Table II. Bond Distances (Å) and Angles (Deg) for $Rh_2(O_2CCF_3)_4(Me_2SO\text{-}d_6)_2$

Distances			
Rh(1)-Rh(1′)	2.409 (1)	F(4)-C(4)	1.319 (5)
O(1)	2.032 (3)	F(5)-C(4)	1.324 (5)
O(2)	2.026 (3)	F(6)-C(4)	1.314 (5)
O(3′)	2.042 (3)	F(7)-C(6)	1.315 (5)
O(4′)	2.040 (3)	F(8)-C(6)	1.311 (5)
O(10)	2.263 (3)	F(9)-C(6)	1.302 (5)
Rh(2)-Rh(2′)	2.407 (1)	F(10)-C(8)	1.300 (6)
O(5′)	2.039 (3)	F(11)-C(8)	1.312 (5)
O(6)	2.033 (3)	F(12)-C(8)	1.261 (6)
O(7)	2.040 (2)	O(1)-C(1)	1.253 (5)
O(8′)	2.029 (3)	O(2)-C(3)	1.245 (4)
O(20)	2.234 (3)	O(3)-C(1)	1.243 (5)
S(10)-O(10)	1.515 (3)	O(4)-C(3)	1.250 (4)
C(10)	1.781 (6)	O(5)-C(5)	1.252 (5)
S(10)-C(11)	1.749 (7)	O(6)-C(7)	1.249 (5)
S(20)-O(20)	1.516 (3)	O(7)-C(5)	1.245 (5)
C(20)	1.771 (6)	O(8)-C(7)	1.254 (5)
C(21)	1.776 (6)	C(1)-C(2)	1.533 (6)
F(1)-C(2)	1.303 (6)	C(3)-C(4)	1.530 (5)
F(2)-C(2)	1.296 (6)	C(5)-C(6)	1.520 (5)
F(3)-C(2)	1.273 (6)	C(7)-C(8)	1.513 (6)
Angles			
Rh(1′)-Rh(1)-O(1)	88.00 (8)	Rh(2)-O(6)-C(7)	117.4 (2)
O(2)	87.83 (7)	Rh(2)-O(7)-C(5)	118.2 (2)
O(3′)	87.88 (8)	Rh(2)-O(8′)-C(7′)	117.9 (2)
O(4′)	87.76 (7)	Rh(1)-O(10)-S(10)	120.1 (2)
O(10)	176.29 (7)	Rh(2)-O(20)-S(20)	120.0 (2)
O(1)-Rh(1)-O(2)	89.8 (1)	O(1)-C(1)-O(3)	130.1 (4)
O(3′)	175.9 (1)	C(2)	113.9 (4)
O(4′)	89.5 (1)	O(3)-C(1)-C(2)	116.0 (4)
O(1)-Rh(1)-O(10)	91.4 (1)	F(1)-C(2)-F(2)	105.5 (5)
O(2)-Rh(1)-O(3′)	89.6 (1)	F(1)-C(2)-F(3)	106.5 (5)
O(2)-Rh(1)-O(4′)	175.6 (1)	F(1)-C(2)-C(1)	111.5 (4)
O(10)	88.5 (1)	F(2)-C(2)-F(3)	109.2 (5)
O(3′)-Rh(1)-O(4′)	90.7 (1)	C(1)	112.0 (4)
O(10)	92.7 (1)	F(3)-C(2)-C(1)	111.8 (4)
O(4′)-Rh(1)-O(10)	95.9 (1)	O(2)-C(3)-O(4)	129.1 (4)
Rh(2′)-Rh(2)-O(5′)	88.45 (8)	O(2)-C(3)-C(4)	114.6 (3)
O(6)	88.08 (8)	O(4)-C(3)-C(4)	116.3 (3)
O(7)	87.30 (7)	F(4)-C(4)-F(5)	106.6 (3)
O(8′)	87.70 (8)	F(6)	107.7 (4)
O(20)	176.31 (8)	C(3)	113.0 (3)
O(5′)-Rh(2)-O(6)	88.9 (1)	F(5)-C(4)-F(6)	108.3 (4)
O(7)	175.7 (1)	C(3)	111.6 (4)
O(8′)	90.8 (1)	F(6)-C(4)-C(3)	109.5 (3)
O(20)	88.1 (1)	O(5)-C(5)-O(7)	129.2 (3)
O(6)-Rh(2)-O(7)	91.0 (1)	C(6)	115.1 (3)
O(8′)	175.8 (1)	O(7)-C(5)-C(6)	115.7 (3)
O(20)	93.2 (1)	F(7)-C(6)-F(8)	105.6 (4)
O(7)-Rh(2)-O(8′)	88.8 (1)	F(9)	108.0 (4)
O(20)	96.1 (1)	C(5)	112.7 (4)
O(8′)-Rh(2)-O(20)	91.0 (1)	F(8)-C(6)-F(9)	108.3 (4)
O(10)-S(10)-C(10)	104.3 (2)	C(5)	112.1 (4)
C(11)	105.9 (3)	F(9)-C(6)-C(5)	109.8 (3)
C(10)-S(10)-C(11)	99.4 (4)	O(6)-C(7)-O(8)	128.8 (4)
O(20)-S(20)-C(20)	103.7 (2)	C(8)	115.1 (4)
C(21)	105.8 (2)	O(8)-C(7)-C(8)	116.0 (4)
C(20)-S(20)-C(21)	99.4 (3)	F(10)-C(8)-F(11)	103.8 (4)
Rh(1)-O(1)-C(1)	117.1 (3)	F(12)	108.7 (5)
Rh(1)-O(2)-C(3)	118.0 (2)	C(7)	111.8 (4)
Rh(1)-O(3′)-C(1′)	116.9 (2)	F(11)-C(8)-F(12)	108.1 (5)
Rh(1)-O(4′)-C(3′)	117.3 (2)	C(7)	109.6 (4)
Rh(2)-O(5′)-C(5′)	116.8 (2)	F(12)-C(8)-C(7)	114.2 (4)

