

C–H⋯N Mediated Hexagonal Network in the Crystal Structure of the 1 : 1 Molecular Complex 1,3,5-Tricyanobenzene–Hexamethylbenzene

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Molecules of 1,3,5-tricyanobenzene are networked with C–H⋯N hydrogen bonds into a symmetrical hexagonal pattern in the crystal structure of the 1 : 1 complex formed by the compound with hexamethylbenzene.

In spite of much recent research on the assembling of supramolecular structures using the directional properties of intermolecular interactions,^{1–7} it should be recalled that such ideas are not entirely new. As far back as 1961, Hassel^{8,9} commented on the hexagonal layered network **1a** of weak N^{δ-}⋯Cl^{δ+} interactions¹⁰ in the crystal structure of cyanuric chloride, which had been reported by Hoppe, Lenne and Morandi in 1957.¹¹ These arguments have been restated recently.¹² Further, in a study of crystalline cyanocinnamic acids, we have observed that C–H⋯N hydrogen bonding between C≡N groups and aromatic H atoms results in the formation of networks such as **1b**.¹³ These ideas and the knowledge of the linearity of hydrogen bonds have led to the identification of 1,3,5-tricyanobenzene **2** as a potential candidate for the formation of the hexagonal C–H⋯N≡C mediated network **1c**.

Compound **2** [crystals from CHCl₃, m.p. 255 °C, IR(KBr) ν/cm^{-1} 3200, 2255, 1440, 920, 680, ¹H NMR (CDCl₃) δ 8.2 (s, 3H), MS (*m/z*, %) 153 M⁺(100%)] was synthesised from mesitylene using literature procedures¹⁴ but single crystals of uncertain quality were obtained for X-ray analysis. However, when a CHCl₃ solution containing equimolar amounts of **2** and hexamethylbenzene **3** (m.p. 168 °C) was evaporated slowly, well-formed crystals of the 1 : 1 complex **4** (m.p. 255 °C) were obtained.

The crystal structure of complex **4**[†] consists of alternating layers of molecules of **2** and **3** (Fig. 3). These layers are shown separately in Figs. 1 and 2 but in the crystal, they are stacked along [001] at a centroid-to-centroid separation of 3.855 Å to optimise π – π interactions. Fig. 1 reveals that the molecules of **2** crystallise according to the hexagonal network **1c**. In both **2** and **3** the molecules lie on special positions but curiously, these are different. While the molecules of **2** are bisected by twofold axes, those of **3** are located on inversion centres. The site symmetry of **2** necessitates that four of the six moderately strong C–H⋯N bonds encircling the molecule [C⋯N, 3.471(4) Å; C–H⋯N, 172(2)°] must be equal while the other two must be perfectly linear (C⋯N, 3.516(6) Å; C–H⋯N, 180°).[‡] Additionally, the molecular plane of **2** is nearly parallel to (110), but this is not required by the crystallographic symmetry. The overall effect is a flat hexagonal array of molecules of **2** linked efficiently by C–H⋯N hydrogen bonds. It is noteworthy that the entire layer is assembled with interactions which are far weaker than O–H⋯O and N–H⋯O hydrogen bonds, the traditional glue for supramolecular construction.

The layers of molecules of **3** in the crystal structure of complex **4** closely resemble the molecular layers in the crystal

structure of pure **3** itself but in general, layering of a planar aromatic hydrocarbon is difficult and the crystal structure of pure **3** is exceptional.¹⁵ Retrieval of all hexamethylbenzene containing structures from the Cambridge Structural Database¹⁶ (1992 release, version 5, 102 589 entries) yielded ten hits (no metal atom) but in many of these, the molecules of **3** are arranged in a herringbone or quasi-herringbone fashion.¹⁵

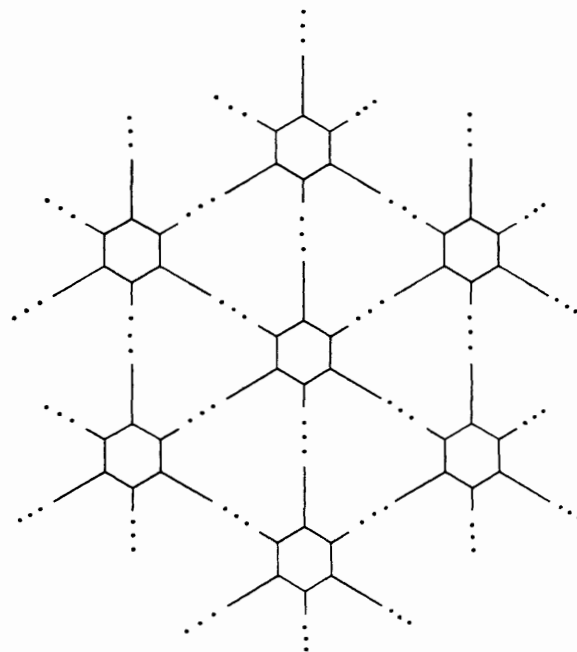


Fig. 1 Layer structure parallel to (110) of 1,3,5-tricyanobenzene molecules in the crystal structure of complex **4**. Note that the molecules are bisected by the *b*-axis which is vertical. C–H⋯N bonds are shown as dotted lines.

