A Robust Two-Dimensional Hydrogen-Bonded Network: The Sulfamide Moiety as a New Building Block for the Design of Molecular Solids

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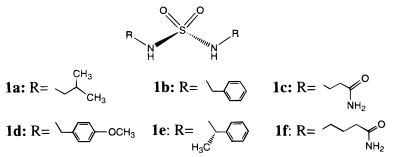
A principal goal of crystal engineering is the ability to manipulate solid-state properties by systematic variations of the molecular structure through alteration of the constituent molecules.[1] Molecular solids with predefined solid-state structures can find many important applications for developing new materials. Current efforts in assembling molecular solids focus mainly on one-dimensional aggregates such as chains, tapes, and columns.[2] Many examples of two-dimensional networks have also been reported.[2h,3] Except for the tetrahedron-centered hydrogen-bonding topology that produces three-dimensional diamondoid networks,[4] little or no control over the assembly in the third dimension has been realized. A recently reported system,[5] based on a 2D network of guanidinium cations and sulfonate anions, offered a very elaborate and advanced example of crystal engineering. Here we report a previously unrecognized 2D structural motif for the design and self-assembly of 3D molecular arrays. This system makes use of the sulfamide functionality of the N,N′-disubstituted sulfamide, as shown by general structure **1**.



Compared to planar H-bonding functionalities such as amide and carboxyl groups that have been extensively used in molecular solid design,[2b,h] the tetrahedral-shaped sulfamide group, surprisingly, has not been employed.[6] For this reason, we have synthesized sulfamides **1a**−**f** and examined their solid-state structures. Compounds **1a**−**f** were prepared by treating the corresponding amines or amino acid esters with sulfuryl chloride.[7] X-ray crystallography (Supporting Information) showed a previously unknown 2D H-bonded network in the crystalline state of all six compounds.[8] As illustrated in Figure 1a, using **1a** as an example, one sulfamide group forms four hydrogen bonds with those of four adjacent molecules. As a result, a rhombic 2D network composed of the sulfamide groups is formed. Despite the significant difference in size and properties of their substituents, these sulfamides assemble in essentially the same way as that shown in Figure 1a. The hydrogen bonds (Table 1) formed by the sulfamide groups of these compounds vary to some extent in their lengths and bond angles. However, all of the S atoms of

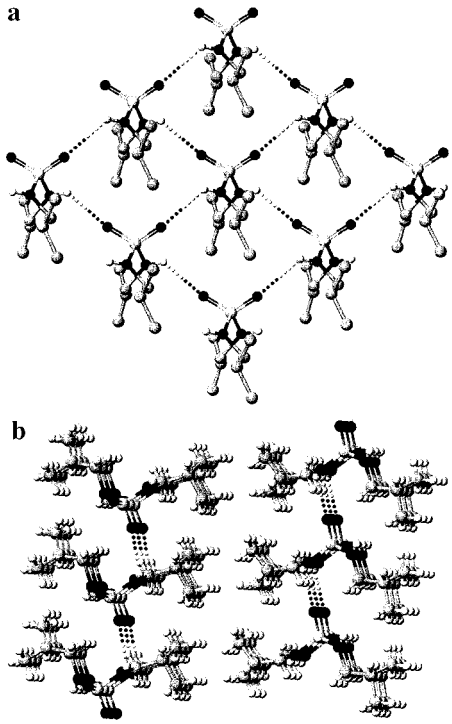


Figure 1. Packing of **1a**. (a) One molecular layer held together by the 2D hydrogen-bonded sulfamide network. The viewing direction is perpendicular to the plane of the 2D network. The isobutyl groups pack above and below the 2D network. All six compounds pack similarly to form layers based on the sulfamide network. (b) Packing of the molecular layers along the third direction. Two layers are shown here. The planes of two 2D sulfamide networks are perpendicular to that of the paper.

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(6) For an example using tertrahedral S atom (sulfone) in solid design, see: Glidewell, C.; Ferguson, G. *Acta Crystallogr.* **1996**, C*52*, 2528.

