A triazine-based three-directional rigid-rod tecton forms a novel 1D channel structure†

Anupama Ranganathan,* Burkhard Clemens Heisen, Ina Dix and Franc Meyer*

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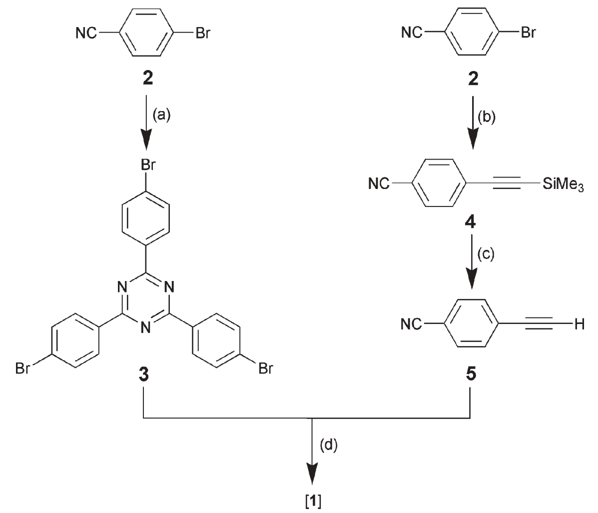
A large, symmetrically substituted triazine-based molecule, synthesized by a copper-free Sonogashira coupling procedure self-assembles to form a novel 1D channel structure that hosts chlorobenzene molecules as guests.

Over the past decade, there has been considerable interest in the synthesis and characterization of compounds containing a 1,3,5-triazine core.[1] The symmetry and structural attributes of the triazine core make it an attractive candidate for exploring a range of material properties such as nonlinear optical,[2] liquid crystalline[3] and luminescent[4] properties. The triazine unit enjoys a one-upmanship over the 1,3,5-benzene core, in that it is more electron withdrawing and possesses a larger nucleophilic susceptibility than the latter. In the field of supramolecular chemistry, triazine derivatives are commonly used as they are well-known to form hydrogen bonds and to favour π–π contacts, and they were recently shown to be involved in attractive anion–π interactions.[5] Triazine-based aggregates assembled with the aid of non-covalent forces have resulted in tubular fibres[6] or three-dimensional porous networks.[7] Metal coordination polymers using the triazine core in the form of interlaced networks and self-assembled cages to catalyze reactions have been extensively studied.[8]

Nanoporous solids based on organic building blocks have the potential for a precise rational design, by employing crystal engineering principles.[9] Recently, Lee and co-workers[10,11] have prepared a family of organic–inorganic composites utilizing the 1,3,5-benzene core, symmetrically substituted with phenylacetylene nitriles, which have been crystallized with silver triflate salts. The resulting silver coordination polymeric networks have an overall honeycomb pattern exhibiting pseudohexagonal channels. Even with sizeable modifications to the organic host tecton, there is a predisposition to channel crystallinity for these complexes. Replacing the central core from benzene to triazine could probably have interesting consequences on the properties of the resulting molecules. Structural insights into the nature of such purely organic tritopic building blocks themselves, however, are rather rare as not many have been crystallized to date. We wanted to explore trigonally symmetric molecules with a central triazine unit, that could serve as a fundamental azaheterocyclic tecton, substituted with long, linear π-conjugated rigid rod residues, the diphenylacetylene moieties. From a synthetic point of view, the potential of triazine as a building block for π-conjugated substances would be interesting to investigate. We chose the compound, 2,4,6-tris(4-(4-ethynylbenzonitrile)phenyl)-1,3,5-triazine, **1** for our study. Despite more emphasis laid on the study of metal-bound tritopic ligands leading to channel structures,[10,11] it is imperative to understand the nature of packing forces that would induce self-aggregation of the pristine ligands with long-armed rigid-rod functionalized substituents, in the absence of any metal-ion directing agent. Although analogous triazine-cored molecules substituted with long-chain alkoxyl groups are known to be liquid-crystalline,[12] to the best of our knowledge, there are no reports on the structural characterization of such large triazine molecules with long-arm C-atom-based substitutions at their C-2, C-4 and C-6 positions. The synthetic preparation and the crystal structure of compound **1** exhibiting an organization that mirrors the structures of metal-bound benzene-derived counterparts is reported here.

