Letter

Supramolecular synthesis of brick wall and honeycomb networks from the T-shaped molecule 5-nitrosalicylic acid

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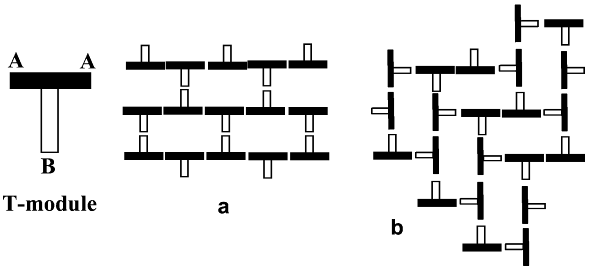
Received (in Montpellier, France) 25th September 2002, Accepted 23rd November 2002
First published as an Advance Article on the web 17th December 2002

The T-geometry of O–H···O and C–H···O hydrogen bonding groups in the title molecule (5-NSA) form a brick wall network that is modularly expanded and transformed to chair cyclohexane and honeycomb architectures in molecular complexes with *trans*-1,4-dithiane-1,4-dioxide and dioxane. The variation in hydrogen bond synthons results in different examples of topologically related (6,3) nets.

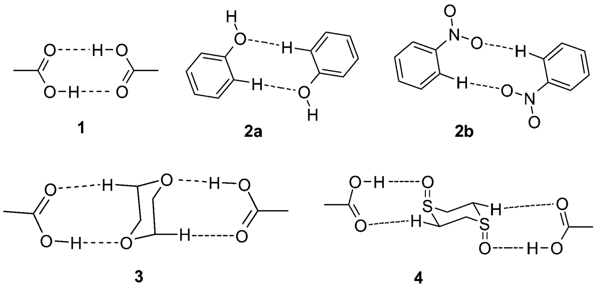
The self-assembly of ladder, brick wall, bilayer, herringbone and honeycomb networks starting from functionalised molecular scaffolds and combinations of metals and bidentate ligands has attracted considerable attention in supramolecular chemistry.[1] The design of such three-connected networks may be traced to T-shaped scaffolds in the retrosynthetic direction (Scheme 1).[2] These diverse architectures exhibit interesting structural variations (*e.g.* interpenetration,[3] guest inclusion, isomerism) and also useful properties (such as porosity, magnetism, nonlinear optics[4]). Two-dimensional brick wall and herringbone networks are topologically identical to the honeycomb grid because they are (6,3) nets.[5] Self-assembly of molecular brick wall and honeycomb structures is controlled by the partial charge of guests in a Ni(II) complex.[6] Honeycomb architectures built from C_3 symmetric precursors, *e.g.* trisubstituted benzene, triazine and cyclohexane scaffolds, are popular targets in organic structures,[7] but they seldom occur in coordination polymer networks.[1b,6] On the other hand, ladder, brick wall, bilayer and herringbone networks are relatively common in metal–organic or coordination polymer structures,[1,8] but there are very few organic examples of these architectures.[9] From this background, we initiated the present study on the construction and modular control of ladder, brick wall and herringbone networks using organic tectons.[10] Some of the factors that should be considered in the crystal engineering[11] of organic networks with T-modules are: (1) a T-geometry at the metal centre is easily achieved in square planar, octahedral and trigonal bipyramidal coordination with appropriate ligands, but it is difficult to design a T-shaped organic molecule given that the standard bond angles at carbon are 109°, 120° or 180°; (2) in coordination polymer networks, the metal atom acts as the node and the ligands serve as the node connectors, whereas in organic networks the molecule is the node and the hydrogen bonds and intermolecular interactions are the node connections; (3) metal–ligand coordination bonds are strong and directional (energy 30–60 kcal mol^{-1}),[1b] whereas hydrogen bonds (O–H···O, N–H···O, C–H···O; energy 2–10 kcal mol^{-1})[12] exhibit moderate directionality in crystals.

