DUNNING, A. J. & VAND, V. (1969). Acta Cryst. 15, 1092.

- GROVE, D. C. & KEENAN, G. L. (1941). J. Amer. Chem. Soc. 63, 97.
- HIGUCHI, W. I., BERNADO, P. D. & MEHTA, S. C. (1967). J. Pharm. Sci. 56, 200.
- JOHNSON, C. K. (1965). ORTEP, A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations. ORNL-3794, Oak Ridge National Laboratory, Tennessee.
- KLUG, H. P. (1968). Acta Cryst. B24, 792.
- LAI, T. F. & MARSH, R. E. (1967). Acta Cryst. 22, 885.
- MESLEY, R. J. & HOUGHTON, E. E. (1967). J. Pharm. Pharmacol. 19, 295.

- MIYAZAKI, H. (1947). Japan J. Pharm. Chem. 19, 133. See also (1951). Chem. Abstr. 45, 3559h.
- O'CONNELL, A. M. & MASLEN, E. N. (1967). Acta Cryst. 22, 134.
- SEYDEL, J. K. (1968). J. Pharm. Sci. 57, 1455.
- SHEINKER, YU. N., POSTOVSKII, I. YA., VORONINA, N. M. & KUSHKIN, V. V. (1957). *Zh. Fiz. Khim.* **31**, 1745.
- SMITH, D. L. (1969). Acta Cryst. B25, 625.
- SUTTON, L. E. (1965). Tables of Interatomic Distances and Configuration of Molecules and Ions. Supplement, 1956– 1959. London: The Chemical Society.
- TRUEBLOOD, K. N., GOLDISH, E. & DONOHUE, J. (1961). Acta Cryst. 14, 1009.

Acta Cryst. (1971). B27, 333

Glycolic Acid: Direct Neutron Diffraction Determination of Crystal Structure and Thermal Motion Analysis*

BY R. D. ELLISON, C. K. JOHNSON AND H. A. LEVY

Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, U.S.A.

(Received 23 February 1970)

Glycolic acid (hydroxyacetic acid) crystallizes in $P_{21/c}$ with a=8.9649, b=10.5634, c=7.8261 Å, $\beta=115.083^{\circ}$, at $24\pm1^{\circ}$ C, with Z=8. The structure was solved directly from single-crystal neutron diffraction data by the 'squared structure amplitude' method followed by symbolic addition and Fourier synthesis. The structure consists of a loose three-dimensional hydrogen-bonded network of two closely similar but crystallographically distinct types of molecules. Averaged interatomic distances corrected for thermal effects deduced from a rigid-body motion analysis are C-C=1.517, C-O(H) in -COOH=1.326, C=O=1.226, C-O(H) in $-CH_2OH=1.420$, C-H=1.116 Å. Averaged O-H distances, corrected with the 'riding model' formula, are 1.009 in the carboxyl and 0.993 Å in the α -hydroxyl groups. With the exception of the aliphatic and α -hydroxyl hydrogen atoms, each molecule is nearly planar. The structure explains the nearly orthorhombic symmetry of the electron spin resonance spectrum of irradiated glycolic acid.

Introduction

Glycolic acid (hydroxyacetic acid) is the simplest member of the α -hydroxycarboxylic acid series. Crystal structure studies have been carried out on relatively few members: the dicarboxylic acids tartronic (Van Eijck, Kanters & Kroon, 1965) (HOOC-CHOH-COOH), tartaric (Okaya, Stemple & Kay, 1966) (HOOC-CHOH-CHOH-COOH), and dihydroxyfumaric (Gupta & Gupta, 1968) (HOOC-COH=COH-COOH); the tricarboxylic acid citric (Johnson, 1966; Glusker, Minkin & Patterson, 1969) (HOOC-CH₂-COHCOOH-CH₂-COOH); and acid salts containing the bisglycolate ion (Golič & Speakman, 1965; Van der Helm, Glusker, Johnson, Minkin, Burow & Patterson, 1968) (HOOC-CH₂-CHCOO⁻-CHOH-COOH). Glycolic acid affords a favorable case for observation of the dimensions of the > COHCOOH group, some of which seem rather variable from member to member: C–C from 1.502 to 1.544, C=O from 1.198 to 1.24, C–OH (carboxyl) from 1.28 to 1.319, C–OH (α -hydroxyl) from 1.39 to 1.426 Å.

A study (Atherton & Whiffen, 1960) of the electron spin resonance spectrum of γ -irradiated glycolic acid revealed an interesting pseudo-symmetry; the authors proposed an orientation in the crystal of the glycolyl radicals produced by irradiation, and by implication that of the parent molecules. The present study permits testing of the suggested orientation and provides an explanation of the pseudo-symmetry.

