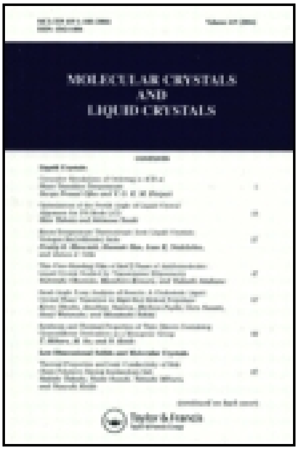

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Microporous Material Based on π-π Stacking of 1,4-Bis(3,6-diphenylpyridazin-4-yl)benzene

Hsien-Chang Kao [a] , Shang-Wei Tang [a] , Jau-Shuenn Wang [a] & Wen-Jwu Wang [a]

[a] Department of Chemistry, Tamkang University, Tamsui, Taipei, Taiwan (ROC)

To cite this article: Hsien-Chang Kao, Shang-Wei Tang, Jau-Shuenn Wang & Wen-Jwu Wang (2006): Microporous Material Based on π-π Stacking of 1,4-Bis(3,6-diphenylpyridazin-4-yl)benzene, Molecular Crystals and Liquid Crystals, 456:1, 193-200

To link to this article: http://dx.doi.org/10.1080/15421400600788708

Mol. Cryst. Liq. Cryst., Vol. 456, pp. 193–200, 2006
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400600788708

Taylor & Francis
Taylor & Francis Group

Microporous Material Based on π-π Stacking of 1,4-Bis(3,6-diphenylpyridazin-4-yl)benzene

Hsien-Chang Kao
Shang-Wei Tang
Jau-Shuenn Wang
Wen-Jwu Wang
Department of Chemistry, Tamkang University,
Tamsui, Taipei, Taiwan (ROC)

*A microporous material constructed by π-π interaction of a twisted H-shape polyaromatic molecule, 1,4-bis(3,6-diphenylpyridazin-4-yl)benzene (**1**) was synthesized and X-ray quality crystals were isolated. The intermolecular distances between the various aromatic rings are within the range of 3.4 ∼ 3.7 Å, which indicate intermolecular π-π interactions. Hexagonal channels with pores of 13 Å width along the c-axis were observed. Interstitial H_2O and MeOH molecules were located within each porous channel.*

Keywords: H-shape molecule; microporous; pyridazine; π-π stacking

INTRODUCTION

Recently, intense research activities have been directed towards the development of open porous frameworks based on the assembly of inorganic compounds, activated carbons, metal-organic frameworks, and organic molecules, into extended motifs held together either by strong metal–ligand bonding or non-covalent interactions, such as hydrogen-bonding, and π-π interactions [1–3]. Porous materials have attracted the attention of chemists due to their nanometer-sized spaces, which may be used to investigate novel phenomena and for applications such as molecular storage and heterogeneous catalysis. These characteristic features are based on their open frameworks,

---

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

Address correspondence to Wen-Jwu Wang, Department of Chemistry, Tamkang University, Tamsui 25137, Taipei, Taiwan (ROC). E-mail: wjw@mail.tku.edu.tw

which are ascribed to a robust porosity that can accommodate various guest molecules within their crystal structures [4,5].

Inorganic porous compounds such as zeolites are widely used in separation, catalysis and exchange. Zeolites frameworks have high stability and crystallinity but of low porosity [6]. Activated forms of carbon have high porosity with a broad pore size distribution, so that many of the channels or cavities are often superfluous and unnecessary for the required porous functions, which leads to poor storage/separation capacity for a specific guest [7].

