

The Crystal Structure of Maleic Anhydride*

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The crystal structure of maleic anhydride, $C_4H_2O_3$, has been determined and refined by an analysis of three-dimensional X-ray diffraction data. The crystals are orthorhombic with space group $P2_12_12_1$; the cell dimensions are:

$$a = 7.180 \pm 0.008, \quad b = 11.231 \pm 0.015, \quad c = 5.39 \pm 0.03 \text{ \AA}.$$

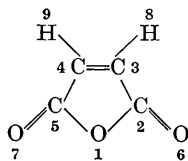
The maleic anhydride molecule is slightly non-planar, the oxygen atom within the five-membered ring lying 0.03 Å from the plane of the other atoms. The nearest intermolecule neighbors are hydrogen and oxygen atoms, but there is no evidence of C-H...O hydrogen bonds.

Introduction

Two considerations prompted us to undertake an investigation of the crystal structure of maleic anhydride (I):

(1) We felt that a careful determination of the interatomic distances and angles would contribute fundamentally to an understanding of the properties of this important compound.

(2) We anticipated that the principal intermolecular contacts would probably be between hydrogen atoms of one molecule and oxygen atoms of its neighbor, and that the geometry of these contacts might throw light on the question of the structural importance of C-H...O hydrogen bonds.



(I)

Experimental

An acicular crystal of commercial, reagent-grade maleic anhydride was mounted in a thin-walled glass capillary with its needle axis (c) parallel to the axis of the capillary. This crystal was used for all experimental measurements. We prepared the following photographs: (1) multiple-film equi-inclination Weissenberg photographs about c for layer lines 0 through 5, using Cu $K\alpha$ radiation; (the fifth layer line, which has an equi-inclination angle of 45.6° , was actually re-

corded at 43.8°); (2) zero-level precession photographs of the (100), (010), and (110) zones, using Mo $K\alpha$ radiation; (3) a Straumanis-type rotation photograph about c , using Cr $K\alpha$ radiation.

The Weissenberg and precession photographs showed the crystal to be orthorhombic with space group $P2_12_12_1(D_2^2)$. Values for a and b were obtained from a least-squares analysis of the Straumanis photograph; c was obtained from the precession photographs which were calibrated from the known values of a and b . The unit-cell dimensions and estimated limits of error are:

$$a = 7.180 \pm 0.008, \quad b = 11.231 \pm 0.015, \quad c = 5.39 \pm 0.03 \text{ \AA} \\ (\lambda \text{ Cr} = 2.2909 \text{ \AA}).$$

The density calculated on the basis of four molecules in the unit cell is 1.498 g.cm.^{-3} .

Intensities on the Weissenberg photographs were estimated visually by two of the authors (R. M. and H. W.), corrected for Lorentz and polarization factors, and averaged. Preliminary scale factors for the six layer lines were obtained by correlation with the precession photographs; later, these scale factors were adjusted by comparing observed and calculated structure factors, the maximum adjustment being 13%. The precession photographs also provided intensity estimates for four reflections (002, 012, 013, and 004) which were not observable on the Weissenberg photographs.

Determination of the structure

Our search for a trial structure began with packing and symmetry considerations and was guided by a large observed intensity for the (220) reflection. The shortness of the c axis (5.4 \AA) indicated that there could be no superposition of atoms in the (001) projection, and we assumed the maximum permissible value of the dihedral angle between the plane of the molecule and the (001) plane to be 60° . (The final results show it to be 66° .)

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A preliminary structure, based on an assumed molecular geometry which turned out to be very close to the final one, was projected onto the (001) plane so as to give satisfactory packing. The molecule was then translated in the a and b directions to yield a maximum calculated intensity for the 220 reflection; structure-factor and electron-density calculations for the low-order reflections gave promising results. However, further structure-factor and electron-density calculations were less encouraging and suggested that the structure was correct in general but wrong in detail. Accordingly, we rotated the molecule about its $O_6 \cdots O_7$ axis until the oxygen atom in the ring (O_1) projected on the opposite side of the $O_6 \cdots O_7$ line. The resulting low-order structure factors and Fourier projection looked considerably more promising. Preliminary