5-Methylpyrazine-2-carboxylic acid is a rare example of an organic crystal structure with the herringbone network.[9c] We report in this paper a new T-shaped tecton, 5-nitrosalicylic acid (5-NSA), that exhibits the brick wall pattern. Further, the brick framework transforms to the hexagonal grid in the molecular complex of 5-NSA with *trans*-1,4-dithiane-1,4-dioxide (DTDO)[13] and dioxane. This shows that organic network solids may be engineered and modularly expanded using O–H···O and C–H···O hydrogen-bonded supramolecular synthons (Scheme 2).[14]

5-NSA has three different hydrogen bond groups on its densely functionalised molecular periphery: COOH group as O–H donor and C=O acceptor, (Ph)C–H donor and OH acceptor, (Ph)C–H donor and (nitro)O acceptor (Fig. 1a). In the crystal structure of 5-NSA ($P\bar{1}$, Fig. 2), the COOH group forms the expected dimer synthon **1** with an O–H···O hydrogen bond (d, θ: 1.70 Å, 178.7°). The other two node connections of the T-molecule extend *via* C–H···O dimers **2a** and **2b** involving activated C–H donors and phenol and nitro O acceptors (2.36 Å, 174.1°; 2.45 Å, 137.2°). The OH group is intramolecularly hydrogen bonded to the COOH (1.75 Å, 147.3°). If the T-module is viewed as having two A and one B type hydrogen bond sites (Scheme 1), then recognition *via* one A···A and



Scheme 1 T-module for the self-assembly of brick wall (a) and herringbone (b) networks.



Scheme 2 Carboxylic acid dimer **1** in 5-NSA, synthons **3** and **4** in molecular complexes with dioxane and DTDO.

DOI: 10.1039/b209350b

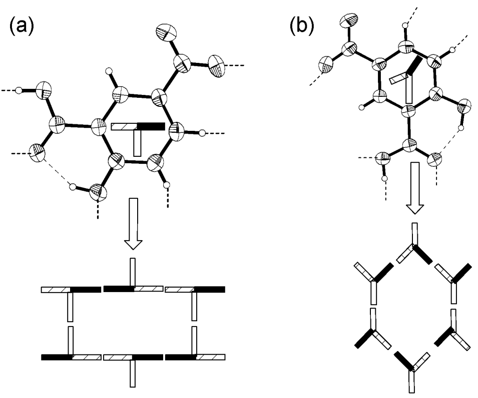


Fig. 1 (a) T-shaped molecule 5-NSA with O–H···O (left), C–H···O (right) and C–H···O (down) hydrogen bond groups in the three directions; (b) Y-geometry of 5-NSA in the dioxane complex.

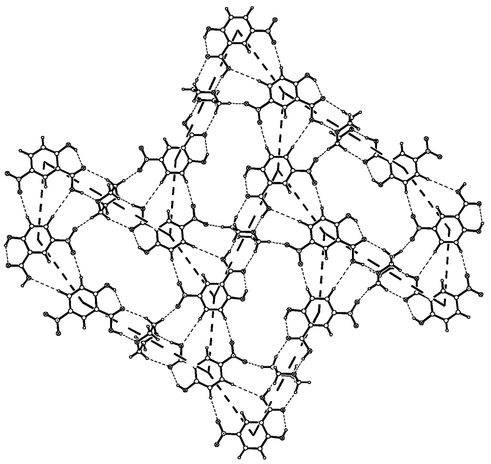


Fig. 3 Crystal structure of (5-NSA)$_2$·dioxane showing the linearly expanded synthon **3** and C–H···O interactions with nitro and carboxyl O atoms in the other two directions with *c*-glide related molecules. Note the pseudo honeycomb network of long dash lines.

two A···B interactions results in the herringbone network;[9c] alternatively, two A···A and one B···B interactions lead to the brick wall architecture (this paper). To our knowledge 5-NSA is the first example of a T-shaped organic *molecule* with the brick wall pattern. In *C*-methylcalix[4]resorcinarene and 4,4′-bipyridine hydrogen-bonded complexes,[9a,b] the T-modules are supramolecular in nature. While brick frameworks are also obtained in guanidinium–sulfonate lamellar architectures,[15] these structures are not built from T-shaped building blocks.

