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Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
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Self-assembly Molecular Complex by 3,6-Di(pyridin-4-yl)-1,2,4,5-tetrazine with Trimesic Acid through H-Bonding

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Published online: 21 Dec 2006.

To cite this article: Chia-Jung Hsu , Shang-Wei Tang , Jau-Shuenn Wang & Wen-Jwu Wang (2006): Self-assembly Molecular Complex by 3,6-Di(pyridin-4-yl)-1,2,4,5-tetrazine with Trimesic Acid through H-Bonding, Molecular Crystals and Liquid Crystals, 456:1, 201-208

To link to this article: http://dx.doi.org/10.1080/15421400600788724

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Mol. Cryst. Liq. Cryst., Vol. 456, pp. 201–208, 2006
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400600788724

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Self-assembly Molecular Complex by 3,6-Di(pyridin-4-yl)-1,2,4,5-tetrazine with Trimesic Acid through H-Bonding

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*The reaction of 3,6-di(pyridin-4-yl)-1,2,4,5-tetrazine (***4-PTA***) with trimesic acid (***TMA***) in methanol solution in a 1.5:1 mole proportion affords molecular complex* ***1****. The structure was confirmed by single crystal X-ray diffraction study. The compound crystallizes in the triclinic space group P-1 with* $a = 9.7625(11)$, $b = 11.7298(13)$, $c = 13.0734(13)$, $\alpha = 68.849(10)^\circ$, $\beta = 72.701(8)^\circ$, $\gamma = 83.937(9)^\circ$ *and* $Z = 2$*. The crystal structure of* ***1*** *shows hydrogen bonding between* **4-PTA** *and* **TMA***, and the presence of an interstitial* H_2O *molecule in the crystal. The zigzag 1-dimensional framework was constructed by the intermolecular hydrogen bond containing* $O{-}H\cdots N$, $O{-}H\cdots O$ *and* $C{-}H\cdots O$ *interactions. The* $\pi{-}\pi$ *interactions are the non-covalent forces operating between the pyridine ring in* **4-PTA** *and benzene ring in* **TMA** *to generate 3-dimensional network.*

Keywords: Hydrogen-bond; multi-compartmental arrays; self-assembly; Trimesic acid; two-dimensional network; zigzag structure

INTRODUCTION

Solid-state organic and metal-organic systems are of increasing interest because of their high potential and wide application for molecular storage, molecular sensing, nano-devices, and catalysis. Understanding of the relationships between molecular structure and crystal structure can help develop the tectonic chemistry or crystal

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

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engineering, but usually it is very hard to predict molecular packing in the solid state. For this reason, using the self-assemblying of supramolecular systems by chemical forces, like coordination bonding, hydrogen bonding, $\pi-\pi$ interactions, π-hydrogen interactions, has become an area of great interest in crystal engineering for the development of tectonic chemistry [1].

Hydrogen bonds play an important role in crystal engineering because of their selectivity and directionality, which can help control the design of various molecular assemblies [2]. A judicious choice of appropriate carboxylic acid donors and pyridine nitrogen acceptors may form short intermolecular O–H···N hydrogen bonds and lead to different types of molecular architectures [1,3]. The building block containing carboxylic acid group can coordinate with variety of complementary functional groups. Generally, trimesic acid (**TMA**) and pyromellitic acid (**PMA**) are frequently used as functional building blocks for the development of tectonic chemistry due to their predictable and interesting supramolecular properties. These carboxylic acids have robust hydrogen bonding abilities and form different types of C–H···O and O–H···N hydrogen bonding with the complementary basic components, such as pyridine, pyrazine, or pyrimidine substituted molecules, to engineering the desired crystal structures [4–8]. We anticipated that the incorporation of distinctive polycarboxylic- and dipyridyl- type building blocks within a binary molecular crystal would lead to formation of new organic crystalline materials with fascinating supramolecular structures.