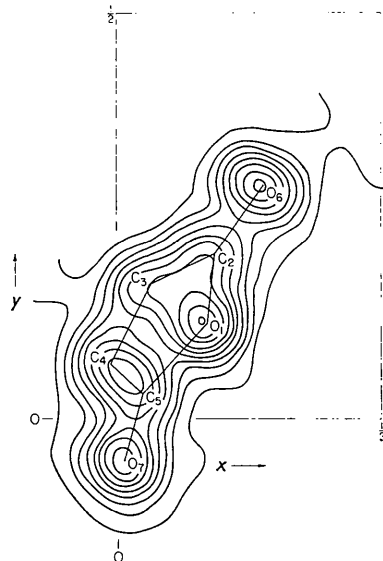


Fig. 1. The final electron density projection onto (001). The contours are at intervals of 1 e.Å^{-3} , beginning with the one-electron contour.

adjustments of the x and y parameters by a trial-and-error method improved the agreement of several reflections, and a complete $hk0$ structure-factor calculation was carried out; the R factor was 0.57. A least-squares calculation coupled with a readjustment of parameters to maintain a reasonable molecular geometry reduced the R factor to 0.30. Eight least-squares cycles together with an adjustment of the average scale and temperature parameters reduced it to 0.13 and completed the two-dimensional refinement.

Starting with the predicted dimensions of the molecule and its projection onto the (001) plane, we projected it onto (100) by a geometrical construction. We then positioned the molecule along the c axis to give reasonable packing, and assigned z parameters to all the atoms. The first three-dimensional structure-factor calculation yielded an R factor of 0.24.

Refinement of the parameters was carried out on the Burrough's 220 computer, using a structure-factor least-squares program developed by Mr A. Hybl. (The same program was used for the two-dimensional calculations.) Three positional and six temperature-factor parameters were refined for the carbon and oxygen atoms; initial positional parameters for the hydrogen atoms were assigned assuming C-H distances of 1.0 Å and were included in the final least-squares calculations. Scale factors for the individual layer lines were adjusted once during the refinement; otherwise, only a single factor was adjusted.

For the initial refinement, consisting of 13 structure-factor least-squares cycles, we chose somewhat arbitrarily the weighting scheme

$$\sqrt{w} = 1/(1 + 2F_o + 0.12F_o^2). \quad (1)$$

During this refinement the R factor dropped to 0.054 and the sum of the weighted residuals,

$$\sum [(\sqrt{w}(F_o^2 - F_e^2))^2],$$

Table 1. The final parameters and their standard deviations

The temperature factors are expressed in the form $T_i = \exp(-\alpha_i h^2 - \beta_i k^2 - \gamma_i l^2 - \delta_i hk - \epsilon_i hl - \eta_i kl)$

	O_1	C_2	C_3	C_4	C_5	O_6	O_7	H_8	H_9
x	0.1706	0.1835	0.0650	-0.0138	0.0476	0.2782	0.0109	0.069	-0.097
σ_x	3	5	5	5	5	5	5	7	7
y	0.1162	0.2037	0.1673	0.0664	0.0305	0.2889	-0.0536	0.215	0.010
σ_y	2	3	3	3	3	2	2	4	4
z	0.5218	0.3393	0.1308	0.1877	0.4373	0.3669	0.5639	-0.036	0.060
σ_z	4	7	7	7	8	8	7	11	13
α	234	226	285	226	230	366	400		
σ_α	4	5	6	6	6	7	8		
β	138	114	121	127	108	134	132		
σ_β	2	3	2	3	2	3	2		
γ	418	496	403	530	572	757	801		
σ_γ	9	14	13	17	15	17	15		
δ	14	-17	38	16	18	-175	-30		
σ_δ	5	7	9	7	7	9	8		
ϵ	-68	6	-114	-147	10	-41	56		
σ_ϵ	11	16	17	17	16	21	21		
η	-11	-56	-22	-94	8	-106	144		
σ_η	8	10	10	12	11	13	12		