deuterio compounds. It might well be asked if the isolation of a different structure for each compound has not arisen merely from the fact that slightly different conditions prevailed during crystallization in each case. We believe the conditions of temperature, concentration, etc., were the same, but of course there may have been slight differences of which we were unaware. A related question in whether both types of crystals may have been present in each case. While we did not check exhaustively, each batch appeared to be homogeneous in this respect. We cannot, however, rule this out altogether.

There are several small but real differences in the intramolecular dimensions from one structure to the other. These are presumably the result of the different intermolecular contacts and not direct consequences of the isotopic substitution. It may also be noted that a comparison of the cell volumes for the Me_2SO and $Me_2SO\text{-}d_6$ adducts of $Rh_2(O_2CCF_3)_4$ shows that the protio compound occupies 614.2 Å^3 per dinuclear molecule while the deuterio compound has an effective volume of 608.2 Å^3. This change of ca. 1% in volume is far too large to be a direct consequence of the smaller effective volume of CD_3; it is simply a consequence of the overall change in packing. It is interesting, however, that the deuterio compound has the structure with the tighter packing.

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Registry No. $Rh_2(O_2CCF_3)_4(Me_2SO\text{-}d_6)_2$, 79769-93-0; $Rh_2(O_2CCF_3)_4(Me_2SO)_2$, 72665-42-0.

Supplementary Material Available: Tables IIA (bond distances and angles involving deuterium atoms in $Rh_2(O_2CCF_3)_4(Me_2SO\text{-}d_6)_2$), III (final positional and thermal parameters), IV (bond distances and angles for $Rh_2(O_2CCF_3)_4(Me_2SO)_2$), V (least-squares planes for both compounds), and listings of observed and calculated structure factors for the two compounds (29 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of the Sulfamide $(t\text{-}BuNH)_2SO_2$

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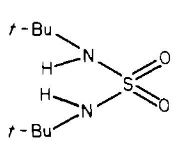
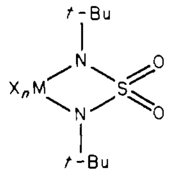
It has been demonstrated recently[3] that the sulfamide $(t\text{-}BuNH)_2SO_2$ (**1**) is a very useful precursor for the synthesis of novel heterocycles such as **2**. Interestingly, if the steric bulk of the *N*-alkyl group is reduced, it is not possible to isolate heterocycles like **2** and only polymeric materials or ring-opened products can be isolated.[4]



1



2

e.g., M = P, X = Cl, *n* = 1
M = P, X = F, *n* = 1
M = P, X = NMe_2, *n* = 1

We are aware of only two previous X-ray crystal structures on sulfamides. The structure of the parent compounds $(H_2N)_2SO_2$ has been determined by Trueblood and Mayer,[5] and

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(1) University of Alabama.
(2) The University of Texas at Austin.
(3) Cowley, A. H.; Mehrotra, S. K.; Roesky, H. W. *Inorg. Chem.* **1981**, *20*, 712–716.
(4) Roesky, H. W.; Mehrotra, S. K.; Platte, C.; Amirzadeh-Asl, D.; Roth, B. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 1130–1136.

