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2,4,6-Tris(4-nitrophenoxy)-1,3,5-triazine: a hexagonal host framework stabilised by the NO_2-trimer supramolecular synthon

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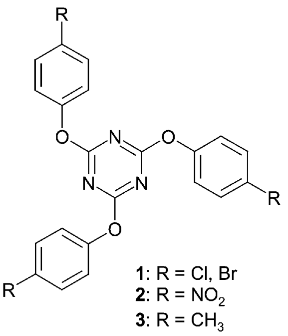
The title molecule forms a honeycomb network of molecular and nitro-trimer synthons with guest species included in the hexagonal voids.

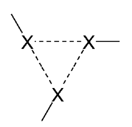
The design of host–guest systems through strong O–H···O, N–H···O, O–H···N and weak C–H···O, C–H···N hydrogen bonds is a current theme in crystal engineering and supramolecular chemistry. Two distinct streams have emerged in recent years for the self-assembly of host frameworks: organic molecules assembled *via* hydrogen bonds and heteroatom interactions,[1] and coordination polymers that use metal–ligand and hydrogen bonds.[2] Our focus on the design of microporous solids has led to the identification of new molecular scaffolds with wheel–axle, hexagonal nanotube and layered-clay architectures that are stabilised by O–H···O, halogen···halogen and C–H···O bonds, respectively.[3] Hexagonal host networks constructed from 2,4,6-tris(4-halophenoxy)-1,3,5-triazine **1** and the robust halogen trimer supramolecular synthon[4] **I** (X = Cl, Br) exhibit versatility and adaptivity for the inclusion of guest species.[3b] Both layer and channel type structures are obtained depending on the nature of halogen in triazine **1** and the shape/size of guest molecule. A notable feature of the *sym*-phenoxytriazine family is that trigonal symmetry in the molecule is routinely carried over into hexagonal/rhombohedral symmetry in the crystal. This is not so common in other trigonal host molecules, *e.g.* trimesic acid, perhydrotriphenylene, cyclotriphosphazene, tri-*o*-thymotide and cyclotriveratrylene.[5] Against this background, we examined the title molecule 2,4,6-tris(4-nitrophenoxy)-1,3,5-triazine **2** as a new scaffold for constructing the hexagonal host framework. Another motivation for studying **2** was that if the target host architecture were obtained *via* NO_2-trimer supramolecular synthon **II** analogous to **I**, then a novel recognition motif of the nitro group would be identified. We report in this paper the realisation of such a goal.

Crystallisation of nitro-triazine **2**† from various solvents afforded diffraction quality crystals from benzene, chloroform, hexachlorobenzene (HCB), tribromobenzene (TBB) and hexamethylbenzene (HMB). Single crystal X-ray analysis showed them to be host–guest adducts in space groups $R\bar{3}$, $P6_3$, $P6_3/m$ or $P\bar{3}$.‡ Host–guest stoichiometry, crystallographic data, cavity type, guest disorder, and O····O/N distances in synthon **II** are summarised in Table 1. Significantly, all five crystal structures are in the hexagonal/rhombohedral system and the host molecules are fully ordered. The honeycomb network is assembled via the alternation of nitro-triazine **2** and nitro-trimer synthon **II** (O···O/N interaction) in the *ab*-plane (Fig. 1); numerous C–H···O/N hydrogen bonds[6] make up the channel walls in the *c*-direction. The hexagonal cavity in **2** has a diameter of 11–12 Å, comparable to that in **1**.[3b,c] Supramolecular isomerism (layer *vs.* channel) and intermolecular interactions (C–H···O/N, Cl···O, π–π) observed in (**2**)·guest structures are similar to clathrates of **1**.[3b] Self-assembly in crystals of **2** is guest-induced because the space group and cavity type is different for different guests, suggesting that the host framework is somewhat flexible. However, recurrence of the symmetrical nitro-trimer synthon **II** in five clathrate structures means that the host architecture is quite stable. Inclusion adducts of **2** have the dual character of stability and flexibility, a feature shared by host–guest systems assembled with weak hydrogen bonds and heteroatom interactions.[3b–d]