Table 2. Observed and calculated structure factors

The five columns in each group contain the values, reading from left to right, of k , $10F_o$, $10|F_c|$, $10A_c$ and $10B_c$. Reflections indicated by an asterisk (*) were omitted from the least-squares refinements; those indicated by the letter a were given half weight

h	k	l	$10F_o$	$10 F_c $	$10A_c$	$10B_c$
0	0	0	2000	2000	0	0
0	60	58	58	58	0	0
0	58	64	64	64	0	0
0	52	32	32	32	0	0
0	113	107	107	107	0	0
10	11	4	4	4	0	0
5	20	16	16	16	0	0
6	15	15	15	15	0	0
12	35	35	35	35	0	0
14	48	1	1	1	0	0
0	250	261	0	261	0	0
2	359	385	0	385	0	0
3	117	118	0	118	0	0
4	121	122	0	122	0	0
5	120	116	0	116	0	0
6	15	15	0	15	0	0
7	63	61	0	61	0	0
8	10	3	0	3	0	0
9	11	4	0	4	0	0
10	11	14	0	14	0	0
11	11	5	0	5	0	0
12	13	12	0	12	0	0
13	12	13	0	13	0	0
14	8	8	0	8	0	0
0	216	202	0	202	0	0
1	268	281	0	281	0	0
2	517	537	0	537	0	0
3	107	106	0	106	0	0
4	52	48	0	48	0	0
5	113	107	0	107	0	0
6	15	11	0	11	0	0
7	22	23	0	23	0	0
8	75	70	0	70	0	0
9	10	8	0	8	0	0
10	27	26	0	26	0	0
11	19	17	0	17	0	0
12	19	17	0	17	0	0
13	4	4	0	4	0	0
14	4	6	0	6	0	0
0	140	141	0	141	0	0
2	180	189	0	189	0	0
3	88	81	0	81	0	0
4	58	55	0	55	0	0
5	116	109	0	109	0	0
6	10	5	0	5	0	0
7	15	11	0	11	0	0
8	67	66	0	66	0	0
9	15	17	0	17	0	0
10	29	35	0	35	0	0
11	12	12	0	12	0	0
13	4	4	0	4	0	0
14	4	0	0	0	0	0
0	193	194	0	194	0	0
1	24	23	0	23	0	0
2	80	78	0	78	0	0
3	88	88	0	88	0	0
4	64	62	0	62	0	0
5	25	24	0	24	0	0
6	26	22	0	22	0	0
7	54	57	0	57	0	0
8	60	62	0	62	0	0
9	33	33	0	33	0	0
10	11	11	0	11	0	0
11	11	12	0	12	0	0
12	9	6	0	6	0	0
13	4	0	0	0	0	0
14	0	0	0	0	0	0
0	222	224	0	224	0	0
1	341	363	0	363	0	0
2	260	267	0	267	0	0
3	138	139	0	139	0	0
4	11	31	0	31	0	0
5	12	10	0	10	0	0
6	32	30	0	30	0	0
7	36	30	0	30	0	0
8	39	43	0	43	0	0
9	32	30	0	30	0	0
10	14	15	0	15	0	0
11	9	4	0	4	0	0
12	4	3	0	3	0	0
13	4	3	0	3	0	0
14	3	3	0	3	0	0
0	277	272	0	272	0	0
1	390	457	0	457	0	0
2	234	246	0	246	0	0
3	114	111	0	111	0	0
4	114	111	0	111	0	0
5	33	32	0	32	0	0
6	98	105	0	105	0	0
7	64	64	0	64	0	0
8	45	40	0	40	0	0
9	35	34	0	34	0	0
10	22	21	0	21	0	0
11	35	35	0	35	0	0
12	16	16	0	16	0	0
13	19	18	0	18	0	0
14	4	4	0	4	0	0
0	222	224	0	224	0	0
1	341	363	0	363	0	0
2	260	267	0	267	0	0
3	138	139	0	139	0	0
4	11	31	0	31	0	0
5	12	10	0	10	0	0
6	32	30	0	30	0	0
7	36	30	0	30	0	0
8	39	43	0	43	0	0
9	32	30	0	30	0	0
10	14	15	0	15	0	0
11	9	4	0	4	0	0
12	4	3	0	3	0	0
13	4	3	0	3	0	0
14	3	3	0	3	0	0

dropped from 1075 to 20; in the last cycle no parameter shift exceeded one-third of its standard deviation.