The next task was to expand the network in a modular fashion using the robust and reliable recognition of carboxylic acid with spacer ligands, *e.g.* 4,4′-bipyridine, phenazine, pyrazine, 2-pyridone, and the recently reported DTDO.[13] Crystallisation of 5-NSA with 4,4′-bipyridine gave salt precipitation; no binary crystals were obtained with phenazine and pyrazine because of a solubility mismatch. Cognisant of the ability of dioxane to form solvates with carboxylic acids *via* synthon **3**,[16] 5-NSA was crystallised from dioxane to extend the dimer synthon **1**. In the crystal structure of (5-NSA)$_2$·dioxane ($P2_1/c$, Fig. 3). The expected synthon **3**, acid–dioxane–acid (O–H···O: 1.64 Å, 168.6°), fortified by a (dioxane)C–H···O(carbonyl) hydrogen bond (2.74 Å, 127.7°), aggregates molecules in the crystal. Hydrogen bond synthons in the other two directions are: C3 and C4 H atoms of the 5-NSA hydrogen bond to the nitro and carboxyl O acceptors of a *c*-glide related molecule, and further this molecule accepts C–H···O bonds from a neighbouring molecule (2.26 Å, 162.4°; 3.07 Å, 176.3°). To complete the structure, a C–H···O hydrogen bond connects dioxane and nitro oxygen (2.43 Å, 128.1°), and 5-NSA has an intramolecular O–H···O bond (1.78 Å, 143.1°). In effect, the T-shaped molecular node in the parent crystal structure adopts a Y-geometry because the same donor and acceptor groups of 5-NSA now engage in different hydrogen bond motifs (Fig. 1b).† The honeycomb network in 5-NSA·dioxane dioxane is a common pattern in organic crystals.[7]

DTDO is a new spacer ligand for the crystal engineering of carboxylic acids.[13] The crystal structure of (5-NSA)$_2$·DTDO‡ ($P2_1/c$, Fig. 4) is stabilised by synthon **4** and exhibits a supramolecular chair cyclohexane topology. Because of the involvement of different donor/acceptor groups in the weaker C–H···O hydrogen bonds the node has an approximate T-geometry and the structure is a polycyclohexane network. The metrics of O–H···O and C–H···O hydrogen bonds are listed in the caption of Fig. 4. Supramolecular chair cyclohexane has been assembled with C–H···π interactions in organic structures,[17] and from a T-module in coordination polymers.[18] A comparison of Figs. 2, 3 and 4 shows how supramolecular synthons control network architecture in these structures. In a perfectly modular strategy, the brick framework of 5-NSA would have expanded to a larger brick wall through synthon **3** (or **4**) with **2a** and **2b** completing the structure. The fact that such a high fidelity in crystal design is not achieved could be because of the subtle influence of molecular

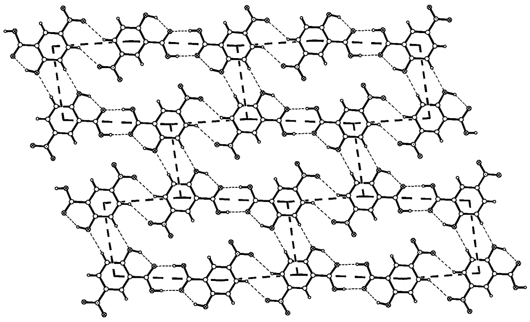


Fig. 2 Crystal structure of 5-NSA mediated *via* synthons **1** and **2**. Note the self-assembly of the T-module *via* like recognition (A···A, B···B) to produce the brick wall architecture. Short dash lines represent H-bonds and long bold dash lines highlight the network pattern in this and subsequent figures.

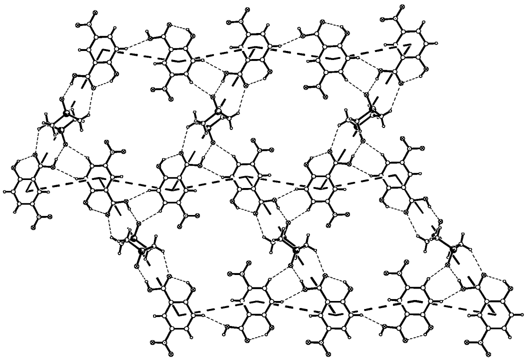


Fig. 4 Crystal structure of (5-NSA)$_2$·DTDO depicted as a chair polycyclohexane network. O–H···O: 1.58 Å, 169.7°; C–H···O: 2.97 Å, 125.6°; 2.46 Å, 154.8°. See ref. 13 for details.

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† The Y-geometry is assigned in such a way that the long node connection (synthon **3**) represents the stem and the short connections (C–H···O interactions) are the two arms.

