ORGANIC LETTERS

2002
Vol. 4, No. 6
921−924

Topological Equivalences between Organic and Coordination Polymer Crystal Structures: An Organic Ladder Formed with Three-Connected Molecular and Supramolecular Synthons

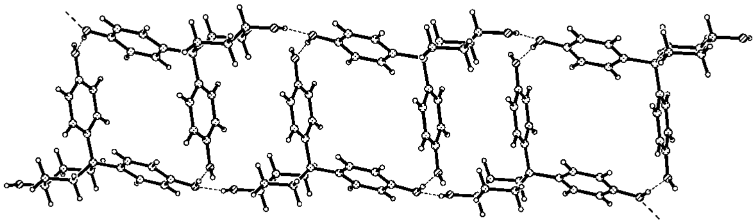
Srinivasulu Aitipamula,[†] Praveen K. Thallapally,[†] Ram Thaimattam,[‡] Mariusz Jaskólski,*[,‡,§] and Gautam R. Desiraju*[,†]

School of Chemistry, University of Hyderabad, Hyderabad 500 046, India, and Center for Biocrystallographic Research, IBCh, Polish Academy of Sciences and Department of Crystallography, Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland

desiraju@uohyd.ernet.in

Received December 21, 2001

ABSTRACT



Crystal engineering of an organic ladder can be achieved with a T-shaped molecule, 4,4-bis(4′-hydroxyphenyl)-1-cyclohexanol, having three hydroxyl functionalities that can form O–H···O hydrogen-bonded helices. The topology of this network structure finds a parallel in three-connected coordination polymers.

From a crystal engineering viewpoint, organic molecular crystals[1−3] and coordination polymers[4−10] are generally considered independently. The structures of coordination polymers follow from the coordination preferences of the metal ion and from the ligand connectivity, and the design exercise is modular. In the packing of “pure” organics, however, most of the interactions are comparable and the crystal structures are more prone to change with small changes in the molecular structure. Yet, at a basic level, all crystal structures are formed in the same way. The need to fill space economically and the tradeoff between close packing and interaction directionality are universal. Therefore it may be useful to draw parallels between crystal structures of organic compounds and coordination polymers. These parallels are necessarily topological in nature and bring out the similarity between organic crystals and coordination polymers in terms of their network structures.

Any organic crystal structure can be treated as a network, and such a depiction facilitates supramolecular retrosynthe-

---

[†] University of Hyderabad.

[‡] A. Mickiewicz University.

[§] Center for Biocrystallographic Research.

(1) Kitaigorodskii, A. I. *Molecular Crystals and Molecules*; Academic Press: New York, 1973; pp 67−71.

(2) Schmidt, G. M. J. *Pure Appl. Chem.* **1971**, *27*, 647.

(3) Desiraju, G. R. *Crystal Engineering*: *The Design of Organic Solids*; Elsevier: Amsterdam, 1989.

(4) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629.

(5) Sharma, C. V. K.; Swenson, J. A.; Rogers, R. D. The Design of Two-Dimensional Polymeric Networks. In *Proceedings of the Symposium on Crystal Engineering*: Rogers, R. D., Zaworotko, M. J., Eds.; *ACA Trans.* **1998**, *33*, 59.

(6) Robson, R. *J. Chem. Soc., Dalton Trans.* **2000**, 3735.

(7) Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474.

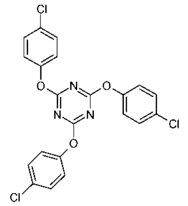
(8) Fujita, M.; Kwon, Y. J.; Sasaki, O.; Yamaguchi, K.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 7287.

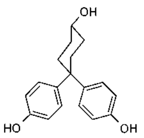
(9) Carlucci, L.; Ciani, G.; Proserpio, D. M. *Dalton Trans.* **1999**, 1799.

