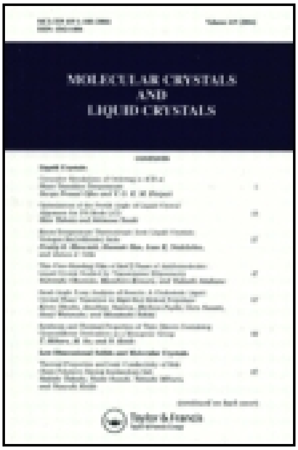

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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To cite this article: Wen-Jwu Wang & Jau-Shuenn Wang (2005): H-Bond Mediated Self-Assembly 1-Dimensional Array of 3,6-Bis(3′-Pyridyl)-1,2,4,5-Tetrazine with Trimesic Acid, Molecular Crystals and Liquid Crystals, 440:1, 147-152

To link to this article: http://dx.doi.org/10.1080/15421400590958214

Mol. Cryst. Liq. Cryst., Vol. 440, pp. 147–152, 2005
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400590958214

H-Bond Mediated Self-Assembly 1-Dimensional Array of 3,6-Bis(3′-Pyridyl)-1,2,4,5-Tetrazine with Trimesic Acid

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3,6-Bis(3′-pyridyl)-1,2,4,5-tetrazine was prepared by reaction of 3-cyanopyridine with hydrazine. Slow evaporation of 3,6-bis(3′-pyridyl)-1,2,4,5-tetrazine with trimesic acid, in a 2:1 molar ratio in methanol afforded single crystals of ***1*** $C_{33}H_{22}N_{12}O_6$, *suitable for X-ray analysis. The product was characterized by spectroscopic and single-crystal X-ray diffraction studies. The hydrogen bond mediated self-assembly of 3,6-bis(3′-pyridyl)-1,2,4,5-tetrazine with trimesic acid molecules generates 1-dimensional multi-compartmental arrays in the solid state as revealed by X-ray crystallographic analysis. The crystal structure of* ***1*** *is monoclinic with* $a = 28.445(3)$, $b = 6.7088(10)$, $c = 33.846(4)$ Å, $\alpha = 90°$, $\beta = 108.112(7°$, $\gamma = 90°$, $Z = 8$, *and space group C2/c. The directional intermolecular hydrogen bonding between 3,6-bis(3′-pyridyl)-1,2,4,5-tetrazine and trimesic acid molecules uses* $O{-}H\cdots N$ *and* $C{-}H\cdots O$ *interactions, together with intramolecular* $C{-}H\cdots N$ *hydrogen bonding, to build up the one-dimensional network structure.*

Keywords: hydrogen-bond; monoclinic; multi-compartmental arrays; one-dimensional network; self-assembly; solid state; trimesic acid

INTRODUCTION

The design of new molecular architectures has generated great interest in crystal engineering over recent years. Especially, much investigation into organic compounds has been carried out using the presence of functional groups that can form strong and stable intermolecular interactions [1]. Therefore, recognizing geometry and functionality at the molecular level has relevant implications in the design of

This work was supported by the National Science Council, Taiwan (ROC), and Tamkang University.

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supramolecular patterns. These patterns in turn can be translated into physical or chemical properties in a solid. Non-covalent interactions have been extensively used in crystal engineering, since they are the fundamental cause of the formation of crystals [2]. Hydrogen bonding, π-π interactions, and π-hydrogen interactions have been used in particular for this purpose. Hydrogen bonding is the most studied intermolecular interaction, presumably due to its frequent presence in organic solid molecules. The selectivity and directional nature of hydrogen bonding has led to its extensive use in the construction and stabilization of large non-covalently bonded molecular and supramolecular structures. Hydrogen bonds are formed when a donor (D−H), with an available acidic hydrogen atom, is brought into intimate contact with an acceptor (A) [3].

