{-1}$, $T (\text{K}) = 200(2)$, 53 859 reflections collected, 1700 unique, 1442 observed ($I > 2\sigma(I)$) reflections, 81 refined parameters, $\text{GOF} = 1.056$, $R_1 = 0.0385$, $wR_2 = 0.1101$, CCDC 688115. **2**-non-solvated: C₂₇H₁₅I₃O₆, $M = 816.09$, monoclinic, $P2_1/c$, $a = 29.911(3)$, $b = 5.6474(6)$, $c = 31.534(4) \text{ \AA}$, $\beta = 103.112(5)^\circ$, $V = 5187.8(10) \text{ \AA}^3$, $Z = 8$, $D_c = 2.090 \text{ g cm}^{-3}$, $\mu = 3.655 \text{ mm}^{-1}$, $T (\text{K}) = 210(2)$, 39 978 reflections collected, 11 892 unique, 8033 observed ($I > 2\sigma(I)$) reflections, 649 refined parameters, $\text{GOF} = 1.008$, $R_1 = 0.0369$, $wR_2 = 0.0761$, CCDC 688116.

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