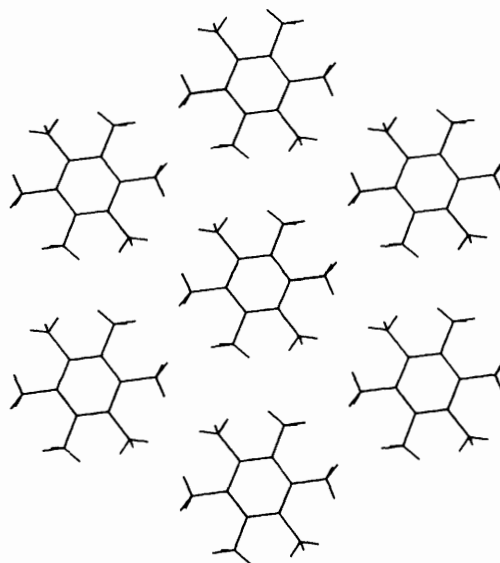


Fig. 2 Layer structure parallel to (110) of hexamethylbenzene molecules in the crystal structure of complex **4**. Each molecule lies on an inversion centre.

[†] Crystal data for complex **4**: C₉N₃H₃·C₁₂H₁₈, *M* = 315.41, monoclinic, *C*2/*c*. *a* = 15.207(3), *b* = 8.839(2), *c* = 14.460(2) Å, β = 110.48(7)°, *Z* = 4, *D*_c = 1.51 Mg m⁻³, μ (Mo-K α) = 0.37 cm⁻¹, *F*(000) = 672.0, *T* = 293 K, 1003 observed (3 σ) reflections out of 1448 collected with 2 < 2 θ < 50°, solution SHELXS86, refinement SHELX76, *R* = 0.049, *R*_w = 0.050, C, N anisotropic, H isotropic. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[‡] This is also true of the N⋯Cl interactions in cyanuric chloride which adopts the same space group *C*2/*c* and the same site symmetry for the molecules.

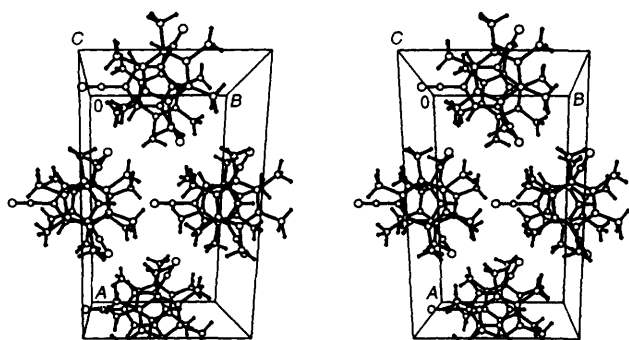
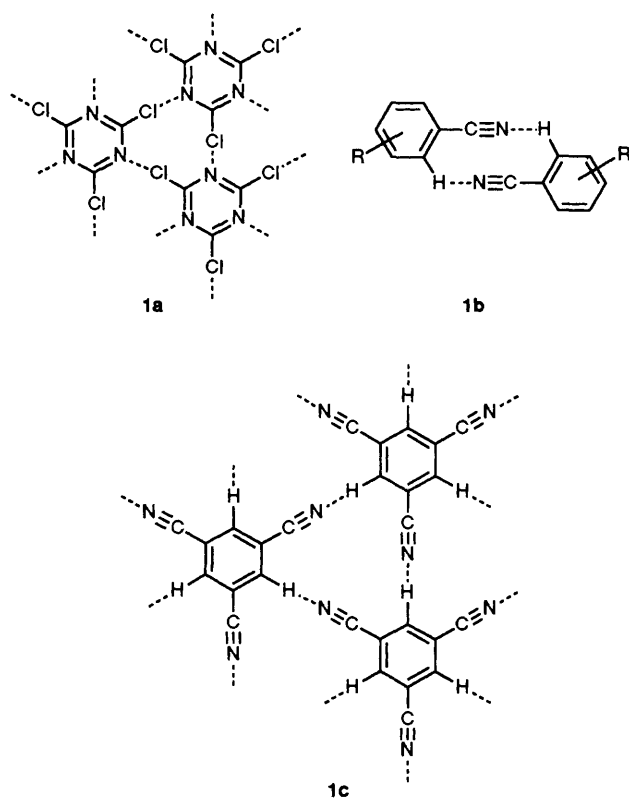


Fig. 3 Stacking of alternate layers of 1,3,5-tricyanobenzene and hexamethylbenzene in the structure of **4** to optimise π - π interactions



It will be of interest to ascertain if the tendency of **2** to layer is strong enough to cause layering of other aromatic hydrocarbon molecules, which might not even form layers in their pure structures, in the structures of the appropriate complexes. Accordingly, investigations into the crystal structures of pure **2** and some of its other complexes are currently under way. Examination of intermolecular interactions through the study of molecular complexes has already been well established.¹⁷

This work reemphasises that supramolecular structures may be built with fairly weak intermolecular interactions and that these structures can be designed using the known directional properties of such interactions.

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