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The Crystal and Molecular Structure of 'Mercury Diethylene Oxide'

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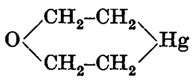
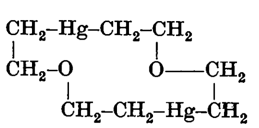
The application of the method of X-ray analysis has shown that the compound $\beta.\beta'$-oxido-diethylmercury quoted in chemical literature under the name 'mercury diethylene oxide', to which the formula (I) is ascribed, has in fact the structure given by formula (II).



(I)



(II)

The crystals are monoclinic. The cell containing four molecules (of II) has the dimensions $a = 19.45$, $b = 4.46$, $c = 14.67$ Å, $\beta = 120.5°$. The space group is C_{2h}^6–$C2/c$.

The molecule occupying the position on the twofold symmetry axis in the lattice is a puckered twelve-membered ring. The bond angle C–Hg–C is only a few degrees less than 180°. Accepting the normal single bond length for C–C and C–O, the value of 2·14 Å was obtained for the Hg–C distance. It is characteristic that the oxygen atom is closer to one mercury atom than to the other, the distances being 2.21 ± 0.1 and 3.30 ± 0.1 Å respectively. The lower value can be interpreted only with the assumption of a more or less realized coordinate link between oxygen and mercury. Consequently the molecule has only the symmetry of a twofold axis and the crystal is a racemic mixture.

Introduction

In the chemical literature on the organo-mercurials we find a certain number of compounds to which a cyclic structure is ascribed with one or more mercury atoms in one ring containing only four, five or six members in totality. If that is so the mercury bond angle ought to be much smaller than 180°, which is in contradiction with the present knowledge of the stereochemistry of mercury. It follows that the proposed structures are either not cyclic at all, or they contain such a number of members that the mercury bond angle of 180° may be realized (i.e. they are polymeric). Besides, the question arises whether a *sp* hybrid bond angle, such as that of the mercury atom, may be considerably deformed, a question which, as it seems, has not been hitherto investigated.

It is to be pointed out that the mercury organic compounds until recently were not examined by the methods of X-ray structure analysis. The main reason lies obviously in the difficulty of locating the carbon atoms in the presence of mercury atoms. Therefore, an X-ray structure analysis of such a compound as mercury diethylene oxide was also of interest from the methodical point of view. The most important information we wish to obtain from such an analysis, exept the mercury bond angle, is the Hg–C bond length. This bond length has been hitherto determined roentgenographicaly only for methyl mercuric chloride (Grdenić & Kitaigorodskiĭ, 1949) with the value of 2·06 Å. (When the present investigation was nearly finished a paper appeared on the structure analysis of α- and β-1-chloromercuri-2-methoxycyclohexanes with the values of C–Hg bond length 2·34 and 2·15 Å respectively (Brook & Wright, 1951).)

From the cyclic organo-mercurials the most convenient for the structure analysis seemed to be the mercury pentamethylene and the $\beta.\beta'$-oxido-diethylmercury or 'mercury diethylene oxide'. The latter was chosen to be examined first. According to Sand (1901) it has a six-membered cyclic structure. The molecular weight of this compound had not been previously determined and the investigation was undertaken with the supposition that the real structure was a twelve-membered cycle with a bruto formula $Hg_2C_8H_{16}O_2$.

Crystallographic and X-ray data

The material used in the investigation was prepared as described by Sand (1901). The crystals were grown by slow evaporation from a solution in benzene. Colourless, bright needles were obtained. The crystals are monoclinic, elongated in the direction of the b axis, with well developed $\{001\}$, $\{100\}$, $\{\bar{1}01\}$ and $\{110\}$. The perfect cleavage parallel to (001), (100) and $(\bar{1}01)$ is the most characteristic property of the crystals. Slightly pressed, they cleave like asbestos into a large number of thin flexible fibres.

