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The Crystal Structure of Sulfamide

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Sulfamide, $SO_2(NH_2)_2$, forms orthorhombic crystals, of space group *Fdd*2, with $a_0 = 9{\cdot}14$, $b_0 = 16{\cdot}85$, $c_0 = 4{\cdot}58_0$ Å, and eight molecules in the unit cell. A three-dimensional investigation by Fourier and least-squares methods, utilizing individual anisotropic atomic temperature factors, has established the structure. The tetrahedral molecule has, within the limits of error, the symmetry *mm*2. The bond lengths are: S–O, $1{\cdot}39_1$ Å; S–N, $1{\cdot}60_0$ Å; and the bond angles: O–S–O, 119·4°; N–S–N, 112·1°; O–S–N, 106·2 and 106·6°. The molecules are packed approximately hexagonally into layers parallel to (010), with four equivalent weak N–H · · · O bonds (3·02 Å) holding each molecule to four neighbors in the layer. The anisotropic temperature factors derived by least squares are qualitatively explicable in terms of the observed intermolecular bonding and packing.

Introduction

The structure of sulfamide, $SO_2(NH_2)_2$, is of interest for a number of reasons. It is closely related to the sulfates and similar compounds of oxygen with second-row atoms in which the nature of the bonding, and in many cases even the precise structural parameters, are still in question (Pitzer, 1948; Wells, 1950; Moffitt, 1950; Pauling, 1952; Kucsman, 1953; Varsani & Ladik, 1953). With the closely related sulfuryl halides, especially the fluoride, a significant discrepancy exists between the results of electron diffraction (Stevenson & Russell, 1939) and microwave and infra-red investigations (Fristrom, 1952; Perkins & Wilson, 1952), particularly with regard to the length of the sulfur–oxygen bond. Finally, the relation of sulfamide to the sulfonamides makes structural information concerning it of potential value in connection with the hypothesis that at least part of the effectiveness of the sulfonamides depends upon their steric similarity to certain essential metabolites.

Experimental

Diamond-shaped crystals of sulfamide were grown from ethyl acetate; they were soft and exhibited no marked cleavage. Rotation and Weissenberg photographs with nickel-filtered Cu $K\alpha$ radiation showed the crystals to be orthorhombic, with

$$a_0=9{\cdot}14,\ b_0=16{\cdot}85,\ \text{and}\ c_0=4{\cdot}58_0\ \text{Å, each}\ \pm0{\cdot}1\%.$$

The density of the crystals was determined by flotation to be 1·807 g.cm.$^{-3}$, which corresponds to eight (calculated 7·99) molecules in the unit cell.

The observed systematic extinctions lead uniquely to the space group *Fdd*2, which has a multiplicity of 16. Consequently, the one sulfur atom of each molecule must lie in one of the eightfold special positions, along the twofold rotation axes parallel to **c**. These special positions are at $(0, 0, z)$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}+z)$, and the corresponding positions related to these by the translations of a face-centered lattice. The z parameter of the sulfur atoms may be arbitrarily set equal to zero with no loss of generality. Since the molecule lies on a twofold axis, the parameters of only one oxygen atom and one nitrogen atom, with its associated hydrogen atoms if possible, need be determined.

Crystals used for intensity measurements were reduced by slicing and dissolving to cylinders about 0·09 mm. in diameter, thus obviating the need for absorption corrections. The cylindrizing operations also reduced extinction effects appreciably. Equi-inclination multiple-film Weissenberg photographs were taken about **c** and **a** for all layer lines with equi-inclination angles less than 30°. The film-to-film factor for non-equatorial layer lines was corrected for obliquity of incidence. Of the 216 independent reflections accessible with Cu $K\alpha$ radiation, 180 were observed, and 17 more were in position to be observed but were too weak, although the ratio between the maximum and minimum observed intensities was about 3000. Independent intensity estimates of the same reflections on different films and from different crystals showed an average deviation of about 9%.