Some results of the present study have appeared in preliminary form (Levy & Ellison, 1967; Ellison & Levy, 1967, 1968).

Experimental

The space group of glycolic acid was determined to be $P2_1/c$ by Hughes & Small (see Atherton & Whiffen,

^{*} Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

1960); these investigators found that the asymmetric unit contains 2 independent molecules. We have redetermined the unit-cell parameters with greater accuracy from the diffractometer settings of 12 Bragg reflections in the 2θ -range $87-156^{\circ}$ (Cu $K\alpha_1$ radiation, $\lambda = 1.54051$ Å, temperature 24 ± 1 °C). The results, in agreement with those of Hughes & Small within the quoted errors, are a=8.9649 (6), b=10.5634 (7), c=7.8261 (7) Å, $\beta=115.083$ (5)° (least-squares standard errors in the least-significant digits are in parenthesis). With 8 molecules in this unit cell, the calculated density is 1.5056 g.cm⁻³; the density measured by flotation of a single crystal in tetrachloroethane-mineral oil is 1.51 g.cm⁻³.

Pijper (1970) has recently determined the structure of glycolic acid by X-ray diffraction. The unit cell upon which his description is based is apparently related to that of the present authors by the transformation A = -a - c, B = -b, C = c.

For neutron diffraction measurements, a large crystal from a commercial preparation was shaped to an oblate ellipsoid of revolution with principal diameters of 0.346 and 0.468 cm and weight 64 mg. Measurements of 2991 Bragg reflections were made with the Oak Ridge Automatic Neutron Diffractometer (Busing, Smith, Peterson & Levy, 1964) at a neutron wavelength of 1.078 Å. Of these, 24 corresponded to the absences of $P2_1/c$ (h0l, l odd) and had zero intensity within experimental error. The remainder corresponded to 2349 non-extinct, independent, symmetrically nonequivalent reflections of which 2109 were non-zero. The data were corrected for absorption (linear absorption coefficient 2.11 cm⁻¹), and reduced to squared structure factors in the usual way (Brown & Levy, 1964). A Wilson analysis (Wilson, 1942) of these data yielded an average temperature factor coefficient $B = 3.11 \text{ A}^2$.

Solution of the structure

The solution of the structure was first attacked unsuccessfully by computation of the gradient-sharpened (Jacobson, Wunderlich & Lipscomb, 1961) Patterson function, and its analysis by means of multiple implication (symmetry minimum) diagrams and superposition diagrams, following a procedure that was successful in the solution of the structure of potassium hydrogen chloromaleate (Ellison & Levy, 1965) from neutron diffraction data. Although some 16 superpositions were made on prominent peaks of the implication diagram, the solution to the structure was not forthcoming. The reason for the failure of the method became clear after the structure was solved: some important peaks were 'missing' from the Patterson function because of cancellation of positive and negative interactions. This cancellation is a difficulty peculiar to neutron diffraction from crystals containing both negative- and positive-amplitude scattering centers, and is especially important for those with a high proportion of hydrogen atoms. In this case there are

8 hydrogen atoms out of 18 atoms in the asymmetric unit; in potassium hydrogen chloromaleate, there are only 2 out of 12.

The assumption that the scattering density is everywhere non-negative underlies not only the usual schemes for interpreting the Patterson function, but also the direct phase-determining relationships utilized in the symbolic addition method (Karle & Karle, 1966). Hence, symbolic addition should not be expected to succeed in the present instance if applied directly to the neutron structure factors. A way of circumventing this difficulty suggested by Karle (1966) is referred to as the 'squared scattering amplitude method'. Briefly, from a set of pseudonormalized structure-factor magnitudes $|\varepsilon_h|$ derived from neutron measurements, there is derived a set of quantities

$$\varepsilon_{\mathbf{b}}^{'2} = 1 + (\beta_2^2 \beta_4^{-1} - 1) \frac{\langle (\varepsilon_{\mathbf{k}}^2 - 1) (\varepsilon_{\mathbf{b}-\mathbf{k}}^2 - 1) \rangle_{\mathbf{k}}}{\langle (\varepsilon_{\mathbf{k}}^2 - 1)^2 \rangle_{\mathbf{k}}}, \quad (1)$$

where $\beta_n = \sum_j f_j^n$ with j ranging over the atoms in the

unit cell; the $|\varepsilon'_h|$ are approximations to a set of pseudonormalized structure factor magnitudes for a structure with the same atomic arrangement as the experimental one, but with all atomic scattering amplitudes squared. The relation is most likely to be reliable when both $|\varepsilon_h|$ and $|\varepsilon'_h|$ are large. Since for this fictitious 'squared scattering amplitude' structure the scattering density is everywhere positive, symbolic addition, and perhaps also methods based on the Patterson function, should be applicable.

