$$\langle E_{\mathbf{h}}^2 E_{-2\mathbf{h}}\rangle = \begin{cases} |\mathbf{h}|>2k_0 : \dfrac{1}{\sqrt{N}} \\ k_0<|\mathbf{h}|<2k_0 : \dfrac{1}{\sqrt{N}}\left(\dfrac{3}{2}\dfrac{|\mathbf{h}|}{k_0}-\dfrac{1}{8}\dfrac{|\mathbf{h}|^3}{k_0^3}-1\right) \\ |\mathbf{h}|<k_0 : \dfrac{1}{\sqrt{N}}\,\dfrac{3}{8}\,\dfrac{|\mathbf{h}|^3}{k_0^3}. \end{cases} \qquad (19)$$

Avec une loi de probabilité uniforme (P_0), le résultat obtenu est:

$$\langle E_{\mathbf{h}}^2 E_{-2\mathbf{h}}\rangle = \frac{1}{\sqrt{N}}$$

quel que soit **h**.

Le fait d'introduire la restriction supplémentaire des 'atomes impénétrables' ne donne un résultat identique que pour les facteurs de structure avec $|\mathbf{h}|$ grand ($|\mathbf{h}|>2k_0$). Pour les autres, les valeurs moyennes obtenues (19) sont différentes. Ce fait est général, on peut prévoir pour toutes les lois de probabilités relatives aux facteurs de structures $E_{\mathbf{h}}E_{\mathbf{k}}\ldots$ une dépendance importante avec $|\mathbf{h}|$, $|\mathbf{k}|\ldots$ lorsque ces modules seront faibles.

Un long travail reste à faire pour trouver les nouvelles lois. Disons que cette méthode sera particulièrement intéressante dans le cas de structures avec un grand nombre d'atomes ayant une forte tendance à l'équipartition ce qui est loin d'être restrictif.

Nous remercions M. Bertaut, Directeur Scientifique au C.N.R.S., de l'intérêt qu'il a porté à ce travail.

References

Bertaut, E. F. (1955). *C. R. Acad. Sci., Paris*, **240**, 938.

Goedkoop, J. A. (1952). *The Phase Problem in X-ray Crystal Analysis*, p. 61. The Pennsylvania State College.

Karle, J. & Hauptman, H. (1950). *Acta Cryst.* **3**, 181.

Lajzérowicz, J. (1964). Thèse d'Etat, Grenoble.

Messiah, A. (1960). *Mécanique quantique*, Tome II. Paris: Dunod.

Nozières, P. (1963). *Le problème à N corps*. Paris: Dunod.

Pines, D. (1963). *Elementary excitations in solids*. Benjamin.

Acta Cryst. (1966). **21**, 12

The Molecular and Crystal Structure of Dimethyl Sulfoxide, $(H_3C)_2SO$

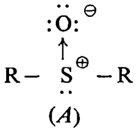
By Robert Thomas*, Clara Brink Shoemaker† and Klaas Eriks
Boston University, Department of Chemistry, 675 *Commonwealth Avenue, Boston, Massachusetts* 02215, *U.S.A.*

(*Received* 28 *June* 1965)

Crystals of dimethyl sulfoxide were studied at 5 °C. They are monoclinic, space group $P2_1/c$, with cell dimensions $a = 5{\cdot}303 \pm 0{\cdot}005$, $b = 6{\cdot}829 \pm 0{\cdot}003$, $c = 11{\cdot}693 \pm 0{\cdot}010$ Å, $\beta = 94°30' \pm 15'$ and 4 molecules per cell. Least-squares refinements were carried out both excluding and including unobserved reflections. For the former case the final R is 7·4 % (507 reflections), for the latter 13·3 % (777 reflections). Although no molecular symmetry is required, the molecule possesses symmetry m within the accuracy of the determination. Bond distances were corrected for librational motion. The distances found (uncorrected values are given in parentheses) are: S–O = 1·531 ± 0·005 Å (1·513), and S–C (average) = 1·798 ± 0·010 Å (1·788). The most important bond angles are O–S–C– (average) 106·7 ± 0·4° and C–S–C 97·4 ± 0·4°. Bond distances, particularly of S–O, angles and packing are discussed.

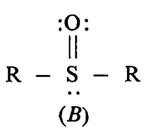
Introduction

A long-standing controversy exists regarding the proper description of the sulfur–oxygen bond. Quantitative discussion of this bond was started by Moffitt (1950) and recently opposing views have been taken in its description by Cruickshank (1961*a*) and by Price & Oae (1962). The difference in viewpoint lies in whether the semipolar (A) or the doubly bonded covalent structure (B) is the major contributor to the resonance hybrid.



$R-\overset{\uparrow\ \ddot{O}:^{\ominus}}{\underset{\cdot\cdot}{S}}{}^{\oplus}-R$

(A)



$R-\overset{:O:}{\overset{\|}{\underset{\cdot\cdot}{S}}}-R$

(B)

Price & Oae base their preference for the semipolar structure on physical and chemical data for sulfones, sulfoxides and sulfonium salts. Cruickshank's treatment, applicable in particular to tetrahedrally coordinated sulfur, concludes that sulfur–oxygen bond shortenings can be explained solely on the basis of $2p-3d-\pi$ bonding.

The structure determination of dimethyl sulfoxide (DMSO) contributes to this discussion a reliable value for the sulfur–oxygen bond length in a sulfoxide. Electron diffraction studies of the substance have been reported (Rundle, 1950, Bastiansen & Viervoll, 1948), but these studies lack in desired accuracy. DMSO forms complexes with many metal halides, such as $SbCl_3$, $SbCl_5$, $SnCl_4$ (Lindquist, 1959) and $NiCl_2$, $CoCl_2$, $PdCl_2$ *etc.* (Cotton & Francis, 1960). A meaningful comparison of the sulfur–oxygen bond length in these complexes with that in the parent molecule now becomes possible.

---

* Present address: Brookhaven National Laboratory, Chemistry Department, Upton, Long Island, New York 11973, U.S.A.

† Permanent address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, U.S.A.

A structure determination of DMSO seemed further appropriate because of its unusual medicinal properties, one of which is its ability to permeate rapidly through the skin (Jacob, 1964). Its effectiveness as a medicine against arthritis and bursitis is still under study.

Experimental

A capillary-enclosed single crystal of DMSO was grown by slow cooling of the reagent grade liquid material to a temperature below 18·6°C, its freezing point. The 0·3 mm diameter glass capillary was mounted on a precession camera during the crystal growth. The cooling was provided by a stream of air which had been passed through a copper coil immersed in an ice–methanol slush. The single crystal was maintained at a temperature of about 5°C and was found to have its needle axis, a, approximately parallel to the axis of the capillary.

Sets of X-ray photographs of ten reciprocal lattice nets were taken with Mo $K\alpha$ radiation, including the hkL with $L=0$ to 4, the hKl with $K=0$ to 3 and the $h,k,2k$. Of the total of 868 unique reflections collected, 91 were systematically absent, 507 were of measurable intensity and 270 were below the limit of observability. The 868 data represent 62% of the total of 1400 unique reflections in the reflection sphere that are formally accessible to the precession instrument.

From the photographs the crystal was found to be monoclinic. The unit-cell dimensions, obtained after calibration of the camera with a sodium chloride crystal, were $a=5{\cdot}303 \pm 0{\cdot}005$, $b=6{\cdot}829 \pm 0{\cdot}003$, $c=11{\cdot}693 \pm 0{\cdot}010$ Å and $\beta=94°30' \pm 15'$; λ Mo $K\alpha=0{\cdot}7107$ Å. The unit-cell volume is $V=422{\cdot}2$ Å^3 and the calculated density is $D_x=1{\cdot}23$ g.cm^{-3} assuming $Z=4$. Since no experimental value for the density of the solid is available, the only possible comparison is with the liquid density of 1·101 g.cm^{-3}. The observed extinctions, $h0l$ with $l=2n+1$ and $0k0$ with $k=2n+1$ determine uniquely the space group $P2_1/c$.

The intensity of each unique reflection was estimated independently from one to four times by visual comparison with a standard intensity scale.

Preliminary data processing*

The scaling and averaging of the photographic X-ray intensity data of DMSO were performed according to a procedure described by Simpson (1963). In this procedure the most probable value of the scaling factor relating intensities belonging to different sets, a and b, is determined as the weighted harmonic mean of the ratios of intensities in the two sets with the same Miller indices. All well-determined ratios of such corresponding intensities which are available contribute to the determination of the scaling factors, and the appropriate weights are the equivalent numbers of observations of the ratios. A study of the precision of the scaling factors so obtained allows a thorough error analysis of the original intensity data, resulting in the evaluation of an estimated standard error associated with the intensity of each reflection. These standard errors, reflecting the precision of the intensity estimations, were used to provide weights in the least-squares refinement of the DMSO structure parameters. Standard errors for the unobserved reflections were arrived at by applying the same error analysis that was used for the observed reflections. In Table 5, the standard error associated with each reflection is given.

Lorentz and polarization corrections were applied to the DMSO intensity data. No correction for absorption was made since with Mo $K\alpha$ radiation $\mu r=0{\cdot}16$ for the crystal used, implying a maximum error of less than 2% by omission of the correction. A Wilson scale-temperature plot was used to determine the initial values of the absolute scale constant K and the overall isotropic temperature factor B. The value of B was 3·05 Å^2 and the value of K did not undergo major changes in subsequent refinement calculations.

For improved resolution in the Patterson and Patterson superposition functions, the intensity coefficients were sharpened with partial origin removal.