Almost all calculations were made on the high-speed computer SWAC, although the first two-dimensional projections were calculated by the *L*-card I.B.M. method of Prof. V. Schomaker. The first three-dimensional structure-factor and Fourier calculations on SWAC were done before installation of the magnetic drum by techniques which utilized only the high-speed memory (Mayer, 1953; Mayer & Trueblood, 1953). However, all of the least-squares refinements and the final structure-factor and Fourier calculations were made with more general routines developed later (Sparks, Prosen, Kruse & Trueblood, 1956). About 15 min. was needed for each cycle of refinement by least-squares which included a structure-factor calculation and solution of the normal equations for the shifts in the position and temperature-factor parameters of each atom; the Fourier syntheses required about 30 min. McWeeny's (1951) form factors were used for oxygen and nitrogen and the James–Brindley (*Internationale Tabellen*, 1935) curve was used for sulfur.

Determination of the structure

A suitable trial structure was rather easily deduced. A Patterson projection on (001) showed prominent S–S peaks and other broad peaks which could be tentatively assigned to S–N and S–O interactions. The resulting rough x and y parameters were refined crudely by consideration of the intensities of certain ($hk0$) reflections and were then used in the calculation of the signs of all 37 ($hk0$) reflections. A Fourier projection on (001) showed a clearly resolved view of the presumably tetrahedral molecule along the twofold axis. Improved parameters from this projection did not differ greatly from the initial set and led to no changes in sign.

Approximate z parameters were next estimated for the two possible configurations of the molecule, one with the oxygen atoms pointing in the positive z direction, and the other with the nitrogen atoms in that direction. Comparison of the observed intensities of certain ($0kl$) reflections with those calculated for each of the two possibilities indicated clearly that the first-mentioned situation was the true one. Although a projection on (100) was calculated, the resolution was not sufficient to permit significant improvement in the estimates of the z parameters.

Consequently, three-dimensional refinement was undertaken, utilizing all 180 observed reflections in successive structure-factor and Fourier calculations. An approximate scale factor and an overall isotropic temperature factor parameter of about 3·0 Å² were estimated by a least-squares comparison of F_o^2 and F_c^2; F_c^2 was evaluated for the once-refined structure. Peak maxima were located by the Gaussian-line method of Carpenter & Donohue (1950) until the final Fourier synthesis, for which the 19-point Gaussian ellipsoid method was employed (Shoemaker, Donohue, Schomaker & Corey, 1950; Donohue & Trueblood, 1952).

After four cycles of Fourier refinement, the last of which included back-shift corrections, the usual 'reliability index', R, was 10·2%. Approximate corrections to the isotropic temperature factors for each atom were then estimated from a difference map, and least-squares refinement of the scale factor, the position parameters, and the individual anisotropic temperature-factor parameters for each atom was started. The progress of the refinement is indicated in Table 1. After one cycle of refinement, R dropped to 7·57%, and decreased only about 0·1% more during additional cycles. The sum of the residuals, $\Sigma\omega(\Delta|F|)^2$, was smaller in the second stage than in the first by a factor of about 2, and then fell an additional 8%, almost all of it in the following cycle. After the first cycle, all of the shifts called for were far smaller than the corresponding standard deviations; thus many more least-squares cycles were run than were strictly needed, chiefly because sulfamide served as the test compound in the development of our least-squares routine, giving valuable information concerning behavior in least squares of this sort in which full anisotropy of each atom is permitted. The rapidity of convergence here resulted chiefly from the fact that the structure had been refined rather carefully by Fourier methods first.

The final least-squares parameters, which are listed

Table 1. *Progress of the least-squares refinement**

Stage	R (%)	$\Sigma\omega(\Delta\|F\|)^2$†	Average $\|\Delta x_i\|$ (Å)	Average $\|\Delta B_{ii}\|$ (Å²)	Average $\|\Delta B_{ij}\|$ (Å²)
1	10·2	8200	0·0078	0·70	0·91
2	7·57	4303	0·0010	0·13	0·14
3	7·50	4001	0·0008	0·05	0·10
4	7·46	3978	0·0006	0·03	0·07
5	7·47	3975	0·0005	0·02	0·06

* The standard deviations for the parameters whose shifts are listed here are about 0·008 Å, 0·3 Å², and 0·6 Å², respectively.
† Arbitrary scale.