‡ (5-NSA)$_2$·DTDO: $P2_1/c$, $a = 6.5864(13)$, $b = 23.353(5)$, $c = 7.0345(14)$ Å, $\beta = 96.07(3)°$, $V = 1075.9(4)$ Å^3 (ref. 13).

components, strong hydrogen bonds and weak interactions on the final crystal structure in organic systems.

To summarise, we report in this paper a novel T-tecton 5-NSA for the self-assembly of brick wall and hexagonal nets. This study also highlights the complementary role of strong and weak hydrogen bond synthons (*e.g.* **1** and **2**) in crystal engineering of organic solids. The strong O–H···O carboxylic acid dimer **1** transforms to linearly extended motifs **3** and **4** in complexes with dioxane and DTDO. The weak C–H···O interactions change from structure to structure, resulting in variation from brick wall to hexagonal networks. We illustrate three tiling patterns of (6,3) nets starting from the same molecular node.

Wells[5] has described crystal structures as periodic networks in the context of inorganic compounds. The diversity of network solids has been explored for a large number of coordination polymers.[1,8] The present study shows that diverse hydrogen bond networks may be accessed from simple building blocks through binary crystallisation. Further work on 2D and 3D organic networks[19] is ongoing in our laboratory.

Experimental

Crystallisation

5-Nitrosalicylic acid was purchased from Lancaster. The compound was dissolved in hot ethanol. Pale yellow, X-ray quality crystals of 5-NSA were obtained after 4 days. Yellow coloured crystals of $(\text{5-NSA})_2$·dioxane were obtained upon recrystallisation from 1,4-dioxane at ambient temperature. A mixture of 3,5-dinitrosalicylic acid hydrate (61.5 mg, 0.25 mmol) and 1,4-dithiane (15 mg, 0.125 mmol) were dissolved in 5 mL of hot 1,4-dioxane with the idea of obtaining (dinitrosalicylic acid)·dithiane cocrystals. But the X-ray diffraction showed these crystals to have the composition $(\text{5-NSA})_2$·DTDO. Dithiane is oxidized to DTDO *in situ* and crystallises with 5-NSA, present as an impurity in dinitrosalicylic acid.

Crystal data

For both structures, O–H hydrogens were refined from difference Fourier maps, C–H hydrogens fixed at idealised geometry, and all hydrogens treated isotropically as riding groups. Structure solution and refinement with SHELX-97.[20]

CCDC reference numbers 198782 and 198783. See http://www.rsc.org/suppdata/nj/b2/b209350b/ for crystallographic data in CIF or other electronic format.

5-NSA. $C_7H_5NO_5$, $M = 183.12$, triclinic, space group $P\bar{1}$, $a = 5.2010(7)$, $b = 8.8753(13)$, $c = 9.2841(13)$ Å, $\alpha = 62.449(2)$, $\beta = 75.388(2)$, $\gamma = 81.657(3)°$, $V = 367.47(9)$ Å^3, $Z = 2$, $D_c = 1.655$ g cm^{-3}, $T = 298$ K, $F(000) = 188$, $\lambda = 0.71073$ Å, $\mu = 0.145$ mm^{-1}, $R1 = 0.0583$ for 1565 $Fo > 2\sigma(Fo)$, $R(\text{int})$ $(= wR) = 0.1693$, data collected on Bruker SMART CCD.

$(\text{5-NSA})_2$·dioxane. $(C_7H_5NO_5)\cdot(C_4H_8O_2)_{0.5}$, $M = 227.17$, monoclinic, space group $P2_1/c$, $a = 5.3656(11)$, $b = 22.995(5)$, $c = 7.9984(16)$ Å, $\beta = 90.79(3)°$, $V = 986.8(3)$ Å^3, $Z = 4$, $D_c = 1.529$ g cm^{-3}, $T = 293$ K, $F(000) = 472$, $\lambda = 0.71073$ Å, $\mu = 0.131$ mm^{-1}, $R1 = 0.0343$ for 1359 $Fo > 2\sigma(Fo)$, $R(\text{int})$ $(= wR) = 0.0854$, data collected on Enraf-Nonius MACH-3 diffractometer.

Acknowledgements

AN thanks the DST (SP/S1/G29/98) for financial support and the X-ray diffraction facility at UH. VSSK thanks the CSIR for a fellowship. RB and MTK acknowledge support from the DF (SFB 452).

