

THE CRYSTAL AND MOLECULAR STRUCTURE OF DIMETHYL SULFONE DIIMINE

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Cogliano and Braude (1) suggested that dialkyl sulfides react with two moles of chloramine to give a series of compounds having the probable general formula $(R_2\overset{+}{S}N\overset{-}{H}NH)_2$, termed a bis(iminodialkylsulfilimine). On the basis of chemical and mass spectrometric data Appel, Fehlhaber, Hänssgen and Schöllhorn (2) have proposed the alternative formula $R_2S(NH)_2$, that is, a dialkyl sulfone diimine. For the same series of compounds, Yellin and Laughlin (3) have also interpreted Raman, nmr and infrared spectra in terms of a tetrahedral diimine structure. We have determined the crystal and molecular structure of dimethyl sulfone diimine by X-ray single-crystal techniques and have found a tetrahedral structure as proposed by Appel et al and by Yellin and Laughlin.

Dr. R. G. Laughlin gave us a crystalline sample of dimethyl sulfone diimine that had been sublimed and then recrystallized from acetonitrile. Crystals of dimethyl sulfone diimine are orthorhombic with unit cell dimensions of $a = 5.44$, $b = 10.59$ and $c = 16.13 \text{ \AA}$. The observed conditions on the Miller indices, hkl , for systematic absences are characteristic of space group F2dd.* From a measured density of 1.324 g cm^{-3} we determine that there are 8 molecules per unit cell (the calculated density for 8 molecules is 1.318 g cm^{-3}). The general multiplicity of space group F2dd is 16; therefore, the sulfur atom of each molecule must lie on a twofold axis in one of the special eightfold positions, $(x,0,0)$, $(1/4 + x, 1/4, 1/4)$ and the corresponding positions related to these by the translations of a face-centered lattice. In this polar space group the x parameter of one set of atoms may be arbitrarily chosen; therefore we set the x parameter of the sulfur atoms equal to zero without loss of generality.

*Sulfamide, $(NH_2)_2SO_2$, crystallizes in space group F2dd with $a = 4.58$, $b = 9.14$ and $c = 16.85 \text{ \AA}$ (4).

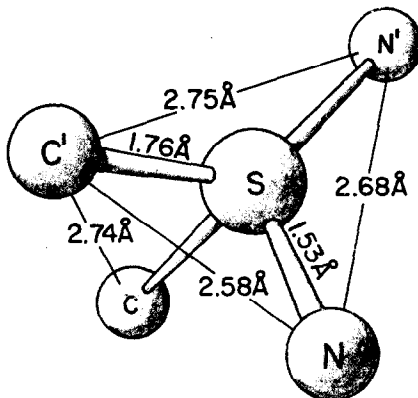
Since each molecule lies on a twofold axis we need to determine the positions of only one carbon atom and one nitrogen atom, along with their associated hydrogen atoms, if possible, to completely define the structure.

Dimethyl sulfone diimine is hygroscopic and forms a crystalline quarter-hydrate (5); hence, crystals were handled in a nitrogen atmosphere and one was selected and enclosed in a Vycor capillary. The crystal was aligned for rotation about the $[011]$ direction and six layer-lines of intensity data were recorded with nickel-filtered $\text{Cu K}\alpha$ radiation using the multiple-film equi-inclination Weissenberg technique. In all, 232 independent reflections were observed out of 295 accessible in the $\text{Cu K}\alpha$ sphere. Intensities were estimated by visual comparison with a calibrated strip made with a selected reflection from the crystal used throughout the study. Of the 232 estimated intensities, the intensities of 8 reflections were less than a minimum observable quantity; these are referred to as "less-thans." The intensities were corrected for Lorentz-polarization effects but not for absorption effects; inter-layer correlations were made using equivalent reflections occurring on different layers.

The structure was solved from a three-dimensional vector map and refined by the full-matrix least-squares method utilizing individual anisotropic thermal parameters. The current agreement index is $R = 0.077$ ($R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$, where F_o and F_c are observed and calculated structure factors). None of the 8 "less-thans" calculated too large.

At this stage of refinement the molecular dimensions are

$$\begin{array}{lll} \text{S-N} = 1.53 \pm .04 \text{ \AA} & \angle \text{NSN}' = 122^\circ \pm 3^\circ & \angle \text{NSC}' = 103^\circ \pm 2^\circ \\ \text{S-C} = 1.76 \pm .05 \text{ \AA} & \angle \text{CSC}' = 103^\circ \pm 3^\circ & \angle \text{NSC} = 113^\circ \pm 2^\circ. \end{array}$$



The S-N distance is essentially that of a double bond as predicted by the Pauling radii (6) and shorter than the 1.60 Å found in sulfamide (4). The S-C distance is 0.05 Å shorter than the 1.81 Å predicted for a S-C single bond. At present, no significance can be attached to the different NSC angles.