Hydrogen-bonded supramolecular structures represent a primary tool for crystal engineering [4–6]. In such a context, trimesic acid (benzene-1,3,5-tricarboxylic acid, **TMA**) is a molecule which predictably forms networks with interesting supramolecular properties as a result of its molecular symmetry and complementary hydrogen-bonding capabilities. Carboxylic acids can form homo- or hetero-dimers with a variety of complementary functional groups (*e.g.* pyridines, 2-aminopyridines and pyrimidines), This has allowed functionalized **TMA** [7], its deprotonated forms [8], or its metal complexes [9, 10] to be exploited as templates in crystal engineering studies. In this contribution we report a one-dimensional network in the co-crystal of **TMA**, 2[3,6-bis(3′-pyridyl)-1,2,4,5-tetrazine]· TMA, **1**, the supramolecular structure of which is effectively an enlargement of **TMA**.

EXPERIMENTAL

3,6-Bis(3′-pyridyl)-1,2-dihydro-1,2,4,5-tetrazine [11]

A mixture of 3-cyanopyridine (10.4 g, 0.1 mol, Aldrich, 98%, b.p. 201°C) and an excess of hydrazine hydrate (10 ml, 0.32 mol, Aldrich) were warmed on a water bath for 6 hr. The solid was collected and crystallized from ethanol as yellow needles, m.p. 233–235°C. The yield was 8.6 g (72%).

3,6-Bis(3′-pyridyl)-1,2,4,5-tetrazine [11]

3,6-Bis(3′-pyridyl)-1,2-dihydro-1,2,4,5-tetrazine (7.0 g) was dissolved in a mixture of glacial acetic acid (300 ml) and water (200 ml) and cooled to 0°C. Sodium nitrite (9.2 g) in cold water (25 ml) was added to this solution slowly with vigorous stirring. The color of the solution turned red-purple. The mixture was neutralized with ammonia solution and the product was collected by filtration. It was crystallized from ethanol to afford purplish red plates, m.p. 201–202°C. The yield was 4.2 g (61%).

2[3,6-Bis(3′-pyridyl)-1,2,4,5-tetrazine] · TMA

Crystals of the compound suitable for single-crystal X-ray analysis were grown by slow evaporation of a methanol solution containing a mixture of 3,6-bis(3′-pyridyl)-1,2,4,5-tetrazine and trimesic acid in a 2:1 molar ratio.

RESULTS AND DISCUSSION

The title compound, 2[3,6-bis(3′-pyridyl)-1,2,4,5-tetrazine] · TMA, **1**, consists of 3,6-bis(3′-pyridyl)-1,2,4,5-tetrazine (**3-pta**) and trimesic acid (**TMA**) in a 2:1 ratio as shown in Figure 1. Molecules of the title compound are linked by O—H· · ·N and C—H· · ·O intermolecular hydrogen-bonding. Within the asymmetric unit of the crystal **1**, both **3-pta**

