

# New supramolecular packing motifs: $\pi$ -stacked rods encased in triply-helical hydrogen bonded amide strands

Matthew P. Lightfoot, Francis S. Mair,\* Robin G. Pritchard and John E. Warren

Department of Chemistry, UMIST, PO Box 88, Manchester UKM60 1QD. E-mail: frank.mair@umist.ac.uk

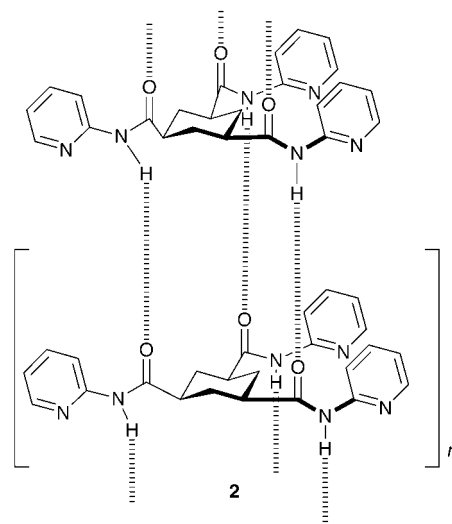
Received (in Cambridge, UK) 30th June 1999, Accepted 18th August 1999

The structure of *N,N',N''*-tris(2-methoxyethyl)benzene-1,3,5-tricarboxamide consists of aryl rings self-assembled using a novel conjunction of organizational motifs into a  $\pi$ -stack surrounded by a triple helical network of hydrogen bonds, in a manner suggestive of a new mode of organization for some columnar liquid crystals.

Central to the goal of crystal engineering is the discovery of molecular building blocks that can assemble in a pre-determined fashion to generate structural components<sup>1</sup> such as sheets,<sup>2</sup> ribbons,<sup>3</sup> tubes<sup>4</sup> and rods.<sup>5</sup> Often the hydrogen bond is used as a method of linking self-complementary molecules into such supramolecular components,<sup>6</sup> just as it is often used by Nature in defining protein structure. During the course of studies directed at the characterisation of alternative linking units, such as alkali metals, we synthesised† the triamide *N,N',N''*-tris(2-methoxyethyl)benzene-1,3,5-tricarboxamide **1**. Here we report its remarkable crystal structure,‡ composed of infinite  $\pi$ -stacked rods supported by a triple helical network of hydrogen bonds (**1<sub>n</sub>**).

The only similar structure in the literature was reported by Hamilton and co-workers in 1995.<sup>7</sup> A cyclohexyl unit was used as the scaffold for three amide functions, all of which pointed in the same direction, approximately perpendicular to the average plane of the ring, so as to generate a perfectly self-com-

plementary building unit held by three C=O–HN hydrogen bonds. The mode of its self-organization is depicted in **2**.



Our supramolecular rod **1** differs from **2** in two important and related respects: the use of an aromatic central scaffold, as opposed to a saturated cyclohexyl ring, and the disposition of the three amide bonds, which are partially tilted in **1** and perpendicular to the ring in **2**.

The central aromatic framework in **1** allows for a further self-assembly mechanism, additional to the three hydrogen bonds, through  $\pi$ -stacking. There is one molecule of **1** in the asymmetric unit (Fig. 1). The stack is generated by the crystallographic  $2_1$  screw axis leading to an inter-ring plane separation of  $b/2$ , as prescribed by the  $P2_1$  space group.‡ The inter-ring centroid distance is therefore 3.62 Å. This is compatible with computed distances in the  $\pi$ -facial arrangement of the gas-phase benzene dimer (3.60 Å),<sup>8</sup> and, inter-