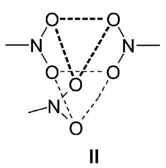
The next objective was to find out how frequently occurring and energetically stable is the nitro-trimer synthon **II**. A search of the Cambridge Structural Database[7] (version 5.22, 245 392 entries) in C–NO_2-containing organic compounds with *R*-factor < 0.10 (5012 hits) gave 97 occurrences of synthon **II** in the range 2.8 < O···O < 3.3 Å when only one O···O trimer was used as the 3D contact criterion. Of these 97 hits, only four crystal structures§ contain the symmetrical variant of synthon **II**; the remaining structures have unsymmetrical motifs. Nitro-triazine **2** is the first example on the recurrence of symmetrical synthon **II** in a family of crystal structures, thereby signifying robustness,¶ and hence may serve as the starting point for future crystal engineering. Recognition between NO_2 groups has been ascribed to the electrostatic stabilisation from multiple



1: R = Cl, Br
2: R = NO_2
3: R = CH_3



I (X = halogen)



II

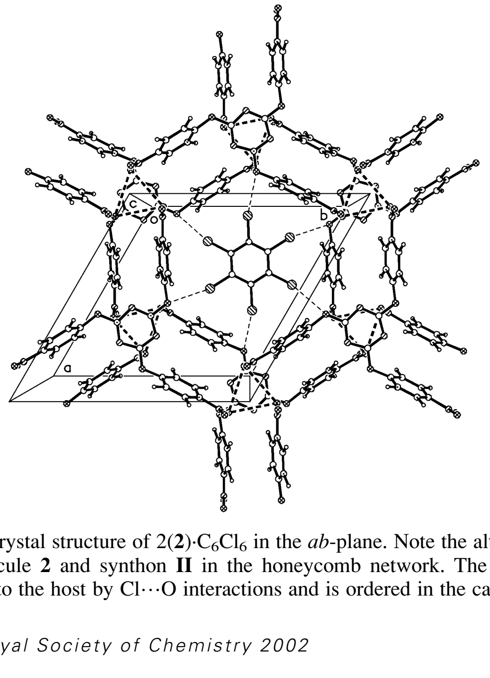


Fig. 1 Crystal structure of 2(**2**)·C_6Cl_6 in the *ab*-plane. Note the alternation of molecule **2** and synthon **II** in the honeycomb network. The guest is bonded to the host by Cl···O interactions and is ordered in the cavity.

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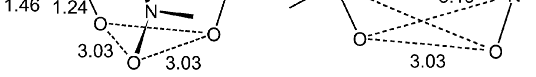
Table 1 Crystal data and structural parameters of some clathrates of 2,4,6-tris(4-nitrophenoxy)-1,3,5-triazine **2**

Clathrate	Space group	a (= b)/Å	c/Å	Guest orientation	Cavity type	Z	$O\cdots O^{c}$/Å	$N\cdots O^{c}$/Å
2(**2**)·C_6H_6[a]	$R\bar{3}$ (no. 148)	14.195(2)	20.941(5)	Disordered	Sandwich layer	3	3.16	3.20
2·3($CHCl_3$)	$P6_3$ (no. 173)	14.617(1)	8.383(1)	Disordered	Channel	2	3.03, 3.15	3.19, 3.22
2(**2**)·C_6Cl_6[a]	$R\bar{3}$ (no. 148)	14.660(1)	20.210(2)	Ordered	Sandwich layer	3	3.19	3.29
2·$C_6H_3Br_3$	$P\bar{3}$ (no. 147)	14.524(1)	8.287(1)	Disordered	Channel	2	3.08, 3.09	3.19, 3.20
3(**2**)·C_6Me_6[b]	$P6_3/m$ (no. 176)	14.443(1)	22.593(2)	Disordered	Layered offset	2	3.05, 3.14	3.21, 3.27

[a] These adducts are isostructural. [b] Two host molecules in the asymmetric unit. [c] Up to 3.3 Å.