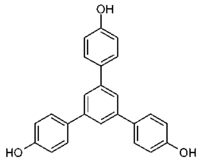
(10) Batten, S. R. *Curr. Opin. Solid State Mater. Sci.* **2001**, *5*, 107.

10.1021/ol017284s CCC: $22.00

sis.[11] The molecules may be conveniently defined as nodes and the supramolecular synthons that connect molecules as node connectors in such a network. Accordingly, the open cage structure of adamantane-1,3,5,7-tetracarboxylic acid may be likened to the diamond network,[12] that of 1,3,5,7-tetrahydroxyadamantane to the 8-connected CsCl,[13] and the structure of 4-(carboxamido)-1-cubanecarboxylic acid to the rare 4-connected NbO network, which also finds a parallel among coordination polymers.[14] Alternatively, and equally conveniently, both molecular and supramolecular synthons may be defined as nodes with the node connections being reduced to mere abstractions. In this sense, the host framework of tris(4-chlorophenoxy)-1,3,5-triazine, **1**, may be described as an alternation of 3-fold symmetrical molecular and supramolecular synthons (Figure 1a).[15] The molecular component is the triazine itself, whereas the supramolecular component is the Cl_3 trimer synthon, **IV**. This is an example of a 3-connected honeycomb network.


1


2


3

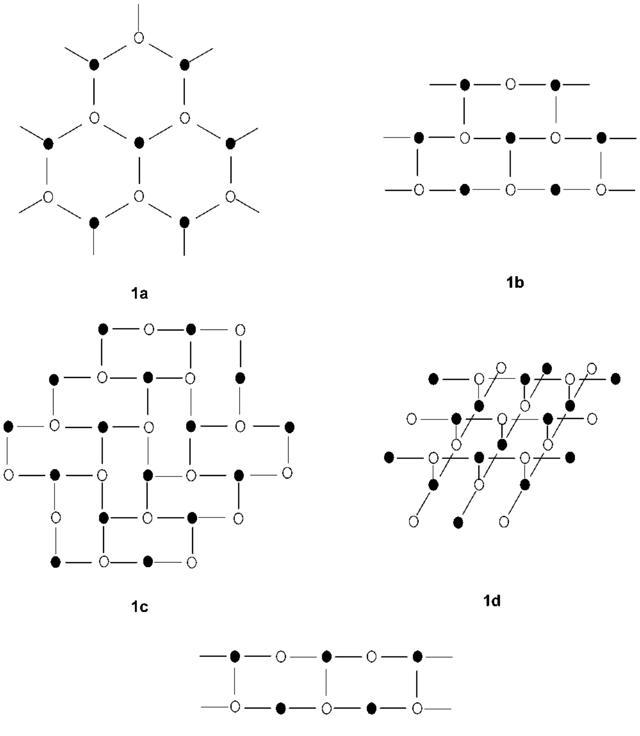
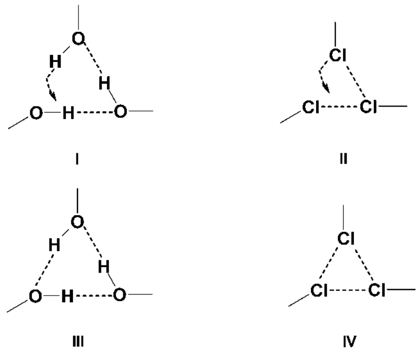

1a
1b
1c
1d
1e

Figure 1. Some typical three-connected networks. Filled and open circles refer to molecular and supramolecular synthons: (a) honeycomb; (b) brick wall; (c) parquet floor; (d) bilayer; (e) ladder. Networks (a) and (e) have organic counterparts that are described, respectively, in ref 15 and in the present work.