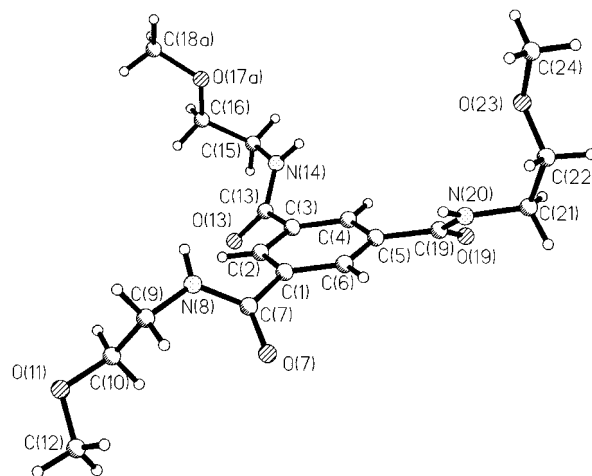
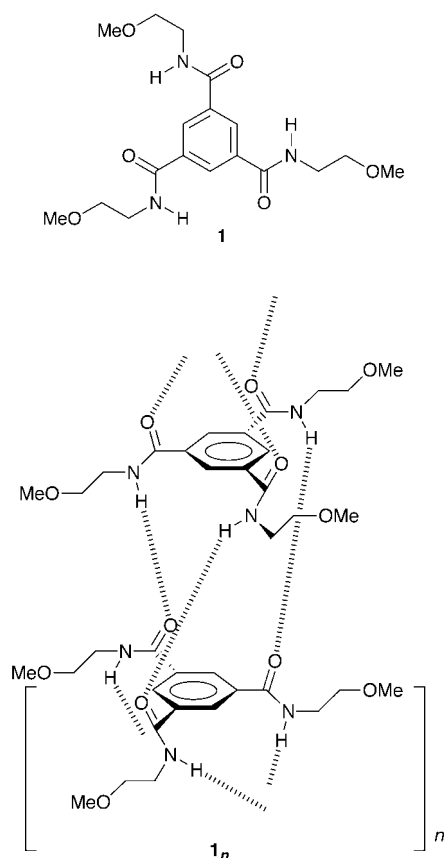
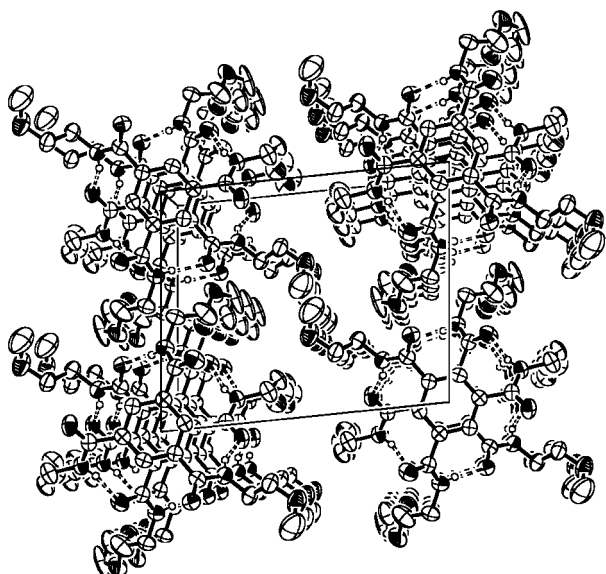


Fig. 1 Molecular structure of **1**. Minor contributor to two-fold disorder in one sidearm is omitted for clarity.



**Fig. 2** Packing diagram of **1**, viewed along the *b*-axis. Non-amide hydrogen atoms and minor contributor to side-arm disorder omitted for clarity.

estingly, is similar to distances inferred from sharp peaks seen in X-ray diffraction patterns of discotic liquid crystalline phases based on aromatic cores.<sup>9</sup>

One such mesophase is composed of molecular cores similar to **1**, but extended using intramolecularly hydrogen bonded bipyridine units.<sup>10</sup> Others are more similar still, being identical to **1** but for longer alkyl chains on each amide function. Thermotropic mesophases are formed by such triamides with pentyl to octadecyl groups.<sup>11</sup> Furthermore, highly viscoelastic phases were formed by these species in organic solvents.<sup>12</sup> The methyl variant was crystallised as a model compound: in *N,N,N'*-trimethylbenzene-1,3,5-tricarboxamide, only a single amide is involved in the third dimension, the other two amides (approximately coplanar with the aryl ring) being involved in generating sheet morphology.<sup>12</sup> The slightly longer alkyl groups of **1** appear to make this mode of organization less favourable. The columnar structure exhibited by **1** may offer a better clue as to the nature of the novel mesophases<sup>11</sup> and lyotropism<sup>12</sup> observed. However, the particular type of primitive rectangular column packing exhibited by **1** (Fig. 2) has not previously been characterised in studies of columnar liquid crystals.<sup>9</sup>

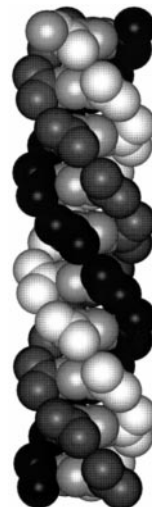
Aromatic amides prefer coplanarity of the carbonyl with the aryl for conjugative reasons, as exemplified in the almost totally planar *N,N,N'*-tris(6-methyl-2-pyridyl)benzene-1,3,5-tricarboxamide.<sup>13</sup> In **2** the amides are virtually perpendicular to the ring,<sup>7</sup> while in **1** the conflict between the demands of conjugation and the demands of intermolecular hydrogen bonding result in partial tilting, so that in place of the three vertical strands in **2**, a triple helical network of hydrogen bonds, as shown in Fig. 3, arises. These pack in the polar *P2*<sub>1</sub> space group with parallel alignment, such that spontaneous generation and resolution of supramolecular chirality has occurred from achiral solutions of **1**. The mean planes of the three amide units make angles of 36.8, 42.4 and 45.5° with the aryl mean plane. All therefore point their dipoles at approximately 60° from the column axis, and are helically wrapped around that axis with a pitch of 21.7 Å. The O–N distances are 2.94, 2.95, and 3.01 Å, in the normal range for amide N(H)–O interactions.

Our attempts to probe the structural effect of replacement of the amide hydrogen with alkali metals continue.

We thank the EPSRC for supporting this research and the referees for their useful comments.