At this point we changed weighting schemes, adopting one which more truly represented our estimates of the reliabilities of the observed quantities F_o^2 . This scheme, which gave greater relative weight to the weak reflections, was

$$w = 1 / (0.1 + 0.1 F_o^2) \quad (2)$$

Five least-squares cycles with this weighting scheme completed the refinement. The final R factor for 479 observed reflections having non-zero weight was 0.055. Unobserved reflections were not included in the R factor; they were included in the least-squares refinement only if the calculated structure factor exceeded the minimum observable value.

The final atomic parameters and their standard deviations are given in Table 1. The observed and calculated structure factors are given in Table 2.

Accuracy of the results

The standard deviations in the positional parameters (Table 1) were calculated from the residuals and the diagonal terms of the least-squares normal equations. The average standard deviation for the heavy atom parameters is about 0.003 Å, leading to a standard deviation in an interatomic distance of about 0.005 Å and a limit of error of 0.015 Å; the limit of error in a bond angle is about 1.0°. The limits of error in the bond distances and angles involving hydrogen atoms are approximately 0.15 Å and 10°, respectively.

The standard deviations in the temperature-factor parameters of the heavy atoms were calculated from the diagonal terms of the 6×6 inverse matrix of the normal equations, and take into account interactions between the six temperature parameters of the same atom. The real meaning of these standard deviations is not clear, since the temperature factors include the effects of absorption, spot shape and other experimental errors. In addition, the coefficients γ may include corrections to the scale factors of the individual layer lines. The standard deviations, then, must be considered relevant only to the temperature-factor parameters themselves and not to the implied thermal motions of the atoms.

Discussion of the results

(i) Bond distances and angles

The bond distances and angles are shown in Fig. 2 and listed in Table 3. Two best planes were calculated by the method of least-squares (Schomaker *et al.*, 1959), with approximate weights assigned to all atoms on the basis of the standard deviations of their parameters. Table 4 gives the results of this calculation.

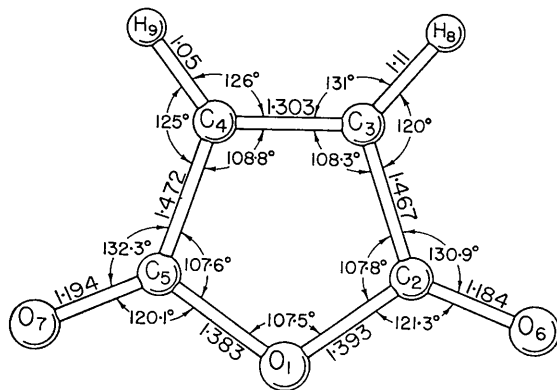


Fig. 2. Bond distances and angles in maleic anhydride.

The three oxygen atoms deviate by about five e.s.d.'s from plane (A) (Table 4), which was calculated from the positions of all nine atoms. The positions of the two hydrogen atoms and of the ring oxygen atom O_1 were excluded from plane (B), which shows the remaining atoms to be coplanar within 0.005 Å; O_1 lies 0.029 Å from plane (B). Accordingly, it seems appropriate to describe the molecule as slightly but significantly non-planar, being puckered at O_1 . It is suggestive that both hydrogen atoms deviate from the molecular plane by approximately the same amount and in the same direction; however, we do not believe these deviations are significant.