Manipulation of functional metal-organic frameworks and organic porous materials are specially intriguing because they are easier to control and fine-tune [8,9]. Hydrogen bonding and π-π interactions have been used in particular for this purpose. Hydrogen bonding is the most studied intermolecular interaction due to its frequent presence in organic frameworks. The selectivity and directional nature of the hydrogen bond has led to its extensive use in the construction and stabilization of large non-covalently bonded organic porous compounds. Although many of them show unique catalytic properties, their frameworks are liable to collapse or deform after removal of guest molecules from the micropores [10]. To date, the number of organic networks with new structural aspects is increasing, but to our knowledge of aromatic and heteroaromatic porous structures sustained by π-π interactions are still scarce. This has prompted us to undertake a program to construct organic solid in which π-π stacking interactions could be predicted to play an important role in the porous material.

In this paper we study a twisted H-shape poly-aromatic molecule, 1,4-bis(3,6-diphenylpyridazin-4-yl)benzene (1), in which π-π stacking of aromatic interactions have been proposed to provide the assembling force that makes the extended aromatic molecules into an overall three-dimensional structure.

The intermolecular distance between various aromatic rings are within the range of $3.4 \sim 3.7\,\text{Å}$ and the dihedral angle between each aromatic and heteroaromatic rings indicates that the large intermolecular π-π interaction is operating in the molecule and a hexagonal channels with pore width 13 Å along the *c*-axis are observed.

EXPERIMENTAL

3,6-Diphenyl-1,2-dihydro-1,2,4,5-tetrazine [11]

A mixture of 3-benzonitrile (10.4 g, 0.1 mol) and an excess of hydrazine hydrate (10 ml, 0.32 mol) were warmed in a water bath for 6 h. The solid was collected and crystallization from ethanol afforded yellow needles (m.p. 233–235°C), which was used directly in the subsequent reaction. The yield was 8.6 g (72%).

3,6-Diphenyltetrazine [11]

3,6-Diphenyl-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 slowly to this solution with vigorous stirring. The color of the solution turned to red-purple. The mixture was neutralized with an ammonia solution and the product was collected by filtration. Crystallization from ethanol afforded purplish red plates, m.p. 201–202°C. The yield was 4.2 g (61%).

^{1}H NMR(300 MHZ, CDCl$_3$), (ppm), J (HZ): 8.67(d, 4H, phenyl-H, $J = 1.8$), 7.63(t, 4H, phenyl-H, $J_1 = 1.8$, $J_2 = 1.4$), 7.62(d, 2H, phenyl-H, $J = 1.4$)

1,4-Bis(3,6-diphenylpyridazin-4-yl)benzene [11]

A mixture of 1,4-diacetylbenzene (2 g, 12.3 mmol) and 3,6-diphenyltetrazine (5.9 g, 25 mmol) in dry THF was warmed in a water bath for

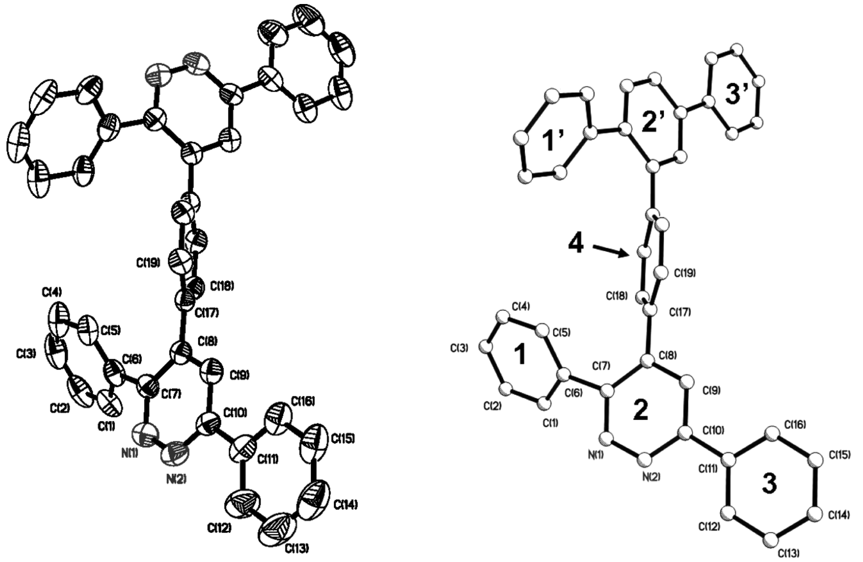

FIGURE 1 ORTEP diagram of 1,4-bis(3,6-diphenylpyridazin-4-yl)benzene. Inset diagram is numbering of the aromatic and hetroaromatic rings.

