

Polar Assembly of *N,N'*-Bis(4-substituted benzyl)sulfamides

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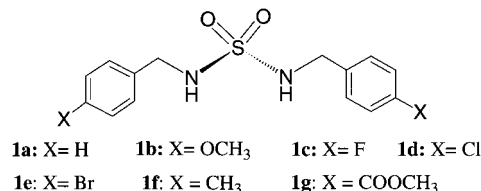
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Presently there is an intense interest in manipulating solid-state properties through systematic alteration of the structures of constituent molecules.¹ Significant progress has been made in the design and synthesis of supramolecular motifs with particular geometric features, i.e., secondary structures. These secondary structures include one-dimensional chains, tapes, and columns² and various two-dimensional (2D) networks.^{2h,3,5} However, little is known about the assembly of these secondary structures into tertiary (or complete) patterns. The only three-dimensional (3D) motifs known are the diamondoid networks formed from the tetrahedron-centered hydrogen-bonding topology.⁴ One area of particular endeavor in crystal engineering is the design of noncentrosymmetric (polar) crystals because of their important physical properties.^{1,9} Currently there is only one foolproof method of forcing a polar space group and that is by choosing a resolved enantiomer. However, the need for synthesizing pure enantiomers often introduces synthetic difficulty that limits the general applicability of the method. Otherwise there are hardly any

existing guidelines for the systematic design of polar organization in solid-state structures.

Recently, we reported a robust 2D hydrogen-bonded sulfamide sheet that leads to the formation of either layered or 3D-networked structures.⁶ Our results clearly established the 2D sulfamide layer as a reliable supramolecular synthon for designing 3D solid-state structures. Here we report a chiral packing motif based on the derivatives of *N,N'*-dibenzylsulfamides, shown as the general structure **1**. The assembly of this class of molecules leads to chiral



2D molecular layers that further assemble into layered 3D polar crystals.

Among the six sulfamides we reported recently,⁶ one compound containing stereocenters packed, as expected, into a noncentrosymmetric space group (*P*₂₁). Interestingly, *N,N'*-bis(4-methoxybenzyl)sulfamide (**1b**), which is achiral, also formed noncentrosymmetric crystals of the space group *P*₂₁. In contrast, the achiral *N,N'*-dibenzylsulfamide (**1a**) crystallized in the centrosymmetric space group *P*₂₁/*c*. Given the very similar molecular structures of **1a** and **1b**, it is obvious that the 4-methoxy group of **1b** is responsible for its noncentrosymmetric packing in the solid state. To probe the generality of forming polar crystals by *N,N'*-bis(4-substituted benzyl)sulfamides, we chose to study the assembly of **1c–g**. This series of compounds offer ease of synthesis and convenience of structural modification. Similar to **1a** and **1b**, these compounds were expected to assemble into 2D layers. Given the robustness of the 2D sulfamide layer,⁶ **1c–f**, with a range of 4-substituents, may provide insight into the assembly of this newly discovered 2D supramolecular synthon.

Compounds **1c–g** were prepared according to the procedure reported by us.⁶ X-ray crystallography⁷ showed that **1c–g** assembled into the 2D layers held by the hydrogen-bonded sulfamide network as described before.⁶ The benzyl groups in each case packed above and below the sulfamide network in the commonly observed herringbone motif.⁸ More interestingly, compounds **1c–g** all packed into the noncentrosymmetric space group *P*₂₁, i.e., their crystal packing was the same as that of **1b**. The crystals examined were therefore all chiral. Since the majority of achiral organic compounds tend to pack into centrosymmetric crystals,^{1,9} this result is very unusual and must represent a rather general phenomenon for this class of compounds.

A closer examination of the crystalline structures of **1a–g** reveals that the sulfamide group consisted of two orthogonally fused, nearly planar *cis*-O=S–N–H units (see the dihedral angle α (*cis*-O=S–N–H) in Table 1). Each such unit was thus similar to a planar *cis* secondary amide group. As a result, the tetrahedral sulfamide group existed in a chiral conformation reminiscent of a substituted spiro[3.3]heptane. Because of the chiral nature of their sulfamide groups, molecules of **1a–g** adopted nearly the same chiral conformation in their solid-state structures. Chiral 2D layers were seen in the crystals of all these compounds. Further stacking of the 2D layers of **1a** and **1b–g** along the third dimension, however, was different. Molecules of **1a** packed into the centrosymmetric space group (*P*₂₁/*c*) due to the stacking of alternating 2D layers consisting of molecules of the opposite chirality (Figure 1a). Molecules of **1b–g**, on the other hand, packed into the noncentrosymmetric space group *P*₂₁ through the stacking of 2D layers consisting of molecules of the same chirality (Figure 1b).

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(7) The crystals were obtained from chloroform by slow cooling from 60 °C in sealed vials. For each compound, at least five single crystals were tested. Under this crystallization condition, only one allotrope was found for each compound. No polymorphism was observed for this series of compounds. The X-ray data of **1c–g** are given in the Supporting Information.