Within experimental error the molecule has the symmetry m , the mirror plane being perpendicular to the molecular plane and passing through O_1 and the midpoint of C_3 - C_4 . There is no significant difference

Table 3. Bond distances and angles

Distance		Angle	
O_1 - C_2	1.393 Å	C_5 - O_1 - C_2	107.5°
O_1 - C_5	1.383	O_1 - C_2 - C_3	107.8
C_2 - C_3	1.467	O_1 - C_2 - C_6	121.3
C_4 - C_5	1.472	O_6 - C_5 - C_3	130.9
C_3 - C_4	1.303	C_2 - C_3 - C_4	108.3
C_2 - O_6	1.184	C_3 - C_4 - C_5	108.8
C_5 - O_7	1.194	C_4 - C_5 - O_1	107.6
C_3 - H_8	1.11	C_4 - C_5 - O_7	132.3
C_4 - H_9	1.05	O_7 - C_5 - O_1	120.1
		C_2 - C_3 - H_8	120
		C_4 - C_3 - H_8	131
		C_3 - C_4 - H_9	126
		C_5 - C_4 - H_9	125

Table 4. Least-squares planes

Plane (A): $0.7686ax - 0.4952by - 0.4051cz = -0.859$
 Plane (B): $0.7724ax - 0.4951by - 0.3979cz = -0.848$

Atom	Plane (A)		Plane (B)	
	Weight	Deviation	Weight	Deviation
O_1	700	0.015	0	0.029
C_2	300	-0.002	300	0.005
C_3	300	0.002	300	-0.002
C_4	300	0.004	300	0
C_5	300	-0.003	300	0.005
O_6	400	-0.014	400	-0.003
O_7	400	-0.014	400	-0.003
H_8	2	0.125	0	0.115
H_9	2	0.134	0	0.123

between the two observed values within each pair of chemically equivalent bond distances and angles, and we shall discuss the molecular dimensions in terms of the average of each pair of observed values.

The C_3 - C_4 distance, 1.303 Å, is significantly shorter than the value 1.334 Å observed in ethylene (Bartell & Bonham, 1957) and usually chosen as the normal C-C double-bond distance. It is far shorter than the value 1.43 ± 0.02 reported in maleic acid (Shahat, 1952), but close to the values found in *p*-benzoquinone by X-ray diffraction (Robertson, 1935) and by electron diffraction (Kimura & Shibata, 1954; Swingle, 1954). A comparison of analogous distances in benzoquinone and maleic anhydride is given in Table 5.

Table 5. Comparison of bond distances in maleic anhydride and *p*-benzoquinone

Bond	Maleic Anhydride	Benzoquinone		
		(a)	(b)	(c)
C-C	1.470	1.50	1.52	1.50
C=C	1.303	1.32	1.31	1.32
C=O	1.189	1.14	1.15	1.23

(a) X-ray; Robertson (1935). No uncertainties given.

(b) E.D.; Kimura & Shibata (1954). Uncertainties (not defined), 0.02 Å.

(c) E.D.; Swingle (1954). Limits of error, 0.04 Å.

The average single-bond C-C distance in maleic anhydride, 1.470 Å, is shorter than the values reported for benzoquinone but slightly longer than the average

value, 1.45 Å, reported in maleic acid. It compares well with the central C-C distance in 1,3-butadiene (1.47 Å; Schomaker & Pauling, 1939) and with many other C-C bond distances in conjugated systems, and implies a double-bond character of about 15%. Further evidence of the double-bond character of the C₂-C₃ and C₄-C₅ bonds is given by the external bond angles at C₂ and C₅, for the O-C-O angles are 11° smaller than the C-C-O angles. Both angles, of course, are larger than normal because of the geometrical requirements of the five-membered ring.

The average C-O distance within the ring, 1.388 Å, is slightly shorter than the value 1.41 usually chosen as the single-bond distance between an oxygen atom and a planar carbon atom (Pauling, 1960, p. 275). There is a wide range of C-O bond distances reported in analogous compounds: 1.40-1.41 Å in furane (Schomaker & Pauling, 1939; Beach, 1941); 1.30 and 1.31 Å in furoic acid (Goodwin & Thomson, 1954); 1.33 and 1.40 Å in ethylene carbonate (Brown, 1954); and 1.39-1.41 Å in diketene (Katz & Lipscomb, 1952; Bregman & Bauer, 1955).

The double-bond C-O distance of 1.189 Å should perhaps be increased by approximately 0.02 Å to take account of the thermal motion implied by the tempera-

ture factors (Cruickshank, 1956*b*). The resulting value, 1.21 Å, is that usually accepted for a C-O double bond.

