A supramolecular carpet formed *via* self-assembly of bis(4,4′-dihydroxyphenyl) sulfone†

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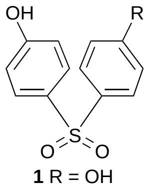
Bis(4,4′-dihydroxyphenyl) sulfone 1 exploits its tetrahedrally disposed complementary hydrogen bonding sites to generate a unique doubly interwoven molecular carpet architecture in the solid state.

The concept of rational design of 2D and 3D frameworks has evoked considerable interest in recent years as many functional properties of solids are dependent on crystal packing.[1,2] A particularly interesting and relevant problem that has been addressed by several groups concerns the preparation of open cage and/or interwoven networks.[3–5] While the former is desired in the context of porous solids, the latter is an associated phenomenon which invariably occurs if $> 50\%$ of a solid would otherwise be empty. Such interpenetration (or catenation) is appreciated for its aesthetic appeal and offers potential host materials if guest molecules can be exploited to prevent interpenetration.[6] Understanding and predicting interpenetration patterns therefore constitutes an important aspect of crystal engineering.

Self-assembly can be an effective strategy for crystal engineering but it requires careful control over molecular symmetry and functionality.[3] In general, tetrahedral molecules with rigid complementary hydrogen bonding sites adapt diamondoid architecture with levels of interpenetration based on the relative size of superdiamondoid cage and the volume of the tecton.[7] We report herein an alternate motif for such compounds which occurs if there is flexibility present in the tecton: interwoven 2D square grids.[8]

A solution of bis(4-chlorophenyl) sulfone (4.0 g) and sodium hydroxide (4.0 g) in Me_2SO (160 ml) and water (40 ml) was maintained at 100 °C for two months. Extractive workup with diethyl ether furnished a mixture of unchanged chloro sulfone, bis(4-hydroxyphenyl) sulfone **1** and 4-chlorophenyl (4′-hydroxyphenyl) sulfone **2**. Chloroform elution on silica gel furnished pure **1** (2%) and **2** (50%).



1 R = OH
2 R = Cl

Non-centrosymmetric crystals of **1** were obtained from acetone–$CHCl_3$ (mp 247–249 °C). The crystal structure‡ reveals an infinite 2D hydrogen bonded network sustained by interaction between hydroxy and sulfone groups (O···O 2.705(7), 2.800(3) Å, Fig. 1). The network generates square cavities with *ca.* 8 × 10 Å dimensions, large enough to facilitate generation of a 2-fold interwoven molecular carpet (Fig. 2). The entangled 2D grids are stabilized by van der Waals and herringbone interactions. A 3D diamondoid architecture is also feasible but presumably packs less efficiently in the absence of an appropriate guest.

The molecular carpet architecture of **1** demonstrates how molecules with flexible hydrogen bonding sites can self-assemble to yield 2D interwoven networks as an alternative to 3D diamondoid architectures. Such networks would be expected to have clay-like intercalation properties and, if appropriate guests can be used to eschew interpenetration, large cavities within the grid.[9] The critical importance of complementarity amongst the hydrogen bonding sites is illustrated by what happens if one hydroxy substituent of **1** is replaced by a chloro substituent. 4-chlorophenyl (4′-hydroxyphenyl) sulfone **2** exhibits a less predictable but nonetheless intriguing crystal structure.§ Compound **2** crystallizes from $CHCl_3$ (mp 150–151 °C) in the non-centrosymmetric space group $P1$ with, remarkably, four molecules in the asymmetric unit. There are two discrete hydrogen bonding motifs: i, simple linear hydrogen bonding between sulfone and hydroxy groups [2.898(6) Å]; ii, cyclic hydrogen bonding involving two of the sulfone O atoms and three hydroxy groups, possibly with two of the hydroxy groups being disordered [Scheme 1, O···O: 2.838(6), 2.881(6),