Structure determination and refinement*

The correct initial model for the crystal structure of DMSO was independently arrived at in two ways: (1) the direct interpretation of the three-dimensional Patterson function, and (2) the production of the structure image by the minimum function superposition of the three-dimensional Patterson function. The initial atomic coordinates deduced in these two ways were virtually identical. Also, if the assumption was made

---

* All data reduction computations were performed on an IBM 7094 computer. Mainly the programs used were kindly supplied by Dr P.G.Simpson and Professor W.N.Lipscomb, Harvard University, Chemistry Department, *viz.* XRDP-1, XRDP-3, WILPLT and PASHCO. Where necessary, supplementary programs were written by one of us (R.T.); *viz.* XRDP-3A, INT-FO.

* The following lists the IBM 7094 computer programs used.

1. W.G.Sly, D.P.Shoemaker & J.H.Van der Hende. *Two- and Three-dimensional Crystallographic Fourier Summation Program for the IBM* 7090 *Computer.* Massachusetts Institute of Technology, Esso Research and Engineering Co. (1962).
2. P.G.Simpson & W.N.Lipscomb. *HASUP, A High Order Minimum Function Program for the IBM* 7090. Department of Chemistry, Harvard University (1963).
3. W.R.Busing, K.O.Martin & H.A.Levy. *ORFLS, A Fortran Crystallographic Least-Squares Program.* ORNL-TM-305, Oak Ridge National Laboratory (1962).
4. W.R.Busing, K.O.Martin & H.A.Levy. *ORFFE, A Fortran Crystallographic Function and Error Program.* Oak Ridge National Laboratory (1962).
5. D.P.Shoemaker. *DISTAN, A Crystallographic Bond Distance, Bond Angle, and Dihedral Angle Computer Program.* Massachusetts Institute of Technology (1963).
6. D.P.Shoemaker & R.C.Srivastava. *VIBELL, Anisotropic Temperature Factor Interpreting Program.* Massachusetts Institute of Technology (1963).

that the sulfur atom was a heavy atom in the structure, the Patterson map allowed only two alternatives for the coordinates of the sulfur atom. Only one of these was consistent with the coordinates found in the minimum superposition map. A comparison of the heavy atom Fourier maps based on each alternative confirmed the sulfur atom position deduced from the superposition map.

Refinement of the structure was carried out by least squares. The full matrix of the normal equations was used, the quantity minimized being $R' = \Sigma\, w(|F_o| - |F_c|)^2$. The weight w of each observation F_o was $w = 1/\sigma^2(F_o)$, where σ is the standard error described in the previous section. Atomic scattering factors used were those for the uncharged sulfur, oxygen, carbon and hydrogen atoms listed in *International Tables for X-ray Crystallography* (1962).

Because the number of unobserved reflections was large (35% of the data) it appeared desirable to carry out separate refinements including and omitting unobserved reflections, to see if the latter would affect the resulting structure. Only the observed reflections were included in the isotropic refinement of the initial model. The starting R index was 22·9%, convergence was achieved after three least-square cycles and an R of 16·2% was reached at the end of the isotropic refinement. In all refinement calculations only one scale factor was used to relate F_o's to F_c's.

A three-dimensional difference Fourier map showed the thermal motion of the atoms to be noticeably anisotropic. Particularly sulfur and oxygen showed large amplitudes of vibration in the y direction. Individual anisotropic temperature factors were applied of the form

$$T_i = \exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\}\,.$$

The starting parameters for the anisotropic refinement were those obtained from the isotropic calculations. Convergence was achieved after two cycles and R became 8·9%.

A new difference Fourier map showed that the applied thermal motion corrections were satisfactory. In addition, the carbon atom sites were roughly tetrahedrally surrounded by broad regions of low positive density located at distances that could represent C–H lengths. The peak definition was poor. Therefore, instead of choosing hydrogen positions directly from the difference map, ideal tetrahedral positions were calculated, with respect to each carbon atom, in such a way that the S–C bond was a threefold axis of the tetrahedron and each hydrogen atom was located in as high a region of difference map density as possible. The assumed C–H length in this procedure was 1·08 Å. The hydrogen atoms thus located were labelled H(ij) with i referring to the particular hydrogen atom and j referling to the corresponding carbon atom. Each H(ij) was now included in the model and assigned the isotropic temperature coefficient which the corresponding carbon atom j had at the end of the isotropic refinement.

The final least-squares cycles with only the observed reflections included the hydrogen atoms, but neither their atomic position parameters nor their isotropic temperature coefficients were varied. With the hydrogen atoms thus included, R dropped to 7·9% before any refinement cycles were calculated. Convergence was achieved after one cycle and the atomic position and temperature factor parameters with their standard errors after four cycles are listed in Tables 1 and 2 respectively. The final value of R with only the observed reflections was 7·4%. The weighted R index $Rw = (\Sigma\, w(F_o - kF_c)^2/\Sigma\, wF_o^2)^{\frac{1}{2}}$ had value 10·3%.

The scaled and corrected absent reflections were then included in the data, each with value $(I_{\min}/3)^{\frac{1}{2}}$ (Hamilton, 1955). $I_{\min}$ had a value 1·0 as determined from the standard intensity scale. Anisotropic cycles were restarted, using the parameters of Tables 1 and 2. Tables 3 and 4 list the results after four cycles, convergence having been reached after three cycles. During these cycles the atomic position and temperature parameters for the hydrogen atoms were held constant as before. As expected, the R values increased attaining values of 13·3% and 31·0%, respectively, for R and Rw. The final list of calculated structure amplitudes given in Table 5 is based on the parameters of Tables 3 and 4.

Discussion

Thermal motion

Comparison of Tables 1 and 2 with Tables 3 and 4 shows a significant difference for some of the parameters calculated with and without inclusion of the unobserved reflections. Standard errors were generally higher for the refinement which included the absences. Often absent reflections are left out in refinement calculations, but in this study, where their number is relatively large, it is difficult to justify their omission.

Hamilton (1955) recommends inclusion of the unobserved intensities, but Vand (1965) concludes that their inclusion in the final stages of refinement is basically incorrect. Perhaps the correct treatment of unobserved reflections depends on the problem under investigation, notably on the ratio of the numbers of unobserved and observed intensities. From the large difference between R and Rw for the calculations including the unobserved in the present study it is quite obvious that the weights of the unobserved were higher than they should have been, and this may account for the significant difference in some of the parameters in the two types of refinement. These high weights were chosen somewhat on purpose, so that the influence on the final parameters could be observed.

As a compromise in calculating the interatomic distances, angles and the thermal vibration amplitudes, the average of the two sets of parameters was taken. This procedure puts more weight on the observed reflections, since they contribute to both refinements. The procedure appears furthermore acceptable because the distances, angles and thermal amplitudes determined by the parameters of the two separate refinements never differ by more than four times the standard deviation. To avoid prejudice the larger standard error was always retained in the averaging process.

The distances, angles and thermal parameters were thus calculated, using the full parameter errors and variance-covariance matrix in the estimation of standard errors including standard errors in the cell parameters. For each principal axis i of the vibration ellipsoids, Table 6 lists the r.m.s. amplitudes U_i and the direction cosines p, q and r with respect to a Cartesian coordinate system having Z parallel to the c axis and X parallel to a^*. Fig. 1 shows the ellipsoids viewed along the $[\bar{1}01]$ axis.

The sulfur atom has the smallest vibrational ellipsoid, consistent with the fact that the center of gravity of the molecule lies close to that atom. In such a case a clearer view of the intramolecular motions is available by subtracting from the total molecular motion the translational component (Caron, Palenik, Goldish & Donohue, 1964). It is assumed that the translational motion of the molecule is represented by the displacements of the sulfur atom. The translational components $T_{\parallel}$ and $T_{\perp}$ parallel and perpendicular to each bond

Table 1. *Atomic position parameters after anisotropic refinement including hydrogen atoms and using only observed reflections*

	x/a	$10^4\sigma(x)$	y/b	$10^4\sigma(y)$	z/c	$10^4\sigma(z)$
S	0·1772	2	0·1599	3	0·1885	1
O	0·8955	7	0·1432	7	0·1641	5
C(1)	0·3108	10	−0·0493	11	0·1290	6
C(2)	0·2887	14	0·3408	10	0·0910	9
H(11)	0·2691		−0·0451		0·0344	
H(21)	0·2329		−0·1795		0·1615	
H(31)	0·5139		−0·0467		0·1461	
H(12)	0·2669		0·2835		0·0036	
H(22)	0·1750		0·4729		0·0950	
H(32)	0·4830		0·3741		0·1139	

Table 2. *β_{ij} coefficients after anisotropic refinement including hydrogen atoms and using only observed reflections**†

	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
S	266 (5)	342 (6)	82 (1)	−37 (4)	22 (2)	−32 (2)
O	272 (12)	436 (17)	137 (6)	−2 (11)	41 (7)	−49 (7)
C(1)	360 (20)	339 (19)	99 (6)	0 (18)	50 (10)	22 (11)
C(2)	558 (29)	242 (17)	149 (11)	−6 (20)	52 (15)	23 (10)
H(11)	382	230	79	0	14	0
H(21)	382	230	79	0	14	0
H(31)	382	230	79	0	14	0
H(12)	552	333	114	0	20	0
H(22)	552	333	114	0	20	0
H(32)	552	333	114	0	20	0

* $10^4\sigma$ is given in parentheses.

† Anisotropic equivalents of the isotropic β_i are listed for the hydrogen atoms.