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Table 1. Selected Structural Parameters for **1a–g**

compd	$d(S-S)$ (Å)	$r(N\cdots O)$ (Å)	$r(N\cdots O)$ (Å)	$a(N-H\cdots O)$ (deg)	$a(cis-O=S-N-H)$ (deg)	space group
1a	4.909	2.431	2.939	118.4	0.8	$P2_1/c$
	5.229	2.287	2.881	126.3	3.3	
1b	4.962	2.436	2.909	115.2	0.8	$P2_1$
	5.187	2.284	2.867	125.2	7.2	
1c	4.978	2.353	2.870	119.0	0.5	$P2_1$
	5.183	2.318	2.872	122.4	5.3	
1d	4.910	2.461	2.955	117.2	1.2	$P2_1$
	5.269	2.237	2.862	129.6	3.0	
1e	4.873	2.448	2.950	117.8	1.3	$P2_1$
	5.243	2.229	2.836	127.6	3.4	
1f	5.267	2.233	2.854	129.1	0.9	$P2_1$
	4.927	2.465	2.964	117.7	4.0	
1g	4.985	2.366	2.885	117.9	0.7	$P2_1$
	5.212	2.244	2.872	128.2	6.6	

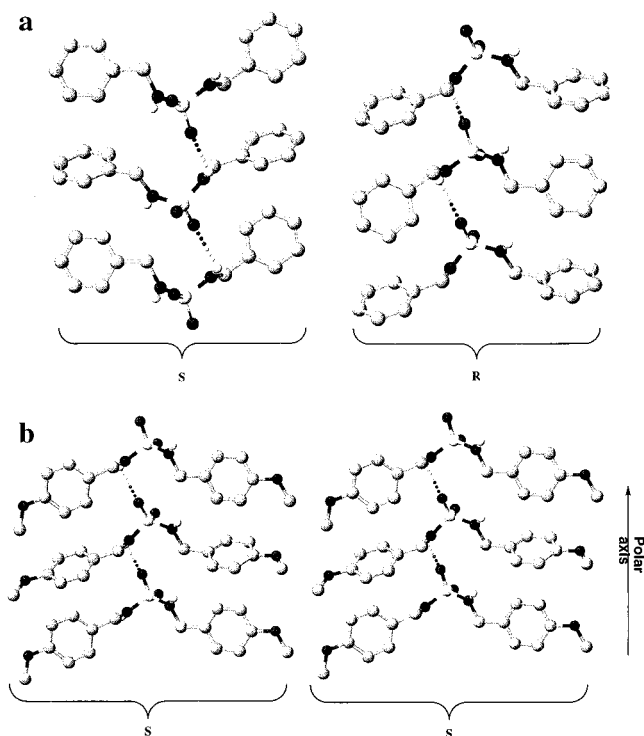


Figure 1. (a) Layered packing of **1a**. Two layers of opposite chirality are shown here. (b) Layered packing of **1b**. Two layers of the same chirality are shown here. The polar direction (arrow) is along the b axis. Compounds **1c–f** show the same packing pattern. Only three molecules are shown for each layer. In the 3D crystals, the molecules in each layer also pack along the direction that is perpendicular to the plane of the paper, i.e., the planes of the 2D sulfamide networks are perpendicular to that of the paper. Hydrogen atoms, except for those of the sulfamide groups, have been omitted for clarity.

Polar single crystals were formed from molecules of the same chirality with dipoles of the sulfamide groups oriented preferentially along one direction of the polar b axis.

Table 1 lists some selected structural parameters and the corresponding space groups for **1a–g**. Given the diversity of the 4-substituents, the above results are very surprising. The polar packing of **1b–g** is to some extent similar to the previously reported layered crystal structures of 4-bromobenzoic anhydride, which was reported to pack in the noncentrosymmetric space group $C2$.¹⁰ However, 4-substituted benzoic anhydrides did not demonstrate the type of generality in forming polar solid-state structures as shown by **1b–g**. For example, 4-chlorobenzoic anhydride was reported to crystallize into the centrosymmetric group $P2_1/c$.^{10a} In fact, our results represent the first example of a homologous series of achiral compounds that undergo spontaneous resolution in the solid state and crystallize into the same noncentrosymmetric group.¹¹

It is not clear what factors are responsible for the polar organization observed in the crystals of these compounds. For example, although it is obvious that interlayer interactions play dominant roles in determining the packing of the 2D layers, it is difficult to imagine how a wide variety of 4-substituents, from the small fluoro (**1c**) to the relatively large methoxy and methoxycarbonyl (**1b** and **1f**) groups, from the isotropically (**1a–f**) to the anisotropically (**1f**) shaped groups, and from electron-donating (**1b**) to electron-withdrawing (**1g**) groups, all act to ensure polar packing in the crystal structures. Nevertheless, given the invariable nature of their packing patterns, this class of compounds has offered an ideal system for both theoretical and experimental inquiries. Based on the 2D layers, theoretical comparison on centrosymmetric and noncentrosymmetric packing patterns should provide insight into the rules governing polar packing of 2D layers along the third dimension. Experimentally, this molecular system for the first time has provided a general platform to the design of structurally polar crystals based on readily available materials and simple chemistry. The resulting polar crystals may lead to materials with a wide range of applications. The lamellar structure shared by all the examined compounds should also provide an unprecedented template for comparing well-ordered functional groups on isomorphous surfaces.^{11b}

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Supporting Information Available: Tables of X-ray data collection/refinement parameters, atomic position parameters, anisotropic displacement parameters, and thermal ellipsoid plots for **1c–g** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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