$O\cdots N/O/C$ interactions between the oxygen atom of one nitro group and the C–NO_2 fragment of another. It has been argued that aggregates of nitro groups are stabilised by O···N and O···O electrostatic interactions beyond their van der Waals radii sum (r_{vdW}: O 1.52, N 1.55 Å), up to 3.3 Å.[8] Based on this model, we propose that the symmetrical array of three NO_2 groups in synthon **II** is stabilised by $O^{\delta-}\cdots N^{\delta+}$ and $O^{\delta-}\cdots O^{\delta+}$ interactions listed in Table 1. The role of dispersive forces is important in these N···O and O···O interactions. The metrics of synthon **II** in **2**·3($CHCl_3$) are displayed in Scheme 1. The fact that the observed N–O distances (1.18, 1.24 Å) are intermediate between $N–O^{opt}$ and N=O bond lengths (1.248, 1.164 Å)[8] confirms the delocalisation of electron density in the NO_2 group. A similar situation is present in the other clathrates. The energy of symmetrical nitro-trimer synthon **II** in H–NO_2 calculated with the RHF/6-31G** basis set is –8.6 kcal mol^{-1} at an O···O distance of 3.05 Å‖ The maximum binding energy of the H–NO_2 dimer is −3.2 kcal mol^{-1} at the MP2/6-31++G** level.[9] The potential energy surface of N···O interaction is very shallow in the distance range 2.8–3.2 Å and almost insensitive to the inter-atomic separation in dimer or trimer motifs. Therefore the O···N/O interactions listed in Table 1 are attractive and stabilising, even though they are quite long (3.0–3.3 Å). From energy calculations, the cumulative strength of numerous weak interactions in nitro-trimer synthon **II** is comparable to a strong hydrogen bond.

The occurrence of N···O synthon **II** in a molecule that is not loaded with NO_2 groups is noteworthy because **2** could have engaged in (Ph)C–H···O(NO_2) type interactions, as say in the clathrates of tetrakis(4-nitrophenyl)methane.[10] While the exact nature of N···O interaction in synthon **II** is not fully understood (in terms of electrostatic/polarisation *vs.* dispersion/van der Waals character), it is clear that our result has implications in the design of symmetrical host lattices. The presence of three-fold molecular symmetry in the triazine heterocycle together with electronegative group on the 4-phenoxy position that aggregate through weak attractive interactions are favourable features for the formation of hexagonal host frameworks. These factors act in concert in **2**: there is carry-over of trigonal molecular symmetry into the crystal, and attractive O···N/O interactions stabilise the nitro-trimer synthon. However, even such an argument has its limits. A hydrophobic group like methyl is not suitable because the 4-tolyloxy derivative **3** has a close-packed crystal structure (in space group *R*3*c*),[11] very different from **1** and **2**.



Scheme 1 Metrics of O···O (a) and N···O (b) interactions (Å) in synthon **II** in the crystal structure of **2**·3($CHCl_3$). Note that N–O bond distances in the NO_2 group (a) are unequal.

The identification of new supramolecular synthons through the number and diversity of crystal structures being analysed expand the crystal engineer's tool kit. Supramolecular synthons incorporating the NO_2 functional group include strong O–H···O_2N, N–H···O_2N hydrogen bonds and weak C–H···O_2N, C–I···O_2N interactions.[12] We update this library with the NO_2-trimer synthon for crystal design.

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Notes and references

† Nitro-triazine **2** was synthesised by condensation of 4-nitrophenol (3 equiv.) with cyanuric chloride (ref. 3*b*).

‡ *Crystal data* for **2**·guest are summarised in Table 1. Final *R*-factor values for these structures are good (0.04–0.08), except the benzene solvate in which guest disorder could not be properly modelled and so *R* is high (0.15). For details on data collection (Rigaku RAXIS IIC and Siemens P4 diffractometer), structure solution and refinement (SHELX-97), see refs. 3*b* and *c*. CCDC reference numbers 181645–181649. See http://www.rsc.org/suppdata/cc/b2/b200152g/ for crystallographic data in CIF or other electronic format.

§ CSD refcodes: HEVRUV, JIPJAT, VINCIE, YIMWIA.

¶ 'Robust' as used in this paper refers to synthon recurrence in a family of crystal structures. See ref. 3*a* for different meanings of this term in the host–guest literature.

‖ Calculations using PC Spartan Pro 1.0, Wave function Inc., USA.

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