The dimensions of the unit cell were obtained by measuring the layer lines of single-crystal rotation and oscillation photographs:

$$a = 19{\cdot}45, \quad b = 4{\cdot}46, \quad c = 14{\cdot}67\ \text{Å}, \quad \beta = 120{\cdot}5^\circ .$$

Copper $K\alpha$ radiation was used (wave-length taken as 1·542 Å). The density determined pycnometrically is 3·30 g.cm.$^{-3}$. For four molecules of $Hg_2C_8H_{16}O_2$ per unit cell the density required is 3·28 g.cm.$^{-3}$. The following systematic absence of reflexions were observed: hkl with $h+k$ odd, $h0l$ with h odd and l odd, $0k0$ with k odd. These absences are characteristic for the space group C_{2h}^6–$C2/c$, with eight mercury atoms in general positions (set (f) in *Internationale Tabellen*). The usual test by means of liquid air showed no pyroelectric effect.

The information listed above was not sufficient to decide between a monomeric and a dimeric structure. If the latter obtains then the molecule has $\bar{1}$ or 2 as the lowest symmetry. In Fig. 1 the possible configurations for dimeric molecules are drawn. The symmetry is $2/m$ for (a) and (b) ('chair' form), mm for (c) and (d) ('boat' form) and 2 for (e) and (f) ('crown' form). The configurations with the same symmetry differ by the relative position of oxygen and mercury atoms, i.e. they may be 'sin' or 'anti'. Since the cell edge is small in the [010] direction and has approximately the value of the effective diameter of a methyl group, the most probable configurations are (a), (e) and (f). For the same reason it followed that the b-axis projection of electron density would give the most important information on the structure.

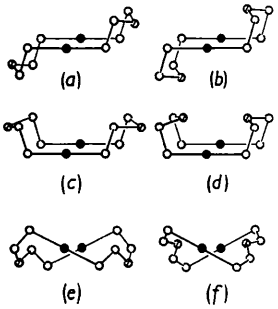


Fig. 1. Possible configurations for dimeric molecule of mercury diethylene oxide (hydrogen atoms are omitted).

Intensity measurements

Nickel-filtered Cu $K\alpha$ radiation was used. All possible reflexions $h0l$ under these conditions were recorded on the oscillation photographs. Relative intensities were determined as follows: The separate oscillation photographs of the 400 reflexion of rock salt were taken with the following range of exposures: 1, 2, 3, 6, 12, 24, 48, 72, 96 (5° oscillation as unity) and developed under standard conditions simultaneously with the oscillation photographs of the examined crystal. From the rock salt reflexion photographs the characteristic curve of the photographic film (optical density plotted against exposure time) was determined. For the purpose of obtaining the integrated reflexions the photographic densities were measured on the equator of each spot using a microphotometer. The recorded densities were converted into relative intensities by means of the characteristic curve. In practice this was possible nearly to the value $D = 2$ for photographic density. This restriction was not disadvantageous since only one reflexion (200) had $D > 2$. Integrated reflexions were obtained by using a planimeter. The smallest value of the integrated reflexion to the largest one was related as 1:1000.

The method for intensity measurements just described was preferred because the great absorption as well as the form of the crystal (the cross section was an irregular elongated hexagon) had considerably influenced the passage of the rays through the crystal and had thus deformed the reflexion curve. For the same reason it was not assumed that the integrated reflexion was proportional to the heigth of the peak, as is usually assumed in visual estimating.

The linear absorption coefficient is $\mu = 550$ cm^{-1}. The correction on the absorption was made very carefully applying the formulae previously described (Grdenić, 1952). The ratio of the smallest absorption factor to the largest was 1:36. The crystal had been dipped into liquid air before it was used for recording photographs. The secondary extinction was not taken into account for there were no systematic discrepancies between observed and calculated F's for those planes for which F was large. The corrections for polarization and Lorentz factors were made in the usual way.

Structure determination

The preliminary x, z co-ordinates of the mercury atom were easily obtained by the usual trial-and-error method neglecting contributions from all other atoms:

$$x_{\text{Hg}} = 0{\cdot}025, \quad z_{\text{Hg}} = 0{\cdot}136 .$$

From these co-ordinates no definitive information about the symmetry and the positions of the molecules can be obtained; the whole molecule may be situated on the centre of symmetry or on the twofold symmetry axis.