Figure 1 shows other possible 3-connected networks. These networks have been recognized many times over in the coordination polymer literature, with the metal atoms acting as the nodes of the network and the ligands acting as the node connections.[16] Topologically equivalent to the honeycomb are the 2-D brick wall (1b) and parquet floor (1c). The 2-D brick wall bilayer (1d) is topologically distinct, as is the 1-D ladder (1e). With this background, the crystal structure of triazine **1** was used as a starting point in the present study. Noting that the hydroxy and chloro groups form similar trimeric synthons of both open helical (**I** and **II**) and closed ring (**III** and **IV**) types (Scheme 1) and also that several supramolecular similarities have been found between these two substituent groups,[17] we have begun a systematic investigation of the crystal packing of trihydroxy

Scheme 1. Open Helix (I and II) and Closed Ring (III and IV) Synthons of the $(OH)_3$ and Cl_3 Type



---

(11) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311.

(12) Ermer, O. *J. Am. Chem. Soc.* **1988**, *110*, 3747.

(13) Reddy, D. S.; Craig, D. C.; Desiraju, G. R. *J. Chem. Soc., Chem. Commun.* **1995**, 339.

(14) (a) Kuduva, S. S.; Craig, D. C.; Nangia. A.; Desiraju, G. R. *J. Am. Chem. Soc.* **1999**, *121*, 1936. (b) Power, K. N.; Hennigar, T. L. Zaworotko, M. J. *Chem. Commun.* **1998**, 595.

(15) Jetti, R. K. R.; Thallapally, P. K.; Xue, F.; Mak, T. C. W.; Nangia, A. *Tetrahedron* **2000**, *56*, 6707.

(16) (a) Zaworotko, M. J. *Chem. Commun.* **2001**, 1. (b) Fujita, M.; Sasaki, O.; Watanabe, K.; Ogura, K.; Yamaguchi, K. *New J. Chem.* **1998**, 189. (c) Dong, Y. B.; Smith, M. D.; Layland, R. C.; Zur Loye, H. C. *Chem. Mater.* **2000**, *12*, 1156. (d) Kondo, M.; Yoshitomi, T.; Seki, K.; Matsuzaka, H.; Kitagawa, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1725. (e) Withersby, M. A.; Blake, A. J.; Champness, N. R.; Cooke, P. A.; Hubberstey, P.; Schröder, M. *New J. Chem.* **1999**, 573.

(17) Robinson, J. M. A.; Kariuki, B. M.; Harris, K. D. M.; Philp, D. *J. Chem. Soc., Perkin Trans. 2* **1998**, 2459.

(18) Bishop, R. *Chem. Soc. Rev.* **1996**, 311.

(19) Caira, M. R.; Horne, A.; Nassimbeni, L. R.; Toda, F. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1717.

(20) Bilton, C.; Howard, J. A. K.; Madhavi, N. N. L.; Nangia, A.; Desiraju, G. R.; Allen, F. H.; Wilson, C. C. *Chem. Commun.* **1999**, 1675.

(21) Allen, F. H.; Kennard, O. *Chem. Des. Autom. News*, **1993**, *8*, 1.

(22) Kolasa, T.; Gunn, D. E.; Bhatia, P.; Basha, A.; Craig, R. A.; Stewart, A. O.; Bouska, J. B.; Harris, R. R.; Hulkower, K. I.; Malo, P. E.; Bell, R. L.; Carter, G. W.; Brooks, C. D. *J. Med. Chem.* **2000**, *43*, 3322.

(23) Crystal data of **2**: $C_{18}H_{20}O_3$, MW = 284.34, triclinic, space group $P\bar{1}$, $a = 6.3490(13)$, $b = 11.310(2)$, $c = 11.464(2)$ Å, $\alpha = 68.38(3)°$, $\beta = 81.51(3)°$, $\gamma = 88.70(3)°$, $V = 756.4(3)$ Å^3, Z = 2, $D_c = 1.248$ g cm^{-3}, $T = 100$ K, F(000) = 304, $\lambda = 0.71073$ Å, $\mu = 0.084$ mm^{-1}, R1 = 0.0439 for 2674 $F_o > 4\sigma(F_o)$. All hydrogen atoms were refined isotropically using SHELXL-97. The data were collected using a KUMA CCD detector and graphite-monochromated Mo Kα radiation. The data set consisted of 7838 observations, which were reduced to 3840 unique data.