In the present work, equation (1) applied to the experimental set of 2349 values of $\varepsilon_{\rm h}$ yielded a set of 239 values of $\varepsilon_{\rm h} > 1$; of these 215 had also $\varepsilon_{\rm h} > 1$. The symbolic addition procedure was then applied using the computer program PHASER (Ammon, 1964; Ammon & Jensen, 1967) with 3 signs arbitrarily chosen to fix the origin and 2 more assigned in 4 combinations. The two combinations judged best (greatest number of signs determined and fewest inconsistent sign indications) had 222 and 220, respectively, determined signs. A Fourier synthesis was prepared with each of these sets; one was interpretable in terms of the expected molecular shape. It showed peaks for all the C and O atoms in the structure and contained only one false peak large enough to be troublesome. No peaks assignable to hydrogen atom positions appeared; since the squared scattering amplitudes for H and C are in the ratio $(-0.378)^2:(0.661)^2=0.325:1$, and because hydrogen peaks should be further reduced by greater thermal amplitudes, their absence is not disturbing. Of the 222 terms used, 217 proved to have correct signs when checked against the final model.

A weighted Fourier synthesis was next computed using structure factor magnitudes derived from the neutron diffraction measurements, signs as given by the C and O positions, and weights (Woolfson, 1956) of

$$\tanh(|F_o||F_c|/32 f_{\rm H}^2)$$

in which $f_{\rm H}$ was corrected for the overall thermal motion as given by the Wilson analysis. This diagram displayed all eight hydrogen atoms in the asymmetric unit and thus completed the solution of the structure.

Refinement

The structure was refined by the method of least squares, in which $\sum w(F_o^2 - S^2 F_c^2)^2$ was minimized. Weights w were set equal to the reciprocal of the variance of the observation, which was estimated according to usual practice (Brown & Levy, 1964) as

$$\sigma_{\rm statistical}^2 + (0.03 \ F^2)^2$$
,

 $\sigma_{\text{statistical}}^2$ being derived from the application of Poisson statistics to the counting data. As refinement proceeded,

it became clear that the two strongest reflections were severely reduced by extinction, and that some 63 others were noticeably affected. These were first omitted from the refinement; in the final stages, the alternate procedure of applying an extinction correction was adopted. In order that the parameters of this correction might be properly adjusted by the method of least squares, the correction was applied to the calculated values in the form

$$F_{\text{corrected}}^2 = F_{\text{calc}}^2 (1 - q_1 Q + q_2 Q^2)$$

in which Q is defined to be $F_{calc}^2/\sin 2\theta$, and F_{calc} is the uncorrected calculated structure factor. This correction is equivalent to that derived by Zachariasen (1965)

$$1 - \frac{P_2}{P_1} g_2 \overline{T} Q + \frac{4}{3\sqrt{3}} \frac{P_3}{P_1} g_2 \overline{T^2} Q^2 - \dots$$

Table 1. Calculated and observed structure amplitudes

The columns contain the Miller index h, the quantity $100F_{calc}$, the quantity $100|F_{obs}|$ adjusted to final scale and corrected for absorption and extinction, and the quantity $100\sigma(|F_{obs}|) = 100\sigma(F_{obs}^2)/2|F_{obs}|$, or, in the entries flagged W, the quantity $100\sigma(F_{obs}^2)$. The flag E indicates that the extinction correction on F_{obs}^2 exceeds 1.05. The reflection 641, flagged X, was deemed to have a gross error in measurement, and was omitted from consideration.

