Hexagonal Supramolecular Networks in the Crystal Structure of the 1 : 1 Molecular Complex Trimethylisocyanurate–1,3,5-Trinitrobenzene

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Trimethylisocyanurate **2** and 1,3,5-trinitrobenzene **3** form a hexagonal C–H···O mediated 1 : 1 complex wherein distinct molecular layers are formed, the molecular symmetry of the components being retained in the crystal.

Crystal engineering,[1] or synonymously solid-state supramolecular synthesis, has been motivated in recent times by aesthetic (symmetry, topology, network properties)[2–4] or utilitarian (NLO, ferromagnets, molecular electronics, nanostructures)[5–7] considerations and in this respect too is to supramolecular chemistry what traditional target-oriented synthesis is to molecular chemistry.[8] In this communication, we report the crystal structure of the 1 : 1 complex **1** between trimethylisocyanurate **2** and 1,3,5-trinitrobenzene **3**. This structure is of relevance because it highlights many current issues in crystal engineering.

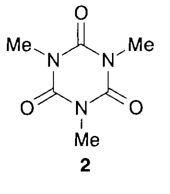
Our interest in compound **2** was motivated primarily by aesthetic considerations. The symmetrical molecular framework in **2** consists only of C–H···O donor and acceptor groups and it seemed that this substance could be used to generate similarly symmetrical or pseudo-symmetrical supramolecular networks. Such goals have been successfully realised in practice with strong[9] and weak[3] hydrogen bonds but it should be noted that, in general, the transformation of molecular symmetry to supramolecular symmetry is not a trivial issue. As is well known, the inversion centre is the only molecular symmetry element which is routinely transferred to the crystal.[10,11] So it comes as no surprise that the crystal structure of pure **2**, though replete with C–H···O hydrogen bonds, is highly three-dimensional with two sets of dovetailed symmetry-independent molecules adopting skewed orientations and retaining none of their intrinsic symmetry in the crystal.[12]†

The many intermolecular forces in organic crystals interact with one another and crystal structures are the result of this, often uneasy, compromise between interactions.[1] Therefore a key emerging strategy in crystal engineering is to dissect and insulate different types of intermolecular interactions from one another so that the consequences of any one particular type are easier to predict and control. In effect, the dimensionality of a crystal structure should be reduced, say through π···π complexation[3] or the use of ionic interactions.[13] To change the three-dimensionally close-packed crystal structure of **2** to one in which the molecular D_{3h} symmetry is retained, we crystallised an equimolar $CHCl_3$ solution of **2** and **3**.[14] Compound **3** was chosen because, like **2**, it also has D_{3h} symmetry. This procedure gave exclusively light-yellow crystals of complex **1** in the form of needles (mp 110–112 °C). When the crystallisation was carried out in CCl_4, small hexagonal tablets were obtained. Data were collected on both types of crystals but these were seen to correspond to the same crystal form.‡

The crystal structure of complex **1** consists of alternating and perfectly flat layers of **2** and **3** molecules. These layers are shown separately in Figs. 1 and 2. Fig. 1 shows that molecules of **2** lie on threefold rotation axes and are connected by C–H···O hydrogen bonds [C···O 3.41 Å, C–H···O 117°] to generate a hexagonal supramolecular net. Fig. 2 shows that the molecules of **3** which lie on a second set of threefold axes, are likewise networked in a hexagonal manner *via* O···O close packing [2.89, 3.08 Å]. The following structural features of the layers of **3** are noteworthy: (*i*) there are no C–H···O bonds within the layers, (*ii*) such layering is seen neither in the crystal structure of pure **3** which (like pure **2**) is three-dimensionally linked with C–H···O bonds[15] nor in the many molecular complexes formed by **3**,[16] (*iii*) there is an unusually large number of intralayer O···O van der Waals contacts. The 3.08 Å contact is similar to that found in hexanitrobenzene (3.07 Å) and confirms Kitaigorodskii's value of the oxygen van der Waals radius.[10]