Table 3. *Atomic position parameters after anisotropic refinement including hydrogen atoms* and using all reflections*

	x/a	$10^4\sigma(x)$	y/b	$10^4\sigma(y)$	z/c	$10^4\sigma(z)$
S	0·1782	2	0·1613	3	0·1888	1
O	0·8933	8	0·1497	9	0·1611	5
C(1)	0·3104	12	−0·0492	11	0·1264	8
C(2)	0·2923	16	0·3375	11	0·0908	11

* The positional parameters for the hydrogen atoms are the same as those in Table 1.

Table 4. *β_{ij} coefficients after anisotropic refinement including hydrogen atoms* and using all reflections*†

	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
S	293 (10)	381 (12)	96 (3)	−37 (3)	31 (4)	−29 (2)
O	289 (17)	465 (20)	157 (6)	13 (11)	85 (8)	−79 (8)
C(1)	423 (25)	291 (21)	118 (6)	69 (16)	59 (9)	34 (11)
C(2)	471 (30)	287 (23)	175 (9)	−36 (15)	14 (14)	−2 (12)

* The β_{ij} parameters for the hydrogen atoms are the same as those in Table 2.

† $10^4\sigma$ is given in parentheses.

direction – *i.e.* the r.m.s. amplitudes in these directions – were therefore calculated for the sulfur atom. Similarly, $U_\parallel$ and $U_\perp$ for each bonded atom. $U'_\parallel$ and $U'_\perp$ then represent the amplitudes after subtraction of the translational component. The results are given in Table 7. It is seen that $U'_\perp$ is larger than $U'_\parallel$ for oxygen as well as the carbon atoms, consistent with a molecular libration.

In cases where such a libration is found a correction must be applied to the bond lengths (Cruickshank 1956,

Table 5. *Observed and calculated structure factors*

Sigmas are the standard errors in the observed structure factors. Unobserved reflections are denoted by an asterisk and are entered under *F(OBS)* with a value $(I_{\min}/3)^{\frac{1}{2}}$.