	1	10 1	n //				1		1 " "					, u 1	1 * "	10 1	· * "	10
···· H 0 0 ····	1 H 6	0 ****	**** p 13			1	1 ···· H 6	1		,	**** N 15	,		,			···· 10	,
	1																1	-
W-1 12 0 4	E 0 627	606 9	1 -27	32 22	-3 -269	266 5	7 196	203 6	0 -118	127 7	0 -56	66 17	-9 -87	92 10	0 80	100 6	-7 182	184
£ 2 1017 990 15	1 -105	105 4	2 -48	71 10	-2 -58	60 9	8 -28	49 14	1 -156	156 6	1 1 1 42	145 9	-8 -167	171 6	C 1 67	672 10	-6 -7	33 1
3 119 121 4	2 -406	395 6	3 1	55 18	¥-1 H	08	9 267	252 6	2 37	53 14	2 - 34	49 26	¥ −7 −18	0 14	E 2 534	530 8	-5 -114	109
4 -67 74 5	3 -102	95 6	4 -36	43 25	0 -39	-7 9	W 10 -36	0 23	3 60	57 15	3 -18	34 42	E -6 -582	579 9	3 253	255 5	-4 13	33 2
5 -91 86 5	1 4 -80S	795 22	W S 24	0 21	1 1 177	373 4			4 139	145 7			-5 62	75 8	1 4 734	748 12	-3 -80	73 1
L 6 632 822 13		37 19	6 10	117.11	2 213	212 4			5 -120	121 6		,	1 -4 511	511 8	5 -272	280 6	w -2 -36	
E 8 685 690 10	7 -129	119 7	**** H 16		L 166	169 5	-11 -15	61 12	2 -121	195 7	-12 -211	213 7	-3 109	768 6	1 1 103	103 7	0 -78	105
9 1 24 16	8 76	80 9		•		69.10	-10 81	86 13	W 8 -22		-11 -155	156 6		400 5	6 -4		1 218	719
10 295 288 5	9 -105	119 7	0 -88	61 18	6-114	114 7	-9 147	140 6	1	• • • •	-10 -137	331 6	E 0 -477	487 8	9 89	91 14	2 -101	98
11 47 66 16	10 -29	57 19	1 -471	477 8	7 -129	141 6	-8 10	32 20	**** 31.11		-9 162	165 6	1 269	270 5	10 55	72 20	w 3 -0	
12 148 142 11	0.1	72 18	2 -91	111 10	8 10	38 22	-7 -98	100 6			[-8 -8-1	852 13	1 2 -439	452 7			138	144
			3 -217	211 7	9 -51	23 29	-6 -203	197 6	-9 -40	58 24	-7 288	282 5	3 39	55 10	**** 31 7	2 ****	5 -103	91
**** H 1 0 ****	н ,	• ••••	4 - 35	15 77	10 130	124 9	-5 -246	238 5	-8 -50	60 18	-6 -452	448 7	E 4 545	546 9			6 158	172
	1	1	5 -121	104 14	1 11 49	69 18	-4 174	177 5	-7 -7	35 30		32 16	5 70	68 11		17 65	7 134	140
1 149 149 3	1 -59	58 9	1				-3 (27	129 5	-6 -113	116 2	C -4 -713	728 11	6 51	64 12	-10 32	40 27	8 -41	62 2
2 -115 119 3	2 130			0		1	-2 100	91 7	-3 /4	82 9	1 -3 -572	578 9.	7 -116	114 8	-9-104	119 7		
L 5 501 502 5								37 14			-2-13/8	12 2/5	0 - 19/	195 5		**	1	
6				0 13			1 -186	189 6	-3 216	212 6	F 0-1766	1100 10	10 -9	LL 16		20 17		60.7
6 -66 9 70	6 -16	50 16		17 41	-10 -10	66.10	2 -98	88 7	- 15	29.28	C 1 V6	182 6				116 2		105 1
7 -168 177 6	1 7 -8	30 28			-8 -328	338 6	3 -270	274 5	0 -121	124 7	1 2 -484	498 8	**** H 4	, 	-4 141	145 6	-7 104	115
8 -267 272 6	8 80	58 12	**** 1 1	1 ****	-7 79	67 12	4 125	129 7	1 38	50 17	3 -51	46 12			-3 -94	93 7	-6 169	162
9 -90 93 10	9 -22	68 15	l		-6 151	159 5	5 61	71 11	2 -194	195 6	£ 4-529	520 B	~12 88	82 15	-2 107	107 6	-5 -74	49 1
10 -103 98 6	10 15	36 31	8-12 43	0 25	-5 300	293 5	6 63	68 13	3 -89	69 10	5 -70	66 10	-11 -140	148 8	-1 -189	185 5		18 1
11 21 62 13	1		-11 -81	86 12	E =4 522	520 8	7 -1 34	142 6	4 95	99 7	E 6 -743	746 12	-10 -17	41 17	0 -10	94 7	-3 -1 30	139
12 -26 55 25	···· × 8	0	~10 ~88	97 11	-3 -316	313 5	8 -79	86 9	W 5 14	0 14	7 -149	125 8	-9 97	92 10	1 -139	137 5	-2 56	66 1
			1 - 9 - 14	0 17	1 -2 -669	668 10	9 -179	165 7	6 125	141 8	8 - 308	308 5	-8 -451	459 8	2 - 394	389 7	W-1 -6	
