X-Ray crystal structure of $C_6H_3(CO_2H)_3$-1,3,5·1.5(4,4′-bipy): a ‘super trimesic acid’ chicken-wire grid

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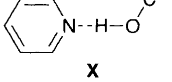
Trimesic acid cocrystallizes with 1.5 equivalents of 4,4′-bipyridine to generate a large distorted hexagonal network with *ca.* 35 × 26 Å internal dimensions: three independent networks interweave to afford a novel threefold two-dimensional corrugated sheet.

Hydrogen-bonded supramolecular synthons represent a primary tool for crystal engineering.[1,2] In such a context, trimesic acid (benzene-1,3,5-tricarboxylic acid, TMA) is a molecule which predictably forms honeycomb networks with interesting supramolecular properties (catenation or interpenetration, polymorphism and inclusion) as a consequence of its molecular symmetry and complementary hydrogen-bonding capabilities.[1] Early work focused upon TMA itself and generated a large number of inclusion compounds, both with and without catenation.[3] That carboxylic acids can form homo- or heterodimers with a variety of complementary functional groups (*e.g.* pyridines, 2-aminopyridines and pyrimidines) has allowed functionalized TMA,[4] its deprotonated forms[5] or its metal complexes[6] to be exploited as templates in crystal engineering studies. In this contribution we report the remarkable networking and interweaving[7] in a cocrystal of TMA, TMA·1.5(4,4′-bipy) **1**, the supramolecular structure of which is effectively an enlarged analogue of TMA that exhibits a novel mode of interpenetration.

The pyridine–carboxylic acid motif, **X**, has previously been exploited to design liquid-crystalline materials and two-dimensional β networks.[8,9] It occurred to us that it should be possible to use simple bifunctional spacer moieties based upon pyridine moieties (*e.g.* pyrazine, 4,4′-bipyridine) to afford fine-tunable chicken-wire motifs with large cavities. A hot solution of propan-2-ol and benzene (3 : 1 ratio) containing 1 and 1.5 equiv. of TMA and 4,4′-bipyridine, respectively, afforded the desired cocrystals of **1** (mp >300 °C) upon cooling and slow evaporation of the solvent at room temperature over a period of two days.

The crystal structure exhibits the desired architecture.† An expanded form of the infinite two-dimensional honeycomb grid seen in TMA is sustained by supramolecular synthon[10] **X**: strong N–H···O hydrogen bonds coupled with complementary C–H···O hydrogen bonds [graph set[11] = $R^2{}_2(7)$, N···O, H···O, N–H···O, C···O, H···O, C–H···O: 2.604(4), 1.470(5) Å, 178.5°, 3.182(5), 2.419(5) Å, 125.2°; 2.719(4), 1.798(4) Å, 157.1°, 3.401(5), 2.683(5) Å, 122.3°; 2.660(4), 1.695(4) Å, 165.3°, 3.116(5), 2.255(5) Å, 133.34°; Fig. 1]. The internal dimensions of the distorted hexagons are 35 × 26 Å compared to just 14 × 14 Å in TMA itself. Self-inclusion is facilitated by the chair conformation of the large hexagon that intercalates and engages in π stacking with two other independent networks. Nevertheless, the other two networks only partially fill these cavities and empty space remains within the layer of interpenetrated networks, Fig. 2. Interpenetrated chicken-wire frameworks have also been seen for coordination polymers but the nature of the interpenetration is somewhat different.[12] This void space is effectively filled in a cog-like manner because of the way adjacent layers stack. To our knowledge, such an architecture (a threefold interpenetrated chicken-wire layer) has not yet been



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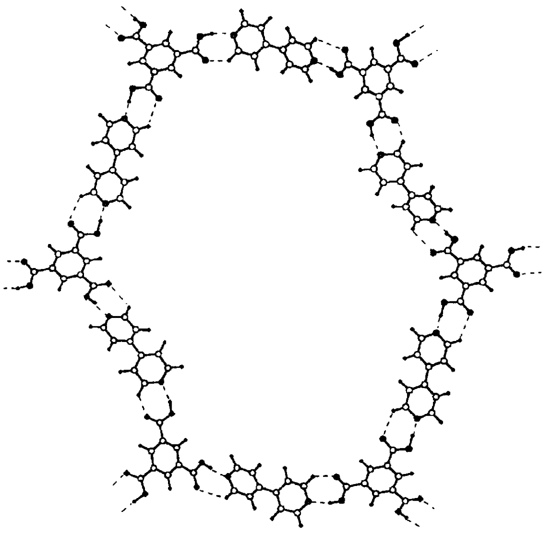

Fig. 1 The non-planar hexagonal unit formed *via* motif **X** in cocrystal **1**. N–H···O and C–H···O hydrogen bonds are illustrated by dashed lines; (⊘) N, ● (O).