H	K	L	F(OBS)	KF(CALC)	SIGMA
0	0	2	53.04	-47.97	3.143
0	0	4	45.63	-41.96	1.664
0	0	6	33.87	30.77	1.235
0	0	8	21.85	-18.21	0.527
0	0	10	11.68	9.60	0.337
0	0	12*	1.70	-0.64	0.061
0	0	14	4.40	-2.87	0.155
0	0	16	3.63	2.43	0.117
1	0	0	36.77	35.36	0.842
1	0	2	90.47	-94.68	9.803
-1	0	2	38.48	34.51	1.907
1	0	4	21.79	21.00	1.249
-1	0	4	20.24	-21.25	0.836
1	0	6	8.02	4.52	0.320
-1	0	6	37.99	35.19	1.883
1	0	8	7.88	-5.26	0.331
-1	0	8	22.20	-21.27	0.735
1	0	10	9.51	7.85	0.423
-1	0	10*	1.58	-2.35	0.049
1	0	12	8.34	-6.52	0.371
-1	0	12	11.93	9.68	0.501
1	0	14*	1.69	2.20	0.061
-1	0	14	7.93	-5.70	0.353
2	0	0	50.75	-52.64	1.072
2	0	2	20.47	17.41	0.592
-2	0	2*	0.92	0.75	0.056
2	0	4	28.42	25.40	1.080
-2	0	4	12.17	-12.64	0.486
2	0	6	29.60	-25.21	1.697
-2	0	6	19.83	18.87	0.657
2	0	8	14.15	11.59	0.538
-2	0	8	3.73	3.32	0.183
2	0	10*	1.66	-0.69	0.063
-2	0	10	16.72	-14.72	0.667
2	0	12	5.96	-4.26	0.265
-2	0	12	10.74	8.73	0.428
2	0	14	4.41	3.32	0.196
-2	0	14*	1.69	-1.20	0.061
3	0	0	31.28	-29.13	0.549
3	0	2	53.95	50.79	2.023
-3.	0	2	3.09	1.28	0.303
3	0	4	15.64	-13.11	0.442
-3	0	4	6.99	8.46	0.240
3	0	6	18.41	-15.89	0.937
-3	0	6	21.89	-21.32	0.756
3	0	8	20.26	15.45	1.031
-3	0	8	19.56	17.09	0.712
3	0	10	8.85	-6.79	0.394
-3	0	10	6.17	-4.82	0.274
3	0	12*	1.68	0.90	0.062
-3	0	12*	1.71	-2.16	0.061
-3	0	14	4.01	3.09	0.197
4	0	0	10.47	-10.39	0.213
4	0	2	20.84	18.46	0.574
-4	0	2	3.67	-2.89	0.359
4	0	4	21.58	-19.96	0.610
-4	0	4	29.08	30.84	0.855
4	0	6	6.81	6.76	0.303
-4	0	6	27.28	-27.12	1.006
4	0	8	4.77	3.36	0.297
-4	0	8*	1.66	2.54	0.063
4	0	10	6.17	-4.75	0.274
-4	0	10	9.62	9.04	0.428
4	0	12	4.23	3.05	0.188
-4	0	12	8.39	-6.83	0.373
-4	0	14	3.04	2.52	0.168
5	0	0*	1.66	1.67	0.062
5	0	2*	1.68	-1.51	0.062
-5	0	2	15.63	-14.75	0.465
5	0	4*	1.66	-2.62	0.062
-5	0	4	20.19	18.03	0.585
5	0	6	8.91	8.10	0.397
-5	0	6*	1.68	-2.34	0.062
5	0	8	7.60	-5.57	0.338
-5	0	8	9.49	-8.32	0.422
5	0	10*	1.43	0.97	0.054
-5	0	10	9.28	8.21	0.413
-5	0	12	4.24	-3.86	0.188
6	0	0	10.34	8.94	0.211
6	0	2	9.38	-8.21	0.340
-6	0	2	4.30	-2.83	0.207
6	0	4	5.64	5.28	0.219
-6	0	4	7.42	-7.37	0.269
6	0	6*	1.51	0.56	0.051
-6	0	6	9.71	7.38	0.432
6	0	8	5.81	-3.75	0.259
-6	0	8	4.19	-3.23	0.204
7	0	0*	1.38	1.16	0.056
7	0	2	8.34	-6.06	0.290
-7	0	2	10.33	8.57	0.347
7	0	4	7.06	4.84	0.262
-7	0	4	11.61	-9.58	0.390
0	1	1	28.07	30.01	1.305
0	1	2	72.77	-68.96	5.257
0	1	3	63.66	-53.98	7.754
0	1	4	44.53	42.02	3.262
0	1	5	26.51	24.42	1.387
0	1	6	20.08	-17.46	0.874
0	1	7	3.01	3.66	0.482
0	1	8*	1.33	-0.58	0.039
0	1	9	3.95	-3.56	0.358
0	1	10	12.40	10.38	0.688
0	1	11	3.95	2.73	0.520
0	1	12	8.25	-6.75	0.524
0	1	13	4.35	-3.59	0.499
0	1	14*	1.86	2.13	0.070
1	1	0	42.72	-43.50	1.966
1	1	1	17.45	-17.13	0.586
-1	1	1	33.38	33.02	2.073
1	1	2	16.17	-11.47	0.498
-1	1	2	42.89	-44.29	1.818
1	1	3	5.83	-6.05	0.631
-1	1	3	29.14	-26.18	2.097
1	1	4	26.18	20.59	1.699
-1	1	4	40.88	36.18	3.926
1	1	5	22.14	18.57	1.381
-1	1	5	4.61	4.95	0.506
1	1	6	12.61	-11.28	0.814
-1	1	6*	1.17	-1.14	0.044
1	1	7	11.48	-10.33	0.802
-1	1	7	4.31	4.42	0.551
1	1	8	12.58	11.67	0.971
-1	1	8	24.35	-21.82	1.464
1	1	9*	1.49	1.18	0.052
-1	1	9	8.34	-7.75	0.643
1	1	10	5.37	-5.49	0.589
-1	1	10	16.96	14.66	1.095
1	1	11*	1.66	-1.24	0.062
-1	1	11	9.06	8.11	0.700
1	1	12	4.24	-2.40	0.955
-1	1	12*	1.71	-2.63	0.061
1	1	13*	1.81	-0.42	0.071
-1	1	13*	1.80	-1.69	0.058
1	1	14	4.55	2.97	1.023
-1	1	14*	1.86	-1.26	0.070
2	1	0	11.40	-8.86	0.343
2	1	1	6.10	-7.67	0.280
-2	1	1	5.16	-5.72	0.223
2	1	2	30.52	30.66	0.900
-2	1	2*	0.97	-0.67	0.054
2	1	3	22.42	22.23	0.768
-2	1	3	2.98	2.62	0.148
2	1	4	19.22	-17.93	0.777
-2	1	4*	1.17	-1.56	0.044
2	1	5	14.67	-13.14	1.327
-2	1	5*	1.25	-1.25	0.041
2	1	6*	1.40	2.56	0.056
-2	1	6	20.73	18.10	1.247
2	1	7	4.22	-5.04	0.461
-2	1	7	6.83	6.89	0.749
2	1	8	8.06	6.80	0.623
-2	1	8	15.81	-15.20	1.021
2	1	9	8.57	6.81	0.661
-2	1	9	9.21	-9.50	0.710
2	1	10	10.39	-9.85	0.802
-2	1	10*	1.61	2.78	0.064
2	1	11*	1.75	-2.89	0.059
-2	1	11*	1.68	1.34	0.062
2	1	12	4.38	4.27	0.700
-2	1	12	4.26	2.76	0.681
-2	1	13	4.42	3.50	0.707
-2	1	14	4.55	-3.74	0.727
3	1	0	21.87	19.50	0.589
3	1	1	8.16	6.74	0.325
-3	1	1	17.77	-17.50	0.555
3	1	2	15.91	14.06	0.375
-3	1	2	30.28	27.93	0.723
3	1	3	10.53	10.45	0.360
-3	1	3	14.88	15.19	0.456
3	1	4	31.69	-27.92	1.204
-3	1	4	24.77	-23.07	0.860
3	1	5	19.85	-17.76	1.282
-3	1	5	6.67	-7.95	0.730
3	1	6	15.75	13.41	1.424
-3	1	6	5.59	5.12	0.612
3	1	7	9.47	8.74	1.025
-3	1	7*	1.54	1.85	0.050
3	1	8*	1.68	-1.49	0.062
-3	1	8	5.94	6.49	0.651
3	1	9*	1.72	2.23	0.060
-3	1	9	4.00	4.39	0.899
3	1	10	4.84	-3.05	0.617
-3	1	10	7.07	-6.39	0.774
3	1	11	4.42	-3.03	0.707
-3	1	11	5.96	-5.77	0.653
3	1	12	5.06	4.09	0.647
-3	1	12	4.94	4.52	0.632
-3	1	13*	1.86	1.92	0.070
4	1	0	23.60	20.65	0.651
4	1	1	8.22	6.86	0.356
-4	1	1	14.69	-14.96	0.536
4	1	2	9.12	-7.80	0.279
-4	1	2	26.01	25.61	0.594
4	1	3*	1.41	-0.58	0.092
-4	1	3	12.77	13.87	0.417
4	1	4	9.96	-7.82	0.441
-4	1	4	9.01	-9.05	0.399
4	1	5*	1.70	-2.71	0.061
-4	1	5*	1.65	-1.38	0.063
4	1	6	13.60	11.10	1.470
-4	1	6	11.00	-12.58	0.849
4	1	7	6.30	6.23	0.690
-4	1	7	9.64	-10.32	0.744
4	1	8	6.08	-5.37	0.938
-4	1	8	14.64	14.27	1.130
4	1	9	4.43	-4.13	0.996
-4	1	9	10.20	9.84	0.788
4	1	10*	1.86	1.99	0.070
-4	1	10	6.09	-6.82	0.668
4	1	11*	1.86	0.23	0.070
-4	1	11*	1.83	-2.07	0.071
5	1	0	8.90	7.54	0.439
5	1	1	4.69	4.92	0.319
-5	1	1	6.29	-5.13	0.302
5	1	2	9.71	-8.15	0.284
-5	1	2	4.13	4.36	0.280
5	1	3*	1.59	-2.94	0.098
-5	1	3*	1.55	0.39	0.100
5	1	4	7.22	7.62	0.391
-5	1	4	6.84	6.63	0.370
5	1	5*	1.83	2.82	0.071
-5	1	5	6.41	6.80	0.703
5	1	6*	1.84	-1.06	0.070
-5	1	6	11.20	-11.36	0.864
5	1	7*	1.86	-1.41	0.070
-5	1	7	9.20	-7.88	0.817
5	1	8	4.54	-3.06	1.018
-5	1	8	6.84	7.95	0.748
5	1	9*	1.87	-1.76	0.069
-5	1	9*	1.84	2.25	0.070
5	1	10	4.53	2.64	1.017
-5	1	10*	1.86	-1.53	0.070
6	1	0	6.09	-4.90	0.378
6	1	1	4.57	-1.43	1.028
-6	1	1	5.83	5.56	0.334
6	1	2*	1.68	-0.51	0.093
-6	1	2	8.56	-8.16	0.311
6	1	3*	1.71	-2.49	0.106
-6	1	3	6.20	-5.36	0.308
6	1	4	6.44	5.57	0.414
-6	1	4	5.34	5.24	0.361
6	1	5*	1.88	2.86	0.069
-6	1	5*	1.87	1.71	0.069
6	1	6	6.35	-5.68	0.696
-6	1	6*	1.87	-1.12	0.069
6	1	7*	1.86	-2.27	0.070
-6	1	7*	1.87	1.58	0.069
-6	1	8*	1.87	-0.73	0.069
-6	1	9*	1.86	-1.61	0.070
7	1	0	8.68	-7.17	0.429
7	1	1	6.04	-4.47	0.307
-7	1	1	6.30	4.87	0.303
7	1	2	3.39	3.43	0.240
-7	1	2	5.96	-5.31	0.252
7	1	3*	1.73	0.90	0.104
-7	1	3*	1.75	-1.01	0.119
-7	1	4*	1.86	-1.23	0.070
-7	1	5	4.48	-3.16	1.005
-7	1	6	4.43	4.75	0.708
-7	1	7	4.37	3.40	0.698
-7	1	8	4.27	-4.06	0.684
0	2	0	25.28	-21.88	0.929
0	2	1	44.04	-42.81	1.595
0	2	2	13.30	13.82	0.457
0	2	4	3.93	-2.60	0.245
0	2	5	18.18	17.67	0.642
0	2	6	8.36	-9.66	0.312
0	2	7	30.14	-28.05	1.064
0	2	8	11.82	10.97	0.441
0	2	9	14.00	12.11	0.522
0	2	10	3.80	-3.28	0.294
0	2	11*	1.66	-2.12	0.078
0	2	12*	1.77	-2.14	0.088
0	2	13*	1.86	-1.45	0.097
1	2	0	20.04	-19.96	0.778
1	2	1	24.06	-23.52	0.835
-1	2	1	54.81	-53.11	2.549
1	2	2	12.04	12.04	0.537
-1	2	2	7.67	7.11	0.357
1	2	3	12.43	12.24	0.460
-1	2	3	11.62	-12.95	0.430
1	2	4	2.98	-4.03	0.342
-1	2	4	18.14	18.63	0.434
1	2	5	15.34	-16.03	0.661
-1	2	5	49.25	45.01	3.869
1	2	6	2.91	3.76	0.272
