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Hydrogen-bonded porous solid derived from trimesic amide

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N,N',N'-Tris(3-pyridyl)trimesic amide, 1, forms a unique P3 symmetrical crystal containing pores with a mean diameter of 8.26 Å.

Supramolecular assembly and crystal engineering are fruitful concepts to use in the design and development of structures with a desired shape. Recently these concepts evolved to be used in the construction of tubular superstructures1 and porous solids.2 Hydrogen bonding is one of the major tools which can be used to achieve the desired order.3 Here we report on the highly ordered infinite bilayer crystal structure of triamide 1,‡ derived from trimesic acid (benzene-1,3,5-triacarboxylic acid) and 3-pyridylamine.§ In contrast to recently designed structures,4 our result was entirely serendipitous. Structure 1 served just as a model for comparison with intramolecularly hydrogen-bonded structure 2, a precursor for extended core discotic liquid crystals of enhanced thermal stability.5

The transparent, hexagon-shaped crystals of 1, obtained upon crystallization from methanol, suggested hexagonal symmetry and prompted us to investigate a single crystal by X-ray diffraction. As indicated in Fig. 1 the asymmetric cell comprises only one third of a molecule while the unit cell is populated by two molecules.§ Intermolecular hydrogen bonding between the pyridyl nitrogens and the amide NHs of adjacent molecules provides the basis for a macrocyclic organization in a rosette-like structure. A 30-membered macrocycle is formed with participation of six molecules and the 3-aminopyridyl units constitute the walls of a cavity with a mean diameter of 8.26 Å (Fig. 2).

The C3-symmetry of the molecule then allows for the creation of an infinite two-dimensional honeycomb grid with repeating units at 13.87 Å in six directions and with a thickness of approximately 8.40 Å. According to Etter’s graph set analysis the nitrogen hydrogen bond donors and acceptors are involved in a R6(30) pattern. Closer inspection reveals the bilayer structure of an ensemble of molecules in one sheet (Fig. 3). The benzene units occupy alternating up and down positions. All the amide carboxyls point outwards, while the pyridyl units orientate their nitrogens inwards in the bilayer structure. This implies that although the crystal is achiral, the structure is a combination of trimesic units of P-helicity with units of M-helicity.

The infinite bilayer sheets themselves belong to a three dimensional super structure in which all the sheets are in fact repeating units placed exactly on top of each other. This results in the formation of a real porous structure with channels of

![Fig. 1 Infinite rosette structure of 1](image1)

![Fig. 2 Cavity in 1 as a result of six-fold intermolecular hydrogen bonding](image2)
nanometer scale diameter and millimeter scale length. The formation of this 3D structure may rest simply on optimal packing. Alternatively it is rationalized by cooperative C–H–O interactions6 (total length 3.39 Å) between each amide oxygen and a pyridyl C–H belonging to an adjacent bilayer.

Methanol is essential to guarantee the stability of the crystals, undoubtedly due to its role as a template and guest filling some of the void space in the interior of the channels, more specifically in the cavity surrounded by the six pyridyl units. The X-ray determination does not allow accurate localization of methanol in I but a molar ratio of 3:1 is estimated. According to the 1H NMR spectrum in [D6]DMSO the molar content of methanol ranges from 1.5 to 3.0, depending on sample preparation. Elemental analysis of the crystals is irreproducible due to partial loss of methanol during analysis while analysis after removal of methanol at high temperature shows a deviation, presumably due to uptake of atmospheric (water) vapours. Upon heating between glass the crystals undergo, far below the melting point, a phase transition at 190 °C, suggesting loss of methanol. In air or in solvents like toluene the crystals become opaque and disintegrate. In pentane, by contrast, the loss of methanol. In air or in solvents like toluene the crystals below the melting point, a phase transition at 190 °C, suggesting due to partial loss of methanol during analysis while analysis after removal of methanol at high temperature shows a difference Fourier map. Refinement converged at a final wR2 value of 0.0973 R1 = 0.0376 [for 1727 reflections with F0 > 4 o(F0)], S = 1.017, for 118 parameters. A final difference Fourier showed no residual density outside -0.20 and 0.24 e Å-3. CCDC 1821632.

† Correspondence address for crystallographic data.
‡ Synthesis of I: Standard reaction of trimesic chloride (0.90, 3.39 mmol) with 3- pyridylamine (1.00 g, 10.6 mmol) afforded a precipitate which after washing with water and diethyl ether and drying in vacuo gave I (1.18 g, 79%), as a white solid. Recrystallization from methanol (200 ml) afforded large, transparent hexagonal crystals, m.p 287–289 °C: δfH(DMSO) 10.87 (s, NH), 9.01 (d, H-2'), 8.82 (s, H-2', 4, 6), 8.39 (dd, H-6'), 8.26 (dd, H-4'), 7.47 (dd, H-5'), 4.15 (s, OH), 3.18 (s, CH3); m/z (ES) (MeOH + H2O2)H2C) Calcd for C24H18N6O3 438.1432. Found: 439.1 (M + H)+ and 219.9 (M + H)+. Analysis (after exhaustive removal of methanol at 150 °C) Calc. C, 65.75; H, 4.14; N, 19.17. Found: C, 64.80; H, 4.17; N, 18.78%.
§ Crystals of I(MeOH) were unloaded from exterior MeOH by repetitive immersion in pentane. Crystals were kept in CD3OD for four days. The crystals remained intact and were then filtered and washed with pentane. The 1H NMR spectrum in [D6]DMSO indicated the complete replacement of MeOH by CD3OD.


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Footnotes and References

Fig. 3 Superimposed bilayer structure of I creating channels.