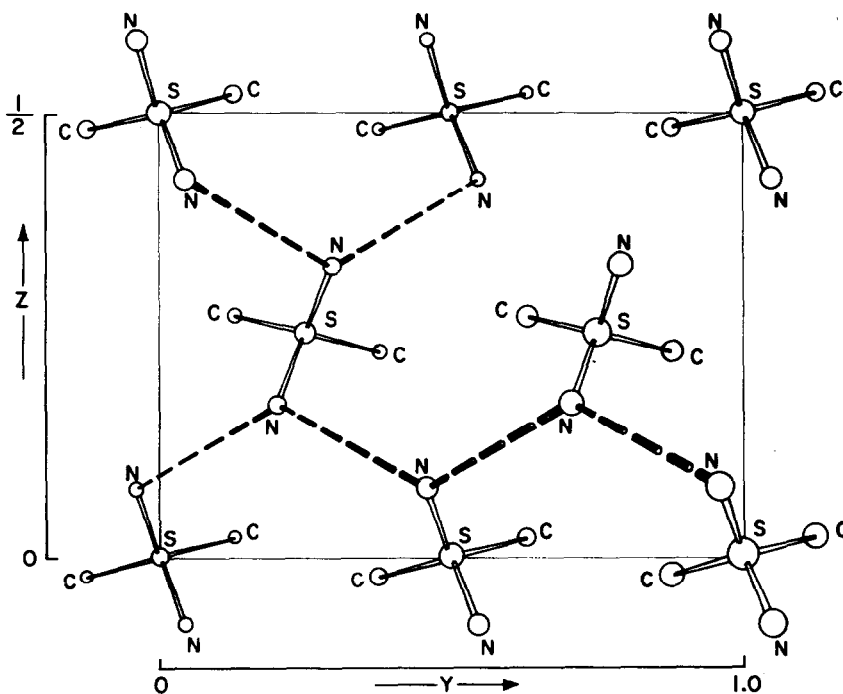
Pertinent distances and angles in a few related molecules are tabulated below. The contraction in S-N bonds on going from S-NH₃ to S-NH₂ to S-NH indicates that the S-N bond acquires more and more π -bond character as p-orbitals become available on the nitrogen atom. The difference in bonds in S-NH₃ and S-NH₂ groups has been noted by the original investigators and has been discussed in detail by Cruickshank (7) in his paper on the role of 3d orbitals in π -bonds in sulfones, sulfamides and related molecules. Among others, Moffitt (8) and Jaffé (9) have discussed the role of d-orbitals in multiple bonds. Along with their X-ray structure determination of ((CH₃)₂N)₂SO₂, Jordan, Warren, Smith and Lipscomb (10) have carried out a LCAO-MO study of d-orbital interactions in (F₂N)₂SO₂.

<u>A-S-B</u>	<u>S-A</u>	<u>S-B</u>	<u>∠ A-S-A</u>	<u>∠ B-S-B</u>	<u>A...A</u>	<u>B...B</u>	<u>Reference</u>
(HN) ₂ S(CH ₃) ₂	1.53 Å	1.76 Å	122°	103°	2.68 Å	2.74 Å	This work
(H ₂ N) ₂ SO ₂	1.60	1.39	112	119	2.65	2.40	Trueblood & Mayer (4)
((CH ₃) ₂ N) ₂ SO ₂	1.62	1.45	113	120	2.72	2.52	Jordan, Smith, Lohr & Lipscomb (10)
(CH ₃) ₂ NSO ₂ Cl	1.69	1.43	-	120	-	2.49	Hargittai (11)
(H ₃ N)SO ₃	1.73	1.48	-	117	-	2.54	Kanda & King (12)
(H ₂ NSO ₃)K	1.60	1.44	-	112	-	2.40	Jeffrey & Stadler (13)
O ₂ SF ₂	1.41	1.53	124	96	2.50	2.29	Lide, Mann & Fristrom (14)

Let us consider a general molecule A₂SB₂. Following Cruickshank's comments on F₂SO₂ we can say that when the S-A bonds have appreciable double bond character and when the S-B bonds are essentially single bonds the A-S-A angle should be significantly greater than the tetrahedral angle (109°28') and the B-S-B angle should be significantly less than the tetrahedral angle; this would apply to (NH)₂S(CH₃)₂ and F₂SO₂ (see above). For a series of sulfones, (RSO₂)₂C=C=NR, Wheatley and his collaborators (15, 16, 17) have found the C-S-C angle to vary from 106.2° to 107.2°. In pyramidal dimethyl sulfoxide, (CH₃)₂SO, the C-S-C angle is 97° (18).

In all cases, the angles will be influenced by ionic and steric factors which generally will tend to increase the A...A and B...B intramolecular distances. As the S-A and S-B bonds both acquire appreciable double bond character the A-S-A and B-S-B angles should approach the tetrahedral value. The final angular values will, of course, be dependent on the nature of each of the bonds and on the various A...A, B...B and A...B interactions.

The short intermolecular distances are $N...C = 3.42$, $C...C = 3.85$ and $N...N = 3.35$ Å. The $N...C$ and $C...C$ distances are reasonable for normal van der Waals contacts. From an electron-density map and a difference map we have not been able to locate any hydrogen atoms. The Raman spectra indicate hydrogen bonding in crystalline dimethyl sulfone diimine (3). Since we have not located the hydrogen atoms we can only say that the most reasonable hydrogen-bonding framework would involve an infinite chain as indicated by the dashed lines; the $N...N$ distances are 3.35 Å.



We anticipate that absorption corrections and further refinement will lead to a more precise molecular geometry and to location of the hydrogen atoms. We would like to locate

the imine hydrogen atom not only because of interest in the hydrogen bonding but also because of interest in the hybridization of orbitals on the nitrogen atom. A linear S-N-H group would imply a hybridization quite different from that for a bent group.

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