The average C-H distance, 1.08 Å, is close to the value commonly chosen as the normal single-bond distance. Maleic anhydride, then, shows none of the apparent shortening of C-H bond distances that has been reported in numerous other X-ray diffraction investigations.

(ii) Packing of the molecules

Drawings of the structure viewed down the *a* and *c* axes are shown in Figs. 3 and 4, respectively; a packing drawing viewed down *c* is shown in Fig. 5.

As was pointed out in the introduction, a principal point of interest in the crystal structure of maleic anhydride is the effect on the molecular packing of interactions between the oxygen atoms and protons attached to carbon atoms. As anticipated, the shortest intermolecular contacts have turned out to be between these atoms. However, there is no indication that these interactions are other than normal van der Waals forces.

Each of the two hydrogen atoms is surrounded by three oxygen atoms of neighboring molecules, the H...O distances being 2.68, 2.74, and 2.76 Å for H₈

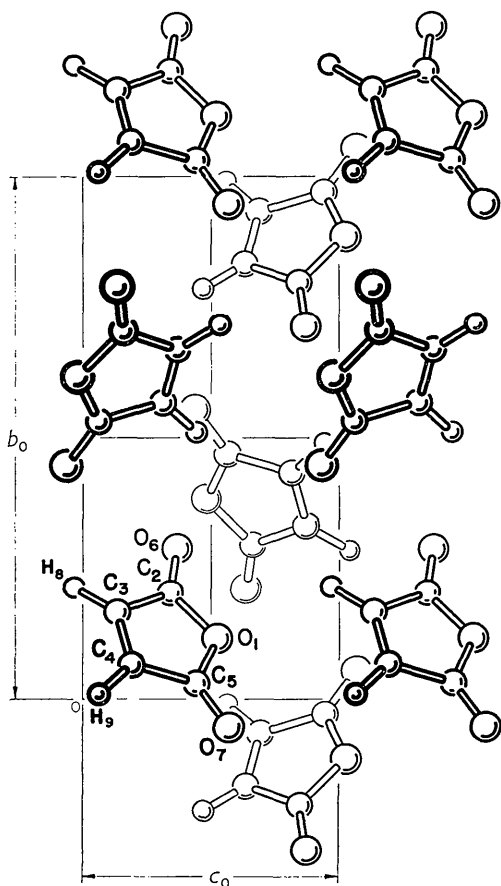


Fig. 3. The structure viewed down the *a* axis.

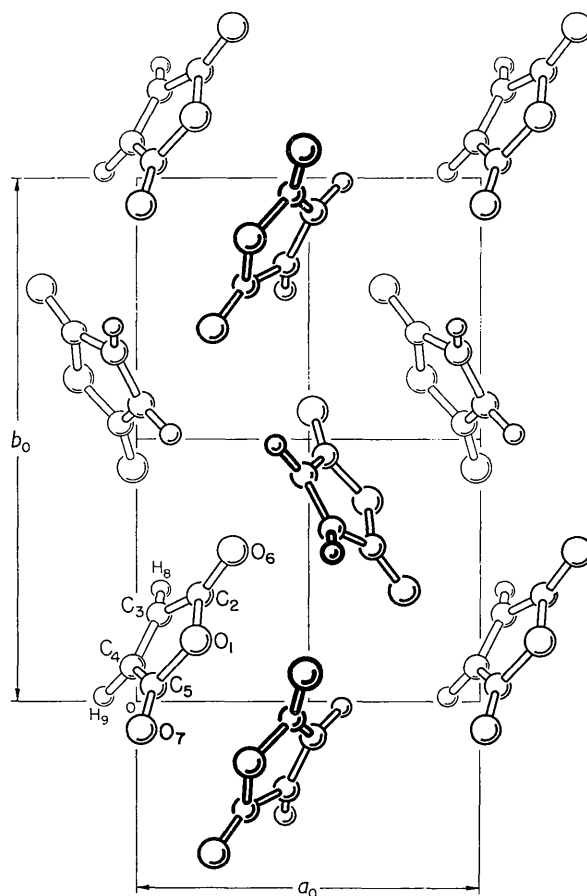


Fig. 4. The structure viewed down the *c* axis.