Examination of Figs. 1 and 2 shows that the structural insulation of **2** and **3** molecules in the crystal of **1** is largely effective. Each of these components forms three-dimensionally close-packed crystals when taken individually but in the complex, molecules of **2** and **3** form separate layers (two-dimensional packing) which fully utilise their D_{3h} molecular symmetry. Yet, complex formation is undoubtedly favourable because the packing coefficients of **1**, pure **2** and pure **3** are respectively 0.71, 0.68 and 0.65. So the interlayer association is also of interest and is shown in Fig. 3. In the alternating layers, molecules of **2** and **3** are staggered and in projection yield an interesting honeycomb structure with the centres of the voids coinciding with the third set of threefold axes. From the colour of the **1** crystals there is no evidence for extensive charge transfer and the interlayer interactions are restricted to weaker C–H···O bonds [C···O, C–H···O: 3.75, 151; 3.82, 154; 3.75 Å, 141°]. To the extent that these very weak interactions are viable,

1 ≡ **2** • **3**



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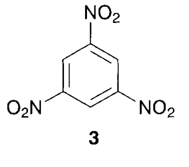

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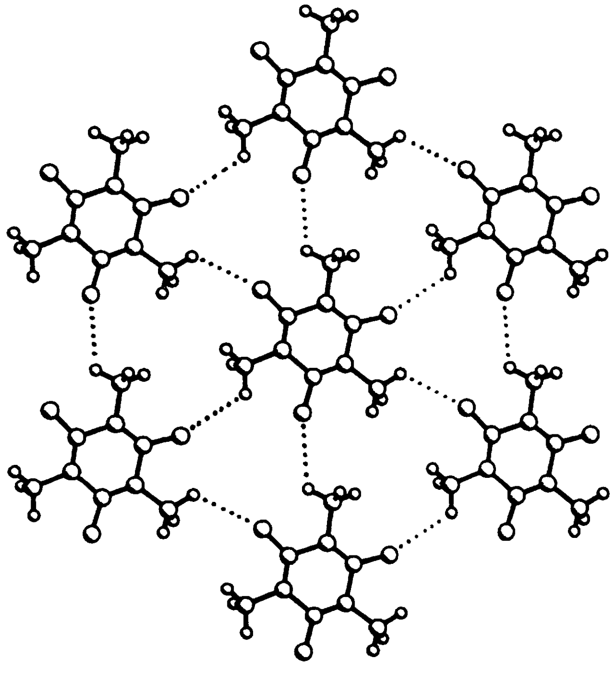

Fig. 1 Layer structure perpendicular to [001] of trimethylisocyanurate molecules in the hexagonal crystal structure of complex **1**. Note that there is only one symmetry-independent C–H···O interaction which is shown as a dotted line.

the layers are not completely insulated structurally from each other.

This work shows that (*i*) weak C–H···O bonds can be used for crystal engineering and supramolecular construction,[17] (*ii*) structural insulation can be an effective device to reduce the dimensionality of a crystal structure resulting in more easily identifiable building blocks, (*iii*) such insulation may decrease the number of structural possibilities available to the system perhaps allowing the successful transfer of molecular symmetry into the crystal.

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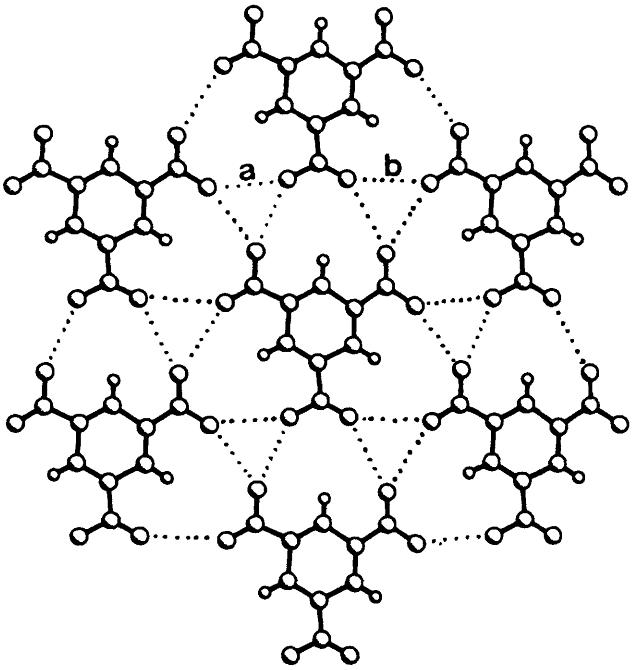