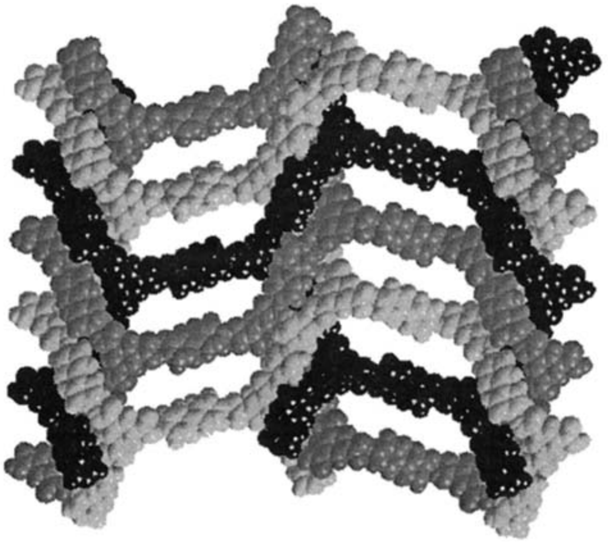

Fig. 2 The threefold two-dimensional chicken-wire networks of **1**. The independent networks are shaded for clarity. Note that void space remains even after catenation of the networks.

observed. However, interpenetrated 'supramolecular carpets' based upon twofold interweaving of square grids have been encountered and twofold layered coordination polymers have also been observed.[13]

The significance of C–H···O hydrogen bonds in supramolecular synthon **X** has been analysed using the Cambridge Structural Database[14] (version 5.11) and has been exploited very recently in a similar context.[15] A total of 60 compounds containing pyridine with at least one *ortho*-H atom and a carboxylic acid moiety (N···O < 3.0 Å) were considered. Of these, 29 compounds were found to exhibit C–H···O interactions (C···O < 3.7 Å, C–H···O 100–180°) with mean C···O distances and C–H···O angles of 3.27 Å and 125.4°, respectively.[16] The majority of the compounds that do not exhibit these interactions are engaged in other strong hydrogen bonds (O–H···O, N–H···O) which compete with the C–H···O hydrogen-bond formation or motif **X**. This observation suggests that C–H···O interactions afford additional stability and rigidity to motif **X** and the generality of this interaction is further supported by the existence of a 3 : 1 cocrystal of TMA with pyridine.‡

In conclusion, the large open networks (Fig. 1) of **1** are built by the strong yet flexible supramolecular synthon **X** and achieve close packing ingeniously in the absence of guest molecule(s) by adopting: (*i*) a chair conformation hexagonal architecture that facilitates two-dimensional interpenetration, (*ii*) staggered stacking of corrugated layers so as to eliminate continuous channels. Although **1** is the first crystal structure to be reported that simultaneously exploits the preceding two features in order to avoid vacuum in its crystal structure, it seems likely that there will be numerous simple analogues with supramolecular synthon **X** and related synthons.

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Footnotes

† *Crystal data* for **1**: $C_{24}H_{18}N_3O_6$, monoclinic, space group $P2_1/c$, a = 11.105(4), b = 10.132(4), c = 18.889(7) Å, β = 99.95(6), U = 2093.30(12) Å^3, Z = 4, D_c = 1.41 Mg m^{-3}, λ = 0.709 30 Å, $F(000)$ = 924. 2582 reflections out of 3671 unique reflections with $I_{\text{net}} > 3\sigma(I)$ measured at 290 K for a crystal of dimensions 0.6 × 0.2 × 0.4 mm on an Enraf-Nonius CAD4 diffractometer using the ω scan mode ($4 < 2\theta < 50°$) afforded on convergence final R-factors of R_f = 0.057 and R_w = 0.055. The H atoms of the OH groups were found *via* difference Fourier map inspection. Other H atoms were placed in calculated positions (C–H = 1.00 Å). All non-hydrogen atoms were anisotropically refined. The crystallographic calculations were carried out using the NRCVAX program package. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/240.

‡ The crystal structure of the cocrystal TMA·3py has been determined in space group $C2/c$, a = 24.587(4), b = 13.994(2), c = 13.610(2) Å, β = 100.75°, U = 4600.2(12) Å^3, Z = 8, W. S. Furey and M. J. Zaworotko, unpublished work.

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