Table 2. *Position parameters*

		Trial structure	Final least squares	Final Fourier	Best value*	σ	σ (Å)
O	x	0·886	0·8848	0·8840	0·8844	0·0007	0·006
	y	0·033	0·0340	0·0337	0·0339	0·0005	0·008
	z	0·17	0·1534	0·1532	0·1533	0·0018	0·008
N	x	0·069	0·0699	0·0695	0·0697	0·0009	0·008
	y	0·067	0·0690	0·0692	0·0691	0·0005	0·008
	z	0·79	0·8050	0·8050	0·8050	0·0020	0·009

* Average of the final least-squares and Fourier parameters.

in Table 2, were used for a final set of observed and calculated Fourier syntheses. The resulting Fourier parameters, also listed in Table 2, were derived by application of the 'n-shift rule' (Shoemaker et al., 1950), with $n = 1{\cdot}6$; the precise choice of a value for n was not critical, for if n had been 1·0 the average difference in atomic position from those listed would have been only 0·0015 Å. The Fourier and least-squares parameters agree very well; the average difference is 0·003 Å, with the maximum difference 0·007 Å. The standard deviations of the parameters, derived in the usual way from the least-squares calculations, are also presented in Table 2. The initial and final values of the temperature-factor parameters, together with their standard deviations, are listed in Table 3; an interpretation of these values is given below. Table 4 gives the observed and calculated peak heights.

Table 3. *Temperature-factor parameters**

		Initial value (Å²)	Final value (Å²)	σ (Å²)
S	B_{11}	3·0	2·5	0·1
	B_{22}	3·3	3·4	0·1
	B_{33}	3·1	2·9	0·1
	B_{12}	0·0	0·5	0·3
O	B_{11}	2·8	3·6	0·3
	B_{22}	3·4	4·7	0·3
	B_{33}	3·1	3·4	0·3
	B_{12}	0·0	−0·1	0·6
	B_{13}	0·0	−0·6	0·6
	B_{23}	0·0	−1·1	0·6
N	B_{11}	3·0	3·7	0·3
	B_{22}	2·9	3·5	0·3
	B_{33}	2·9	4·0	0·4
	B_{12}	0·0	−1·1	0·6
	B_{13}	0·0	−1·7	0·8
	B_{23}	0·0	1·5	0·6

* Defined so that the temperature factor is $\exp[-(B_{11}h_1^2+B_{22}h_2^2+B_{33}h_3^2+B_{12}h_1h_2+B_{13}h_1h_3+B_{23}h_2h_3)]$. If the form which includes a factor of 2 with each cross-term is preferred, the B_{ij} listed here, and their standard deviations, should be halved.

Table 4. *Peak heights in final Fourier syntheses*

Atom	Max. ϱ_o (e.Å⁻³)	Max. ϱ_c (e.Å⁻³)	ϱ_o/ϱ_c
S	32·6	32·3	1·01
O	11·3	11·2	1·01
N	9·4	9·2	1·02

Although a careful search was made for the two hydrogen atoms in both the observed and difference syntheses, no peaks clearly attributable to them could be found. Several low diffuse peaks lie within about 0·5–1 Å of the position expected for one of these atoms, along what is presumably a weak N–H · · · O hydrogen bond, but none is sufficiently near the nitrogen atom to be readily identifiable. It is possible that the hydrogen atoms are not ordered; the rather high apparent temperature factors for the nitrogen atom and the softness of the crystals, which is a manifestation of the absence of any strong hydrogen bonds, are in accord with this possibility.

