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Two-Dimensional Molecular Layers: Interplay of H-Bonding and van der Waals Interactions in the Self-Assembly of *N,N′*-Dialkylsulfamides

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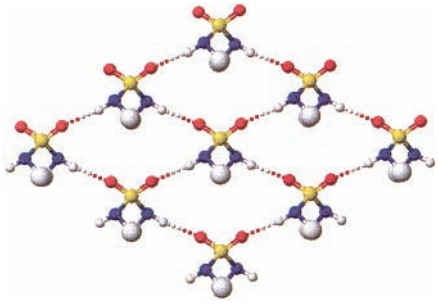
ABSTRACT



***N,N′*-Dialkylsulfamide molecules assemble into solid-state structures consisting of 2D layers. The 2D layers are based on a hydrogen-bonded network of the sulfamide groups and the close-packing of alkyl groups on both sides of the 2D H-bonded network. The thickness of a 2D layer is proportional to the size of the alkyl substituents. The interplay of H-bonding and van der Waals interactions leads to stable 2D layers that pack into 3D structures.**

Lately there has been intense interest in designing supramolecular synthons that predictably assemble into molecular crystals.[1] One attractive strategy involves the design of reliable 2D building blocks which reduce a 3D problem into a one-dimensional one.[2] We discovered recently that sulfamide groups of *N,N′*-disubstituted sulfamides assemble into a novel 2D H-bonded network.[3] Such a 2D sulfamide network tolerates a variety of substituents and therefore may serve as a general supramolecular synthon for the systematic tuning of 3D solid-state structures. Here we report the packing of *N,N′*-dialkylsulfamides **1**. The interplay of H-bonding and van der Waals interactions leads to stable 2D

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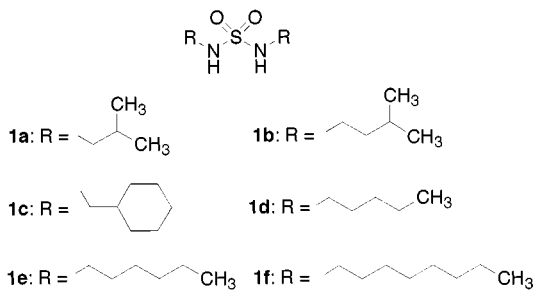
layers whose thickness can be tuned by adjusting the alkyl groups without affecting the overall layered packing.



N,*N*′-Diisobutylsulfamide (**1a**), which was found to assemble into a layered 3D structure, was the only dialkylsulfamide we examined before.[3a] To investigate the assembly of dialkylsulfamides with both straight or branched chain alkyl substituents, **1b**−**f** were prepared by treating the corresponding amines with sulfuryl chloride based on the procedures we reported.[3a] X-ray quality crystals of **1b**−**f** were obtained from chloroform or from a mixture of ethanol/chloroform by slow cooling from 60 °C. Results from X-ray crystallography[4] show that in the solid-state structures of **1b**−**f**, as in that of **1a**, each sulfamide group forms four H-bonds with those of four adjacent molecules, leading to 2D H-bonded networks consisting of the sulfamide groups.

The alkyl groups extend from both sides of the 2D H-bonded network, leading to 2D layers whose thickness is defined by the length of the constituent molecules (Figure 1). As shown in Table 1, the thickness of a 2D layer is proportional to the size of the alkyl substituents of the constituent molecules, ranging from 9.81 Å (**1a**) to 18.04 Å (**1f**) in the solid-state structures of the examined compounds.

Table 1. Selected Structural Parameters for the 2D Layers

structure	d(S···S) (Å)	d(N···O) (Å)	α(N-S-N-C) (deg)	$d_{\text{inter-chain}}$ (Å)	thickness of layer (Å)
1a	5.281	2.897	51.3	3.732	9.812
		3.058	55.8	4.430	
1b	5.313	2.972	53.4	4.095	12.094
	5.029	2.948	59.9	4.277	
1c	5.281	2.967	49.2	3.854	13.838
		3.018	52.3	4.100	
1d	5.253	2.994	60.7	4.149	12.374
1e	5.293	3.024	62.4	4.135	14.118
1f	5.296	5.296	62.1	4.136	18.040