A viable reaction protocol was sought after in order to procure compound **1** with minimum amount of side-products. In this regard, a copper-free Sonogashira coupling reaction[13] was carried out (Scheme 1 and ESI†).‡

Crystallization of **1** from chlorobenzene at 4 °C gave tiny colourless, plate-shaped single crystals suitable for X-ray diffraction



Scheme 1 *Reagents and conditions*: (a) CF_3SO_3H, $CHCl_3$, RT; (b) ethynyltrimethylsilane, Et_3N, CuI, $(PPh_3)_4Pd$, 80 °C; (c) K_2CO_3, MeOH, RT; (d) copper-free Sonogashira reaction conditions: **3**, $(AllylPdCl)_2$, $P(t\text{-}Bu)_3$, **5**, DABCO, acetonitrile–toluene (1.5–50 mL), RT.

Institut für Anorganische Chemie, Georg-August Universität Göttingen, Tammannstrasse 4, D-37077 Göttingen, Germany.
E-mail: franc.meyer@chemie.uni-goettingen.de;
tr.anupama@hotmail.com; Fax: (+49) 551 30 3063;
Tel: (+49) 551 39 3012

† Electronic supplementary information (ESI) available: Syntheses of precursors **3**, **4** and **5** by adapted published procedures. Synthetic procedure, full spectroscopic data, figures and other crystal structure information for **1**. See DOI: 10.1039/b706627a

studies.§ The single crystals of **1** could be bent and stretched, a property, like plastic, that is quite uncharacteristic of single crystalline materials. Compound **1** crystallizes in the monoclinic $P2_1/c$ space group, with one molecule of **1** and one chlorobenzene solvent molecule in the asymmetric unit. The chlorobenzene is disordered, but refined stably without having to use any geometric constraints. The molecular structure of **1** is depicted in Fig. 1. The phenyl C–C bond distances are ∼1.40 Å. The C≡C and C≡N bond lengths are ∼1.20 and ∼1.15 Å, respectively. The C–N bond lengths of the triazine rings are all ∼1.35 Å. The molecule is not planar but it rather exploits a sphere-surface like shape, which is reminiscent of the strained, bowl-shaped geometry observed for related benzene-cored molecules bound to silver metal ions.[10] The average deviation of atoms from the mean plane of the molecule **1** in the asymmetric unit is 0.789 Å.

The UV-vis absorption peak of **1** is shifted to a longer wavelength ($\lambda_{\max}$ = 353 nm) from that of 1,3,5-triazine ($\lambda_{\max}$ = 272 nm) due to the expansion of the π-conjugation system. A sharp emission peak (λ_{em}) is observed at 386 nm (ESI,† Fig. S5).

The crystal structure analysis reveals the formation of a distinct channel structure. These channels, visible along 1D when viewed down the *b*-axis, are occupied by chlorobenzene molecules (Fig. 2), with a 1 : 1 molar ratio of **1** and chlorobenzene in the crystals. Channels are formed by cavities, enabled by relatively weak non-classical C(sp^2)–H···N hydrogen bonds[9] between neighboring molecules of **1**.

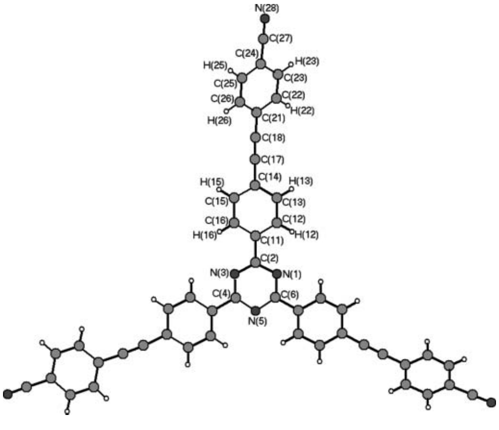


Fig. 1 Molecular structure of **1**. Atom numbering for some of the atoms has been omitted for clarity.