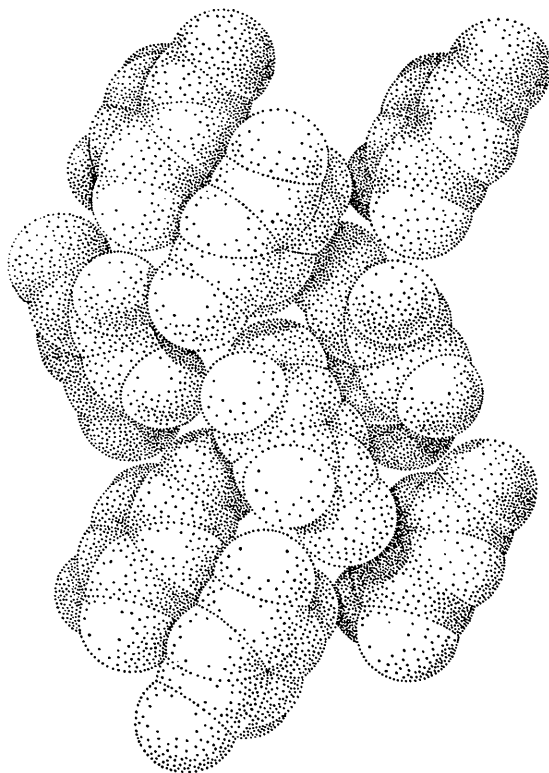


Fig. 5. A packing drawing of the structure viewed down the c axis.

and 2.84, 2.89, and 3.03 Å for H_9 (the second decimal is of little, if any, significance). The sum of the van der Waals radii is given by Pauling (1960) as 2.6 Å. In both cases the arrangement of the oxygen atoms about the hydrogen is roughly tetrahedral with respect to the H-C bond, and it is apparent that the $H \cdots O$ interactions have none of the geometric properties associated with what is usually called a hydrogen bond. An interesting structural feature (Fig. 4) is the formation of zig-zag chains of molecules along the b direction, adjacent molecules within the chain being held together (if that is the appropriate phrase) by two C-H \cdots O interactions.

(iii) The temperature factors

In discussing the thermal motions implied by the temperature-factor parameters of the individual atoms one must bear in mind that, because of the lack of adequate inter-layer scaling, the parameters γ which describe the motions in the c direction are not well determined. Nevertheless, the pattern of atomic motion derived from the temperature-factor parameters of Table 6 seems to be a reasonable one; moreover, there does not appear to be any systematic adjustment of the γ values which would lead to a more reasonable pattern.

In Table 6 are listed the magnitudes of the three principal axes of the thermal ellipsoids for each atom and their direction cosines relative to the crystallographic axes. As expected, the largest thermal motions are associated with the carbonyl oxygen atoms O_6 and O_7 . For both of these atoms the direction of maximum motion is perpendicular to the corresponding C-O bond and is inclined by about 35° (in opposite senses) to the plane of the molecule; in both cases the direction of minimum motion is within 10° of parallel to the C-O bond.

Table 6. The principal temperature factors and their direction cosines relative to the crystallographic axes

Atom	Axis i	B_i	g_i^1	g_i^2	g_i^3
O_1	1	7.08	0.124	0.988	-0.091
	2	5.39	0.687	-0.152	-0.711
	3	4.37	0.716	-0.026	0.698
C_2	1	6.50	-0.089	0.704	0.705
	2	5.22	-0.396	0.624	-0.674
	3	4.60	0.914	0.339	-0.223
C_3	1	6.98	0.691	0.633	-0.350
	2	5.61	-0.545	0.774	0.323
	3	4.27	0.475	-0.033	0.879
C_4	1	7.85	0.326	0.637	-0.698
	2	5.58	-0.458	0.753	0.473
	3	3.97	0.827	0.165	0.537
C_5	1	6.73	0.054	0.091	0.994
	2	5.60	0.331	0.938	-0.103
	3	4.70	0.942	-0.335	-0.020
O_6	1	10.41	-0.628	0.653	-0.424
	2	8.90	-0.475	0.110	0.873
	3	4.06	0.616	0.750	0.241
O_7	1	10.29	0.057	0.435	0.899
	2	8.58	0.960	-0.271	0.070
	3	5.64	0.274	0.859	-0.433