-1	2	6	20.19	-20.46	0.980
1	2	7*	1.32	1.30	0.059
-1	2	7	23.38	-21.74	1.135
1	2	8*	1.42	0.31	0.073
-1	2	8	3.34	3.34	0.436
1	2	9	8.72	7.45	0.450
-1	2	9	3.58	1.72	0.470
1	2	10	6.23	-5.75	0.403
-1	2	10	6.30	6.35	0.408
1	2	11	7.15	-6.53	0.463
-1	2	11	6.08	5.37	0.394
1	2	12	4.41	3.10	0.414
-1	2	12	4.30	-3.47	0.403
1	2	13	4.63	3.21	0.433
-1	2	13	6.78	-5.29	0.439
2	2	0	7.18	7.24	0.217
2	2	1*	0.74	0.58	0.035
-2	2	1	15.87	16.69	0.548
2	2	2	4.63	2.81	0.218
-2	2	2	14.31	-12.75	0.475
2	2	3	4.48	-6.05	0.152
-2	2	3	31.16	-27.43	1.221
2	2	4	7.45	-8.05	0.280
-2	2	4	15.91	14.25	0.359
2	2	5	12.21	-11.83	0.784
-2	2	5	8.06	7.39	0.416
2	2	6	5.57	6.82	0.506
-2	2	6*	1.30	-1.46	0.060
2	2	7	18.29	18.15	0.895
-2	2	7*	1.39	1.33	0.075
2	2	8	3.82	-4.53	0.358
-2	2	8	7.83	-6.82	0.507
2	2	9	6.88	-6.44	0.445
-2	2	9	6.27	-5.62	0.407
2	2	10*	1.75	0.25	0.089
-2	2	10	5.61	4.49	0.363
2	2	11*	1.82	-2.11	0.085
-2	2	11	7.46	7.90	0.483
2	2	12*	1.90	2.93	0.096
-2	2	12*	1.83	-1.54	0.085
2	2	13	4.80	3.41	0.449
-2	2	13	4.63	-4.06	0.435
3	2	0	17.63	15.82	0.407
3	2	1	31.78	30.93	0.897
-3	2	1	30.74	29.38	1.039
3	2	2	12.37	-12.50	0.414
-3	2	2	6.17	-5.83	0.320
3	2	3	15.18	-13.52	0.457
-3	2	3	8.20	9.15	0.293
3	2	4*	1.24	-1.67	0.042
-3	2	4	6.37	-7.17	0.262
3	2	5*	1.56	0.85	0.083
-3	2	5	21.43	-21.09	0.924
3	2	6	6.21	6.69	0.460
-3	2	6	10.06	9.06	0.518
3	2	7	12.18	9.67	0.878
-3	2	7	11.70	11.32	0.603
3	2	8	4.25	-3.51	0.557
-3	2	8	4.00	-2.78	0.375
3	2	9	12.07	-9.53	0.871
-3	2	9	6.85	-5.61	0.443
3	2	10*	1.88	2.17	0.097
-3	2	10*	1.78	0.34	0.087
3	2	11	4.71	3.44	0.441
-3	2	11*	1.84	1.83	0.084
3	2	12*	2.00	-0.36	0.104
-3	2	12*	1.91	-0.54	0.095
-3	2	13*	1.98	1.32	0.092
4	2	0	4.85	4.39	0.267
4	2	1	23.53	22.13	0.612
-4	2	1*	1.48	-1.69	0.070
4	2	2	12.02	-10.81	0.427
-4	2	2	6.16	6.72	0.276
4	2	3	18.21	-16.10	0.499
-4	2	3	22.71	22.35	0.619
4	2	4	6.61	7.08	0.305
-4	2	4	11.80	-11.44	0.305
4	2	5	6.40	5.76	0.481
-4	2	5	17.61	-18.67	0.810
4	2	6*	1.84	0.59	0.085
-4	2	6	4.25	4.50	0.398
4	2	7*	1.88	-1.49	0.097
-4	2	7	9.34	8.78	0.532
4	2	8*	1.92	-2.33	0.095
-4	2	8*	1.82	0.94	0.085
4	2	9*	1.95	-2.29	0.093
-4	2	9*	1.87	1.08	0.097
4	2	10*	2.00	1.23	0.104
-4	2	10*	1.91	-1.53	0.095
4	2	11*	2.04	3.06	0.102
-4	2	11	6.39	-5.75	0.480
-4	2	12*	2.01	1.92	0.103
-4	2	13	4.98	4.29	0.468
5	2	0	5.05	-3.88	0.265
5	2	1	4.18	-5.15	0.245
-5	2	1	11.36	-10.83	0.389
5	2	2*	1.72	0.83	0.075
-5	2	2	6.12	5.23	0.294
5	2	3	4.20	-3.83	0.245
-5	2	3	7.69	7.55	0.291
5	2	4	4.49	3.72	0.264
-5	2	4	4.23	-3.90	0.321
5	2	5	7.20	5.06	0.653
-5	2	5	6.97	-6.47	0.452
5	2	6	4.87	-4.30	0.639
-5	2	6*	1.94	1.08	0.093
5	2	7	4.92	-4.40	0.462
-5	2	7*	1.95	0.94	0.093
5	2	8*	2.05	1.03	0.101
-5	2	8*	1.99	1.89	0.091
5	2	9*	2.08	2.62	0.100
-5	2	9	6.53	6.32	0.491
5	2	10*	2.09	0.46	0.099
-5	2	10*	2.03	-3.63	0.102
-5	2	11	7.35	-6.18	0.552
6	2	0	4.76	-2.58	0.867
6	2	1	9.12	-8.85	0.347
-6	2	1*	1.66	-1.00	0.078
6	2	2	5.30	3.65	0.316
-6	2	2*	1.80	0.62	0.087
6	2	3	8.08	7.43	0.287
-6	2	3*	1.69	-3.09	0.107
6	2	4*	1.60	-1.91	0.097
-6	2	4*	1.66	0.44	0.093
6	2	5*	2.11	-0.96	0.098
-6	2	5*	2.07	3.09	0.100
6	2	6*	2.11	-1.44	0.098
-6	2	6*	2.08	-1.24	0.100
6	2	7*	2.11	-2.12	0.098
-6	2	7	5.06	-4.16	0.475
-6	2	8*	2.09	2.60	0.099
-6	2	9	5.09	3.14	0.478
7	2	0*	1.49	-0.52	0.069
7	2	1*	1.54	-1.57	0.084
-7	2	1	3.79	3.28	0.394
7	2	2*	1.77	1.82	0.088
-7	2	2*	1.79	-1.69	0.087
7	2	3	6.30	5.00	0.324
-7	2	3	6.55	-5.94	0.312
-7	2	4	2.83	2.57	0.236
-7	2	5	5.18	5.63	0.484
0	3	1	4.95	-5.56	0.194
0	3	2	4.00	2.70	0.182
0	3	3	37.62	36.69	1.509
0	3	4	7.92	6.42	0.263
0	3	6	9.06	-8.17	0.187
0	3	7	3.89	4.22	0.274
0	3	8*	1.61	1.92	0.097
0	3	9	8.38	7.90	0.494
0	3	10*	1.90	2.16	0.109
0	3	11	7.02	-7.00	0.460
1	3	0	11.33	8.17	0.491
1	3	1	3.82	-5.55	0.234
-1	3	1	31.34	-30.05	1.222
1	3	2	4.06	-3.31	0.253
-1	3	2	10.98	-8.77	0.490
1	3	3*	0.90	1.15	0.057
-1	3	3	47.17	48.03	4.022
1	3	4	2.50	-2.25	0.200
-1	3	4	10.69	10.42	0.479
1	3	5	17.60	-10.32	1.612
1	3	5*	1.31	1.53	0.079
-1	3	6	3.49	-2.92	0.292
1	3	7	16.84	14.56	1.108
-1	3	7	15.86	-16.33	1.044
1	3	8*	1.69	3.02	0.107
-1	3	8*	1.63	-3.22	0.095
1	3	9	7.01	-7.21	0.678
-1	3	9	14.88	14.48	1.049
1	3	10*	1.97	-1.76	0.119
-1	3	10*	1.90	1.53	0.123
1	3	11*	2.09	0.39	0.124
-1	3	11	6.64	-6.30	0.642
2	3	0*	1.57	-2.35	0.082
2	3	1	15.09	14.12	0.500
-2	3	1	19.55	-18.85	0.839
2	3	2	4.35	-3.79	0.321
-2	3	2	2.91	-1.77	0.400
2	3	3	14.62	-13.90	0.474
-2	3	3	7.38	-7.70	0.365
2	3	4*	1.08	-0.83	0.048
-2	3	4	2.91	-3.46	0.283
2	3	5	13.13	12.86	1.194
-2	3	5	17.82	16.14	1.072
2	3	6	5.82	5.52	0.284
-2	3	6*	1.46	1.44	0.089
2	3	7*	1.75	2.60	0.104
-2	3	7	12.43	-11.16	0.818
2	3	8*	1.88	-2.76	0.110
-2	3	8*	1.76	1.26	0.103
2	3	9	9.84	-9.62	0.765
-2	3	9	5.73	6.54	0.553
2	3	10*	2.12	-1.69	0.134
-2	3	10*	2.00	0.21	0.129
2	3	11	6.10	5.82	0.589
-2	3	11*	2.12	-0.20	0.134
3	3	0*	1.33	1.85	0.078
3	3	1	6.22	7.31	0.281
-3	3	1	22.65	23.88	0.820
3	3	2*	1.42	1.94	0.073
-3	3	2	8.40	9.34	0.373
3	3	3	16.18	-16.71	0.517
-3	3	3	28.00	-28.77	0.960
3	3	4*	1.32	-0.76	0.059
-3	3	4	3.63	-3.92	0.289
3	3	5	15.47	15.36	1.018
-3	3	5	7.91	6.04	0.614
3	3	6*	1.65	1.22	0.094
-3	3	6*	1.61	-2.25	0.097
3	3	7	7.04	-7.83	0.682
-3	3	7*	1.90	2.73	0.109
3	3	8*	2.12	-3.21	0.134
-3	3	8*	1.99	2.10	0.117
3	3	9*	2.22	-1.36	0.140
-3	3	9	5.06	-3.98	0.680
3	3	10*	2.31	1.48	0.146
-3	3	10*	2.17	0.64	0.131
-3	3	11	5.51	4.58	0.740
4	3	0	6.32	5.70	0.309
4	3	1	14.71	-14.05	0.507
-4	3	1	26.35	26.03	0.977
4	3	2*	1.60	-1.36	0.081
-4	3	2	3.82	3.07	0.527
4	3	3	3.75	-4.37	0.262
-4	3	3	10.55	-9.89	0.440
4	3	4*	1.54	-1.42	0.067
-4	3	4*	1.48	0.70	0.070
4	3	5	7.13	7.35	0.689
-4	3	5	5.00	-4.50	0.674
4	3	6*	1.71	0.19	0.106
-4	3	6*	1.69	-0.57	0.092
4	3	7	6.32	-6.39	0.611
-4	3	7	7.54	9.84	0.729
4	3	8*	2.38	0.18	0.141
-4	3	8*	2.23	0.41	0.139
4	3	9*	2.44	3.83	0.248
-4	3	9	7.54	-9.02	0.728
5	3	0*	2.00	-1.11	0.091
5	3	1	10.84	-9.73	0.415
-5	3	1	3.93	1.91	0.410
5	3	2*	1.73	-1.55	0.075
-5	3	2*	1.72	-2.21	0.075
5	3	3	7.48	7.93	0.291
-5	3	3*	1.60	2.55	0.097
5	3	4*	1.71	1.45	0.076
-5	3	4*	1.65	-0.84	0.062
5	3	5*	2.47	-2.60	0.157
-5	3	5	5.77	-5.40	0.776
5	3	6*	1.68	-0.45	0.093
-5	3	6*	1.71	1.41	0.091
5	3	7*	2.55	-0.66	0.162
-5	3	7	7.41	9.04	0.717
-5	3	8*	2.48	1.12	0.157
-5	3	9*	2.51	-4.96	0.154
6	3	0*	1.92	-2.66	0.095
6	3	1	3.98	3.42	0.300
-6	3	1	7.07	-6.67	0.340
6	3	2*	1.80	1.89	0.087
-6	3	2*	1.80	-0.45	0.087
6	3	3	4.43	4.01	0.308
-6	3	3	4.13	3.87	0.310
6	3	4*	1.84	0.40	0.070
-6	3	4*	1.81	-1.01	0.071
6	3	5	6.52	-5.40	0.876
-6	3	5*	2.62	-3.04	0.158
6	3	6*	1.30	-1.07	0.080
-6	3	6*	1.54	0.40	0.084
7	3	0*	2.77	-0.42	0.168
7	3	1	5.98	5.03	0.333
-7	3	1	6.05	-4.73	0.311
-7	3	2*	1.76	-0.05	0.088
-7	3	3*	1.73	2.09	0.105
0	4	0	26.26	-23.88	0.900
0	4	1	25.23	23.82	0.664
0	4	2	14.62	12.99	0.476
0	4	3	5.25	-4.03	0.166
0	4	4*	1.03	1.45	0.050
0	4	8	10.57	8.72	0.230
1	4	0	14.00	-11.13	0.522
1	4	1	15.79	13.53	0.523
-1	4	1	5.76	5.24	0.272
1	4	2	14.76	12.80	0.659
-1	4	2*	1.19	2.19	0.065
1	4	3	16.47	-14.67	0.546
-1	4	3	12.76	11.91	0.435
1	4	4	5.99	-4.94	0.346
-1	4	4	7.40	6.62	0.401
1	4	8*	1.68	-1.24	0.093
-1	4	8	10.30	7.91	0.315
2	4	0	10.26	8.15	0.615