The two-dimensional Fourier synthesis on (010) was carried out at 6° intervals with the use of the Beevers & Lipson strips. To the coefficients $F(h0l)$ were attributed those signs that had been calculated from the contributions of the mercury atoms. It was assumed that the signs of the all structure amplitudes would be determined only by the mercury atom. All observed $F(h0l)$ were taken into summation, 139 in totality. On the projection (Fig. 2) all atoms are well resolved. Molecules in the lattice are not situated on the symmetry centres but on the twofold symmetry axis. The x, z co-ordinates directly evaluated from the projection are listed on Table 1. The values of the mercury parameters evaluated from the projection map are practically equal to those estimated by trial and error.

For calculating the structure amplitudes $F_c(h0l)$ the atom scattering factors for mercury from the *Internationale Tabellen* (1935, vol. 2, p. 573) and for oxygen and carbon from the tables given by Cox & Goodwin (1936) were used. All F_c were multiplied by an average temperature factor $\exp[-B(\sin\theta/\lambda)^2]$ with $B = 4$ Å^2. The observed structure amplitudes were put on the absolute scale by being multiplied with an appropriate factor. This factor was obtained as the mean value of all ratios between each of the calculated and observed structure amplitudes. After this was done the electron-density map (Fig. 2) was put on the absolute scale. The contours for mercury atoms are at intervals of 10 e.Å^{-2}, and those for carbon and oxygen at intervals of 1 e.Å^{-2}. The areas with negative density are indicated by broken lines.

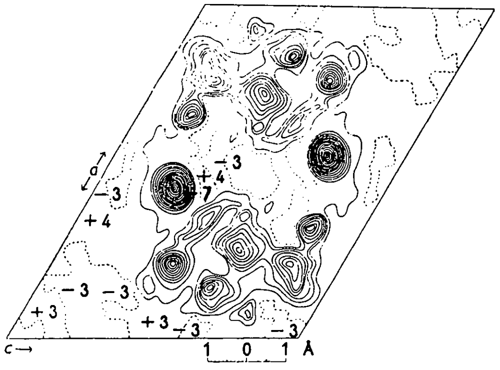


Fig. 2. Electron-density projection on (010). Contours at intervals of 10 e.Å^{-2} for mercury atoms and at intervals of 1 e.Å^{-2} for carbon and oxygen atoms. Areas with negative density are surrounded by broken lines.

Diffraction effect and accuracy of co-ordinates

On the projection map, as was expected, there appeared many spurious peaks and minima with negative density. The contours due to the carbon and oxygen atoms are quite deformed, especially those of low density value. This is caused by the lack of convergency, since the reflexions of high order were rather strong: the ratio of the smallest and largest value of F_o was as 1:23·3. However, the typical ring around the mercury atom did not appear. Spurious peaks, on the other hand, appeared even at such distances from the mercury atom as are not to be expected according to the formula of Bragg & West (1930). The reason, most probably, lies in the fact that the summation had to be computed without a number of reflexions (about ten) which, because of great absorption, had not been recorded. Besides, it seems that the method of taking the photographs and of the intensity measurement was not wholly satisfactory. For this reason no attempt was made to correct the projection for series-termination errors by the methods hitherto described.

The influence of the diffraction effect on the accuracy of the co-ordinates was studied in a similar manner to that used by Robertson & Woodward (1940) in the paper on the structure of the platinum phthalocyanine. The platinum atom has only two electrons less than the mercury atom. Actually the magnitude of the diffraction effect is nearly equal in both cases, as may be estimated by the heights of spurious peaks. The highest spurious peak occurring between the atoms of mercury and oxygen has the value 6 e.Å^{-2}, the height of the peak of the oxygen atom being 11 e.Å^{-2}. In Fig. 3 the cross-section through both the mercury and oxygen peak is shown. The total number of electrons per atom was evaluated out to the contour lines of 1 e.Å^{-2}. The value of 77 electrons was obtained for the mercury atom, 5, 4, 6, 3 electrons for the carbon atoms C_1, C_2, C_3, C_4 respectively, and 6 electrons for the oxygen atom. It is difficult to give an analysis of the accuracy of locating the light atoms. Therefore, it was assumed that the positions of peaks (except that of the mercury atom) had been influenced by the spurious peaks whose magnitude was of the order of the peak between mercury and oxygen. From purely geometrical consideration it was deduced that the greatest possible error in the location of maxima could not exceed 0·1 Å.