3 h followed by addition of 2.5% KOH/MeOH solution into the mixture. The solid was collected and crystallized by slow diffusion of a THF solution into MeOH. The crystal is colorless needle, m.p. 271–273°C. The yield was 3.57 g (53%).

RESULTS AND DISCUSSION

The title compound 1,4-bis(3,6-diphenylpyridazin-4-yl)benzene is shown in Figure 1. Crystal data and structure refinement parameter are listed in Table 1. A twisted H-shaped conformation is formed by two 3,6-diphenylpyridazine units linked together by benzene at the *para*-position (1,4-position). The torsion angle between the two pyridazine units (ring 2–ring 2′) is 70°, as shown in Figure 2a. The benzene linked at the 4-position of two pyridazine units makes the ring 1, ring 2 and ring 4 to lie in different planes, creating a twisted H-shape conformation and a packing structure consisting of a 3-D network. Figure 2b shows the two phenyl rings (ring 1 and ring 3) attached to pyridazine ring at 3 and 6 position. These two rings (ring 1 and ring 3) make dihedral angles of 43° and 6.8° with the pyridzaine ring (ring 2), respectively. The

TABLE 1 Crystal Data and Structure Refinement Parameter [12]

Empirical formula	C160 H104 N16 O20
Formula weight	2570.59
Temperature	273(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, *Pbcn*
Unit cell dimensions	a = 16.3407(7) A alpha = 90 deg.
	b = 10.8145(5) A beta = 90 deg.
	c = 18.6069(8) A gamma = 90 deg.
Volume	3288.1(3) A^3
Z, Calculated density	1, 1.298 Mg/m^3
Absorption coefficient	0.087 mm^−1
F(000)	1336
Crystal size	0.6 × 0.5 × 0.3 mm
Theta range for data collection	2.19 to 28.36 deg.
Limiting indices	$-18 \leq h \leq 21$, $-14 \leq k \leq 14$, $-24 \leq 1 \leq 22$
Reflections collected/unique	33608/4064 [R(int) = 0.0485]
Completeness to theta = 28.36	98.7%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4064/0/223
Goodness-of-fit on F^2	1.057
Final R indices [I > 2sigma(I)]	R1 = 0.0915, wR2 = 0.2166
R indices (all data)	R1 = 0.1320, wR2 = 0.2354
Extinction coefficient	0.0035(7)
Largest diff. peak and hole	0.502 and −0.466 e.A^ −3