compounds. The main idea here is that trigonal or tripod shaped molecules decorated with (three) hydroxy groups at the extremities can, in principle, form network structures of the type shown in Figure 1 with an alternation of molecular (the molecule itself) and supramolecular (**I** or **III**) synthons. At the outset, we recognized that while synthons **I** and **III** are common enough in the literature,[18−20] (476 and 11 hits in the CSD[21] among a total of 4501 non-carboxylic acid and non-carbohydrate compounds that contain a C−OH fragment), there are no examples known at present where a trihydroxy compound adopts an extended 3-connected network mediated by $(OH)_3$ synthons as indicated in Figure 1. Structures of this type would therefore need to be specifically designed.

The targeted molecule, 4,4-bis(4′-hydroxyphenyl)-1-cyclohexanol, **2**, was prepared by literature procedures,[22] and its crystal structure was determined.[23] Figure 2 shows the individual molecule. The cyclohexane ring has the chair conformation, and the hydroxy substituent is equatorial. The geometry at the 4-position is tetrahedral. All of these features confer a T-shape to the molecule. Figure 3 shows the crystal structure of triol **2**. The ladder structure and alternation of molecular and supramolecular synthons are easily recognized. There are three distinct O−H···O hydrogen bonds in the trimer synthon **I** (D (Å), d (Å), θ (deg): O(phenol)−H···O(alcohol) 2.60, 1.62, 171; O(phenol)−H···O(phenol) 2.64, 1.67, 171; O(alcohol)−H···O(phenol) 2.74, 1.78, 163) and their metrics are in accord with the donor and acceptor capabilities of the phenolic and alcoholic OH groups in the molecule. The donor and acceptor capabilities of all hydroxy groups are fully satisfied in this structure. The rungs of the ladder are located at two different separations corresponding to the sizes of the phenyl and cyclohexyl spacers along [010], which is the ladder length. The ladders are hydrogen-bonded in an infinite homodromic chain so that the helical structure runs down [100]. The three branches of the molecular "T" are not all the same, and it is interesting to note that the rungs of the ladder are formed with axial phenyl groups while the sides of the ladder are formed with equatorial phenyl and cyclohexyl groups. The reason for this, almost surely, is the phenyl−phenyl interactions between the more proximal phenyl rungs. Figure 4 is a stereoview that shows this interaction. The perpendicular distance between phenyl residues is as small as 3.20 Å. At such a separation, the lateral overlap between rings is necessarily minimal and the interaction is probably of the electrostatic type.

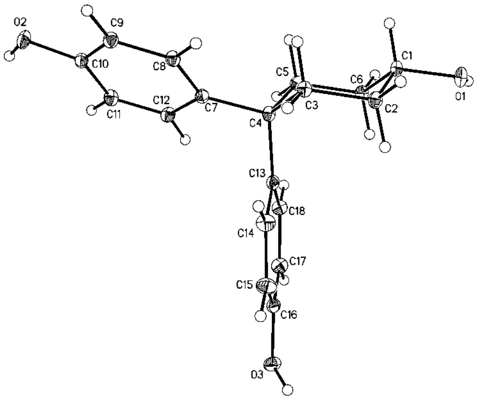


Figure 2. ORTEP diagram of the single molecule of triol **2**.