Recent studies have focused on hydrogen bonding motifs of carboxylic acids with complementary functional groups containing polypyridine as basic unit because of their high success rate [9]. We have already reported the synthesis and crystal structure of the 3,6-di(pyridin-3-yl)-1,2,4,5-tetrazine (**3-PTA**) with trimesic acid (**TMA**), which forms one-dimensional network and have a chain saw-like structure. Herein we describe a new tectonic system of 3,6-di(pyridin-4-yl)-1,2,4,5-tetrazine (**4-PTA**) and its complementary complex with**TMA**. We report a detail synthesis, how the molecular complexes assemble, and what the complementary intermolecular interactions are.

EXPERIMENTAL

3,6-di(pyridin-4-yl)-1,4-dihydro-1,2,4,5-tetrazine [10]

A mixture of 4-cyanopyridine (10.4 g, 100 mmol, Aldrich, 98%, m.p.78–80°C) and an excess of hydrazine monohydrate (10 mL, Lancaster,

98 + %) were heated in a water bath at 80°C for 3 hr. The solid was collected and crystallized from ethanol. Orange crystalline needles were separated on slow evaporation, m.p.240–242°C. The yield was 13.3 g (56%).

3,6-di(pyridin-4-yl)-1,2,4,5-tetrazine(4-PTA) [10]

3,6-Di(pyridin-4-yl)-1,4-dihydro-1,2,4,5-tetrazine (7.0 g, 26 mmol) dissolved in a mixture of glacial acetic acid (300 mL) and water (200 mL) and the solution was cooled to 0°C. Sodium nitrite (9.2 g) in cold water (25 mL) was then added slowly while vigorously stirring; the reaction mixture turned into a red-purple color. The mixture was neutralized with an ice cooled ammonia solution (TEDIA, 28–30%) and the product was collected by filtration. It was recrystallized from ethanol. Purplish red plates were formed on slow evaporation, m.p.261– 262°C. The yield was 6.2 g (90%).

1.5[3,6-di(pyridin-4-yl)-1,2,4,5-tetrazine]·[Trimestic Acid] (1.5[4-PTA]·[TMA])

Trimestic acid (**TMA**) and 3,6-di(pyridin-4-yl)-1,2,4,5-tetrazine **(4-PTA)** in 1:1.5 molar ratio dissolved in methanol solution. The solution was then left undisturbed at room temperature for a week. Single X-ray quality crystals of **1.5[4-PTA]·[TMA]** were formed on slow evaporation.

X-ray Structural Study

A colorless single crystal of molecular complex **1**(**1.5[4-PTA]·[T-MA]·[2H_2O]**) was suitable for x-ray analysis. The diffraction data were collected with Siemens P4 diffractometer using graphite monochromatized Mo–Kα radiation ($\lambda = 0.71073$Å) at 293 K. The unit-cell parameters were determined from least squares refinements setting angles of 4930 reflections with 2θ in the range $1.86 < 2\Theta < 25^{\circ}$. The structure was solved by direct methods using the program SHELXS-97 [11]. The refinement and all other calculations were carried out using SHELXL-97 [11].

RESULT AND DISCUSSION

The flow chart for synthesis of **4-PTA** is presented in Scheme 1. Samples of 4-cyanopyridine and hydrazine monohydrate were heated together under reflux to obtain 3,6-di(pyridin-4-yl)-1,4-dihydro-1,2,4,5-tetrazine. The product was oxidized by nitrous acid

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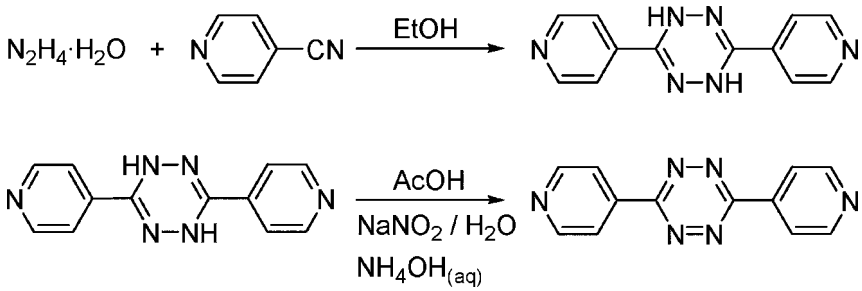