Table 5 (*cont.*)

H	K	L	F(OBS)	KF(CALC)	SIGMA
2	4	1	5.86	-5.26	0.313
-2	4	1	11.34	-9.80	0.486
2	4	2	3.24	-3.24	0.320
-2	4	2	6.67	-5.52	0.416
2	4	3	2.94	-2.02	0.301
-2	4	3	9.46	9.01	0.340
2	4	4	3.57	-4.36	0.284
-2	4	4	6.27	5.44	0.389
2	4	8	6.93	-5.34	0.353
-2	4	8*	1.68	-2.00	0.092
3	4	0	13.32	11.23	0.747
3	4	1	13.42	-12.97	0.575
-3	4	1	10.11	-9.39	0.600
3	4	2	14.56	-14.03	0.649
-3	4	2*	1.47	-1.74	0.070
3	4	3	7.05	7.37	0.299
-3	4	3*	1.33	-1.29	0.078
3	4	4	4.10	3.74	0.327
-3	4	4	3.95	-5.14	0.435
3	4	8	4.89	-3.24	0.345
-3	4	8	6.44	-4.18	0.358
4	4	0*	1.97	1.86	0.092
4	4	1	8.74	-8.00	0.411
-4	4	1*	1.55	-0.72	0.083
4	4	2	6.60	-6.96	0.411
-4	4	2	3.95	3.68	0.388
4	4	3	6.22	6.58	0.291
-4	4	3	6.50	-7.69	0.304
4	4	4	7.04	7.40	0.437
-4	4	4	11.41	-8.96	0.860
4	4	8*	1.69	-0.48	0.092
-4	4	8*	1.73	-1.35	0.105
5	4	0*	2.00	-2.37	0.091
5	4	1*	1.63	0.56	0.080
-5	4	1	6.13	4.92	0.456
5	4	2*	1.75	2.55	0.089
-5	4	2	4.22	3.06	0.581
5	4	3*	1.65	2.33	0.110
-5	4	3	6.87	-7.08	0.321
5	4	4*	1.75	0.72	0.074
-5	4	4*	1.71	-3.72	0.076
5	4	8	3.36	1.79	0.384
-5	4	8*	1.61	0.92	0.097
6	4	1	5.57	4.54	0.418
-6	4	1	3.95	2.99	0.412
6	4	2	4.36	3.15	0.598
-6	4	2*	1.80	-0.37	0.087
6	4	3*	1.72	-2.22	0.106
-6	4	3*	1.71	-0.00	0.106
6	4	4*	1.86	-3.18	0.070
-6	4	4*	1.83	2.11	0.071
0	5	1*	1.29	1.04	0.060
0	5	2	22.49	22.42	0.773
0	5	3	4.85	-5.40	0.194
0	5	4	14.21	-12.25	0.472
0	5	10*	1.77	-2.17	0.102
1	5	0	21.32	17.86	0.731
1	5	1*	1.32	-1.93	0.059
-1	5	1	5.52	4.99	0.295
1	5	2*	1.34	-2.13	0.058
-1	5	2	11.76	9.62	0.575
1	5	3*	1.22	0.99	0.085
-1	5	3	5.08	-5.04	0.237
1	5	4	10.67	-10.07	0.578
-1	5	4	5.42	-4.82	0.337
1	5	10*	1.76	2.14	0.103
-1	5	10	8.29	-6.45	0.422
2	5	0*	1.84	0.89	0.085
2	5	1	4.96	-3.39	0.264
-2	5	1	5.59	4.54	0.299
2	5	2	15.99	-14.53	0.713
-2	5	2	3.48	-3.59	0.479
2	5	3	3.21	2.77	0.330
-2	5	3*	1.30	0.93	0.080
2	5	4	9.88	8.76	0.536
-2	5	4*	1.33	-1.74	0.058
2	5	10	4.21	3.31	0.351
-2	5	10	4.27	-2.71	0.357
3	5	0	10.33	-8.50	0.750
3	5	1	3.68	-3.25	0.276
-3	5	1*	1.51	-1.51	0.068
3	5	2*	1.58	-1.36	0.082
-3	5	2	6.06	-5.85	0.378
3	5	3	3.53	2.94	0.264
-3	5	3	3.45	3.31	0.259
3	5	4	12.16	11.64	0.659
-3	5	4	9.68	7.22	0.836
3	5	10*	1.60	1.50	0.097
-3	5	10	4.15	3.52	0.347
4	5	0	7.43	-4.83	0.540
4	5	1*	1.60	1.31	0.081
-4	5	1	3.88	-3.89	0.292
4	5	2	4.11	4.68	0.405
-4	5	2	9.78	-8.32	0.665
4	5	3*	1.58	1.99	0.098
-4	5	3*	1.55	1.22	0.100
4	5	4*	1.66	0.24	0.062
-4	5	4	7.56	6.10	0.652
4	5	10	2.19	-1.14	0.250
-4	5	10	3.70	3.02	0.311
5	5	0	4.77	-2.94	0.516
5	5	1	3.98	2.94	0.300
-5	5	1*	1.64	-1.38	0.079
5	5	2*	1.77	1.90	0.088
-5	5	2	4.28	-3.07	0.423
5	5	3*	1.68	-1.29	0.108
-5	5	3*	1.66	-0.66	0.109
5	5	4*	1.79	-3.37	0.072
-5	5	4*	1.75	-3.30	0.074
6	5	1*	1.57	0.59	0.082
-6	5	1*	1.57	0.69	0.082
-6	5	2	5.84	4.06	0.431
6	5	3*	1.72	-1.92	0.106
-6	5	3*	1.72	-0.92	0.106
0	6	0	16.95	13.60	0.720
0	6	1	6.11	5.40	0.240
0	6	2	5.88	-5.87	0.267
0	6	3*	1.32	-0.24	0.078
0	6	4*	1.36	-2.18	0.057
0	6	12*	1.42	0.48	0.073
1	6	0	6.30	4.77	0.519
1	6	1	3.56	2.44	0.268
-1	6	1*	1.45	-1.31	0.071
1	6	2	10.40	-9.30	0.509
-1	6	2	3.61	2.71	0.495
1	6	3	3.30	-3.24	0.247
-1	6	3*	1.34	0.56	0.077
1	6	4	5.75	4.16	0.397
-1	6	4	5.10	-5.70	0.352
1	6	12	2.95	-1.56	0.246
-1	6	12	3.42	1.87	0.287
2	6	0	8.12	-5.81	0.517
2	6	1	3.69	-3.81	0.277
-2	6	1*	1.51	-0.75	0.068
2	6	2*	1.56	0.45	0.066
-2	6	2	6.06	4.43	0.377
2	6	3*	1.43	1.71	0.090
-2	6	3*	1.42	-1.79	0.091
2	6	4	6.09	5.12	0.487
-2	6	4	5.50	-4.89	0.343
3	6	0	8.89	-5.82	0.565
3	6	1*	1.59	-1.31	0.081
-3	6	1*	1.58	0.80	0.082
3	6	2	8.44	6.97	0.525
-3	6	2	3.99	2.45	0.551
3	6	3	3.73	3.74	0.280
-3	6	3*	1.51	-0.02	0.103
3	6	4*	1.61	-1.00	0.064
-3	6	4*	1.57	1.25	0.066
4	6	0*	2.00	-1.99	0.091
4	6	1*	1.64	0.37	0.079
-4	6	1*	1.63	-0.78	0.080
4	6	2	4.24	4.15	0.417
-4	6	2*	1.73	-1.86	0.075
4	6	3*	1.63	-0.13	0.111
-4	6	3*	1.61	-0.36	0.097
4	6	4	5.00	-3.94	0.398
-4	6	4	4.90	6.04	0.390
5	6	1*	1.63	-0.17	0.080
-5	6	1*	1.63	0.20	0.080
5	6	2*	1.79	-0.29	0.087
-5	6	2	4.33	-3.61	0.597
5	6	3*	1.70	-0.87	0.107
-5	6	3*	1.69	-0.99	0.107
0	7	1*	1.56	-0.24	0.083
0	7	2*	1.61	-2.65	0.080
0	7	3	3.56	-2.99	0.199
1	7	0	4.94	-2.85	0.470
1	7	1*	1.57	0.19	0.082
-1	7	1	3.83	2.39	0.288
1	7	2*	1.63	-0.46	0.080
-1	7	2	3.95	-3.48	0.388
1	7	3*	1.48	1.38	0.105
-1	7	3	6.25	-5.43	0.292
2	7	0	4.97	-2.88	0.538
2	7	1	3.91	-1.10	0.408
-2	7	1	3.90	2.57	0.294
2	7	2	4.08	3.33	0.402
-2	7	2*	1.66	-0.95	0.078
2	7	3*	1.54	1.36	0.101
-2	7	3*	1.54	0.62	0.101
3	7	1*	1.65	-1.03	0.079
-3	7	1	3.99	-2.50	0.301
3	7	2*	1.75	2.44	0.074
-3	7	2*	1.73	2.33	0.075
3	7	3*	1.62	1.03	0.112
-3	7	3	3.89	4.08	0.292
4	7	1*	1.65	1.84	0.079
-4	7	1	4.00	-3.58	0.301
4	7	2*	1.79	-1.00	0.087
-4	7	2*	1.78	2.13	0.087
4	7	3*	1.68	0.42	0.108
-4	7	3*	1.68	1.10	0.108
0	8	1*	1.66	-1.58	0.078
1	8	1*	1.66	-1.05	0.078
-1	8	1	4.05	-2.36	0.420
2	8	1*	1.66	-0.56	0.078
-2	8	1*	1.66	1.71	0.078
-2	8	3	3.98	-3.05	0.409
3	8	1	4.01	2.28	0.420
-3	8	1	4.03	2.60	0.303