H 2 0 ****	0 -31	6 99	-8 -150	151 6	-1 -265	262 5	10 76	88 17	1 97	70 15	9 64	76 10	-7 302	306 6	1 3 -54	537 9	0 137	157
6 -161 IV.	1 1 145	145 5	-7 267	271 5	E 0 -//3	718 11			w 8 -j+	0 28	10 -89	87 13	-6 /4	69 10	1	62 12	(·'''''''	101
F 1 -8-0 819 12	1 1016	1011 16	-6 256	164 6	2 201	197 6		,				, 		152 5	1 5 -106	100 6	2 57	
2 -129 128 1	6 106	108 8		19 11	1 1 20	261 5	>10 82	87.16	1	,		1	-1 -207	201 6		76 10	1 100	74 1
1 - 1 - 1 - 1 - 1	r 5 880	886 14	-1 -144	141 6	4 454		-10 02	56 18	-8 -81	62 23	-12 19	15 77	-7 -159	161 5	8 -70	46 20	5 -61	61.2
4 -160 156 4	6 147	138 7	-7 -10	44 8	5 -49	33 19	-8 -26	36 19	-1 -1	13 81	-11 -65	65 16	-1 250	244 5	9 -14	169 6	6 61	75 1
5 168 167 4	W 7 29	0 13	-1 53	48 6	1 6 -440	0 16	-7 -61	45 19	-6 -141	160 7	-10 -14	43.15	1 0 -581	584 9	1		7 52	57 2
6 -294 295 5	8 -20	25 28	0 15	40 6	7 -169	166 6	-6 120	137 7	-5 -516	517 9	-9 -53	59 15	1 408	413 7	····	2 ****	1	
7 18 67 12	9 233	235 6	1 213	215 4	8 -274	272 5	-5 -231	231 5	w-4 -7	0 14	-8 147	152 6	2 266	268 5			**** H 12	2
8 2 69 12	10 -33	63 19	2 57	75 6	9 44	61 12	-4 371	368 6	-3 -300	296 5	-7 -187	392 7	3 -199	201 4	-11 -279	257 9		
9-414 406 7	1		3 259	264 5	10 38	51 21	(-3 -193	196 5	-2 110	108 7	-6 259	255 5	4 111	111 6	-10 77	87 13		0 2
10 -48 53 14	•••• н 9	0	L -199	192 5	11 15	31 44	-2 142	141 6	-1 184	183 5	-> 54	55 10	5 -	28 25	-9 -205	198 7	-7 -9	50 2
11 -124 97 12			5 -181	177 5			-1 21	6 99	0 -147	148 5	-4 164	167 4	6 -192	202 6	-8 -255	256 5	-6 -60	
12 -62 5/ 26	1 31	36 19	6 -243	246 5		1	0 -67	41 14	1 -05	176 6	-3 769	101 6	/ -0	38 77	-7 -320	370 6	-3 -202	214
****	1 - 395	392 /		69.11	wall all	• 11	2 102	201 6	1 -168	410 0		26.16	v a -17		-6 -259	266 6	V	
, , , ,	L =224	210 5	0 03 0 18	69 17	-10 -197	201 2	1 -185	185 5	6 -110	105 11	0 248	261 6	10 42	A0 19	1	964 15	-2 18	119
1 14 17 5	5 -226	276 6	10 -44	76 61	-9 22	26.9	4 290	287 6	5 -261	267 6	E 1 -596	613 9		~ .,		671 7	-2 101	·
E 2 859 840 11	6 176	179 5	¥ 11 -7	0 22	-8 -151	165 6	5 -63	73.11	6 0	36 28	2 111	285 5		2 ****	-7 -11	406 7	0 -20	47.1
3 27 38 10	7 -17	46.15			-7 -7	40 18	6 88	62 15	7 69	67 19	3 -30	40 13			-1 -204	200 5	1 -101	95
4 -1 42 9	8 65	75 14	**** H 2		-6 171	175 5	7 15	29 23	1		4 208	210 5	¥+12 35	0 17	0-42	425 7	2 -98	109 1
5 23 36 15	9 -16	44 24			-5 -170	161 5	¥ 8 26	0 20	**** # 13	1	5 330	326 6	-11 77	70 15	E 1 -616	615 10	3 -231	235
E 6 -623 619 10			-12 -83	88 15	-4 123	123 4	9 -59	69 16			E 6 592	591 9	-10 27	39 19	2 -205	203 5	4 -65	71 1
7 -63 82 10	**** H 10	• ••••	-11 91	87 13	-3 89	106 6			w -7 -48	0 27	2 127	123 7	w-9 6	0 13	L 3 -933	9-8 14	w s -33	10 2
8 251 249 6	1		-10 -128	129 6	-2 -235	237 5			-6 37	56 19	8 226	227 5	-3 62	61 14		0 15	6 19	56 2
9 28 75 9	0 165	165 6	-9 144	143 2	-1 127	128 5				123 9	9 -00	/4 10	-/	+66 6	5 -17	174 7	1	
10 161 154 8	1 -261	259 6	-8 -395	396 7	0 132	138 5		170 7	- 10	10 01			38	55 15	6 152	148 6		,
	1.1 2	0 16		697 R	2 40	76 8	-8 -58	72 14	-1 -1	55 13		•		102 4	- a - 4	0 22	-7 70	