SCHEME 1 Synthetic route used to obtain the 3,6-di(pyridin-4-yl)-1,4-dihydro-1,2,4,5- tetrazine and 3,6-di(pyridin-4-yl)-1,2,4,5-tetrazine.

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TABLE 1 Crystallographic and Structure Refinement Data for Crystal 1 [16]

Formula	$C_{27}\ H_{22}\ N_9\ O_8$
Formula weight	600.54
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
A(Å)	9.7625(11) Å
b(Å)	11.7298(13) Å
c(Å)	13.0734(13) Å
α (deg)	68.849(10)
β(deg)	72.701(8)
γ(deg)	83.937(9)
V(Å^3)	1333.1(2)
Z	2
Absorption coefficient	0.114
F(000)	622
Crystal size	$0.38 \times 0.30 \times 0.18$ mm
Theta range for data collection	1.86 to 25.00 deg.
Limiting indices	$0 < h < 11,\ -13 < k < 13,\ -14 < l < 15$
Reflections collected/unique	4930/4630 [R(int) = 0.0264]
Completeness to theta = 25.00	98.5%
Absorption correction	Empirical
Max. and min. transmission	0.4684 and 0.4480
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4630/0/477
Goodness-of-fit on F^2	1.022
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0514$, $wR_2 = 0.1143$
R indices (all data)	$R_1 = 0.0974$, $wR_2 = 0.1352$
Largest diff. peak and hole	0.244 and -0.221 e·Å^{-3}

to 3,6-di(pyridin-4-yl)-1,2,4,5-tetrazine and the pH value was adjusted to neutral with a solution of ammonia, resulting in the precipitation of the product. Mixing **TMA** and **4-PTA** (1:1.5 molar ratio) in methanol solution followed by slow solvent evaporation resulted in colorless single crystal of molecular complex **1** that were suitable for x-ray diffraction analysis.

Analysis of the x-ray crystallographic data of molecular complex **1** and the structure refinement parameters are given in Table 1. Selected bond lengths and bond angles are summarized in Table 2.

Molecular complex **1** crystallizes in the enantiomorphous space group *P*–1. The molecular structure of **1** is shown in Figure 1. During refinement it was observed that O8 atom of the water molecule was disordered. It was difficult to refine the closely connected hydrogen atoms, suggesting that there are very weak interactions around the H_2O. The two-dimensional structure of **1** is given in Figure 2.

The **4-PTA** molecule is linked with **TMA** and H_2O based on O–H···N, O–H···O hydrogen bonds. The two pyridine groups of **4-PTA** are interconnected with **TMA** by intermolecular O3–H31···N7 and O6–H6O···N1 hydrogen bonding with angles 176(3)° and 171(4)°. Besides this, **4-PTA** is also interconnected with H_2O by intermolecular O7–H7OA···N6 hydrogen bonding with angles 169(4)° generating one-dimensional infinite chain structure. **TMA**

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TABLE 2 Selection Bond Lengths [Å] and Angles [deg] for Crystal **1**