(7) Typically, the reaction is carried out by dropwise addition of a solution of sulfuryl chloride in chloroform to a solution of the corresponding amine in chloroform at 0 °C. The reaction mixture was warmed to room temperature, stirred for 3−12 h, and washed with acidic and basic aqueous solutions. Evaporation of chloroform results in a pure product. In the case where the product was insoluble in the reaction medium, the pure product was obtained by simple filtration. **1c**,**d** were prepared by reacting sulfuryl chloride with *β*-alanine ethyl ester and *γ*-aminobutyric acid methyl ester, respectively, leading to the corresponding sulfamide dicarboxylic ethyl esters that were then converted into the sulfamide dicarboxamides (**1c**,**d**) by aminolysis (30% NH_3 in water).

(8) (a) A search of the Cambridge Structural Database for structures containing the disubstituted sulfamide substructure yielded only one relevant example. The crystal structure of *N,N′*-di-*tert*-butylsulfamide[8b] shows that the constituent molecules assemble into a hydrogen-bonded, one-dimensional network. (b) Atwood, J. L.; Cowly, A. H.; Hunter, W. E.; Mehrotra, S. K. *Inorg. Chem.* **1982**, *21*, 435.

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Table 1. Selected Structural Parameters for the 2D Hydrogen-Bonded Network Composed of the Sulfamide Group and Thickness of Individual Layers

structure	*d* (S···S) (Å)	*r* (N−H···O) (Å)	*r* (N···O) (Å)	α (N−H···O) (deg)	thickness (Å)
1a	5.281	2.388	2.897	118.3	9.812
		2.545	3.058	119.1	
1b	4.909	2.431	2.939	118.4	13.345
	5.229	2.287	2.881	126.3	
1c	5.153	2.246	2.905	133.4	9.665
1d	4.962	2.436	2.909	115.2	17.367
	5.187	2.284	2.867	125.2	
1e	5.286	2.506	3.073	124.2	13.993
	5.341	2.325	3.038	140.4	
1f	5.139	2.099	2.953	174.4	11.732

the 2D networks lie in the same plane, resulting in the formation of a sheet of sulfamide moieties.

Based on this 2D network and the tetrahedral shape of the sulfamide groups, the sulfamide molecules pack with their long axes parallel to each other and their substituents tilted relative to the plane of the 2D H-bonded network (Figure 1a). This arrangement facilitates the formation of the 2D molecular layers.[9] The 2D layers formed by **1a**,**b**,**d**,**e** assemble in the third dimension in an organized way through van der Waals interaction between terminal groups of the substituents R of adjacent layers. For **1d**, a weak C−H···O interaction between methoxy O and aromatic H atoms is also responsible for interlayer packing in the third dimension. Due to the dense packing of constituent molecules within a layer, penetration (interdigitation) of R groups into the adjacent layer is not observed. Figure 1b shows the layered packing of **1a**. **1b**,**d**,**e** show the same layered packing as that in Figure 1b. Structural variation involving either terminal (**1b** vs **1d**) or middle positions (**1b** vs **1e**, introduction of chiral groups) of substituents does not interfere with assembly of the sulfamide sheets. Chiral **1e**, as expected, crystallizes in the noncentrosymmetric space group P2(1). Achiral **1d**, surprisingly, also packs in this space group. This class of compounds may thus offer a new approach for designing noncentrosymmetric crystals. Varying the thickness of each layer (Table 1), as defined by the length of its constituent molecules, is a way to adjust intersheet distances.

The robustness of the sulfamide sheet is further desmonstrated with **1c**,**f**. The expectation was that the primary amide groups of **1c**,**f** might interrupt the 2D sheets by forming unwanted hydrogen bonds with the sulfamide moiety. Large single crystals of **1c**,**f** were obtained from a water solution by slow evaporation of solvent at 30 °C. X-ray diffraction[10] revealed again the existence of a 2D H-bonded sulfamide sheet in the crystals of **1c**,**f**. Instead of disrupting the 2D H-bonded network, the primary amide groups form eight-membered cyclic dimer hydrogen bonds[11] that assemble the layers in the third dimension.[12] Thus, in **1c**,**f**, a 3D H-bonded network is formed. Figure 2 show the 3D network formed by **1c**. This implies that assembly of analogues of **1c**,**f** is very likely to offer a general strategy for constructing hierarchical, 3D H-bonded structures. This approach should simplify the study of molecular assmbly in the solid state by fixing the first two dimensions and focusing on the last remaining dimension.