No detailed comparison of the observed and calculated structure factors (Table 8) will be made here. All observed planes were included in the evaluation of the final R value of 7·5%.

Discussion of the structure

The sulfamide molecule

The molecular dimensions of sulfamide are indicated in Fig. 1 and Table 5. Comparable dimensions of some related molecules are listed in Table 6.

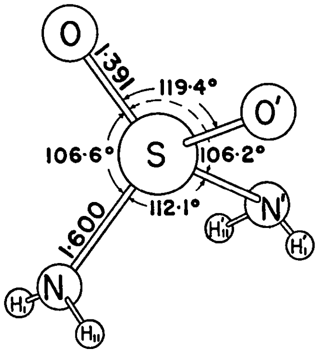

Fig. 1. The sulfamide molecule.

Table 5. *Intramolecular distances and angles**

	Distance	E.s.d.		Angle	E.s.d.
S–O	1·391 Å	0·008 Å	O–S–O′	119·4°	0·8°
S–N	1·600	0·009	N–S–N′	112·1	0·7
			O–S–N	106·6	0·5
O–O′	2·402	0·016	O–S–N′	106·2	0·5
N–N′	2·654	0·016			
O–N	2·401	0·011			
O–N′	2·394	0·011			

* O′ and N′ are equivalent to O and N respectively by operation of the twofold axis.

The sulfamide molecule, exclusive of the hydrogen atoms, has the symmetry *mm*2 in the crystal although only the twofold axis is required by the space group; thus the O–N and O–N′ distances are the same within experimental error and the O–S–N and O–S–N′ angles are likewise not significantly different. The S–O distance is unusually short; only in the microwave study of sulfuryl fluoride has a similar bond been reliably reported as short or shorter, and there is an unresolved discrepancy with the electron-diffraction results for this molecule (Table 6). [Table 6 does not include the distances and angles reported in many early and two-dimensional studies of sulfates, sulfites, and related molecules because the parameters were not determined by precise methods; however, the only one of these distances reported to be comparably short is that in sodium sulfite, 1·39 Å (Zachariasen & Buckley, 1931).]

It is apparent from Table 6 that in almost every

Table 6. *Bond distances and angles in sulfamide and related molecules**

Molecule	Distances (Å)		Angles (°)		Method†	Reference
	S–O	S–N	O–S–O	O–S–N		
$O_2S(NH_2)_2$	1·39	1·60	119	106, 107	3*X*	This Work
KO_3SNH_2	1·44	1·57	110, 114	106, 107	3*X*	Brown & Cox, 1940
$K_2(O_3S)_2NH$	1·44–1·45	1·66	112–114	103–107	3*X*	Jeffrey & Jones, 1955
$KO_3SN_2O_2$	1·43	1·63	108, 116	106, 108	3*X*	Cox *et al.*, 1949
O_3SNH_3	1·47–1·49	1·73	114–119	92–102	2*X*	Kanda & King, 1951
$(CH_3SO_2)_2CCNCH_3$	1·43		118		3*X*	Wheatley, 1954
$KOSO_2OC_2H_5$	1·44–1·49‡		110–116‡		3*X*	Jarvis, 1953
	1·60§		101–109§			
SO_2	1·432		119·5		*M*	Kivelson, 1954
	1·43		119		3*X*	Post *et al.*, 1952
	1·43		120		*E*	Schomaker & Stevenson, 1940
SO_3	1·43		120		*E*	Palmer, 1938
SOF_2	1·412		—		*M*	Ferguson, 1954
SO_2F_2	1·37		129·6		*M*	Fristrom, 1952
	1·43		130		*E*	Stevenson & Russell, 1939
$SOCl_2$	1·45		—		*E*	Palmer, 1938
SO_2Cl_2	1·43		120		*E*	Palmer, 1938
$C_5H_8SO_2$	1·44		114		3*X*	Jeffrey, 1951
S_4N_4		1·62		106	*E*	Lu & Donohue, 1944
		1·60		102	2*X*	Clark, 1952

* All values, except those determined by microwaves, have been rounded off to the nearest 0·01 Å or to the nearest degree.