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Table I. Pertinent Crystallographic Parameters for $(t\text{-BuNH})_2SO_2$

cryst system	monoclinic	cell const	
space group	$P2_1/c$	a, Å	9.720 (3)
density (calcd), g cm^{-3}	1.19	b, Å	9.887 (3)
obsd reflctns	1242	c, Å	12.076 (4)
R	0.030	β, deg	90.46 (3)
R_w	0.036	cell vol, Å^3	1160.5
μ, cm^{-1}	2.53	Z	4

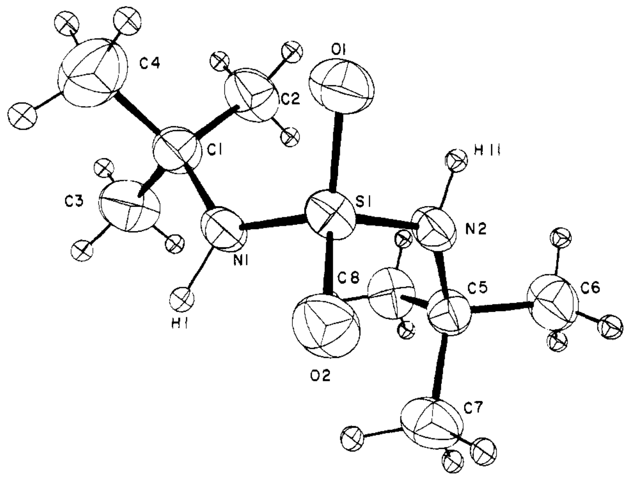


Figure 1. View of the $(t\text{-BuNH})_2SO_2$ molecular structure showing the atom numbering scheme.

that of the permethylated analogue $(Me_2N)_2SO_2$ has been reported by Lipscomb et al.[6] The present work therefore represents the first single-crystal X-ray diffraction study of a symmetrical dialkylsulfamide.

Experimental Section

N,*N'*-Di-*tert*-butylsulfamide, $(t\text{-BuNH})_2SO_2$ (**1**), was prepared according to the method of Bermann and Van Wazer.[7] Clear, colorless crystals of **1** suitable for X-ray diffraction were grown by recrystallization from a 6:1 CH_2Cl_2/pentane solution.

X-ray Crystallography. The data crystal (0.5 mm on edge) was sealed under a dry-nitrogen atmosphere in a 0.5-mm o.d. Lindemann glass capillary. Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation. The diffracted intensities were collected by the ω–2θ scan technique in a manner similar to that described previously.[8] One independent quadrant of data was measured out to $2\theta < 44°$, and a slow scan was performed on a total of 1242 unique reflections. The intensities were corrected for Lorentz and polarization effects but not for absorption. A summary of pertinent crystallographic parameters is presented in Table I.

The structure was solved with the direct-methods program[9] and refined with the SHELX system.[10] All hydrogen atoms were located on difference Fourier maps and allowed to ride on the bonded atom. The average C–H bond length is 1.00 Å, while the H–C–H and C–C–H angles average 109 and 110°, respectively.

Results and Discussion

The molecular structure and labeling scheme for $(t\text{-BuNH})_2SO_2$ (**1**) are shown in Figure 1, and a stereoview of the unit cell is provided in Figure 2. Bond distances and angles are presented in Table II, and the atomic positional and thermal parameters are listed in Tables III and IV, respectively.