Table 6. *The ellipsoids of thermal vibration**

Atom	i	U_i	p	q	r
S	1	0·1948 (38) Å	0·9806	0·0973	−0·1704
	2	0·2370 (38)	0·1186	0·3982	0·9096
	3	0·3025 (40)	−0·1563	0·9121	−0·3790
O	1	0·1838 (62)	0·9493	−0·1178	−0·2914
	2	0·2845 (68)	0·2924	0·6711	0·6813
	3	0·3608 (64)	−0·1152	0·7320	−0·6715
C(1)	1	0·2169 (76)	0·8874	−0·0230	−0·4605
	2	0·2535 (103)	−0·2744	0·7762	−0·5676
	3	0·3018 (89)	0·3705	0·6300	0·6825
C(2)	1	0·2403 (90)	0·3388	0·9342	−0·1120
	2	0·2738 (82)	0·9348	−0·3477	−0·0727
	3	0·3373 (113)	0·1069	0·0800	0·9911

* $10^4\sigma$ (U_i) is given in parentheses.

Table 7. *Intramolecular vibration amplitudes**

Atom	Bond	$T_{\parallel}$ (Å)	$T_{\perp}$ (Å)	$U_{\parallel}$ (Å)	$U_{\perp}$ (Å)	$U'_{\parallel}$ (Å)	$U'_{\perp}$ (Å)
O	S–O	0·2007 (36)	0·3808 (49)	0·2115 (61)	0·4472 (63)	0·0108 (71)	0·0664 (80)
C(1)	S–C(1)	0·2603 (39)	0·3435 (49)	0·2651 (96)	0·3631 (73)	0·0048 (104)	0·0198 (88)
C(2)	S–C(2)	0·2739 (36)	0·3332 (49)	0·2770 (106)	0·4128 (77)	0·0031 (112)	0·0796 (91)

* $10^4\sigma$ is given in parentheses.

1961*b*; Busing & Levy, 1964). The intramolecular distances presented in Table 8 include this correction; the uncorrected values for the bond distances are given in parentheses. Since the vibration ellipsoids for atoms O and C(2) are larger than that for C(1) (Tables 6 and 7) the corrections for the S–O and S–C(2) bond lengths are larger than that for S–C(1). Intramolecular angles are listed in Table 9, and Fig. 2 gives a diagram of the molecule with its bond lengths and angles.

Structure of the molecule

The conclusions reached in this section would not change substantially if the coordinates from refinement without unobserved reflections were used. For comparison we have also listed in Tables 8 and 9 the corresponding distances (corrected for thermal motion) and angles based on coordinates of Table 1, *i.e.* excluding the unobserved reflections.

The sulfur–oxygen bond length of 1·531 ± 0·005 Å is significantly longer than the electron diffraction value of 1·47 ± 0·04 Å (Bastiansen & Viervoll, 1948, Rundle 1950). It is also longer than the 1·43 Å observed in many sulfones (Cruickshank, 1961*a*), consistent with the chemical fact that the S–O linkage in sulfoxides is weaker than that in sulfones. The Schomaker–Stevenson (1941) single-bond value for S–O is 1·69 Å.

In the trimethyloxosulfonium ion $[(CH_3)_3SO]^+$ the sulfur–oxygen distance is only 1·45 ± 0·01 Å (Zimmer-

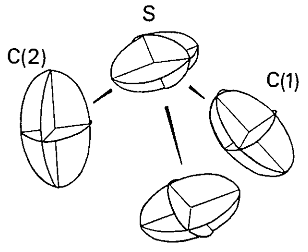


Fig. 1. View along [$\bar{1}$01] of the ellipsoids of thermal vibration of the DMSO molecule.

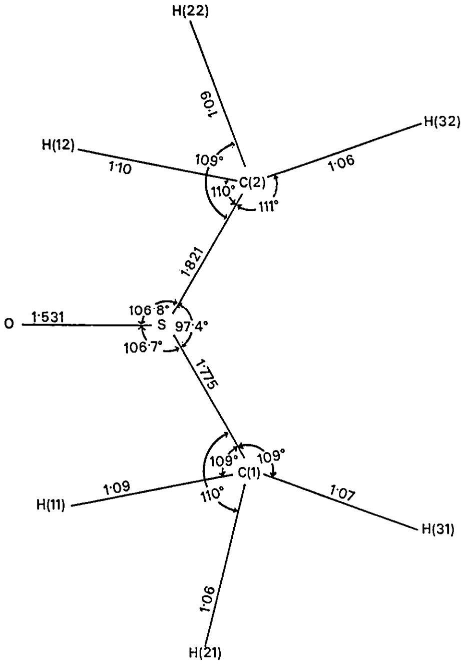


Fig. 2. Diagram of DMSO molecule with bond lengths and angles.

mann, Barlow & McCullough, 1963; Coulter, Gantzel & McCullough, 1963). The appreciable shortening of 0·08 Å can be considered as being due to the higher positive charge on the sulfur atom in the ion. Jaffé (1954) points out that the increased electron affinity of the sulfur atom would lead to a lowering of the energy of the 3*d* orbitals and consequently to an appreciable overlap integral for 2*p*-3*d* π-bonding. The bond distances for the trimethyloxosulfonium ion and the DMSO molecule are also consistent with the proposition (Sass, Vidale & Donohue, 1957; Caron, Palenick, Goldish & Donohue, 1964) that increasing opposite charges across a bond have a shortening effect on the bond length.

The S–O bond length (uncorrected for thermal motion) in the complex dimethyl sulfoxide – boron trifluoride is 1·517 Å (McGandy, 1961). Apparently this bond length is affected very little, if at all, by the complex formation. If the semipolar structure (*A*) contributed to a high degree to the overall configuration of the DMSO molecule, then one would expect an appreciable increase of the S–O distance in the BF_3 complex, where the oxygen atom becomes formally neutral. Such an increase is not to be expected if the main contribution is from structure (*B*), since the formally neutral oxygen still has a lone pair available for bonding to BF_3 and the π-bonding orbitals are localized. The results therefore tend to support the proposition that the S–O bond shortening in DMSO is largely a result of $2p-3d$ π-bonding.

The molecular dipole moment of DMSO is reported as $\mu = 3{\cdot}96 \pm 0{\cdot}04$ D (Dreizler & Dendl, 1964) and $\mu =$ 3·96 D (Cotton & Francis, 1960). The main contribution to this dipole moment is from the S–O bond moment, which is estimated at 3·0 D by Cumper & Walker (1956). This value is lower than the 4·7 D to be expected if the S–O bond is principally a semipolar bond, but

Table 8. *Intramolecular bond distances*

Distances uncorrected for thermal motion in parentheses

	Distance		
	Based on average coordinates	Based on refinement with observed reflections only	σ
S–O	1·531 (1·513) Å	1·521 Å	0·005 Å
S–C(1)	1·775 (1·771)	1·766	0·008
S–C(2)	1·821 (1·805)	1·827	0·011

Table 9. *Intramolecular angles**

	Angles		
	Based on average coordinates	Based on refinement with observed reflections only	σ
O–S–C(1)	106·7°	106·7°	0·4°
O–S–C(2)	106·8	107·5	0·4
C(1)–S–C(2)	97·4	98·2	0·4
H(11)–[C(1)–C(2)]–H(12)	4		
H(21)–[C(1)–C(2)]–H(22)	10		
H(31)–[C(1)–C(2)]–H(32)	5		

* For dihedral angles, atoms enclosed in brackets define the intersection line of the planes.

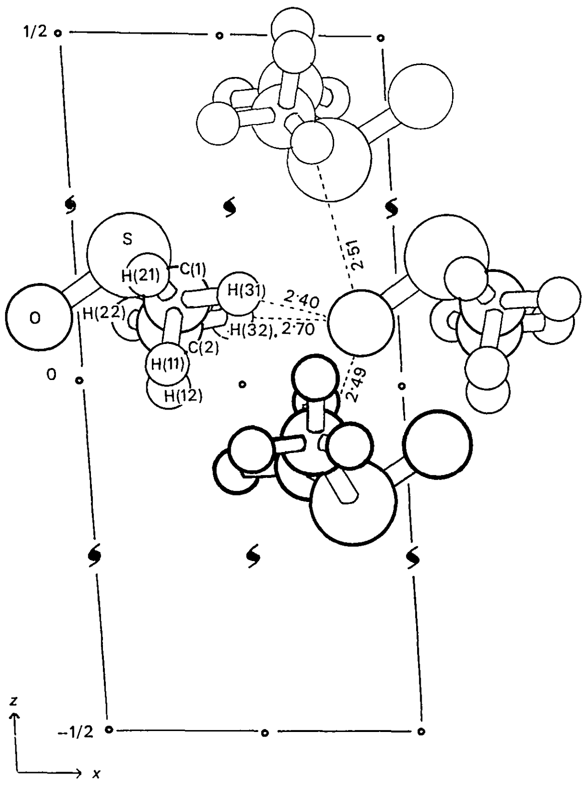


Fig. 3. Part of the structure projected along the *b* axis, showing short H---O intermolecular contacts.

only slightly higher than the 2·7 ± 0·2 D value to be expected if the bond is principally covalent. If our conclusion is correct that the covalent structure (*B*) is the main contributor to the resonance hybrid, then this bond moment must result largely from the lone pairs on the sulfur and oxygen atoms and from the difference in size of the sulfur and oxygen orbitals (Coulson, 1961).