† *X*, X-ray diffraction; 2, two-dimensional; 3, three-dimensional; *M*, microwaves; *E*, electron diffraction.

‡ Not involving the esterified oxygen atom.

§ Involving the esterified oxygen atom.

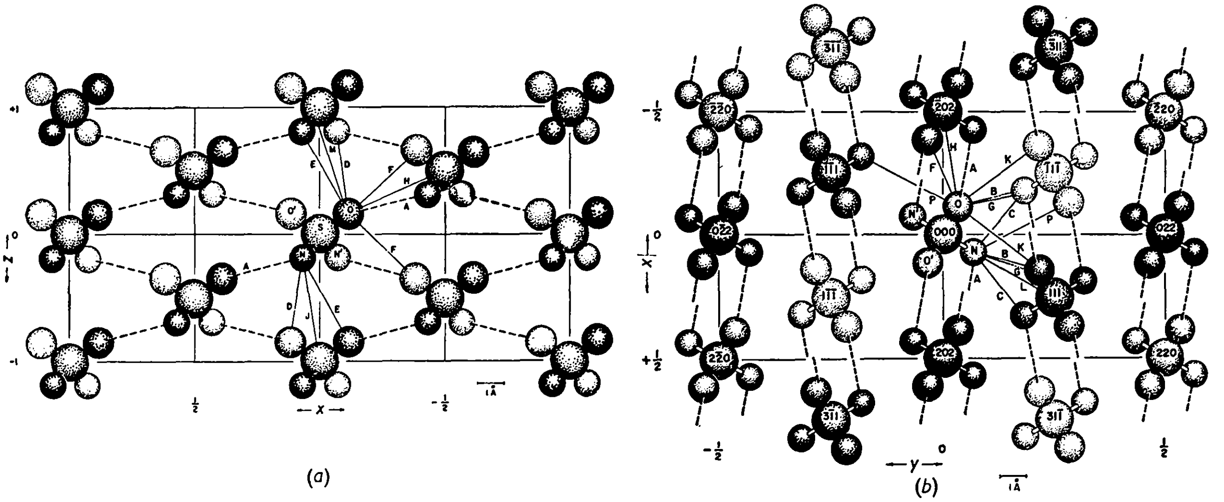

Fig. 2. (*a*) One of the layers of molecules, viewed along **b**. The lettered contact distances are listed in Table 7. (*b*) A portion of the structure viewed along **c**. The lettered contact distances are listed in Table 7. The numbers on the sulfur atoms represent the position of the atom in *quarter-translations* (see text).

molecule which has been studied carefully the S–O and S–N distances are *both* appreciably shorter than the single-bond distances, about 1·69 and 1·73 Å respectively, predicted from conventional radii (Pauling, 1940). A similar situation holds for the S–O and S–*X* distances in the thionyl and sulfuryl halides. In almost all of these molecules the S–O distance is comparable to or even shorter than that predicted for a conventional covalent double bond, while the distance to the other atom corresponds to a bond order of about 1·5 or greater if one interpolates in the usual way. Various models and explanations have been proposed in the references cited in the Introduction, but none seems adequate. The operation of a number of different opposing effects is suggested by the fact that although the F–S–F angle in the fluorides of Table 6 is less than 93°, the O–S–O angle when there are only two oxygen atoms in the molecule is usually 118° or more, and the N–S–N angle has an *intermediate* value. One can offer tentative explanations for the observations in terms of varying hybridization of the usual atomic orbitals and partial multiple bond and ionic character, but a rationalization of all of the observations probably must await precise measurements on some of the simple oxygen-acid salts, and resolution of the conflicting reports concerning sulfuryl fluoride.