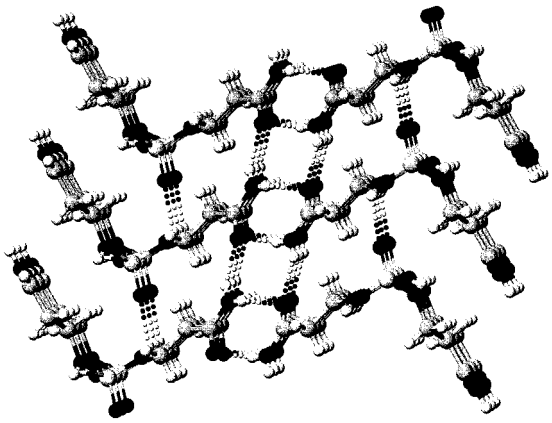

Figure 2. Layered packing of **1c**. A 3D hydrogen-bonded network is observed in the solid-state structure of **1c**, which is based on the 2D sulfamide networks (perpendicular to the plane of the paper) and the 1D hydrogen-bonded network involving the terminal primary amide groups. The packing of **1f** shows the same pattern.

Compared to planar amide and carboxyl groups, the sulfamide moiety introduces features for crystal engineering: (1) Because of its tetrahedral geometry, the sulfamide moiety offers an additional dimension to the H-bonded network. (2) The constituent molecules assemble with their substituents extending above and below the planes of the H-bonded 2D networks. This not only helps the self-assembly of the 2D molecular layers with adjustable thickness but also introduces systematically the ancillary molecular functionality along the third dimension. (3) Since each 2D layer provides two faces of well-ordered terminal groups, stacking of the layers in the third dimension is reinforced by the noncovalent interaction between the individual terminal groups. Such 2D layers may serve as templates for designing solid-state structures with sandwiched guest layers.

We have demonstrated a novel 2D H-bonded network composed of the sulfamide moiety of N,N′-disubstituted sulfamide. The 2D H-bonding motif is retained despite changes in the substituents of the sulfamide molecules. Therefore, formation of molecular layers is tunable by changing the substituents of the sulfamide molecules. Assembly of 2D layers in the third dimension, through either H-bonding or van der Waals interaction, has been achieved. Efforts to designed layered materials based on N,N′-dialkyl- or N,N′-diarylsulfamides and 3D molecular arrays, based on sulfamide dicarboxamides and sulfamide dicarboxylic acids, are being made. N,N′-Disubstituted sulfamides with two different substituents are also being designed and synthesized. These unsymmetrical sulfamides may assemble into molecular layers with two different surfaces. Polar-organized crystals may result from the assembly of these 2D layers. Incorporation of the 2D sulfamide network into self-assembled monolayers should significantly enhance the stability of the monolayers. The corresponding results will be reported later.

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Supporting Information Available: X-ray, atomic, and thermal data for **1a**−**e** (31 pages, print/PDF). X-ray crystallographic data, in CIF format, for **1a**−**e**, are available on the Web only. See any current masthead page for ordering information and Web access instructions.

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(9) The layered structures formed by **1b**,**d**,**e** are to some extent similar to previously reported 2D layered crystal structures of 4,4′-disubstituted *meso*-hydrobenzoin: (a) Pennington, W. T.; Chakraborty, S.; Paul, I. C.; Curtin, D. Y. *J. Am. Chem. Soc.* **1988**, *110*, 6498. (b) Swift, J. A.; Pal, R.; McBride, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 96.

(10) The X-ray data of **1a**−**e** are given in the Supporting Information. The X-ray data of **1f** will be published as a separate paper: Gong, B.; Zheng, C.; Zhang, J. *Acta Cryst*allogr., in press.

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(12) (a) The eight-membered cyclic dimer hydrogen bonds form via the amide *syn*-H atoms. N···O, N−H···O observed: **1c**, 2.963 Å, 169.3°; **1f**, 2.946 Å, 175.4°. (b) The amide *anti*-H atoms form additional hydrogen bonds to amide carbonyl O atoms of the neighboring cyclic hydrogen bond dimers, which links the cyclic dimer hydrogen bonds into a ribbonlike network. N···O, N−H···O observed: **1c**, 2.960 Å, 156.3°; **1f**, 2.981 Å, 152.1°.