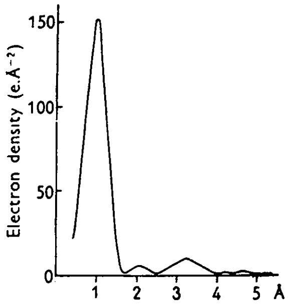


Fig. 3. Cross-section through both mercury and oxygen peaks. Between these two peaks lies the highest spurious peak of all that occurs on the projection.

Certain information on the reliability of the results can be obtained from the correlation factor defined as $R = \Sigma\{|F_o|-|F_c|\}\div|F_o|$. The result is $R = 0{\cdot}17$ (the reflexions which had not been observed because of the great absorption were omitted). It may be pointed out that there was only one structure amplitude $F(12,0,\bar{4})$ with the sign determined by the oxygen and carbon atoms. The comparison of the observed and calculated structure factors is given in Table 3.

Description of the structure

The parameter y_{Hg} was evaluated by the trial-and-error method. The accuracy of the result is less than that of x_{Hg} and z_{Hg}, since the highest order of k was

Table 1. *Final co-ordinates*

	x	x	z
Hg	0·024	0·220	0·136
C_1	0·137	0·002	0·208
C_2	0·176	0·204	0·301
C_3	0·138	0·238	0·409
C_4	0·084	0·462	0·414
O	0·112	0·321	0·303

Table 2. *Bond lengths and angles*

Hg–C_1	2·14 Å	C_4–Hg–C_1	176°
C_1–C_2	1·49 Å	Hg–C_1–C_2	93°
C_2–O	1·37 Å	C_1–C_2–O	102°
O–C_3	1·42 Å	C_2–O–C_3	96°
C_3–C_4	1·49 Å	O–C_3–C_4	90°
C_4–Hg	2·14 Å	C_3–C_4–Hg	103°