The molecular environment

Fig. 2 shows diagrammatically the arrangement of molecules in the structure. The molecules are packed in an approximately hexagonal array in layers parallel to (010); Fig. 2(*a*) is a view of one of these layers, and Fig. 2(*b*) is a view along **c** indicating the way in which the layers pack together. The dashed lines in Fig. 2(*a*) indicate the four equivalent presumed hydrogen bonds which bond each molecule to four others in the layer. Since the hydrogen atoms were not located, it is not certain that these contacts can properly be described as hydrogen bonds; however, the distance (3·02 Å) is appreciably shorter than that of any other contact, and corresponds to a weak N–H · · · O bond (Donohue, 1952). The S–N · · · O angle of 111° supports this interpretation and the fact that the N · · · O–S angle is 156° suggests one reason for the weakness of the bond, since, to the extent that the unshared pairs of electrons on the oxygen atom are localized, they are very unfavorably placed for interaction with the proton. The weakness of the bond is in accord with the observed softness of the crystals.

Table 7 lists the unique intermolecular distances smaller than 4·2 Å; the accompanying letter is used to identify the distance (or one equivalent to it) in Fig. 2 and in the ensuing text. The subscripts attached to the atoms indicate, in terms of *quarter-translations*, the position of the sulfur atom in the molecule of which the atom is a part; thus O_{111} is attached to the sulfur atom at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and $N_{00\bar{4}}$ is attached to the sulfur atom at $(0, 0, \bar{1})$. Atoms without subscript are attached to the sulfur at the origin.

The shortest out-of-plane contact, B (3·14 Å), from oxygen to the nitrogen atom of the molecule at $(-\frac{1}{4}, \frac{1}{4}, \frac{3}{4})$, cannot be a hydrogen bond; the O · · · N–S configuration is nearly linear, the angle at the nitrogen atom being 167° and consequently no hydrogen atom can lie near this O · · · N line. The only other short distance, C (3·18 Å), between nitrogen atoms of molecules in adjacent layers, might be a very weak N–H · · · N bond. The angles of interest in this connection are: S–N · · · $N_{\bar{1}1\bar{1}}$, 110°; S–N · · · N_{111}, 121°; $N_{\bar{1}1\bar{1}}$ · · · N · · · N_{111}, 107°; $O_{20\bar{2}}$ · · · N · · · $N_{\bar{1}1\bar{1}}$, 136°; and $O_{20\bar{2}}$ · · · N · · · N_{111}, 61°. The first four of these angles are consistent with the possibility that this is a hydrogen bond, with the N–H on the molecule at the origin pointing toward $N_{\bar{1}1\bar{1}}$. The great departure of the fifth angle from the tetrahedral value might then explain the weakness of this interaction (or its equivalent, coming from N_{111}) since, as with the N–H · · · O bond, the unshared pair on the accepting atom is unfavorably situated.

The anisotropy of the temperature factors derived in the least-squares refinement can be interpreted qualitatively in terms of the intermolecular distances and suggested hydrogen bonding scheme. Since none of the presumed hydrogen bonds is very strong, they should not produce marked anisotropy, nor should they limit vibration markedly. However, the stronger N–H · · · O bonds are almost entirely in the *xz* plane, and primarily in the *x* direction. Thus, for the molecule as a whole, and particularly for the sulfur atom, situated approximately at the center of gravity, it might be expected that B_{11} would be smallest, B_{33} intermediate, and B_{22} the largest. The values of the B_{ii} for sulfur in Table 3 are entirely in accord with this picture. For the lighter oxygen atom, the individual values are all roughly one-third larger, with B_{22} still significantly larger than the others, although now B_{11} and B_{33} are the same within experimental error. Each oxygen atom makes one short contact (A, 3·02 Å) and four intermediate contacts (D, E, F, F, 3·5 Å) in the *xz* plane and only one fairly short contact between layers (B, 3·14 Å); all other distances to atoms in adjacent layers (G, K, P) are 3·74 Å or more. Hence it is reasonable that B_{22} is the largest of the B_{ii} for the oxygen atom.