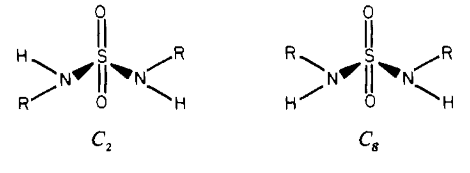
Table II. Bond Distances (Å) and Bond Angles (Deg) in $(t\text{-BuNH})_2SO_2$

S–O(1)	1.434 (2)	S–O(2)	1.434 (2)
S–N(1)	1.615 (2)	S–N(2)	1.616 (2)
N(1)–C(1)	1.492 (4)	N(2)–C(5)	1.496 (4)
N(1)–H(1)	1.00	N(2)–H(11)	1.03
C(1)–C(2)	1.517 (4)	C(1)–C(3)	1.518 (4)
C(1)–C(4)	1.522 (5)	C(5)–C(6)	1.533 (4)
C(5)–C(7)	1.519 (4)	C(5)–C(8)	1.528 (4)
O(1)–S–O(2)	118.7 (1)	O(1)–S–N(1)	110.6 (1)
O(2)–S–N(1)	104.5 (1)	O(1)–S–N(2)	103.6 (1)
O(2)–S–N(2)	108.6 (1)	N(1)–S–N(2)	110.8 (1)
S–N(1)–C(1)	127.4 (2)	S–N(2)–C(5)	127.5 (2)
C(1)–N(1)–H(1)	116.6	C(5)–N(2)–H(11)	112.3
H(1)–N(1)–S(1)	113.3	H(11)–N(2)–S(1)	113.4
N(1)–C(1)–C(2)	111.4 (2)	N(1)–C(1)–C(3)	105.2 (2)
C(2)–C(1)–C(3)	109.5 (3)	N(1)–C(1)–C(4)	110.5 (3)
C(2)–C(1)–C(4)	110.2 (3)	C(3)–C(1)–C(4)	109.9 (3)
N(2)–C(5)–C(6)	103.9 (2)	N(2)–C(5)–C(7)	111.4 (2)
C(6)–C(5)–C(7)	109.9 (3)	N(2)–C(5)–C(8)	111.0 (2)
C(6)–C(5)–C(8)	110.0 (3)	C(7)–C(5)–C(8)	110.4 (3)

Table III. Atomic Positions in Fractional Coordinates for $(t\text{-BuNH})_2SO_2$

atom	x/a	y/b	z/c
S	0.24896 (7)	0.51174 (7)	0.51535 (5)
O(1)	0.3536 (2)	0.6072 (2)	0.5462 (2)
O(2)	0.1408 (2)	0.4840 (2)	0.5922 (1)
N(1)	0.1702 (2)	0.5601 (2)	0.4039 (2)
C(1)	0.2237 (3)	0.6516 (3)	0.3159 (2)
C(2)	0.3679 (3)	0.6117 (4)	0.2817 (3)
C(3)	0.1257 (4)	0.6340 (4)	0.2184 (3)
C(4)	0.2218 (4)	0.7979 (4)	0.3550 (3)
N(2)	0.3338 (2)	0.3738 (2)	0.4940 (2)
C(5)	0.2792 (3)	0.2428 (3)	0.4498 (2)
C(6)	0.3846 (3)	0.1378 (3)	0.4898 (3)
C(7)	0.1386 (3)	0.2105 (3)	0.4971 (3)
C(8)	0.2729 (4)	0.2443 (4)	0.3234 (2)
H(1)	0.0685 (2)	0.5492 (2)	0.4074 (2)
H(2)	0.3935 (3)	0.6717 (4)	0.2197 (3)
H(3)	0.4378 (3)	0.6208 (4)	0.3385 (3)
H(4)	0.3698 (3)	0.5175 (4)	0.2586 (3)
H(5)	0.1492 (4)	0.6936 (4)	0.1605 (3)
H(6)	0.1232 (4)	0.5354 (4)	0.1923 (3)
H(7)	0.0312 (4)	0.6513 (4)	0.2425 (3)
H(8)	0.2597 (4)	0.8626 (4)	0.2907 (3)
H(9)	0.2814 (4)	0.8074 (4)	0.4224 (3)
H(10)	0.1253 (4)	0.8242 (4)	0.3733 (3)
H(11)	0.4350 (2)	0.3900 (2)	0.4724 (2)
H(12)	0.3775 (3)	0.1291 (3)	0.5747 (3)
H(13)	0.4812 (3)	0.1587 (3)	0.4620 (3)
H(14)	0.3598 (3)	0.0548 (3)	0.4614 (3)
H(15)	0.0596 (3)	0.2761 (3)	0.4693 (3)
H(16)	0.1445 (3)	0.2114 (3)	0.5830 (3)
H(17)	0.1166 (3)	0.1198 (3)	0.4757 (3)
H(18)	0.2491 (4)	0.1557 (4)	0.2944 (2)
H(19)	0.3635 (4)	0.2656 (4)	0.2971 (2)
H(20)	0.2017 (4)	0.3112 (4)	0.2990 (2)