Table 3. *Observed and calculated structure factors*

$h0l$	F_o	$\frac{1}{8}F_c$	$h0l$	F_o	$\frac{1}{8}F_c$	$h0l$	F_o	$\frac{1}{8}F_c$
200	63	+71	608	0	+2	14,0,6	3	+5
400	31	+42	$60\bar{8}$	41	+30	14,0,$\bar{6}$	27	−33
600	31	+37	6,0,10	14	−15	14,0,8	4	−6
800	15	+21	6,0,$\overline{10}$	11	+7	14,0,$\bar{8}$	0	+2
10,0,0	0	+3	6,0,12	0	+1	14,0,$\overline{10}$	33	+26
12,0,0	11	−8	6,0,$\overline{12}$	28	−25	14,0,$\overline{12}$	0	−4
14,0,0	14	−13	6,0,$\overline{14}$	0	+1	14,0,$\overline{14}$	22	−16
16,0,0	13	−14	6,0,$\overline{16}$	14	+12	14,0,$\overline{16}$	0*	+5
18,0,0	13	−13	6,0,$\overline{18}$	0	+2	14,0,$\overline{18}$	5	+7
20,0,0	9	−10	802	34	+43	16,0,2	5	−9
002	16	−19	$80\bar{2}$	46	+45	16,0,$\bar{2}$	12	+16
004	52	−61	804	0	+2	16,0,4	9	+12
006	13	+18	$80\bar{4}$	39	−33	16,0,$\bar{4}$	11	+9
008	25	+26	806	22	+24	16,0,6	0	+1
0,0,10	9	−12	$80\bar{6}$	43	−32	16,0,$\bar{6}$	17	−19
0,0,12	11	−13	808	0	+3	16,0,$\bar{8}$	13	−7
0,0,14	14	+11	$80\bar{8}$	29	+30	16,0,$\overline{10}$	28	+24
0,0,16	4	+3	8,0,10	10	−11	16,0,$\overline{12}$	0	0
202	16	−16	8,0,$\overline{10}$	25	+19	16,0,$\overline{14}$	23	−17
$20\bar{2}$	6	+3	8,0,12	0	+3	16,0,$\overline{16}$	0*	+4
204	41	−48	8,0,$\overline{12}$	22	−24	16,0,$\overline{18}$	0*	+7
$20\bar{4}$	63	−70	8,0,$\overline{14}$	0*	−4	18,0,2	0	−3
206	26	+31	8,0,$\overline{16}$	14	+13	18,0,$\bar{2}$	0	+7
$20\bar{6}$	0	+2	8,0,$\overline{18}$	0	0	18,0,4	7	+7
208	19	+20	10,0,2	27	−34	18,0,$\bar{4}$	16	+16
$20\bar{8}$	40	+40	10,0,$\bar{2}$	43	+44	18,0,$\bar{6}$	12	−13
2,0,10	21	−21	10,0,4	6	+6	18,0,$\bar{8}$	15	−11
2,0,$\overline{10}$	0*	−9	10,0,$\bar{4}$	12	−15	18,0,$\overline{10}$	15	+16
2,0,12	0*	−5	10,0,6	15	+18	18,0,$\overline{12}$	5	+3
2,0,$\overline{12}$	20	−21	10,0,$\bar{6}$	37	−37	18,0,$\overline{14}$	14	−12
2,0,14	10	+10	10,0,8	5	−7	18,0,$\overline{16}$	4	+1
2,0,$\overline{14}$	5	+9	10,0,$\bar{8}$	19	+22	18,0,$\overline{18}$	7	+7
2,0,$\overline{16}$	6	+6	10,0,10	5	−8	20,0,2	0	0
402	39	−34	10,0,$\overline{10}$	30	+25	20,0,$\bar{2}$	0	+3
$40\bar{2}$	37	+39	10,0,$\overline{12}$	23	−20	20,0,$\bar{4}$	15	+15
404	30	−34	10,0,$\overline{14}$	14	−10	20,0,$\bar{6}$	5	−9
$40\bar{4}$	54	−63	10,0,$\overline{16}$	16	+13	20,0,$\bar{8}$	14	−11
406	30	+33	10,0,$\overline{18}$	0	+2	20,0,$\overline{10}$	7	+9
$40\bar{6}$	20	−9	12,0,2	18	−24	20,0,$\overline{12}$	11	+8
408	14	+13	12,0,$\bar{2}$	32	+35	20,0,$\overline{14}$	9	−8
$40\bar{8}$	49	+50	12,0,4	5	−8	20,0,$\overline{16}$	7	−3
4,0,10	22	−19	12,0,$\bar{4}$	5	+3	22,0,$\bar{2}$	0	0
4,0,$\overline{10}$	0*	−6	12,0,6	10	+13	22,0,$\bar{4}$	11	+10
4,0,12	0	−2	12,0,$\bar{6}$	48	−42	22,0,$\bar{6}$	0	−3
4,0,$\overline{12}$	24	−22	12,0,8	5	−8	22,0,$\bar{8}$	13	−11
4,0,14	7	+8	12,0,$\bar{8}$	0*	+12	22,0,$\overline{10}$	11	+5
4,0,$\overline{14}$	0	+4	12,0,$\overline{10}$	34	+25	22,0,$\overline{12}$	13	+9
4,0,$\overline{16}$	9	10	12,0,$\overline{12}$	11	−13	22,0,$\overline{14}$	5	−6
602	40	−48	12,0,$\overline{14}$	15	−12	22,0,$\overline{16}$	3	−4
$60\bar{2}$	43	+45	12,0,$\overline{16}$	4	+9	24,0,$\bar{6}$	3	+1
604	17	−16	12,0,$\overline{18}$	5	+6	24,0,$\bar{8}$	8	−8
$60\bar{4}$	45	−46	14,0,2	9	−14	24,0,$\overline{10}$	0	+2
606	39	+31	14,0,$\bar{2}$	22	+24	24,0,$\overline{12}$	7	+8
$60\bar{6}$	27	−25	14,0,4	11	+12	24,0,$\overline{14}$	3	−3
			14,0,$\bar{4}$	11	+7			

* Not observed because of the great absorption.