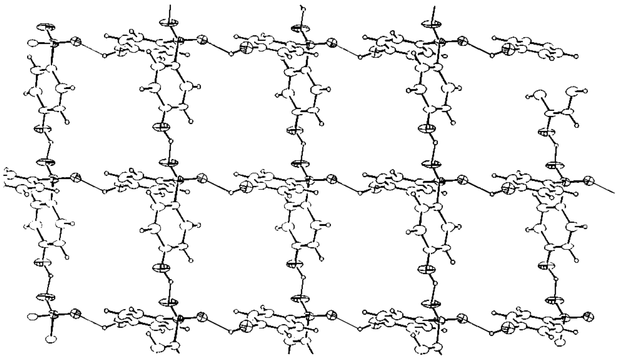


Fig. 1 ORTEP diagram of **1** illustrating a single hydrogen bonded network

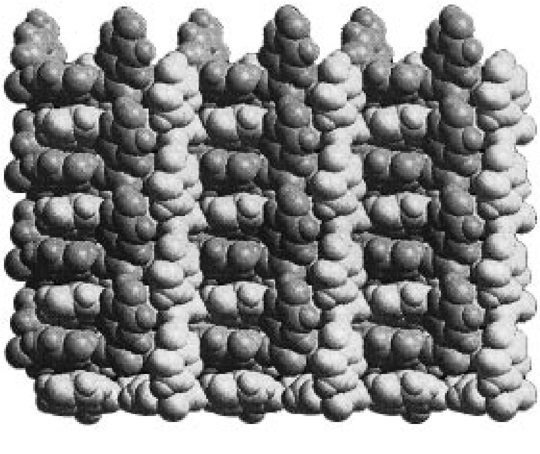
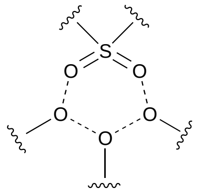


Fig. 2 A space filling diagram of the interwoven supramolecular carpet architecture of **1**. The two independent grids are colour coded for clarity.



Scheme 1

3.019(6), 2.913(6) Å]. Furthermore, there are two different kinds of aryl–aryl stacking interactions: between chlorophenyl and hydroxyphenyl groups and between adjacent chlorophenyl groups. The mean interplanar distances and dihedral angles of these two stacking interactions are 3.74 and 3.60 Å, 2.9 and 3.4° respectively.

Compounds **1** and **2** illustrate clearly the importance of self-assembly to crystal engineering. Compound **1** demonstrates how tetrahedral moieties with complementary hydrogen bonding sites are capable of self-assembling into a predictable 2D motif if the hydrogen bonding sites are robust and flexible. However, **2** demonstrates how even minor changes in functionality can lead to unusual and unpredictable crystal packing.

Footnotes

† This ChemComm is also available in enhanced multi-media format *via* the World Wide Web: http://chemistry.rsc.org/rsc/cccenha.htm

‡ *Crystal Data* for **1**: 4,4′-Dihydroxyphenyl sulfone, $M = 249.26$, orthorhombic, $C2cb$, $a = 8.1572(10)$, $b = 19.2757(21)$, $c = 15.0471(20)$ Å, $V = 2365.9(5)$ Å^3, $Z = 8$, $D_{\mathrm{calc}} = 1.40$ Mg m^{-3}, $\lambda = 0.70930$ Å, $F(000) = 1032.921$ reflections with $I_{\mathrm{net}} > 3\sigma$ (I_{net}) out of 1121 unique reflections measured at 290 K for a crystal of dimensions 0.3 × 0.2 × 0.4 mm on an Enraf-Nonius CAD4 diffractometer using the ω scan mode ($4 < 2\theta < 50°$) afforded, on convergence, final values of $R_{\mathrm{f}} = 0.077$ and $R_{\mathrm{w}} = 0.089$. The H atom of one of the two OH groups was found *via* difference Fourier map inspection. Other H atoms were placed in calculated positions (C–H = 1.0 Å). All non-hydrogen atoms were anisotropically refined. The crystallographic calculations were carried out using NRCVAX program package. Atomic coordinates, bond lengths and angles, and thermal parameters for both **1** and **2** (see below) have been deposited at the Camrbidge Crystallograpic Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/360.

Since submission of this article an account of the structure of **1** has been published. See G. Ferguson and C. Glidewell, *Acta Crystallogr., Sect. C*, 1996, **52**, 2528.

§ *Crystal Data* for **2**: As for **1** but 4-hydroxyphenyl, 4′-chlorophenyl sulfone, $M = 267.96$, triclinic, $P1$, $a = 7.6401(11)$, $b = 9.2850(11)$, $c = 17.6630(13)$ Å, $\alpha = 93.04(2)$, $\beta = 91.51(3)$, $\gamma = 108.64(2)$, $V = 1184.35(24)$ Å^3, $Z = 4$, $D_{\mathrm{calc}} = 1.503$ Mg m^{-3}, $\lambda = 0.70930$ Å, $F(000) = 552$. 3591 reflections with $I_{\mathrm{net}} > 3\sigma$ (I_{net}) out of 4149 unique reflections measured at 290 K for a crystal of dimensions 0.4 × 0.2 × 0.2 mm afforded values of $R_{\mathrm{f}} = 0.042$ and $R_{\mathrm{w}} = 0.047$.

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