Previous structural work on sulfamides[5,6] has established the approximate orthogonality of the N–S–N and R–N–R planes.[11] An *N*,*N'*-dialkylsulfamide is therefore capable of existing in C_2 and C_S conformations. The preference of (*t*-



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(5) Trueblood, K. N.; Mayer, S. W. *Acta Crystallogr.* **1956**, *9*, 628–634.

(6) Jordan, T.; Smith, H. W.; Lohr, L. L., Jr.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1963**, *85*, 846–851.

(7) Bermann, M.; Van Wazer, J. R. *Synthesis* **1972**, *576*–577.

(8) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45–53.

(9) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368–376.

(10) Sheldrick, G. SHELX 76, program system for crystal structure determination, 1976.

(11) This observation has been ascribed by Lipscomb et al.[6] to the optimization of both N → S and O → S pπ–dπ bonding in this conformation. Rotation of the NR_2 groups by 90° would result in increased competition of the N and O lone pairs for the available S(3d) orbitals.

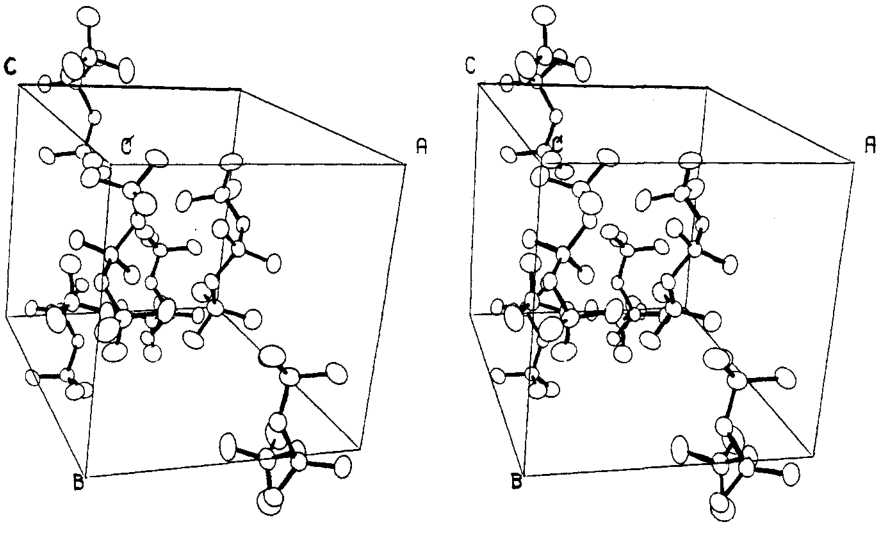

Figure 2. Stereoview of the unit cell for (t-BuNH)$_2$SO$_2$.

Table IV. Thermal Parameters[a] for (t-BuNH)$_2$SO$_2$

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	0.0276 (4)	0.0393 (4)	0.0340 (4)	−0.0019 (3)	0.0005 (3)	0.0002 (3)
O(1)	0.035 (1)	0.044 (1)	0.051 (1)	−0.009 (1)	−0.0035 (9)	−0.005 (1)
O(2)	0.035 (1)	0.054 (1)	0.038 (1)	0.001 (1)	0.0082 (9)	0.002 (1)
N(1)	0.025 (1)	0.048 (2)	0.042 (1)	0.010 (1)	−0.000 (1)	0.000 (1)
C(1)	0.041 (2)	0.052 (2)	0.043 (2)	0.012 (2)	0.001 (1)	−0.003 (2)
C(2)	0.047 (2)	0.089 (3)	0.057 (2)	0.018 (2)	0.013 (2)	−0.004 (2)
C(3)	0.064 (2)	0.096 (3)	0.054 (2)	0.028 (2)	−0.015 (2)	−0.012 (2)
C(4)	0.087 (3)	0.052 (2)	0.081 (3)	0.015 (2)	0.005 (2)	−0.004 (2)
N(2)	0.027 (1)	0.039 (1)	0.044 (1)	−0.001 (1)	−0.003 (1)	0.002 (1)
C(5)	0.041 (2)	0.037 (2)	0.047 (2)	−0.004 (1)	−0.005 (1)	0.000 (1)
C(6)	0.058 (2)	0.040 (2)	0.082 (3)	−0.001 (2)	−0.012 (2)	0.008 (2)
C(7)	0.045 (2)	0.051 (2)	0.072 (2)	−0.007 (2)	−0.000 (2)	−0.013 (2)
C(8)	0.066 (2)	0.060 (2)	0.049 (2)	−0.012 (2)	−0.005 (2)	0.002 (2)