**** * * 0 ****	- i - i	2 12	-5 18	16.15	1 -251	252 4	-7 -1 32	131 6	-1 66	65 11	-12 127	141 9	-3 327	332 6	9 -201	180 10	w-6 11	
	5 24	48 13	-4 -261	257 5	4 -316	318 6	-6 -58	59 14	0 70	58 14	-11 179	179 7	-1 -42	54 10	1		-5 112	133
E 0 696 683 10	6 -212	212 4	-3 60	58 9	5 270	271 5	-5 -213	210 6	W I -21	0 14	¥~10 22	0 13	-1 -105	112 5	**** H 9		-4 -181	188
1 -123 124 4	7 -177	\$72 7	E -2 -390	385 6	6 30	32 23	-4 216	213 5	2 208	208 7	-9 209	209 6	0 -28	54 10			-3 38	18 5
2 157 160 4	8 23	44 24	E -1 399	401 6	7 287	785 6	-3 327	334 6	3 145	150 8	₩8 -20	0 15	1 -412	418 7	-10 -59	64 18	-2 -95	100 1
3 273 266 4	9 -1 38	123 12	0 -406	410 6	8 262	260 5	1 19	35 20		129 9	-7 -59	70 10	2 175	168 4	-9 104	116 10	1 -1 149	151
1 4 -574 571 9			1 242	149 4	9 48	40 26		42.14	1 2 00	99 12	1	-9 12	1 3 51	56 11	× -8 30	0 15	1	27 3
5 160 162 5	1	3	1, 2, 94	au 9	1 10 39	0 21	1 - 117	115 4	1°'	51 25	1	773 11		160 4	-7 -84	07 8	1 , 80	50 1
0 /0/ /0/ 9	W 1 #74	0 14	176	174 4		,	2 -10	49 14	**** H 1L	,		27 18	6 140	174 4	1 2 0	94.9	1 1 1	126
A 281 284 4	بعبر ا	75 12	5 -102	107 4	<u>، ، ،</u>		3 -110	107 8	1	-	1 -2 +25	430 7	7 -116	136 6	-4 -28	278 4	4 - 34	58.
9 21 46 12	1 -1 40	144 7	6 -474	431 7	-11 767	231 7	6 6	10 83	×-5 3	0 24	1 -1 465	469 7	8 -85	93 9	-3 263	262 5	5 18	46 2
¥ 10 -18 0 21	W 4 -24	0 13	7 45	50 15	w-10 -14	0 20	5 270	265 6	-4 220	223 7	0 24	44.11	9 1	26 40	-2 -238	248 5	1	
11 66 69 16	5 204	198 5	8 -194	178 6	-9 300	293 5	w 6 -2	0 13	-3 -64	62 17	1 241	246 5	10 78	84 16	-1 39	391 7	**** H 14	, .
	6 56	79 13	9 196	181 5	-8 -112	114 8	7 -121	131 8	-2 194	191 7	703	418 7	l		0 11	113.2		
**** # 5 0 ****	7 -38	20 51	10 -66	79 1-	-7 184	187 6] 8 -6)	81 13		56 19	3 58	98 6	···· × 6	· ····	1 160	150 6	¥ =6 8	۰.
	8 -30	27 -2	11 61	64 18	-6 -197	200 5	9 -193	187 9	0 150	158 8	4 484	477 8			2 34	345 6	-5 246	238
1 172 172 4	1		L		-5 377	379 6	l		1 114	115 10	5 -259	258 5	-12 159	170 13	3 31	320 6	-4 176	191
2 23 36 10	**** H 12	0	••••• × 3	,		49 12	1 **** H 10		2 23	222 7	6 260	252 5	-11 -15	46 23	4 -15	162 7	-3 323	323
C 3 557 558 9	1		L		1 -3 528	525 8			3 39	22 -9	7 209	213 6	-10 27	67 22	5 6	61 13	-2 97	102 1
4 -73 81 7	0 -203	201 6	-12 17	55 22	-2 89	99 6		8	1	41 19 8	0 -36	29 17		142 6	6 -19	194 7	-1 440	454
5 -375 361 6	1 1 1	54 12	-11 -37	54 20	1 -1 127	116 11	1	70 10	> -62	67 73	3 300	475 B	-2 330	179 9		58 18	1 2 50	53 2
0 -131 152 6	1	205 5		47.70	1 1 4	662 9	- 144	161 4				30 10	-/ 100	498 P	1 * *	30.37	200	(n))) ·
8 67 6916	1			65 17	2 -110	130 4		57 14	1		···· H 1	,		28 24		, ,	1 144	10
9 89 85 9	5 161	159 8	-7 100	112 2	3 300	558 6	1 10	0.16	-4 -75	55 27	1		t - 695	694 11	1 ""		6 39	62
10 57 59 18	6 12	40 27	W-6 15	0 12	4 -62	75 9	-3 -168	166 6	-3 -116	118 12	-12 57	48 23	-3 -287	289 5	w-10 -	0 28	1 "	
11 55 26 47	1 -0	41 22	-5 -108	113 6	5 263	267 6	-2 -46	62 12	-7 -9-	95 16	-11 114	111 10	-2 162	166 5	-9 16	163 8	1	
	1			45.12	هه ۱	30 26	-1 -456	452 7	-1 28	60 19	-10 187	182 5	-1 236	231 5	- A 11	106 10	1	