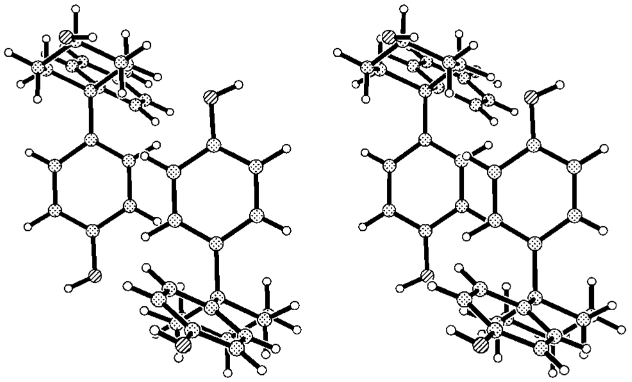


Figure 4. Stereoview of interacting equatorial phenyl rings in the proximal rungs of the ladder in triol **2.** The very short perpendicular distance of 3.20 Å between the rings is compensated for by a large centroid−centroid separation of 5.77 Å.

Rigidity of the selected molecule seems to be important in the design of such a ladder network structure. We have

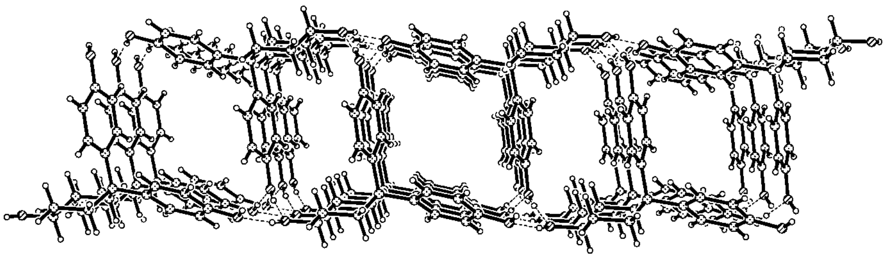


Figure 3. Ladder formation in the crystal structure of triol **2**. The length of the ladder is along [010], and the hydrogen bonded helices run down [100]. Notice the irregular spacing of the rungs.

found recently that conformational flexibility in 1,3,5-tris-(4-hydroxyphenyl)benzene, **3**, results in an unusually compact structure with five O−H···O interactions in a finite cooperative hydrogen bonded chain, accompanied by close packing of the phenyl residues.[24] The molecular shape in the crystal is not easily predicted for a very flexible molecule like **3**, thereby making crystal engineering difficult. In contrast, it is possible to assume that the rigid triol **2** will maintain its T-shape in the crystal thereby leading to the ladder architecture. At the present time, it is not possible to predict why the ladder structure is preferred to the brick wall, parquet floor, and other alternatives. Examination of related derivatives with different spacer groups and substituents is expected to lead to some of these alternative networks.

In summary, a comparison of organic and coordination polymer structures in terms of networks is likely to lead to new and interesting crystal structures for the former, opening up new strategies for crystal engineering.[25,26]

Acknowledgment. G.R.D. and M.J. thank the DST-KBN for a collaborative grant (INT/POL/008/00). S.A. and P.K.T. thank the CSIR, New Delhi for the award of a JRF and SRF, respectively. The research of M.J.was partially supported by the HHMI. G.R.D. acknowledges financial support from CSIR project 01(1570)/99/EMR-II.

Supporting Information Available: X-ray data and details of refinement procedure for triol **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

OL017284S

---

(24) Thallapally, P. K.; Katz, A.; Carrell, H. L.; Desiraju, G. R. *Chem. Comm.* **2002**, 344.

(25) An entirely different strategy for the construction of an organic ladder has been recently described. See: Nguyen, V. T.; Ahn, P. D.; Bishop, R.; Scudder, M. L.; Craig, D. C. *Eur. J. Org. Chem.* **2001**, 4489.

(26) Organic brick walls have been constructed with *C*-methylcalix[4]-resorcinarene and 4,4′-bipyridine spacers wherein the T-shaped modules are in themselves supramolecular. See: Zhang, Y.; Kim, C. D.; Coppens, P. *Chem. Comm.* **2000**, 2299. MacGillivray, L. R.; Reid, J. L.; Ripmeester, J. A. *Chem. Comm.* **2001**, 1034.