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Supramolecular graphyne: a C(sp)-H···N hydrogen-bonded unique network structure of 2,4,6-triethynyl-1,3,5-triazine

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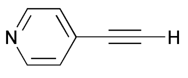
The crystallization of 2,4,6-triethynyl-1,3,5-triazine (2) leads to a π-stacked layered structure of a C(sp)–H···N hydrogen-bonded unique hexagonal network structure, which may be regarded as a supramolecular analogue of a hitherto unknown graphyne network: in-plane intermolecular interactions are short and linear H···N contacts (2.31 and 2.34 Å) and the interlayer separation is 3.23 Å.

Graphyne[1] is a hypothetical novel carbon allotrope which has a layered structure of a unique two-dimensional hexagonal network involving not only sp^2- but also sp-carbon atoms (Fig. 1a). Reflecting its characteristic structural features, this material has been predicted to have interesting conductive, electronic and optical properties.[1] Despite its great interest and high potential as an advanced material, however, the graphyne network has been unknown so far,[2] and only related compounds possessing its substructure have been synthesized and investigated.[3] An alternative way of developing the graphyne chemistry would be to assemble its supramolecular analogue, in which a part of the carbon–carbon covalent bonds in the network are replaced by non-covalent bonds. Ready accessibility of the materials by self-assembling processes from simple molecular building blocks is of great synthetic advantage. In this study, we examine such a supramolecular approach to the graphyne network using C–H···N hydrogen bonds.[4]

We have recently shown[5] that 4-ethynylpyridine (**1**) formed a straight tape structure through short and linear C(sp)–H···N contacts in the solid state. These findings prompted us to investigate the crystal structure of 2,4,6-triethynyl-1,3,5-triazine (**2**), since this compound can be considered to have the D_{3h} symmetric three-fold superimposed structure of **1**. Herein we report the preparation and X-ray crystal structure analysis of **2**, which indeed revealed the formation of a graphyne-like network structure formed by self-complementary C(sp)–H···N hydrogen bonding (Fig. 1b). There is a continuing interest in the design and construction of organic solid materials with a specific supramolecular arrangement, including hexagonal network structures.[6]



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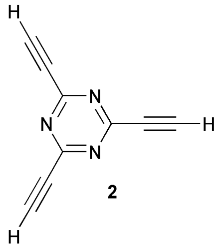

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Compound **2**† was prepared as relatively stable colorless solid by desilylation of 2,4,6-tris[(trimethylsilyl)ethynyl]-1,3,5-triazine (**3**)[7] with potassium fluoride in MeOH–THF (1 : 1) at room temperature. Single crystals of **2** suitable for X-ray diffraction study were grown by sublimation and the X-ray data were collected at −120 °C. The crystal structural analysis‡ of **2** revealed the formation of a layered structure with a unique two-dimensional hexagonal network (Fig. 2). The network is not strictly D_{3h} symmetric, but rather C_2 symmetric, involving not one but two types of short C(sp)–H···N contacts. Thus, compound **2** forms a head-to-tail polar tape through the first short C(sp)–H···N contact (H···N distance 2.31 Å, dashed lines in Fig. 2). The C–H–N angle is 180° and the molecules in the tape are located on a crystallographic two-fold axis. The tapes are connected to each other through the second short C(sp)–H···N contact (H···N distance 2.34 Å, C–H–N angle 172.1°, dotted lines in Fig. 2) to form a polar network, which is stacked in antiparallel fashion (Fig. 3), resulting in a centrosymmetric packing with space group $C2/c$. The linearity of the C–H–N