[a] Anisotropic thermal parameters as defined in ref 10.

BuNH)$_2$SO$_2$ for the C_2 conformation (Figure 1) presumably stems from minimization of the steric interactions between the t-Bu groups. The steric demands of the t-Bu groups are also evident in the following structural features: (i) the S–N–C bond angles in **1** (127.4 (2)°) are significantly larger than those in (Me$_2$N)$_2$SO$_2$ (117.9 (4) and 119.7 (4)°)[6] and (ii) the normals to the C–N–C and N–S–N planes in (Me$_2$N)$_2$SO$_2$ are 89.4°, while those to the C–N–H and N–S–N planes in **1** are increased to 101.8° on account of increased R···O interaction.

Unfortunately, structural data are not available for other N,N′-disubstituted sulfamides. However, it seems reasonable to conjecture that the energy difference between the C_2 and C_S conformations will decrease as the steric bulk of the alkyl moiety diminishes. In turn, the less rigid nature of a sulfamide such as (MeNH)$_2$SO$_2$ may be a factor in the tendency of this molecule to form polymers rather than discrete heterocycles when treated with active halides.

The sums of the bond angles at nitrogen in **1** are 357.3 and 353.2° at N(1) and N(2), respectively. The geometry at nitrogen is thus between trigonal planar and tetrahedral, but nearer to trigonal planar. A similar nitrogen geometry was found in (Me$_2$N)$_2$SO$_2$ (S_N = 350.5°). The S–N bond distances in **1** are 1.615 (2) and 1.616 (2) Å and thus substantially less than the sum of the covalent radii for sulfur and nitrogen (1.75 Å).[12] Similar S–N bond shortening has been observed in the sulfamides (NH$_2$)$_2$SO$_2$ (1.600 (9) Å) and (Me$_2$N)$_2$SO$_2$ (1.623 (5) Å). Trigonal-planar or near-trigonal-planar nitrogen geometries and short N–element bond distances are an increasingly familiar feature of the structures of many N–S and N–P compounds.[13]

The geometry of the O$_2$SN$_2$ unit varies very little in **1**, (H$_2$N)$_2$SO$_2$, and (Me$_2$N)$_2$SO$_2$. Like the S–N bond distances, the S–O bond distances of these sulfamides fall in the order (Me$_2$N)$_2$SO$_2$ (1.441 (5) and 1.449 (5) Å) > **1** (1.434 (2) Å) > (H$_2$N)$_2$SO$_2$ (1.391 (8) Å). This ordering follows the electronegativities of the amide groups.

The crystal structure appears to be held together by weak hydrogen bonds between H(1) and the O(2) of an adjacent molecule. The N–H···O angle is 180°, and the H···O separation is 2.06 Å. The N···O distance for a normal hydrogen bond is 2.9 Å;[14] in **1** it is 3.06 Å.

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Registry No. **1**, 13952-67-5.

Supplementary Material Available: A table of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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(12) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(13) For example, d_{SN} = 1.648 (2) Å in (Me$_2$N)$_2$SF$_2$ (Cowley, A. H.: Riley, P. E.; Szobota, J. S.; Walker, M. L. *J. Am. Chem. Soc.* **1979**, *101*, 5620–5624). For a discussion of this phenomenon in aminophosphines, see: Cowley, A. H.; Davis, R. E.; Remadna, K. *Inorg. Chem.* **1981**, *20*, 2146–2152 and references therein.

(14) Hamilton, W. C.; Ibers, J. A. "Hydrogen Bonding in Solids: Methods of Molecular Structure Determination"; W. A. Benjamin: New York, 1968; p 16.