O1–C7	1.320(3)	O1–C7–C1	112.4(2)
O2–C7	1.205(3)	O4–C8–C3	120.7(2)
O3–C8	1.284(3)	O3–C8–C3	116.1(2)
O4–C8	1.220(3)	O5–C9–O6	122.7(3)
O5–C9	1.206(3)	O5–C9–C5	123.4(2)
O6–C9	1.314(3)	N1–C10–C11	123.7(3)
N2–N3	1.325(3)	N1–C14–C13	123.7(3)
N4–N5	1.314(3)	N2–C15–N4	124.5(2)
N8–N9	1.321(3)	N2–C15–C12	118.4(2)
N8–C27	1.338(3)	N4–C15–C12	117.1(2)
N9–C27	1.338(3)	N3–C16–N5	124.6(2)
C10–N1–C14	117.1(3)	N3–C16–C19	118.3(2)
N3–N2–C15	117.8(2)	N5–C16–C19	117.1(2)
N2–N3–C16	117.3(2)	N6–C17–C18	123.4(3)
N5–N4–C15	117.6(2)	N6–C21–C20	124.2(3)
N4–N5–C16	117.8(2)	N7–C22–C23	121.9(3)
C21–N6–C17	116.6(3)	N7–C26–C25	122.3(3)
C26–N7–C22	119.2(2)	N8–C27–N9	124.8(2)
N9–N8–C27	117.9(2)	N8–C27–C24	117.7(2)
O2–C7–C1	123.8(2)	N9–C27–C24	117.5(2)

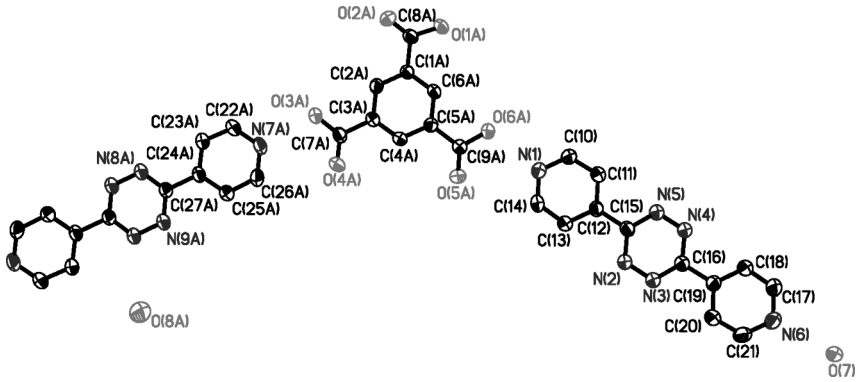

FIGURE 1 ORTEP diagram of molecular complex **1**, hydrogen atoms are omitted for clarity.

is also interconnected with H_2O provided intermolecular O7–H7OB···O4 and O1–H1O···O7 hydrogen bonding with angles 171(4)° and 161(4)°, forming a two-dimensional framework. The **4-PTA** is also linked with **TMA** and H_2O by C–H···O hydogen bonds. Selected hydrogen bond distances and bond angles are summarized in Table 3.

In the literature reported so far, the structure formed by the reaction of 4,4′ -bipyridine with **TMA** appeared as 3-fold interweaving (6,3) networks with parallel interpenetration [12–14] and the structure formed by the reaction of 2[3,6-bis(pyridin-3-yl)-1,2,4,5-tetrazine] with **TMA** [15] formed a chain saw-like molecular complex. The

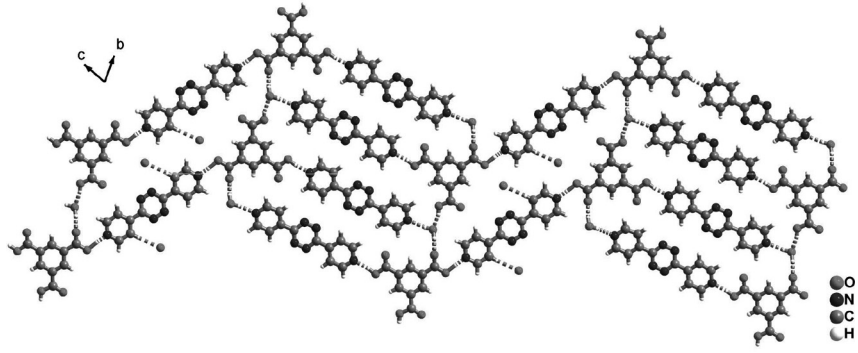

FIGURE 2 Two-dimensional structure of molecular complex **1**.