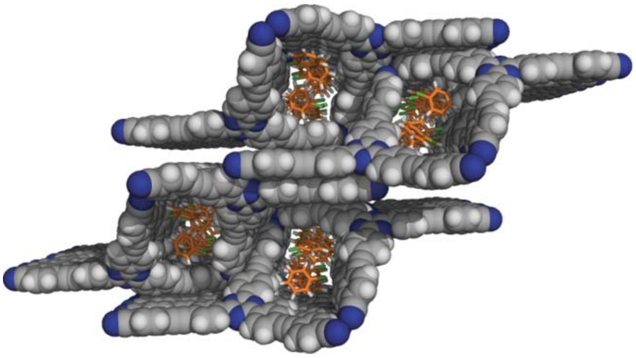


Fig. 2 Space-filling representation of the channels filled by chlorobenzene molecules, viewed parallel to the *b* cell axis.

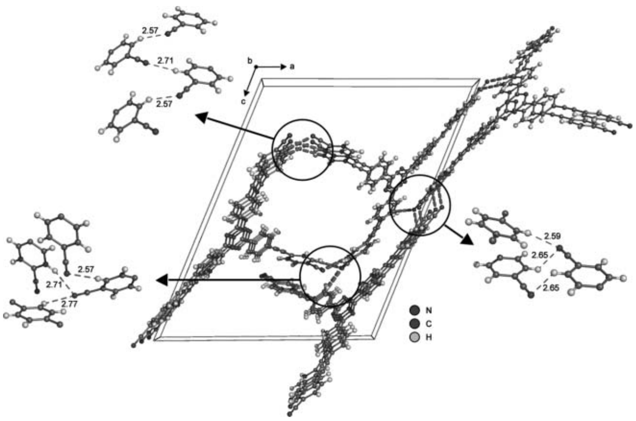


Fig. 3 C–H···N hydrogen bonds (depicted as dashed lines) in the crystal structure of **1**. Guest molecules are not shown.

Two of the three long cyano-substituted diphenylacetylene arms of each molecule are oriented toward another of its kind, held to each other through C(sp^2)–H···N interactions between C–H donors of the phenyl ring of one arm interacting with the N atom of the cyano groups of the adjacent molecule. These associations give rise to rhombus-shaped cavities. The cavity diameter is roughly 7 Å at its narrowest constriction, its axis being parallel to the *b* cell axis. The third rigid arm is associated with the adjacent arm of a neighbouring molecule through additional C–H···N bonds. The H···N distances of five unique hydrogen bonds are in the range of 2.57–2.77 Å, on average shorter than the sum of their van der Waals radii (2.75 Å) and the corresponding C–H···N angles vary between 123 and 163° (see Fig. 3 and ESI,† Table 1). The H···N distances are longer and relatively weaker in comparison to those observed between C(sp)–H donors and N (aza and cyano) acceptors.[14] In contrast to the weak C(sp)–H···N interactions observed in a recently reported structure of 2,4,6-tris(4-ethynylphenoxy)-1,3,5-triazine,[15] however, they are fairly shorter.

The crystal lattice of **1** (see Fig. 2) is somewhat reminiscent of known self-assembling nanotubes that are composed of certain organic tectons such as flat, disk-shaped cyclic or helical peptides,[16] non-disk shaped calixarenes[17] and resorcinarenes,[18] *etc.* These supramolecular nanotubes are usually formed through a network of intermolecular hydrogen bonds or π···π stacking interactions. The internal diameter of the cavity found in the structure of **1** (7 Å at its narrowest) is comparable to that of the above-mentioned organic nanotubes whose inner diameters vary in the range 5–13 Å. **1** could thus serve as a promising building block for the self-assembly fabrication of novel nanotube-like structures.