On the other hand, each nitrogen atom makes only

Table 7. *Intermolecular distances**

I. Primarily parallel to (010)

Atoms	Distance	Identifying letter	Atoms	Distance	Identifying letter
O to N_{202}	3·02 Å	A	O to $S_{\bar{2}02}$	3·89 Å	H
O to N_{004}	3·48	D	N to $S_{00\bar{4}}$	3·92	J
O to N'_{004}	3·48	E	O to S_{004}	4·06	M
O to $O_{\bar{2}02}$	3·55	F			

II. Primarily out of the plane parallel to (010)

Atoms	Distance	Identifying letter	Atoms	Distance	Identifying letter
O to $N_{\bar{1}13}$	3·14	B	O to $O_{\bar{1}1\bar{1}}$	4·00	K
N to N_{111}	3·18	C	N to S_{111}	4·02	L
O to $N_{\bar{1}1\bar{1}}$	3·74	G	O to $N_{\bar{1}\bar{1}1}$	4·10	P

* Subscripts refer to the position of the sulfur atom of the molecule in quarter-translations (see text). The identifying letters have been assigned alphabetically in order of increasing distance.

Table 8. *Observed and calculated structure factor amplitudes for sulfamide*[*]

h	k	l	$\|F_o\|$	$\|F_c\|$
00	04	00	1692	1536
00	08	00	—	57
00	12	00	306	301
00	16	00	236	256
00	20	00	105	64
02	02	00	1360	1462
02	04	00	—	90
02	06	00	384	413
02	08	00	606	657
02	10	00	415	405
02	12	00	298	319
02	14	00	441	421
02	16	00	92	99
02	18	00	190	179
02	20	00	97	93
04	00	00	107	84
04	02	00	311	357
04	04	00	236	260
04	06	00	97	99
04	08	00	608	628
04	10	00	263	282
04	12	00	489	519
04	14	00	—	23
04	16	00	306	284
04	18	00	115	101
04	20	00	156	143
06	02	00	207	211
06	04	00	355	399
06	06	00	572	590
06	08	00	182	190
06	10	00	422	435
06	12	00	—	32
06	14	00	158	168
06	16	00	—	28
08	00	00	384	400
08	02	00	—	0
08	04	00	468	482
08	06	00	—	47
08	08	00	368	374
08	10	00	62	89
08	12	00	97	97
08	14	00	—	38
10	02	00	269	283
10	04	00	148	134
10	06	00	278	254
10	08	00	—	31
10	10	00	170	144
01	01	01	1050	989
01	03	01	1470	1362
01	05	01	571	557
01	07	01	684	645
01	09	01	284	305
01	11	01	307	327
01	13	01	297	289
01	15	01	231	240
01	17	01	176	156
01	19	01	117	97
01	21	01	73	76
03	01	01	712	762
03	03	01	254	274
03	05	01	776	921
03	07	01	254	233
03	09	01	388	406
03	11	01	466	425
03	13	01	223	243
03	15	01	187	203
03	17	01	209	205
03	19	01	78	82
05	01	01	232	216
05	03	01	349	354
05	05	01	374	400
05	07	01	312	274
05	09	01	477	480
05	11	01	170	163
05	13	01	310	296
05	15	01	254	218
05	17	01	83	91
05	19	01	139	139
07	01	01	321	335
07	03	01	371	377
07	05	01	186	208
07	07	01	417	431
07	09	01	148	140
07	11	01	193	217
07	13	01	100	115
07	15	01	66	86
09	01	01	321	286
09	03	01	173	199
09	05	01	226	252
09	07	01	214	198
09	09	01	103	119
09	11	01	173	143
11	01	01	148	122
11	03	01	159	143
11	05	01	126	127
00	02	02	427	423
00	06	02	910	859
00	10	02	550	556
00	14	02	338	313
00	18	02	198	177
02	00	02	441	427
02	02	02	424	452
02	04	02	684	625
02	06	02	502	501
02	08	02	654	613
02	10	02	307	246
02	12	02	321	304
02	14	02	—	54
02	16	02	173	171
02	18	02	—	52
04	02	02	790	808
04	04	02	306	338
04	06	02	533	475
04	08	02	111	72
04	10	02	346	310
04	12	02	148	132
04	14	02	254	236
04	16	02	—	46
04	18	02	136	133
06	00	02	581	600
06	02	02	103	88
06	04	02	404	400
06	06	02	170	167
06	08	02	212	224
06	10	02	145	148
06	12	02	248	256
06	14	02	—	4
06	16	02	196	188
08	02	02	354	346
08	04	02	56	74
08	06	02	134	185
08	08	02	—	48
08	10	02	229	198
08	12	02	—	22
10	00	02	229	212
10	02	02	61	55
10	04	02	179	179
10	06	02	56	66
10	08	02	134	152
01	01	03	117	149
01	03	03	142	159
01	05	03	309	315
01	07	03	449	415
01	09	03	379	389
01	11	03	251	248
01	13	03	170	186
01	15	03	114	135
01	17	03	78	103
03	01	03	455	428
03	03	03	354	350
03	05	03	393	392
03	07	03	321	337
03	09	03	234	228
03	11	03	235	250
03	13	03	89	81
03	15	03	47	74
03	17	03	108	109
05	01	03	552	445
05	03	03	519	425
05	05	03	262	244
05	07	03	234	215
05	09	03	142	154
05	11	03	78	91
05	13	03	128	124
05	15	03	108	83
00	00	04	196	210
00	04	04	248	263
00	08	04	271	282
00	12	04	212	257
02	02	04	377	315
02	04	04	234	233
02	06	04	312	284
02	08	04	89	121
02	10	04	209	210
02	12	04	—	17
02	14	04	153	161
04	00	04	371	384
04	02	04	103	103
04	04	04	318	339
04	06	04	66	81
04	08	04	218	217
04	10	04	73	66
04	12	04	131	114
01	01	05	204	226
01	03	05	116	136
01	05	05	139	165
01	07	05	—	50
01	09	05	91	117
01	11	05	56	77
03	01	05	173	143
03	03	05	184	171
03	05	05	78	83
03	07	05	139	139
03	09	05	89	76
05	01	05	103	97
05	03	05	176	130
05	05	05	134	102