The packing of the alkyl substituents on either sides of the sulfamide sheet closely parallels that of the H-bonded sulfamide network. The alkyl groups in each 2D layer arranged into a rhombic pattern when viewed along their long axes (Figure 2), reflecting the same arrangement of the sulfamide groups found in the H-bonded 2D network. The S···S spacings in the 2D network range from 5.0 to 5.3 Å,

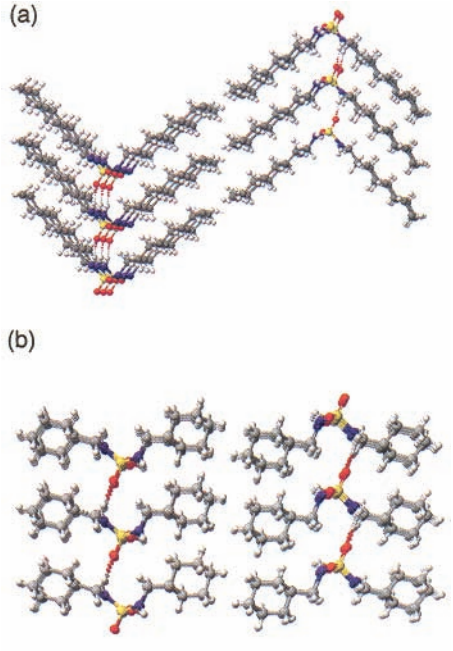


Figure 1. Layered packing of (a) **1f** and (b) **1c**. The planes of the 2D sulfamide networks are perpendicular to that of the paper. The straight chain alkyl groups pack more densely than the branched chains, resulting in more curved conformations for **1d**−**f** than for **1a**−**c**.

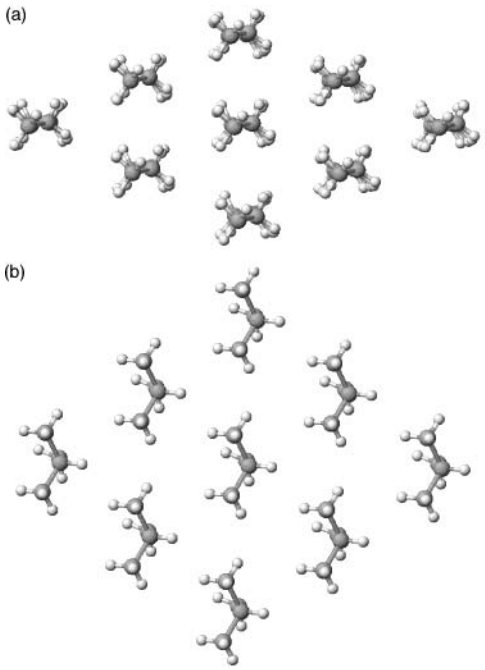


Figure 2. Packing of the alkyl substituents in the solid-state structures of (a) **1f** and (b) **1a**. Viewed along the long axes of the alkyl groups.

which would leave substantial free volume between the alkyl groups if they aligned normal to the plane of the 2D H-bonded network. To achieve optimum van der Waals contacts, the alkyl groups are all tilted relative to the plane of the 2D H-bonded network. In the 2D layers of **1d**−**f**, the straight-chain alkyl groups showed interchain spacings of ∼4.1 Å (Table 1). This packing of alkyl substituents is very similar to that of alkanethiol monolayers on gold surface, in which all the alkyl chains are titled relative to the substrate surface to adjust for the otherwise too large S···S spacing (4.97 Å).[5] Figure 3 shows the interlocking of the H atoms