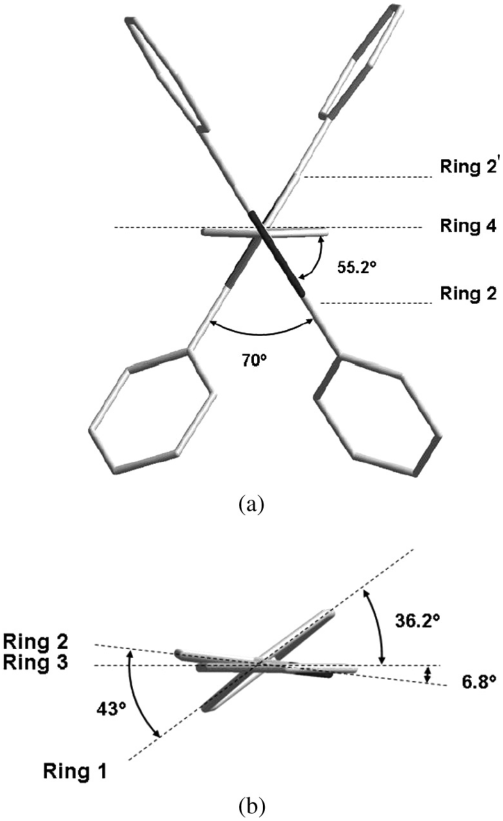

FIGURE 2 a) Dihedral angle of Ring 2, Ring 4 and Ring 2′. B). Dihedral angle of Ring 1, Ring 2, and Ring 3, solvent molecules hydrogen atoms have been omitted for clarity.

dihedral angle between ring 1 and ring 2 is greater than between ring 2 and ring 3. This may due to the repulsion between the hydrogen atoms at 2-position of ring 1 and at 6-position of ring 4 whereas ring 3 is far away from ring 4 and it experiences less repulsion. Moreover, steric hindrance between ring 2 and ring 4 makes the dihedral angle 55.2°. None of the aromatic or heteroarometic rings lie in the same plane, which impedes the formation of π-stacked packing structure.

The twisted H-shape conformation of 1,4-bis(3,6-diphenylpyridazin-4-yl)benzene is organized into stair-like 1-D chains along *a*-axis by pyridazine and phenyl-phenyl intermolecular interactions. The pyridazine rings reveals an anti stacked orientation to neighbor molecule along *b*-axis with a distance 3.8 Å, while the other two phenyl

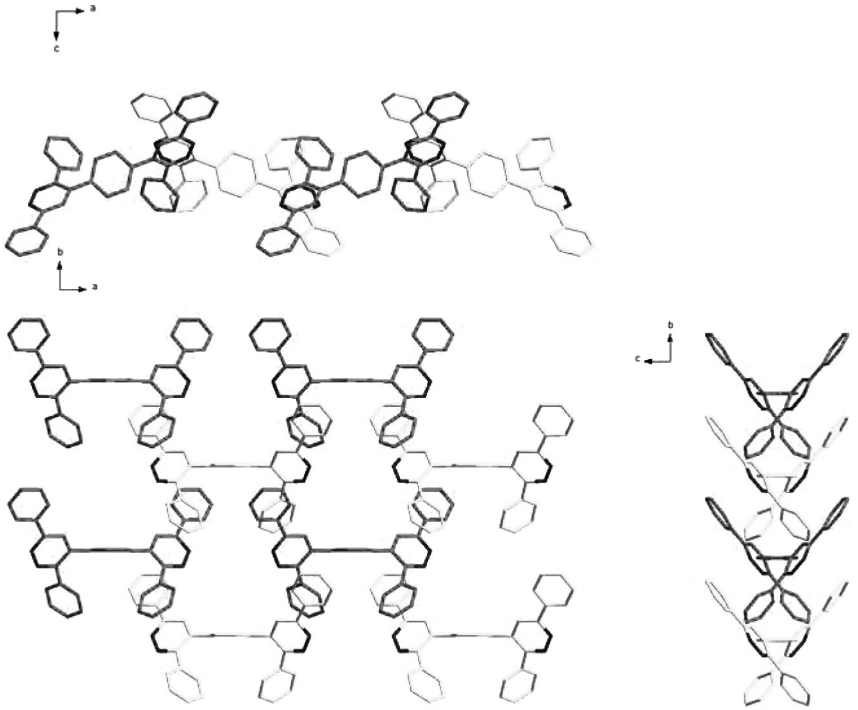

FIGURE 3 2-D representation of the crystal cell viewing down the *a*-axis, *b*-axis and *c*-axis exhibit the molecular packing solvent molecules have been omitted for clarity. (See COLOR PLATE XVIII)

rings separated by a face to face orientation with other unit and the distance between the rings is 4.9 Å. Furthermore, the 3,6-diphenylpyridazine forms a pseudo-zigzag chain along the *b*-axis. Overall, each H-shape unit is connected with four other units through eight identical offset π-π interactions, forming an unusually compact, ordered, and stable molecular solid. Figure 3 shows a 2D representation of the crystal cell.