only $k = 5$. The following was obtained:

$$y_{\mathrm{Hg}} = 0{\cdot}220 \pm 0{\cdot}005 \, .$$

The y co-ordinates for the oxygen and carbon atoms were estimated on the assumption that the bond lengths C–C and C–O were near to the normal values. The final co-ordinates are given in Table 1.
To these co-ordinates correspond the values of bond lengths and bond angles listed in Table 2.
It cannot be stated that the mercury bond angle on one hand and the carbon and oxygen bond angles on the other are actually less than 180° and 100° respectively. The x, z co-ordinates were obtained directly from the projection and therefore they were not free from the influence of the diffraction effect. When the uncertainty of the positions of carbon and oxygen, estimated as 0·1 Å (see above), is taken into account a model of the same configuration can be proposed with the angles of 180° for mercury and from 100° to 108° for carbon and oxygen.

It must be pointed out that the proposed model is the only possible one which can be deduced from the Fourier projection data and which is not in contradiction with the known stereochemical facts. There are two possible models with symmetry 2 and with oxygen atoms in 'sin' configuration: the first with the C_3 atom 'above' and the second with C_3'below' the oxygen atom. It has been established that in fact only the second possibility occurs. The molecular model in relation to the crystal lattice is shown in Figs. 4 and 5.

The characteristic feature of the molecule is the short distance Hg–O; the value 2·21 Å was obtained from the above set of parameters. This value is much smaller than the sum of van der Waals' radii (2·90 Å), and, even when the inaccuracy of the co-ordinates is taken into account, it cannot be greater than 2·40 Å; therefore the mean value of 2·30±0·1 Å is the most reliable. Of course so short a distance between the mercury atom and the nearer oxygen atom may only be interpreted on the assumption that both atoms are linked together in a particular manner. Thanks to the unshared oxygen p electrons and the incomplete mercury outer shell it is very probable that a kind of coordinate link occurs with a more or less pronounced negative charge in the case of the mercury and a positive charge in the case of the oxygen atom. The steric conditions in the molecule are also favourable for the realization of the hybrid sp^2 bond with mercury and p^3 bonds with oxygen atoms. It is evident that the rigidity of the configuration depends upon this mercury–oxygen relation. If it persists even in the free molecules dissolved in a solvent, then it is very likely that the separation of the antipodes will succeed (e.g. using the chromatography on the optical active adsorbent). However, it may be that the configuration of free molecules differs from that in the crystal and therefore the short Hg–O distance observed may be mainly a lattice effect.

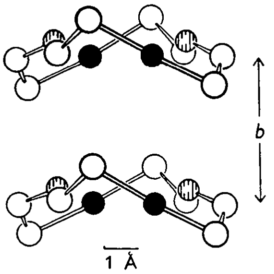


Fig. 4. Packing of molecules of mercury diethylene oxide along the b-axis direction.

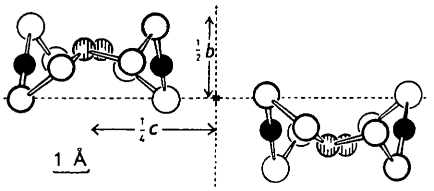


Fig. 5. Packing of molecules of mercury diethylene oxide along the c-axis direction viewed against the [$\bar{1}$02] direction. Only two molecules antipodes are shown.

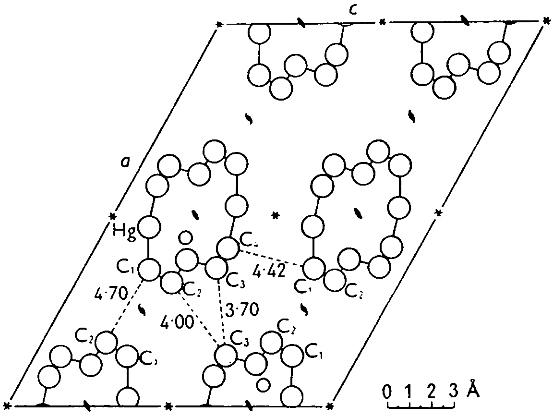


Fig. 6. Structure of mercury diethylene oxide projected on (010). Van der Waals contacts are shown by broken lines.