The nature of interaction between the host **1** and the halogenated guest molecules is essentially governed by a few very 'soft' C–H···Cl and C–H···π contacts, wherein the C–H of the phenyl rings of **1** point toward the chloro substituent of the guest and the C–H group of the guest points toward the midpoint of the C≡C bond of the host, respectively (ESI,† Fig. 8). Extensive π–π interactions of the face-to-face type are observed throughout the crystal packing. The centroid–centroid distance between the triazine rings and the neighbouring phenyl rings, for example, is ∼4.0 Å, being offset by an angle of 35° between the ring normal and the centroid vector. For this reason π-stacking interaction can also be considered to play a vital role in determining the packing. In essence, the structure is stabilized by weakly attractive, directional non-classical hydrogen bonding interactions and π-stacking.[9]

At around 260 °C, **1** transforms to a black material without significant weight loss, presumably *via* a polymerization process. Interestingly, the IR spectrum of a sample that has been heated to 500 °C is almost unchanged to that of pristine **1**, still showing the $\nu(\mathrm{C{\equiv}N})$ stretch at around 2225 cm^{-1} and characteristic bands for the phenyl rings. A more detailed investigation of the thermal behavior of **1** is planned.

Another future target is to replace the cyano group at the *para* position of the terminal phenyl rings of **1** by different substituents (such as hydrogen bond donor groups) with a view to accessing larger supramolecular arrays. The channels may offer the possibility of removing the chlorobenzene molecules to afford a porous tubular material or to substitute the guests with other planar aromatic molecules, which could also determine the possibility of shape selectivity of the guest molecules. Such exchange studies are underway.

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Notes and references

‡ EI MS *m/z* (%) = 684 (100) $[\mathrm{M}]^+$, 228 (45) $[\mathrm{NCC_6H_4CCC_6H_4CN}]^+$. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ/ppm, 8.84 (d, 6H, ^4J = 8.6 Hz, ^3J = 1.9 Hz; $\mathrm{H_a}$), 7.76 (d, 6H, ^4J = 8.6 Hz, ^3J = 1.9 Hz; $\mathrm{H_b}$), 7.68 (s, 6H, $\mathrm{H_c}$, $\mathrm{H_d}$ – accidentally degenerate). ^{13}C NMR ($\mathrm{CDCl_3}$) δ/ppm, 171.0 (triazine-C), 126.6, 127.8, 128.9, 132.0, 132.1, 132.2, 136.3 (aromatic C), 118.4 ($\mathrm{C{\equiv}N}$), 111.9 ($\mathit{C}\text{–}\mathrm{C{\equiv}N}$), 90.4, 93.3 ($\mathrm{C{\equiv}C}$). IR 2224 cm^{-1} ($\mathrm{C{\equiv}N}$).

§ *Crystal structure analysis* for **1** $[\mathrm{C_{48}H_{24}N_6{\cdot}C_6H_5Cl}]$, M = 797.28, monoclinic, space group $P2_1/c$, a = 23.491(2), b = 6.4678(6), c = 30.258(3) Å, β = 112.384(3)°, V = 4250.7(7) Å^3, D_c = 1.262 g cm^{-3}, Z = 4. Colorless plate-shaped crystal (0.26 × 0.04 × 0.01 mm). X-Ray data were collected on a Bruker three-circle diffractometer attached to a CCD area detector and a mirror system for the Cu-Kα radiation (90 kV, 45 mA), λ = 1.54184 Å at 100(2) K. Absorption correction was applied using the SADABS program (Siemens, USA, 1995). A total of 22030 reflections were collected up to θ = 64.3° of which 6389 are independent among 5354 observed $[F_\mathrm{o} > 4\sigma(F_\mathrm{o})]$. The structure solution (SHELXS-97) and refinements on F_o^2 (SHELXL-97) gave R(obs.) = 0.0467 [R(all) = 0.0567] and Rw(obs.) = 0.1180 [Rw(all) = 0.1256] for 743 parameters; min. and max. residual electron densities were −0.33 and 0.25 e Å^{-3}. All non-H atoms were refined anisotropically. The diffraction pattern showed very weak reflections (on average 0.127 of the intensity of the reflections for the cell reported here) that would correspond to a supercell with a tripling of the b axis. This appears to arise from a partial ordering of the chlorobenzene molecules that are disordered in the smaller cell. Since this order/disorder phenomenon is primarily a matter of crystallographic interest and does not affect the chemical conclusions reported here we may investigate it further and report the results in a crystallographic journal. CCDC 644237. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b706627a

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