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TABLE 3 Analysis of Potential Hydrogen Bond Lengths and Bond Angles

D–H···A	D–H	H···A	D–A	Deg.
O7–H7OB···O4^{vi}	0.99(5)	1.75(5)	2.722(3)	171(4)
O1–H1O···O7^{iv}	0.83(5)	1.76(5)	2.552(3)	161(4)
O7–H7OA···N6^{iv}	0.84(5)	1.96(5)	2.782(3)	169(4)
O6–H6O···N1^{iii}	0.95(5)	1.69(5)	2.631(3)	171(4)
O3–H31···N7^{i}	1.31(4)	1.28(5)	2.589(3)	176(3)
O4–H31···N7^{i}	1.31(4)	2.41(4)	3.245(3)	119(3)
C2–H2···O3	0.88(2)	2.51(2)	2.793(3)	100.01(18)
C6–H6···O6	0.95(2)	2.38(2)	2.756(3)	103.1(17)
C17–H17···O1	1.04(4)	2.54(4)	3.343(4)	133(3)
C20–H20···N3	0.88(3)	2.52(3)	2.827(4)	101(2)
C21–H21···O5^{v}	0.97(3)	2.46(4)	3.134(4)	126(2)
C22–H22···O8	1.00(4)	2.46(4)	3.350(5)	148(3)
C23–H23···O8^{ii}	0.92(4)	2.48(4)	3.384(4)	171(3)

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

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molecular complex **1** exhibits atwo-dimensional zigzag network. This type of network is due to the presence of complementary H_2O molecule in the crystals that interconnect the **4-PTA** and **TMA**. The molecular packing diagram is shown in Figure 3.

The pyridine ring in **4-PTA** and benzene ring in **TMA** contribute weak edge-to-edge $\pi-\pi$ interaction to support 3-dimensional crystal

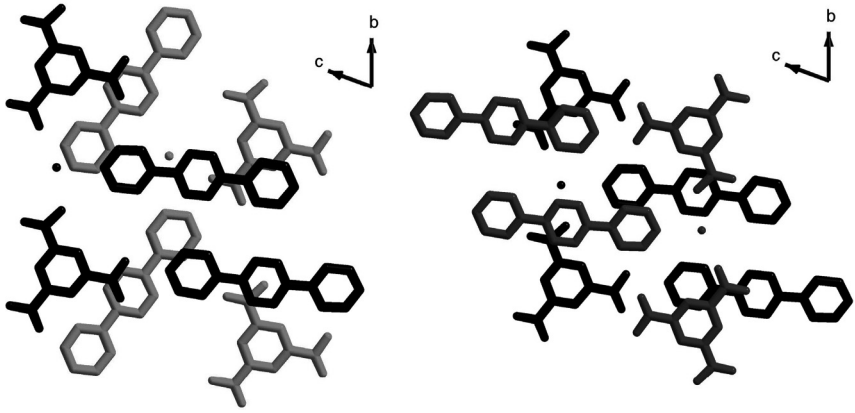

FIGURE 3 Packing diagrams of molecular complex **1** between layer 1 and layer 2 (left) and layer 2 and layer 3 (right). Hydrogen atoms are omitted for clarity.

packing. The distance between two closely layers [N6 to C22] and [C21 to C23] are 3.5(5)Å and 3.7(4)Å), respectively.

CONCLUSION

In this work we present the synthesis of **4-PTA** and the single crystal X-ray structure of molecular complex **1**. It forms zigzag supramolecular architecture using intermolecular hydrogen bonding between the **4-PTA**, **TMA** and H_2O.

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[16] CCDC 284425 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, +44 1223 336408. Hydrogen atoms are omitted for clarity.