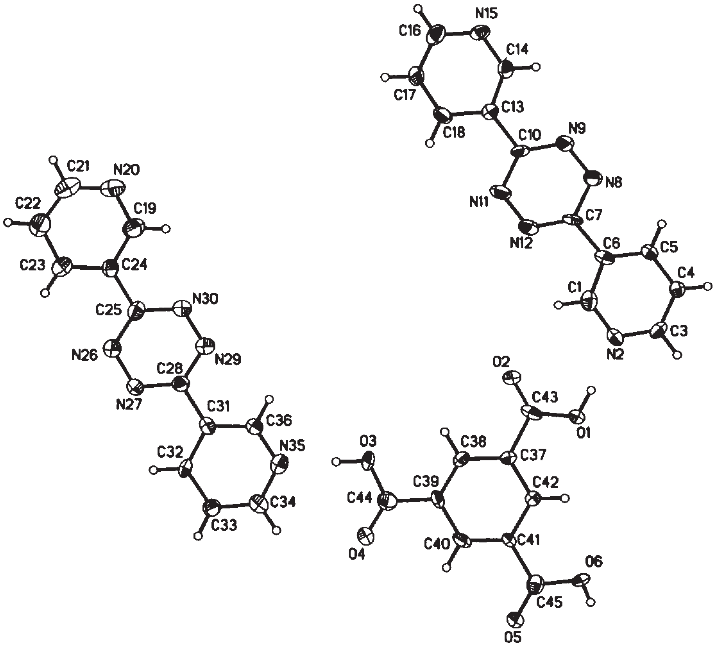

FIGURE 1 The structure and atom-numbering scheme of **1**.

TABLE 1 Hydrogen-Bonding Geometry Close Contacts (Å, °)

D–H···A	D–H	H···A	D–H···A	
O1–H43···N2^{i}	0.93(7)	1.73(7)	2.649(9)	169(6)
O3–H44···N35^{ii}	0.95(6)	1.67(6)	2.605(1)	171(5)
O6–H45···N15$'^{iii}$	0.71(6)	1.95(6)	2.652(1)	171(7)
C1–H1···O2^{iv}	0.93(1)	2.56(6)	3.246(1)	130(3)
C16–H16···O5$'^{v}$	0.93(1)	2.39(5)	3.182(1)	142(4)

Symmetry codes: (i) 1/2 − x, 1/2 − y, − z; (ii) x, 1 + y, z; (iii) 1 − x, y, 1/2 − z; (iv) 1/2 − x, 1/2 − y, − z; (v) 1 − x, − 1 + y, 1/2 − z.

molecules are interconnected with a trimesic acid molecule by means of intermolecular Ol–H43···N2, C1–H1···O2 and O3–H44···N35 hydrogen-bonding, with angles of 169(6)°, 130(5)° and 171(5)° respectively. The carboxylate group of the trimesic acid exhibits further hydrogen-bonding O6–H45···N15′ and C16–H16···O5′ with a **3-pta** of the adjacent asymmetric unit, with angles of 171(7)° and 142(6)° respectively, to build up the expanded one-dimensional network structure. The hydrogen bond parameters are listed in Table 1. For two neighboring chains, the molecules extend the one-dimensional network in the reverse direction through anti-parallel packing as shown in Figure 2. In the asymmetric unit, only one of the **3-pta** molecules generates an intermolecular hydrogen-bond with the adjacent asymmetric unit to create molecular ribbons. The other **3-pta** does not intereact with the adjacent asymmetric unit, therefore the one-dimensional chains form branches of **3-pta** molecules, that mutually interdigitate. In the packing as shown in Figure 3., TMA is connected to

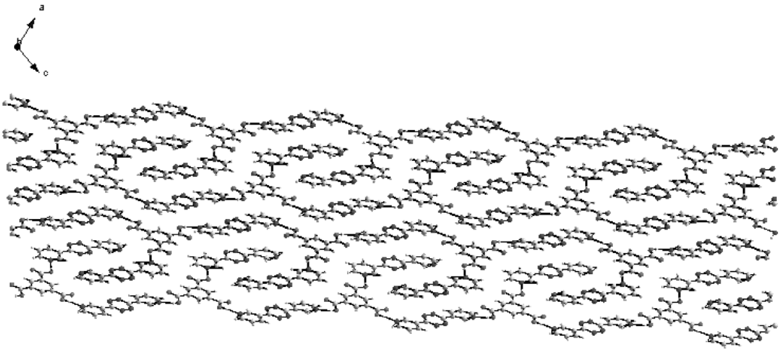

FIGURE 2 The expanded structure of **1**, showing the molecular ribbons projected onto the *ac* plane.