The results of a rigid-body treatment of the temperature factors (Cruickshank, 1956a) show the largest translational vibration to be in the direction of the long axis of the molecule ($O_6 \cdots O_7$) with a mean square amplitude of 0.07 \AA^2 ; the translational amplitudes along the short axis and in the out-of-plane direction are about 0.05 \AA^2 . The magnitudes of the angular oscillations are nearly the same (35°) about all three axes. The agreement between the observed vibration amplitudes U_{ij} and those calculated from the rigid-body motions is rather poor, particularly for the carbonyl oxygen atoms O_6 and O_7 . To explain satisfactorily the individual atom vibrations it appears to be necessary to consider not only the simple rigid-body motions but also some bending of the C=O bonds.

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Determination of the Anomalous Scattering Factor $\Delta f''$ for Chlorine

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Measurements of the Bijvoet inequality for the c zone of L-tyrosine hydrochloride are reported. The measured values of the Bijvoet inequality vary between half and twice the calculated value, but there is a good agreement in sign in almost all cases. These large variations between the observed values and those calculated from the structure are explained by the possible errors in the atomic coordinates and errors in the measurement of the Bijvoet inequality. The imaginary part of $\Delta f''$ for chlorine for $\text{Cu } K\alpha$ is estimated to be 0.67 ± 0.21 . The absolute configuration of L-tyrosine is also obtained.

1. Introduction

During recent years, the anomalous dispersion method of measuring the phases of X-ray reflections has proved to be successful in elucidating the structure of non-centric crystals (Ramachandran and Raman, 1956, Raman, 1959, Doyne, Pepinsky & Watanabé, 1957). This method of estimating the phases depends on measuring the difference in intensity between pairs of inverse reflections \mathbf{H} (hkl) and $\bar{\mathbf{H}}$ ($\bar{h}\bar{k}\bar{l}$) produced by the imaginary component $\Delta f''$ of the atomic scattering factor. Since the value of ΔI depends on $\Delta f''$, the estimated value of the phase angle also depends on the actual value of $\Delta f''$ used. The values ordinarily used are those calculated by Hönl (James, 1954) or by Dauben and Templeton (1955), the former using the wave-mechanical theory and the latter a semi-theoretical method. It seems desirable now to determine experimentally the values of $\Delta f''$ for the following reasons. The measurements on NaClO_3 (Ramachandran and Chandrasekharan, 1957) indicated that there was not very good agreement between the magnitude of $(\Delta I/I)_{\text{th}}$ and $(\Delta I/I)_{\text{exp}}$.

* We have now received the information from Dr J. R. Townsend that only certain crystals of ZnO exhibit this anomaly regarding the Bijvoet inequality and therefore the peculiar results reported earlier require reassessment.

although the sign of the two agreed in most cases. Harrison, Jeffrey and Townsend (1958) found in their measurements of anomalous dispersion effects in ZnO a peculiar periodic variation, which cannot be explained by using a common value of $\Delta f''$ for each Zn atom. They concluded that, if more than one identical anomalous scatterer occurs in the unit cell, it may be necessary to compute the anomalous crystal structure factor directly.* Bijvoet while determining the absolute configuration of NaBrO_3 found that it gave an exactly opposite configuration to that of its isomorphous pair NaClO_3 and suspected that the occurrence of more than two identical anomalous scatterers in the unit cell was the cause of this (personal communication to Prof. G. N. Ramachandran). Thus it appears that two types of experimental study of the anomalous dispersion effects are needed:

(i) One is to find out accurately the value of $\Delta f''$ using simple compounds like ZnS. This can then be used to test the conclusions of wave-mechanical theory, for example to see whether there is any dependence of $\Delta f''$ on $(\sin \theta/\lambda)$.

(ii) Secondly, it is necessary to find out whether the values of $\Delta f''$ so obtained can be directly carried over to more complicated structures containing a number of identical anomalous scatterers in the unit cell.