GLYCOLIC ACID: DIRECT	NEUTRON	DIFFRACTION	DETERMINATION
-----------------------	---------	-------------	---------------

.....

	-	+ 29440044 + A
	5	· · · · · · · · · · · · · · · · · · ·
	2	
		Austicate Sarahelate salatelate Antica fait Lateridate Lateriate Sarahela estate fata
	10	
	2	
	-	
	-	
	2	
		· ####################################
	2	
	2	
	;;;	
	2	
	2 4	·
	• •	
	2 -	
	- :	· 1/2 ·
	2	
	2 -	NALA¥#BE4X44 5 VENESSES 5 VERESSES 2 465050 5 465055655555554555654 0 801-645004655655656 0 801-647005565885
	<u> </u>	
	21	
	2 9 2	2284888282.824242 / 2.222824894000 / / / / / / / / / / / / / / / / / /
	- :	
Ľ.	<u>و</u> :	
10	2 7	
9	1	
-	. :	9 1 3 - 1 0
		• • • • • • • • • • • • • • • • • • •
٥ľ	* .	
able	× 72 ×	
Table	2 2 1 H H H	
Table	· · · · · · · · · · · · · · · · · · ·	
Tablé	· · · · · · · · · · · · · · · · · · ·	
Table	H, FC FO T N FC FC	
Table	FO C H, FC FO C H, FC FC	
Table	ΓC FO C H, FC FO C H FC FC FC	
Table	H LC LO C H LC LO L H LC LO L H LC LC	
Table	0 [H LC TO [H. CC TO [H. CC TO [H TC	
Table	C TO C H TC TO C H TC TO C H TC TO C TO	
Table	ж ГС ГО Г м ГС ГО Г н. ГС ГО Г м ГС ГС •••• к10 4 ••••• • •••• 2 ••••• 8 ••••• 8 ••••• ••••• 11 5 •	
Table	и к сс го с и к сс го с н. сс го с н. сс го с н. к с го с	
Table	10 [K LC 10 [K LC 10 [H LC 10]	
Table	ис го г и и го г и и го г и и го г и и го го г и и и го г и и и го и и и и и и и и и и и и и и и и и и и	
Table		
Table	10 [] H [C] O [] H [C] O [] H [C] O [] H [C] O [] H [C] O [] H [C] O [] H [I] O [] O [] H [I] O [] O [] H [I] O [] O [] H [I] O [] O [] H [I] O [] O [] H [I] O [] O [] H [I] O [] O [] H [I] O [] O [] H [I] O [] O [] H [I] O [] O [] H [I] O [] O [] H [I] O [] O [] H [I] O [] O [] H [I] O [] O [] H [I] O [] O [I	
Table	رد مو دا ۲۰۰۰ منا ۲۰ در دار ۲۰۰۰ منا ۲۰۰۰ منا ۲۰۰۰ منا ۲۰۰۰ د دو دا ۲۰۰۰ ۲۰۰۰ ۲۰۰۰ در ۱۰ ۲۰۰۰ منا ۴۰ درما منا ۲۰۰۰ منا ۲۰۰۰ منا ۲۰۰۰ منا ۲۰۰۰ منا ۲۰۰۰ ۲۰۰۰ منا ۲۰۰۰ ۲۰۰۰ ۲۰	
Table	W CC 00 C W CC 00 W S 3 000 W	
Table	1 H 12 10 H 12 10 H 12 10 H 12 14 14 14 14 14 14 14 14 14 14 14 14 14 14 14 14 14 14	
Table	101 N C 01 N C 0	
Table	رد ۱۵ ۲ × ۱۵ ۲۵ × ۲۵ ۵۵ × ۲۵ ۵۵ × ۲۵ ۵۵ × ۲۵ ۵۵ × ۲۵ ۵۵ × ۲۵ ۵۵ × ۲۵ ۲۵	
Table	и и и и и и и и и и и и и и и и и и и	
Table	0 2 K L2 10 K K L2 10 K K K K K K K K K K K K K K K K K K	
Table	ارد او از	
Table	H 12 10 (H 12 10 1 H	
Table	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	
Table	i 10 H LC 10	
Table	, נכ נסן אונכ נסן אונז זי. ני נו נסן אונכ נסן אונכ נסן אונכ נסן אונכ נסן אונכ נסן אוני נסן גווא גע נסן אוני נסן אוני נסן אוני נסן אוני ני	
Table	ער נכ נס ר אונכ נס ר אונ	
Table	ال « از ۱۵ ز ۵۰	
Table	رد او دار از او دار ا دو دار از او دار از ا دو دار او دار از او د	
Table	γ ₁ το το τ΄ με το τ΄ με το τ΄ με το τ Ματά το	