The average value of 1·798 ± 0·01 Å for the sulfur–carbon bond is not significantly different from that found by applying the Schomaker–Stevenson rule (1941) so that, as expected, this is essentially a normal covalent single bond. It is also in agreement with the value of 1·78 ± 0·01 Å reported for the trimethyloxosulfonium ion. The values of 1·82–1·84 reported in the electron diffraction studies are somewhat higher. There is no straightforward explanation for the fact that the two chemically equivalent sulfur–carbon distances are found to be 0·05 Å different. Possibly the σ-values found from least-squares refinement are somewhat on the low side. It may be noted that the difference between the two S–C distances is slightly larger in the refinement that excludes the unobserved reflections.

The O–S–C and C–S–C angles of 106·8 ± 0·4 and 97·4 ± 0·4° compare with the electron diffraction values of 106 ± 6 and 100 ± 5°. In the trimethyloxosulfonium ion the average O–S–C angle is 112·5 ± 0·5° and the average C–S–C angle is 106·0 ± 0·5°. Consequently the pyramid formed by the oxygen and two carbon atoms as base and the sulfur atom at the apex is much flatter in the trimethyloxosulfonium than it is in the DMSO

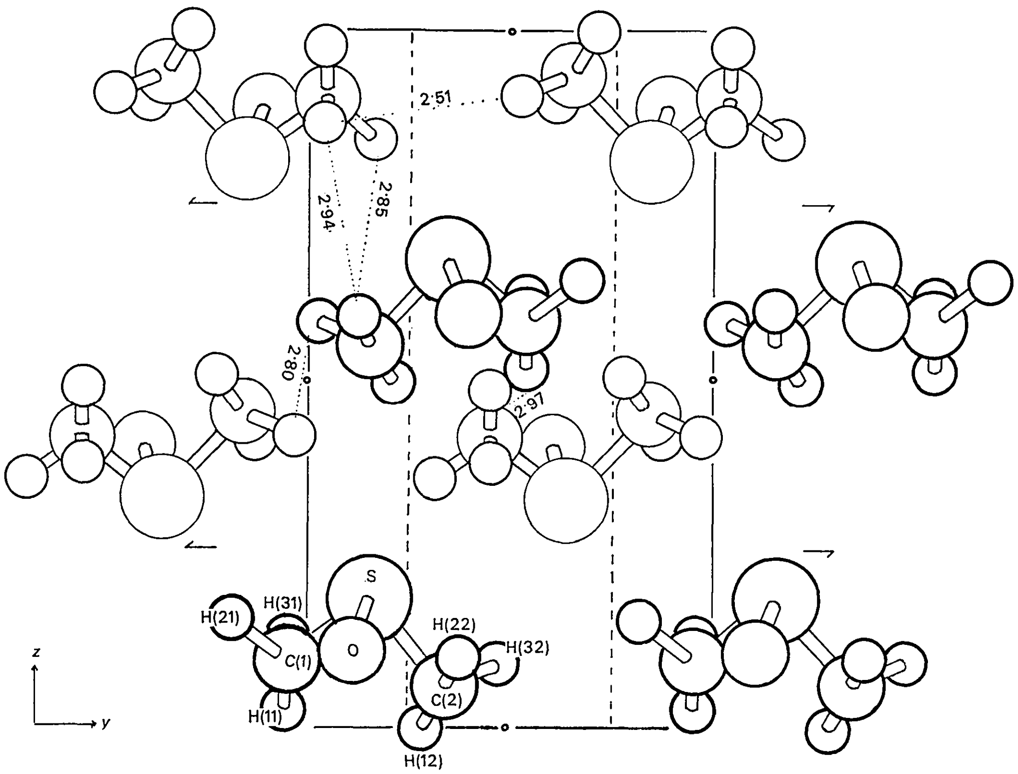


Fig. 4. DMSO structure projected along the *a* axis, showing some of the H---H intermolecular contacts.

molecule. The value for the perpendicular distance from the apical sulfur atom to the base plane is 0·706 Å in DMSO and only 0·370 Å in the trimethyloxosulfonium ion.

The dihedral angles in Table 9 show that the hydrogen atoms of the two methyl groups are only very slightly staggered when viewed along the C(1)–C(2) connecting line. Considering that the hydrogen positions were not required to possess any symmetry one can conclude that within the error of the determination the DMSO molecule has m (C_s) point symmetry, implying perfectly eclipsed H atoms.

Intermolecular contacts

All intermolecular distances below 3·0 Å are either of the type H–O or H–H. Four short H–O contacts were found with lengths 2·70, 2·51, 2·49 and 2·40 Å. They are indicated in Fig. 3 which shows a projection of the structure along the *b* axis. They are estimated to be in error by ±0·03 Å so that even the distance of 2·40 Å cannot be considered significantly shorter than the value of 2·60 ± 0·1 Å given by Pauling (1960). Fig. 3 also reveals the fact that each H atom of carbon C(1) makes a short H---O contact, while only one hydrogen atom [H(32)] of carbon C(2) does so. This is consistent with the finding above that the thermal ellipsoid of carbon atom C(2) was larger than that of C(1).

There are 8 short H---H distances of 2·51, 2·56, 2·71, 2·71, 2·80, 2·85, 2·94 and 2·97 Å. None of these is shorter than the H---H distance of 2·4 ± 0·1 Å given by Pauling (1960). Some of the contacts are shown in Fig. 4, which gives the projection of the structure along the *a* axis. The figure also reveals the corrugated layer structure of the crystal, with S–O dipoles and methyl groups alternating in planes parallel to *ab*.

This work was supported in part by the National Institute of Dental Research under grant number 1T1 DE 116-01. The X-ray data were taken by Mr Thomas L. Nunes under sponsorship of the National Science Foundation, Undergraduate Research Participation Program G 15876. Most of the computations were carried out at the Massachusetts Institute of Technology Computation Center.

Note added in proof. – Since submission of this paper, Viswamitra & Kannan (1966) have reported a structural study of DMSO at −60 °C. Aside from a coordinate transformation and a shift in origin their crystallographic parameters are the same as those reported here. Their cell dimensions indicate a 4·3% volume concentration of the unit-cell between 5° and −60 °C. Their reported S–O and S–C(1) bond lengths, uncorrected for thermal motion, are 1·471 ± 0·008 Å and 1·801 ± 0·0096 Å, respectively, and their S–C(1) and S–C(2) distances are found equal within ±1σ. The reported values for the bond distances agree to within ±3σ with ours, while the angles agree to within ±2σ. For comparison the *R* value reported by Viswamitra & Kannan is 0·129 and the refinement was carried out anisotropically, omitting H atoms. Their X-ray data include only *Hkl* with *H* = 0 to 3.

References

Bartell, L. S. (1962). *Tetrahedron*, **17**, 177.

Bastiansen, O. & Viervoll, H. (1948). *Acta Chem. Scand.* **2**, 702.

Busing, W. R. & Levy, H. A. (1964). *Acta Cryst.* **17**, 142.

Caron, A., Palenik, G. J., Goldish, E. & Donohue, J. (1964). *Acta Cryst.* **17**, 102.

Cotton, F. A. & Francis, R. (1960). *J. Amer. Chem. Soc.* **82**, 2986.

Coulson, C. A. (1961). *Valence*. 2nd ed. London: Oxford Univ. Press.

Coulter, C. L., Gantzel, P. K. & McCullough, J. D. (1963). *Acta Cryst.* **16**, 676.

Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 757.

Cruickshank, D. W. J. (1961*a*). *J. Chem. Soc.* p. 5486.

Cruickshank, D. W. J. (1961*b*). *Acta Cryst.* **14**, 896.

Cumper, C. W. N. & Walker, S. (1956). *Trans. Faraday Soc.* **52**, 193.

Dreizler, H. & Dendl, G. (1964). *Z. Naturforsch.* **19*a***, 512.

Hamilton, W. C. (1955). *Acta Cryst.* **8**, 185.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Jacob, S. W. (1964). Private communication; University of Oregon Medical School.

Jaffé, H. H. (1954). *J. Phys. Chem.* **58**, 185.

Lindquist, I. (1959). *Acta Chem. Scand.* **13**, 420.

McGandy, E. L. (1961). Ph. D. dissertation, Boston Univ.

Moffitt, W. E. (1950). *Proc. Roy. Soc.* A **200**, 409.

Pauling, L. (1960). *The Nature of the Chemical Bond.* Ithaca: Cornell Univ. Press.

Price, C. C. & Oae, S. (1962). *Sulfur Bonding*. New York: The Roland Press Co.

Rundle, R. E. (1950). Private communication quoted by Allen, P. W. & Sutton, L. E. *Acta Cryst.* **3**, 46 .

Sass, R. L., Vidale, R. & Donohue, J. (1957). *Acta Cryst.* **10**, 567.

Schomaker, V. & Stevenson, D. P. (1941). *J. Amer. Chem. Soc.* **63**, 37.

Simpson, P. G. (1963). Ph. D. dissertation, Harvard University.

Vand, V. (1965). Gatlinburg Meeting, A.C.A., Abstracts of Papers, p. 78.

Viswamitara, M. A. & Kannan, K. K. (1966). *Nature, Lond.* **209**, 1016.

Zimmermann, I. C., Barlow, M. & McCullough, J. D. (1963). *Acta Cryst.* **16**, 883.