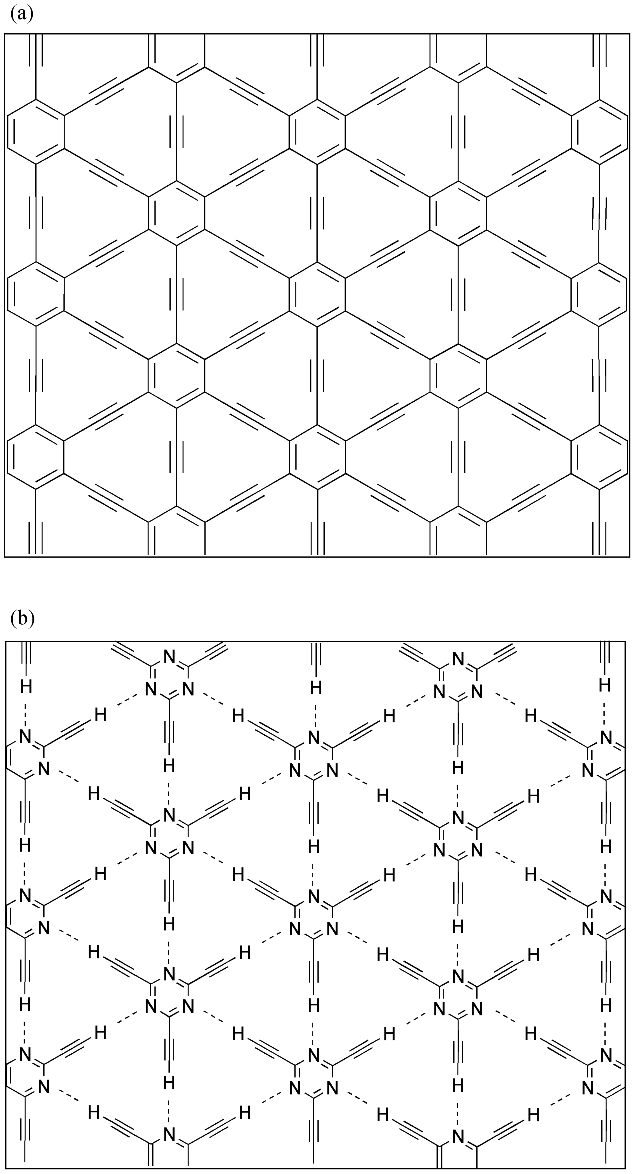

Fig. 1 Two-dimensional hexagonal network structures of (a) graphyne and (b) "spramolecular graphyne".

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moieties coupled with the short N···H distances found in the structure suggest that weak C(sp)–H···N hydrogen bonding interaction[3] plays the dominant role in the determination of the crystal structure. It is interesting to note that all of the nitrogen and hydrogen atoms in compound **2** participate in the C(sp)–H···N interaction in a cooperative manner, resulting in a planar and robust two-dimensional array. Each two-dimensional sheet is essentially planar and the dihedral angle between the layers is 0°, resulting in a parallel stacking of the layers. The interplanar separation found in the crystal structure of **2** (3.23 Å) is shorter than that of graphite (3.4 Å) and, therefore, there would be significant π-stacking interaction between the layers of **2**.