References

1 (*a*) M. J. Zaworotko, *Chem. Commun.*, 2001, 1; (*b*) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.
2 M. Kondo, M. Shimamura, S. Noro, S. Minakoshi, A. Asami, K. Seki and S. Kitagawa, *Chem. Mater.*, 2000, **12**, 1288.
3 S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1461.
4 O. R. Evans and W. Lin, *Acc. Chem. Res.*, 2002, **35**, 511.
5 A. F. Wells, *Structural Inorganic Chemistry*, 5th edn., Oxford University Press, Oxford, 1984.
6 H. J. Choi and M. P. Suh, *J. Am. Chem. Soc.*, 1998, **120**, 10 622.
7 (*a*) *Comprehensive Supramolecular Chemistry*, vol. 6, eds. D. D. MacNicol, F. Toda and R. Bishop, Pergamon, Oxford, 1996; (*b*) A. Nangia, *Curr. Opin. Solid State Mater. Sci.*, 2001, **5**, 115.
8 For selected examples, see: (*a*) M. Fujita, Y. J. Kwon, O. Sasaki, K. Yamaguchi and K. Ogura, *J. Am. Chem. Soc.*, 1995, **117**, 7287; (*b*) H. Gudbjarston, K. Biradha, K. M. Poirier and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1999, **121**, 2599; (*c*) S. R. Batten, B. F. Hoskins and R. Robson, *Chem. Eur. J.*, 2000, **6**, 156; (*d*) Y. Diskin-Posner, G. K. Patra and I. Goldberg, *Chem. Commun.*, 2002, 1420; (*e*) Z.-Y. Fu, X.-T. Wu, J.-C. Dai, S.-M. Hu and W.-X. Du, *New J. Chem.*, 2002, **26**, 978; (*f*) P. Gamez, P. de Hoog, O. Roubeau, M. Lutz, W. L. Driessen, A. L. Spek and J. Reedijk, *Chem. Commun.*, 2002, 1488.
9 (*a*) Y. Zhang, C. D. Kim and P. Coppens, *Chem. Commun.*, 2000, 2299; (*b*) L. R. MacGillivray, J. L. Reid and J. A. Ripmeester, *Chem. Commun.*, 2001, 1034; (*c*) P. Vishweshwar, A. Nangia and V. M. Lynch, *J. Org. Chem.*, 2002, **67**, 556; (*d*) S. Aitipamula, P. K. Thallapally, R. Thaimattam, M. Jaskólski and G. R. Desiraju, *Org. Lett.*, 2002, **4**, 921.
10 P. Brunet, M. Simard and J. D. Wuest, *J. Am. Chem. Soc.*, 1997, **119**, 2737.
11 G. R. Desiraju, *Crystal Engineering, The Design of Organic Solids*, Elsevier, Amsterdam, 1989.
12 For monographs on hydrogen bonding, see: (*a*) G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, Oxford, 1997; (*b*) G. R. Desiraju and T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press, Oxford, 1999.
13 V. S. S. Kumar, A. Nangia, A. K. Katz and H. L. Carrell, *Cryst. Growth. Des.*, 2002, **2**, 313 and references cited therein.
14 G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311.
15 K. T. Holman, A. M. Pivovar, J. A. Swift and M. D. Ward, *Acc. Chem. Res.*, 2001, **34**, 107.
16 V. S. S. Kumar, S. S. Kuduva and G. R. Desiraju, *J. Chem. Soc., Perkin Trans. 2*, 1999, 1069.
17 (*a*) T. Steiner, M. Tamm, A. Grzegorzewski, N. Schulte, N. Veldman, A. M. M. Schreurs, J. A. Kanters, J. Kroon, J. van der Maas and B. Lutz, *J. Chem. Soc., Perkin Trans. 2*, 1996, 2441; (*b*) K. Biradha and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1998, **120**, 6431.
18 Y.-B. Dong, M. D. Smith, R. C. Layland and H.-C. Loye, *Chem. Mater.*, 2000, **12**, 1156.
19 B. R. Bhogala, P. Vishweshwar and A. Nangia, *Cryst. Growth Des.*, 2002, **2**, 325.
20 G. M. Sheldrick, SHELX-97, Program for the Solution and Refinement of Crystal Structures, University of Göttingen, Germany, 1997.