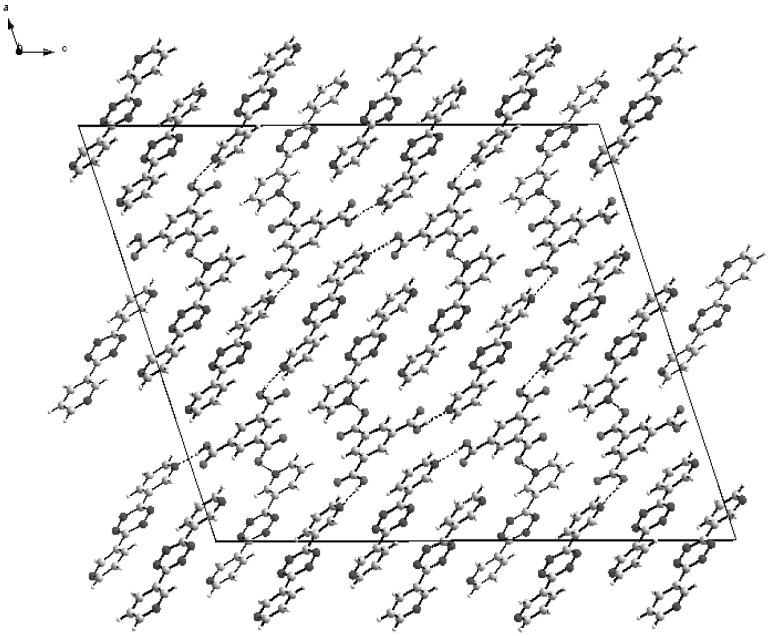

FIGURE 3 The unit cell packing diagram of **1**.

TABLE 2 Crystal Data of **1** [12]

$C_{33}H_{22}N_{12}O_6$
$M_r = 682.63$
Monoclinic, C2/c
a = 28.445(3) Å
b = 6.7088(10) Å
c = 33.846(4) Å
$\alpha = 90^\circ$
$\beta = 108.112(7)^\circ$
$\gamma = 90^\circ$
$V = 6138.91(3)$ Å
Z = 8
5508 Reflections collected
5395 Independent reflections $R_{int} = 0.0937$
Absorption correction: empirical
$T_{min} = 0.3539$, $T_{max} = 0.3366$
Refinement method: Full-matrix least-squares on F^2
Data/restraints/parameters: 5395/0/472
Goodness-of-fit on F^2: 0.957
Final R indices [I $> 2\sigma$(I)]: $R1 = 0.0975$, $wR2 = 0.0595$
R indices (all data): $R1 = 0.3511$, $wR2 = 0.0951$
Largest diff. Peak and hole: 235 and –233 e nm^{-3}

$D_x = 1.477\,\mathrm{Mg/m^3}$
$\theta = 2.25$–25.00°
$\mu = 0.107\,\mathrm{mm^{-1}}$
$T = 293(2)$ K
$0.55 \times 0.13 \times 0.05$ mm
Wavelength = 0.71073 Å
F(000) = 2816
$h = 0 < 33$
$k = 0 < 7$
$l = -40 < 38$

three **3-pta** molecules by O–H···N and C–H···O interactions, in which only two of the **3-pta** extend to generate intermolecular hydrogen-bonds with the adjacent trimesic acid molecules through O6–H45···N15′ and C16–H16···O5′ interactions, that consequently maintain the one-dimensional structure.

Within the asymmetric unit of **1**, the **3-pta** and trimesic acid molecules are nearly planar. The dihedral angles between **3-pta** and TMA are 7.3° and 5.1° respectively. For the trimesic acid, the two O atoms of the carboxylate groups are slightly displaced from the plane of the aromatic ring. The dihedral angles of the carboxylate groups O1/O2/C43/C37, O3/O4/C44/C39 and O5/O6/C45/C41 with respect to the attached aromatic rings are 4.0°, 4.9° and 3.6°, respectively.

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[12] Supplementary crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (deposition number CCDC 274478). Copies can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44(0)-1223-336033 or E-mail: deposit@ccdc.cam.ac.uk].