Hydrogen-bonded porous solid derived from trimesic amide

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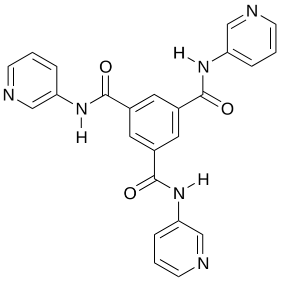
***N,N′,N″*-Tris(3-pyridyl)trimesic amide, 1, forms a unique $P\bar{3}$ symmetrical crystal containing pores with a mean diameter of 8.26 Å.**

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 superstructures[1] 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]



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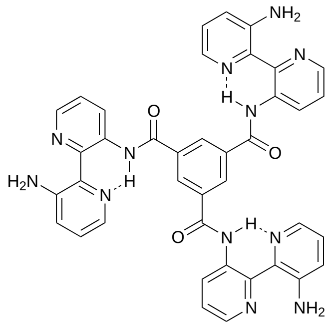

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The transparent, hexagon-shaped crystals of **1**, obtained upon crystallization from methanol, suggested hexagonal symmetry and prompted us to investigate a single crystal by X-ray diffraction. As indicated in Fig. 1 the asymmetric cell comprises 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 C_3-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[6] graph set analysis the nitrogen hydrogen bond donors and acceptors are involved in a $R_6^6(30)$ 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 carbonyls 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

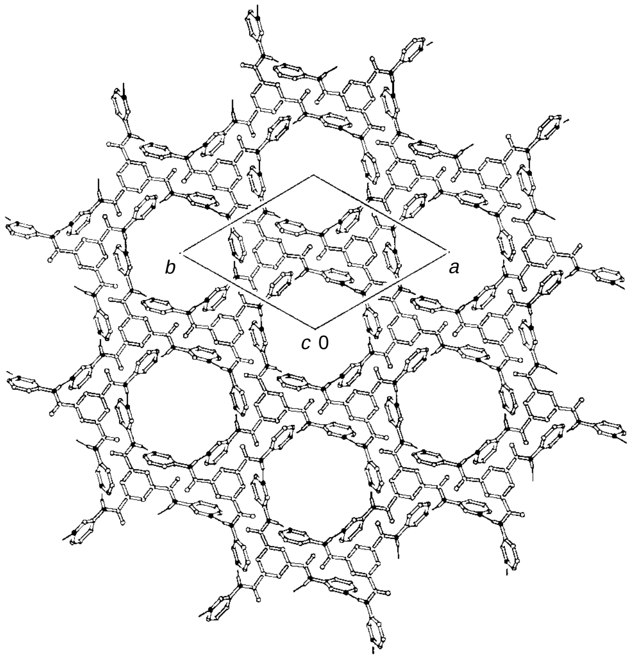

Fig. 1 Infinite rosette structure of **1**

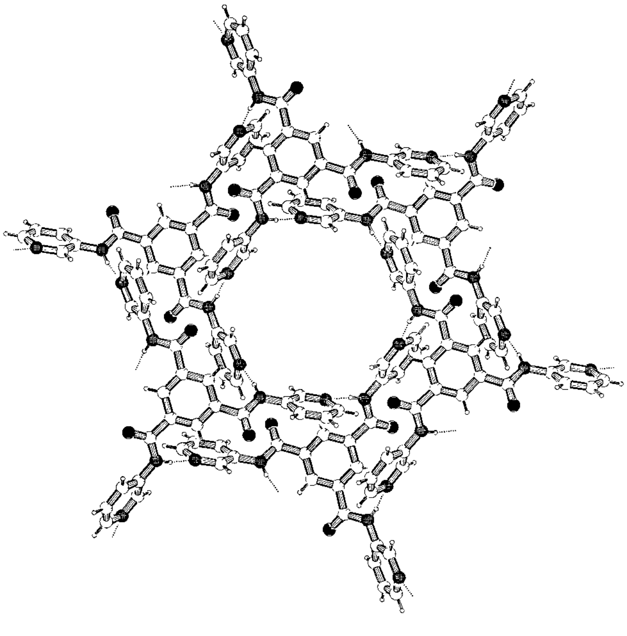

Fig. 2 Cavity in **1** as a result of six-fold intermolecular hydrogen bonding

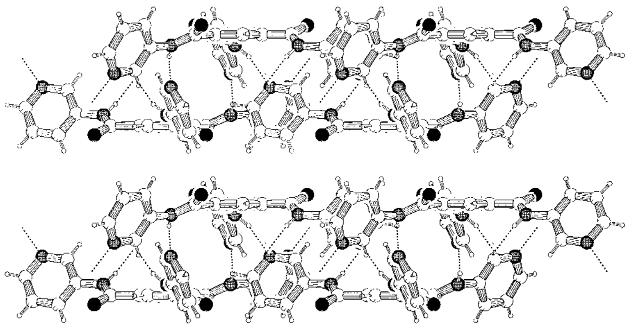

Fig. 3 Superimposed bilayer structure of **1** creating channels

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 interactions[7] (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 **1** but a molar ratio of 3 : 1 is estimated. According to the ^{1}H NMR spectrum in $[^2\mathrm{H}_6]$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 crystals are stable.