The 1-D chains along *a*-axis are propagating in the *b* directions. The strand running along the *b*-axis exhibits separation of benzene in every unit and the distance between the centroids of interplanar benzene is 12.3 Å. This layer-like arrangement creates void spaces that are made hydrophilic by the surrounding pyridazines. The overall result is π-stacked strands with hydrophilic channels along the *c*-axis, wherein the intra-channel water and solvent are located. Figure 4 is the space-filling diagram along *c*-axis.

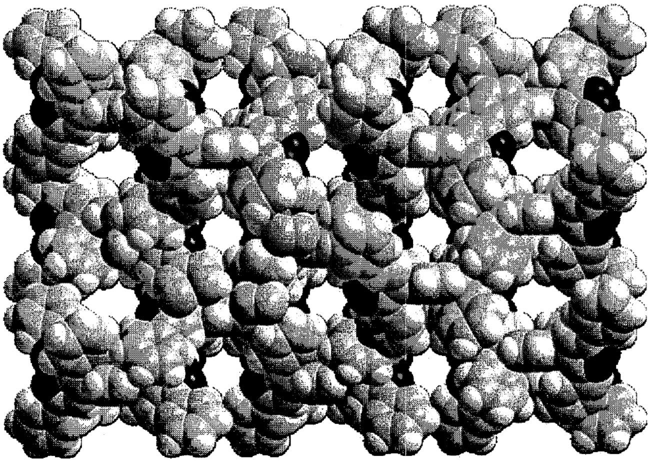

FIGURE 4 Space-filling diagram along *c*-axis, solvent molecules have been omitted for clarity.

CONCLUSION

This study has shown an organic microporous material formed by intermolecular π-stacking interactions between 1,4-bis (3,6-diphenyl-pyridazin-4-yl) benzene. Such new porous material may prove highly interesting in host-guest applications since the intra-channel interactions are much different and distinct from the forces holding the channel framework together.

REFERENCES

[1] Batten, S. R. & Robson R. (1998). *Angew. Chem. Int. Ed.*, *37*, 1460.
[2] Blake, A. J., Champness, N. R., Hubberstey, P., Li, W. S., Withersby, M. A., & Schrtder, M. (1999). *Coord. Chem. Rev.*, *183*, 117.
[3] Kitagawa, S. & Kawata, S. (2002). *Coord. Chem. Rev.*, *224*, 11.
[4] Yaghi, O. M., O'Keeffe, M., Ockwig, N. W., Chae, H. K., Eddaoudi, M., & Kim, J. (2003). *Nature*, *423*, 705.
[5] Moulton, B. & Zaworotko, M. J. (2001). *Chem. Rev.*, *101*, 1629.
[6] Li, H., Laine, A., O'Keeffe, M., & Yaghi, O. M. (1999). *Science*, *283*, 1145.
[7] Zhou, Y., Zhu, H., Chen, Z., Chen, M., Xu, Y., Zhang, H., & Zhao, D. (2001). *Angew. Chem. Int. Ed.*, *40*, 2166.
[8] Seki, K. (2001). *Chem. Commun.*, 1496.
[9] Chui, S. Y., Lo, S. M. F., Charmant, J. P. H., Orpen, A. G., & Williams, I. D. (1999). *Science*, *283*, 1148.
[10] Lai, S. F., Cheng, C.Y., & Lin, K. J. (2001). *Chem. Commun.*, 1082.

[11] Geldard, J. F. & Francis, L. (1965). *J. Org. Chem.*, *30*, 318.

[12] CCDC 284419 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.)_44_1223/336–033; E-mail: deposit@ccdc.cam.ac.uk].