Fig. 2 Layer structure perpendicular to [001] of 1,3,5-trinitrobenzene molecules in the crystal structure of complex **1**. There are two symmetry-independent O···O van der Waals contacts indicated: a (2.890 Å) and b (3.083 Å)

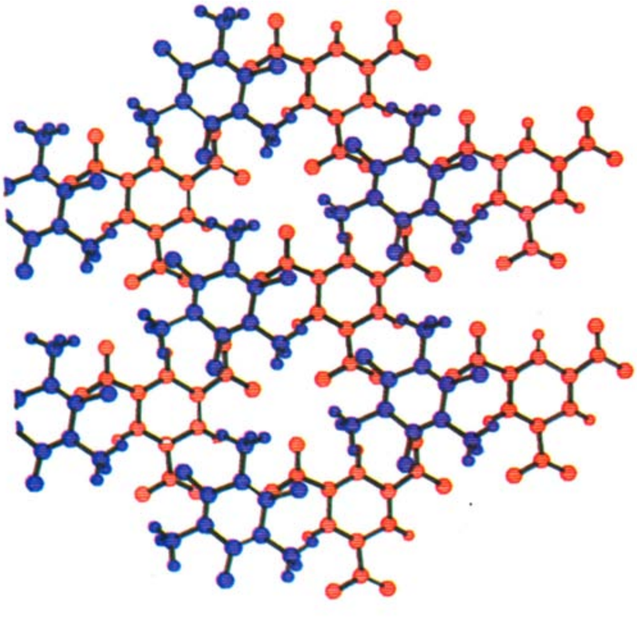

Fig. 3 Arrangement of alternate layers of trimethylisocyanurate (blue) and 1,3,5-trinitrobenzene (red) in the structure of **1**. Notice the honeycomb arrangement.

Footnotes

† The original determination (ref. 12) does not include H-atoms. We carried out a full structural analysis which yielded accurate H-atom positions. *Crystal data* for compound **2**: $C_6H_9N_3O_3$, M = 171.16, monoclinic, $P2_1/c$, a = 8.142(1), b = 13.393(1), c = 14.822(1) Å, β = 100.88(1)°, V = 1587.0(2) Å^3, Z = 8, $F(000)$ = 720, D_c = 1.433 Mg m^{-3}, μ(Mo-Kα) = 1.2 cm^{-1}, T = 293 K, 2508 non-zero (2σ) reflections out of 2821 collected with $2 < 2\theta < 50°$, solution SHELXS-86, refinement SHELXL-93 on F^2, R = 0.061, wR_2 = 0.152, C, N, O anisotropic, H isotropic.

‡ *Crystal data* for complex **1**: $C_6H_3N_3O_6{\cdot}C_6H_9N_3O_3$, M = 384.28, hexagonal, $P\bar{6}$, a = 8.708(2), c = 6.085(3) Å, V = 399.4(2) Å^3, Z = 1, $F(000)$ = 198, D_c = 1.597 Mg m^{-3}, μ(Mo-Kα) = 1.4 cm^{-1}, T = 293 K, 339 non-zero (2σ) reflections out of 817 collected with $5 < 2\theta < 55°$, Enraf-Nonius FAST area detector with rotating anode X-ray source, solution SHELXS-86, refinement SHELXL-93 on F^2, R = 0.091, wR_2 = 0.260, C, N, O anisotropic, H isotropic. Refinement was also attempted in the alternative trigonal space group $P3$ but the quality of the results obtained was inferior. 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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