[*] All F_o and F_c have been multiplied by 10.

one short (A, 3·02 Å) and two intermediate (D, E, 3·5 Å) contacts in the plane, and between planes makes contact with two other nitrogen atoms at 3·18 Å (C) and with an oxygen atom at 3·14 Å (B). Hence it is not unexpected that B_{22} for nitrogen is appreciably smaller than for oxygen, and about the same as for sulfur. In fact, for the nitrogen atom, B_{22} is perhaps slightly smaller than B_{33}, although the difference is not much greater than the standard deviation of either and hence is hardly significant.

It is undoubtedly true that anisotropic temperature factors derived in the present manner will reflect any anisotropic errors in intensity measurement arising from absorption and similar effects. However, it seems likely that these errors will appear as an overall anisotropy, and that significant individual variations, of the sort noted here, are more likely to reflect real thermal effects, particularly since 'bond corrections' appear to be much less significant than thermal effects (McWeeny, 1954). During the present investigation, it was gratifying to note that the marked anisotropic ripples present in the original difference maps (which varied appreciably for the different atoms) were effectively removed in later syntheses based on phases calculated with the improved temperature factors derived primarily by least-squares methods.

Note added in proof, 18 *June* 1956.—Lide, Mann & Fristrom (1956) have recently re-investigated the microwave spectrum of sulfuryl fluoride and report the following structural parameters: S–O, 1·405 Å; S–F, 1·530 Å; O–S–O, 123°55′; F–S–F, 96°8′. These values differ significantly from those reported earlier by Fristrom (1952) and more nearly agree with the electron-diffraction results, the differences being approximately at or within the stated limits of error of the two studies.

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