The packing of the molecules in the lattice is a close one. In the b-axis direction the closest intermolecular approach is equal to the translation period, i.e. 4·16 Å. In the $a\,b$ plane the closest approach is 4·70 Å and occurs in the direction of the diagonal through the CH_2-groups of the carbon atoms C_1 and C_2 rerespectively. The layers parallel to (001) are mutually in contact at 4·42 Å through the CH_2 groups of the C_1 and C_4 carbon atoms belonging to the molecules connected by the glide plane c, and also through the CH_2 groups of both C_3 as well as C_3 and C_2 on the molecules connected by the n plane, the closest approach being 3·70 and 4·00 Å respectively (Fig. 6). No intermolecular contact was found between the mercury atoms, between the mercury and the carbon atoms, or between the oxygen and carbon atoms. In the discussion of the packing of the molecules the criteria of Kitaĭgorodskiĭ (1946, 1948) were taken into account. According to Kitaĭgorodskiĭ the space group C^6_{2h} is possible for the molecules with symmetry $\bar{1}$ or 2, but it is less probable. The packing conditions in the *b*-axis direction are determinant since the packing here occurs at right angles to the *a c* layer. In the case of mercury diethylene oxide the puckered form of the ring enables the close approach of the molecules also in the *b*-axis direction even when the molecules are occupying the twofold symmetry axis positions. The perfect cleavage already quoted is also well explained by the observed molecular arrangement, as may be seen easily from the above description.

The author wishes to thank Prof. M. Paić at whose laboratory (Physical Institute, Faculty of Science) the main part of the experimental work has been performed.

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The Crystal Structure of Sulfur Dioxide*

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Oscillation diagrams have been obtained of single crystals of sulfur dioxide at $-130\pm5°$ C. The unit cell is orthorhombic and contains four molecules. Cell dimensions are: $a = 6{\cdot}07$, $b = 5{\cdot}94$, $c = 6{\cdot}14$ Å (all $\pm0{\cdot}01$ Å). The most probable space group is *Aba*.

The four sulfur atoms in the unit cell lie in face-centered positions. The parameters of the oxygen atom are: $x = 0{\cdot}140$, $y = 0{\cdot}150$, $z = 0{\cdot}118$. The length of the S–O bond is $1{\cdot}430\pm0{\cdot}015$ Å, the intramolecular O–O distance is $2{\cdot}46\pm0{\cdot}01$ Å; the O–S–O angle is $119°\pm2°$.

Introduction

Giauque & Jones (1948) have reported calorimetric evidence of disorder in solid sulfur dioxide close to the melting point. To account for the disorder they postulated a structure in which adjacent molecules are paired with their molecular planes 90° apart and with the O–O sides of the triangles together. A structure of this type, it was felt, offered a number of possibilities for orientational disorder.

Sulfur dioxide is one of a large number of substances of chemical importance whose crystal structures have not been studied because they happen to be liquids or gases at room temperature. Techniques and apparatus have been developed which make single-crystal X-ray investigations of such compounds feasible down to the temperature of liquid air (Kaufman & Fankuchen, 1949; Abrahams, Collin, Lipscomb & Reed, 1950; Post, Schwartz & Fankuchen, 1951). In this paper the determination of the crystal structure of sulfur dioxide, using these techniques, is described.

Experimental

The low-temperature X-ray camera used in the investigation has been described elsewhere (Post, Schwartz & Fankuchen, 1951). Specimens of sulfur dioxide suitable for X-ray diffraction studies were obtained by distilling 99·8% pure sulfur dioxide gas into thin-walled pyrex glass capillary tubes immersed in liquid nitrogen. When half to three-quarters full of solid sulfur dioxide the capillary tubes were sealed with a flame.

Powder diagrams and single-crystal oscillation diagrams were obtained using filtered copper and molybdenum radiation. To avoid possible difficulties in structure determination due to disorder near the melting point, all X-ray diagrams used in this investigation were obtained at $-130\pm5°$ C., approximately 60° C. below the melting point.

Experimental difficulties were appreciable; single crystals suited for X-ray diffraction purposes were grown with great difficulty and generally began to break up into fragments soon after X-ray exposures were begun. The crystals, moreover, showed a marked

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