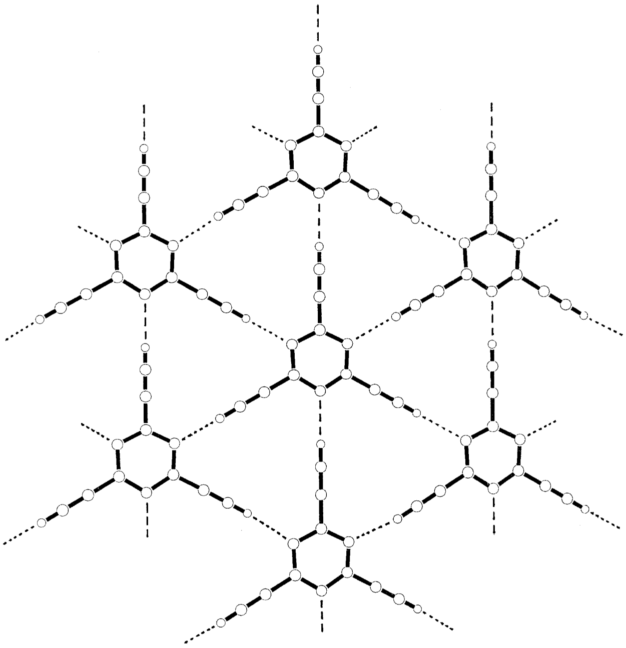

Fig. 2 Packing arrangement of **2** in the crystal. Short C–H···N contacts are shown by dashed lines (H···N 2.31, C···N 3.27 Å, C–H–N 180°) and dotted lines (H···N 2.34, C···N 3.30 Å, C–H–N 172.1°).

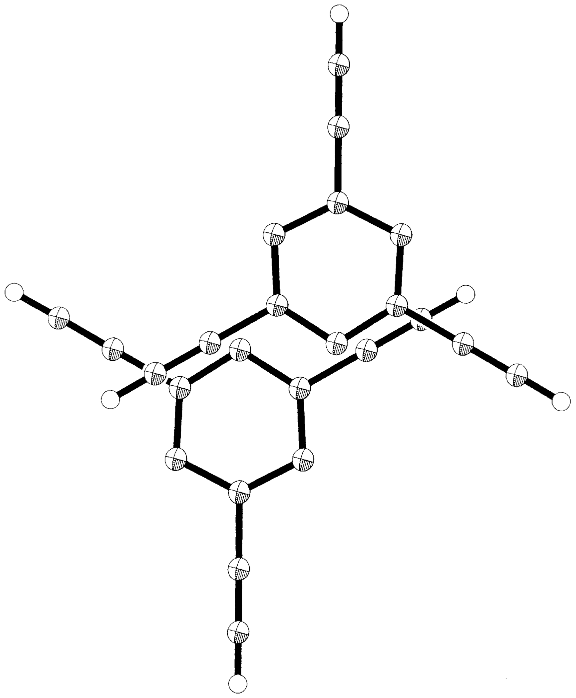

Fig. 3 A face-to-face overlap between molecules of **2** in the crystal. The interplanar distance and dihedral angle are 3.23 Å and 0°, respectively.

In conclusion, this work describes a successful application of supramolecular strategy for the construction of an elusive graphyne-like network using the weak C–H···N hydrogen bonding interaction. Further exploitation of this approach using other non-covalent interactions, as well as a detailed investigation of the properties of the assembled materials are in progress.

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Notes and references

† *Spectroscopic data for* **2**; mp 121 °C (dec.) (Found: M$^+$, 153.0331. $C_9H_3N_3$ requires *M*, 153.0327); ν_{max} (KBr)/cm^{-1} 3200, 2116, 1496, 1336, 954, 832, 756, 738 and 526; δ_H (300 MHz, $CDCl_3$) 3.44 (3H, s); δ_C (75 MHz, $CDCl_3$) 79.45, 82.34 and 159.87; *m/z* (FD) 153 (M$^+$, 100%).

‡ *Crystal data for* **2**: $C_9H_3N_3$, $M = 153.03$, colorless plate, 0.25 × 0.25 × 0.01 mm, monoclinic, space group $C2/c$, $D_c = 1.371$ g cm^{-3}, $a = 14.44(1)$, $b = 8.570(5)$, $c = 7.505(5)$ Å, $\beta = 119.31(1)°$, $V = 809.9(9)$ Å^3, $Z = 4$, $T = 153$ K, Mo-K$_\alpha$ radiation. A total of 898 unique reflections ($2\theta_{max} = 54.9°$) were collected, of which 586 observed reflections [$I > 3\sigma(I)$] were used in the structure solution (direct methods) and refinement (full-matrix least-squares) to give the final $R = 0.041$ and $R_w = 0.050$. Residual electron density is 0.18 e Å^{-3}. CCDC reference number 193181. See http://www.rsc.org/suppdata/cc/b2/b208813b/ for crystallographic data in CIF or other electronic format.

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