To provide evidence for the accessibility of the channels for external molecules, a methanol–CD_3OD exchange experiment was conducted¶ and the ^{1}H NMR spectrum in $[^2\mathrm{H}_6]$DMSO unambiguously demonstrates the complete disappearance of non-deuteriated methanol from the crystals. Analogous experiments have been conducted in other trimesic acid derivatives and in other tectonic molecules.[8] The calculated density of **1** without guests amounts to 1.0395 g cm^{-3} and of **1·3** MeOH to 1.267 g cm^{-3}. This relatively low density contrasts with the higher density of many trimesic derivatives including the parent acid (1.449 g cm^{-3}).[9]

The presence of C_3-symmetry tends to induce void space in crystals, which Nature may compensate for by producing concatenated or interpenetrated structures or by incorporation of appropriate guest molecules. To our surprise, up to now no X-ray data are available on symmetrical secondary trimesic amides. In trimesic acid three-fold interpenetration of two-dimensional layers composed of three parallel molecules is observed,[9] unless guests like pyrene and ethanol are built in.[10] A pattern such as the one found in compound **1** is, to the best of our knowledge, unprecedented. It seems that in this particular molecule an acceptable compromise is found between void space, concatenation of molecules and inclusion of guests. The formation of a bilayer structure in compound **1** is reminiscent of the Piedfort units observed in other C_3-symmetric systems like 2,4,6-tris[4-(2-phenylpropan-2-yl)phenoxy]-1,3,5-triazine,[11] in which two π-stacked molecules are mutually rotating by 60° to resemble a spatially filled hexagonal system.

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Footnotes and References

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‡ *Crystal structure data* for **1**: $C_{24}H_{18}N_6O_3$, M_r = 438.45, colourless, block-shaped crystal (0.3 × 0.5 × 0.5 mm), trigonal, space group $P\bar{3}$ (no. 147) with a = 13.8762(10), c = 8.4005(5) Å, V = 1400.80(17) Å^3, Z = 2, D_c = 1.039 g cm^{-3}, F(000) = 456, μ(Mo-Kα) = 0.7 cm^{-1}, 4819 reflections measured, 2135 independent, R_{int} = 0.0288, 1.7° < θ < 27.5°, ω scan, T = 150 K, Mo-Kα radiation, graphite monochromator, λ = 0.71073 Å on an Enraf-Nonius CAD4 Turbo diffractometer on rotating mode. Data were corrected for Lp effects and for a linear instability of 1% of the reference reflections, but not for absorption. The structure was solved by automated direct methods (SHELXS96). Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL96); no observance criterion was applied during refinement. Electron density in a disordered solvent area (the unit cell contains a channel parallel to the c-axis, through the origin, with a volume of 450 Å^3 and containing 111 electrons per c-translation period, suggesting the presence of approximately six molecules of methanol) was taken into account in the refinement *via* PLATON/SQUEEZE. Where relevant, data cited above are given without disordered solvent contribution. Positional parameters for hydrogen atoms were included in the refinement; initial values were obtained from a difference Fourier map. Refinement converged at a final $wR2$ value of 0.0973 $R1$ = 0.0376 [for 1727 reflections with $F_o > 4\,\sigma(F_o)$], S = 1.071, for 118 parameters. A final difference Fourier showed no residual density outside −0.20 and 0.24 e Å^{-3}. CCDC 182/632.

§ *Synthesis* of **1**: Standard reaction of trimesic chloride (0.90 g, 3.39 mmol) with 3-pyridylamine (1.00 g, 10.6 mmol) in THF (20 ml) in the presence of triethylamine (1.6 ml, 1.13 g, 11.2 mmol) afforded a precipitate which after washing with water and diethyl ether and drying *in vacuo* gave **1** (1.18 g, 79%) as a white solid. Recrystallization from methanol (200 ml) afforded large, transparent hexagonal crystals, mp 287–289 °C; $\delta_{\mathrm{H}}([^2\mathrm{H}_6]$DMSO) 10.87 (s, NH), 9.01 (d, H-2′), 8.82 (s, H-2, 4, 6), 8.39 (dd, H-6′), 8.26 (ddd, H-4′), 7.47 (dd, H-5′), 4.15 (s, OH), 3.18 (s, CH_3); *m/z* (ES) (MeOH + HCO_2H) Calc. for $C_{24}H_{18}N_6O_3$ 438.142. Found: 439.1 (M + H)$^+$ and 219.9 (M + 2 H)$^{2+}$. 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 **1**·(MeOH)$_x$ were unloaded from exterior MeOH by repetitive immersion in pentane. Crystals were kept in CD_3OD for four days. The crystals remained intact and were then filtered and washed with pentane. The ^{1}H NMR spectrum in $[^2\mathrm{H}_6]$DMSO indicated the complete replacement of MeOH by CD_3OD.

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