## Notes and references

† *Experimental data for 1*: Methoxyethylamine (18.35 ml, 0.21 mol) was added to a solution of benzene-1,3,5-tricarbonyl trichloride (18.79 g, 0.07



**Fig. 3** Diagram of **1** showing triple-helical hydrogen bonding network. Each O, C, N(H)–O helical strand is a different shade of grey. Hydrogen atoms and methoxyalkyl side-arms omitted for clarity.

mol) and Et<sub>3</sub>N (29.59 ml, 0.21 mol) in Et<sub>2</sub>O (350 ml) at 0 °C. The solution was stirred at room temperature for 20 h. The resultant yellow powder was filtered and dissolved in CHCl<sub>3</sub> and then washed with 2 M HCl (aq.) (2 × 50 ml). Solvent removal and recrystallisation from hot EtOH produced colourless needles in a yield of 56%. A second crop of crystals was obtained giving a combined yield of 78%. Satisfactory C, H and N analyses were obtained.

‡ *Crystal data for 1*: C<sub>18</sub>H<sub>25</sub>N<sub>3</sub>O<sub>6</sub>, *M* = 379.41, monoclinic, space group *P2*<sub>1</sub>, *a* = 10.776(3), *b* = 7.241(3), *c* = 13.028(3) Å, β = 95.84(3)°, *U* = 1011.4(6) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.246 Mg m<sup>-3</sup>, μ = 0.094 mm<sup>-1</sup>, (Mo-Kα, λ = 0.71069 Å), *F*(000) = 404, *T* = 393 K. Rigaku AFC6S diffractometer, crystal size 0.2 × 0.3 × 0.2 mm, θ<sub>max</sub> 25.02°, 1944 reflections measured, 1944 unique. Final *R*<sub>w</sub> = [Σw(*F*<sub>o</sub><sup>2</sup> – *F*<sub>c</sub><sup>2</sup>)/Σ(*wF*<sub>o</sub><sup>2</sup>)]<sup>1/2</sup> = 0.1629 for all data, conventional *R* = 0.0636 for 1337 observed reflections. Data was of insufficient quality to determine absolute configuration. Disorder on one side chain was modelled to occupancies of 78:22%. Only the major contributor is shown. CCDC 182/1381. See <http://www.rsc.org/suppdata/cc/1999/1945/> for crystallographic data in .cif format.

- G. R. Desiraju, *Chem. Commun.*, 1997, 1475; G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311; C. B. Aakeröy, *Acta Crystallogr., Sect. B*, 1997, **53**, 569; D. Braga and F. Grepioni, *Coord. Chem. Rev.*, 1999, **183**, 19.
- X. Zhao, Y.-L. Change, F. W. Fowler and J. W. Lauher, *J. Am. Chem. Soc.*, 1990, **112**, 6627; F. Garcia-Tellado, S. J. Geib, S. Goswami and A. D. Hamilton, *J. Am. Chem. Soc.*, 1991, **113**, 9265; M. J. Krische, J.-M. Lehn, N. Kyritsakas and J. Fischer, *Helv. Chim. Acta*, 1998, **81**, 1909; J. J. Wolff, F. Gredel, T. Oeser, H. Irgartinger and H. Pritzkow, *Chem. Eur. J.*, 1999, **5**, 29.
- J.-M. Lehn, M. Maskal, A. DeCian and J. Fischer, *J. Chem. Soc., Perkin Trans. 2*, 1992, 461; M. W. Hosseini, R. Ruppert, P. Schaeffer, A. DeCian, N. Kyritsakas and J. Fischer, *Chem. Commun.*, 1994, 2135; R. Macías, N. P. Rath and L. Barton, *J. Organomet. Chem.*, 1999, **581**, 39; J. C. MacDonald and G. M. Whitesides, *Chem. Rev.*, 1994, **94**, 2383.
- M. R. Ghadini, J. R. Granja, R. A. Milligan, D. E. McRee and N. Khazanovich, *Nature*, 1993, **366**, 324.
- I. S. Choi, X. Li, E. E. Simanek, R. Akaba and G. M. Whitesides, *Chem. Mater.*, 1999, **11**, 684.
- S. Subramanian and M. J. Zaworotko, *Coord. Chem. Rev.*, 1994, **137**, 357.
- E. Fan, J. Yang, S. J. Geib, T. C. Stoner, M. D. Hopkins and A. D. Hamilton, *J. Chem. Soc., Chem. Commun.*, 1995, 1251.
- P. Hobza, H. L. Selze and E. W. Schlag, *J. Am. Chem. Soc.*, 1994, **116**, 3500.
- S. Chandrasekhar and G. S. Ranganath, *Rep. Prog. Phys.*, 1990, **53**, 57.
- A. R. A. Palmans, J. A. J. M. Vekemans, H. Fischer, R. A. Hikmet and E. W. Meijer, *Chem. Eur. J.*, 1997, **3**, 300.
- Y. Matsunaga, N. Miyajima, Y. Nakayasu, S. Saki and M. Yonega, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 207.
- K. Hanabusa, C. Koto, M. Kimura, H. Shirai and A. Kakehi, *Chem. Lett.*, 1997, 429.
- B. König, O. Möller, P. Bubenitschek and P. G. Jones, *J. Org. Chem.*, 1995, **60**, 4291.