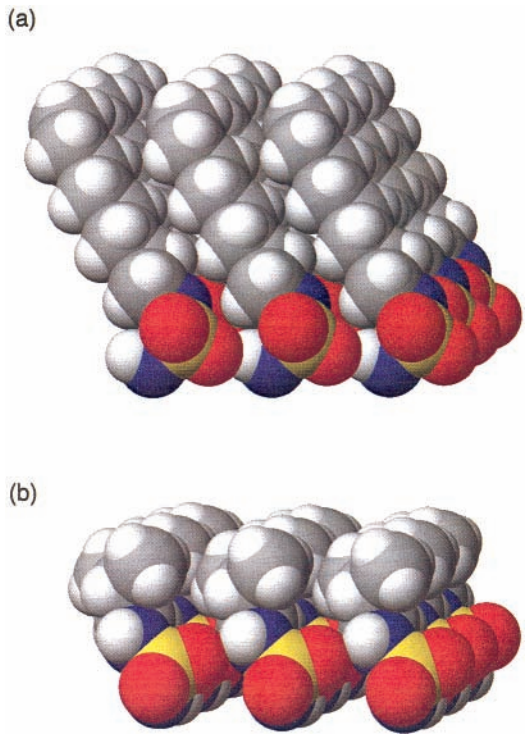


Figure 3. Interlocking of the alkyl substituents in the solid-state structures of (a) **1f** and (b) **1a**. The substituents below the sulfamide networks are removed for clarity of view.

at neighboring octyl groups in a 2D layer consisting of **1f**. Such van der Waals interactions between the alkyl groups provides an additional driving force for forming the 2D layers. In the 2D layers of **1a**−**c**, the bulkier branched alkyl groups are less tilted but still show extensive van der Waals contacts, reflecting the flexibility of this supramolecular motif in accommodating alkyl groups of various size and shape.

As a result of this packing, the sulfamide molecules are not fully extended. This is realized by the N−S−N−C torsional angle ((N−S−N−C) in Table 1) being much smaller (∼50° to 60°) than the 180° that is required for a fully extended conformation. In other words, the tetrahedral-shaped sulfamide group introduces a "twist" in these molecules, which leads to V-shape conformations.

The alkyl groups of **1d**−**f** are all equally distanced, reflecting the relatively isotropic, cylindrical shape of these straight chains along the directions that are perpendicular to the normal of the 2D layers. Each of the anisotropically shaped branched chain alkyl groups of **1a**−**c**, however, is related in two different ways to its adjacent neighbors. As a result, two different interchain distances are observed. Packing of the side chains also affects the distances between the sulfamide groups, with one S···S (or N···O) distance between the H-bonded sulfamide groups in the 2D layers of **1d**−**f** and two different S···S (or N···O) distances in those of **1a**−**c**. Therefore, on one hand, the H-bonded sulfamide network defines the overall packing pattern in the 2D layers; on the other hand, the different shapes of the alkyl substituents also cause minor adjustment in the H-bonding pattern of the sulfamide groups. The interplay of the two types of interactions, H-bonding between the sulfamide groups and van der Waals interaction between the alkyl groups, leads to stably assembled 2D layers. Further assembly of the 2D layers along the third dimension is achieved by van der Waals contacts, mainly between the terminal methyl groups on a predictable one-to-one basis. The importance of the lateral packing of the alkyl substituents to the stability of the 2D layers will be further probed by incorporating alkyl groups that lead to minimum lateral contact surfaces. These groups include the very small methyl, the very bulky *tert*-butyl, and other similar, sphere-shaped groups that provide insufficient van der Waals contact surfaces. Will the 2D H-bonded network still be stable in the presence of these groups? If not, what type of alternative H-bonding pattern will be observed?

In summary, we have examined the assembly of *N*,*N*-dialkylsufamides with both straight-chain and branched alkyl substituents in the solid state. The 2D H-bonded sulfamide networks persist in the solid-state structures of these molecules. The thickness of a 2D layer is defined by the size of the alkyl substituents, which provides a convenient platform for tuning the 2D layers without affecting the overall 3D packing pattern. The alkyl groups pack in such a way as to satisfy the 2D H-bonded network and to realize optimum interchain van der Waals contacts. The 2D sulfamide networks also adjust to reflect the different shapes and sizes of the alkyl groups. This system not only provides insights into designing molecular crystals but also has implications for other fields such as LB films and self-assembled monolayers.[6] Oligosulfamides and polysulfamides may lead to oligomeric and polymeric materials that are extensively H-bonded.

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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 **1b**−**1f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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