336

._

if the polarization factors P_n are set to unity (as is appropriate for neutron scattering), the identification

$$q_1 = g_2 \overline{T}, \quad q_2 = \frac{4}{3\sqrt{3}} g_2 \overline{T^2}$$

is made, and terms of higher order in Q are ignored. Thus our form assumes that \overline{T} and $\overline{T^2}$, $\overline{T^n} \equiv (-1)^n (1/A) d^n A/d\mu^n$, where A is the transmission factor as a function of the linear absorption coefficient, are independent of the orientation of the crystal and the scattering angle, an assumption that is plausible in the present case. This correction was highly successful in that all observed intensities were brought into satisfactory agreement with calculation. The most severe correction factor is 0.6241.

Table 1 lists values of the calculated and observed structure factor magnitudes. The latter have been corrected for absorption and extinction and placed on the final scale. The errors listed are values of $\sigma(F_{obs}^2)/2F_{obs}$ except for the weakest reflections, flagged with the symbol W, for which $\sigma(F_{obs}^2)$ is listed instead; $\sigma(F_{obs}^2)$ is the standard error corresponding to the least-squares weight. Table 2 lists the final parameters of the structure. The agreement achieved is indicated in the following table:

Reflections	Number	R(F)	$R(F^2)$	σ_1
All*	2348	0.092	0.056	1.07
$F^2 > \sigma(F^2)$	1748	0.060	0.051	1.18

In this table $R(F^n) \equiv \sum (|F_{obs}|^n - |SF_{calc}|^n) / \sum |F_{obs}|^n$ and $\sigma_1 \equiv \sum w (F_{obs}^2 - S^2 F_{calc}^2)^2 / (N-P)$ where N is the num-

* One reflection, 641, judged to be a gross error in measurement, has been omitted; see Table 1. ber of reflections in the group and P=167 is the number of parameters fitted by least-squares (54 positional coordinates, 108 coefficients of the anisotropic temperature factors, 1 scale factor, 2 extinction correction parameters, and 2 atomic scattering amplitudes).

Description of the structure

Fig. 1 shows stereoscopic drawings of individual molecules of glycolic acid, along with the atoms of neighboring molecules to which they are hydrogen bonded, viewed in a direction 25° to the normal to the plane of the carboxyl group. The interatomic distances shown in this Figure have not been corrected for effects of thermal motion. Bond angles are given in Fig. 2. The two molecules are closely similar, both in dimensions and in conformation. The bond distances and angles are all within the range of the better determined values from previous studies of similar molecules, and none is in disagreement with expected values. The configuration of atoms $C - C < O^{O}$ of each molecule is quite closely planar. There is also evident a tendency for the acid hydrogen atom [H(11) or H(12)] and the oxygen atom [O(21) or O(22)] of the α -hydroxy group to lie in this plane, as indicated by the following conformation angles:*

* Conformation angle A-B-C-D is defined to be the azimuth of \overrightarrow{CD} with respect to \overrightarrow{BA} about the vector \overrightarrow{BC} as polar axis of a right-handed system; that is, the clockwise angle from the projection of \overrightarrow{BA} to the projection of \overrightarrow{CD} viewed in the direction \overrightarrow{BC} .

Table 2. Parameter	s oj	f the	structure	of	glycol	lic	acid	
--------------------	------	-------	-----------	----	--------	-----	------	--

Least-squares standard errors are given in parenthesis.

	Fractional	position paran		Thermal parameter* $\times 10^5$					
	x	У	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(11)	-64 (1)	-2448 (1)	2251 (1)	961 (11)	404 (6)	1608 (17)	25 (6)	382 (11)	-62(8)
O(11)	-1316(2)	-1886(1)	897 (2)	1560 (20)	525 (9)	2137 (26)	205 (10)	-137(17)	-137(12)
H(11)	-1273(3)	-954 (2)	1161 (3)	1664 (34)	593 (16)	2700 (54)	154 (18)	296 (33)	-53(22)
O(31)	980 (1)	- 1877 (1)	3534 (2)	1131 (16)	470 (8)	2307 (27)	31 (9)	41 (16)	- 99 (12)
C(21)	-97 (1)	-3861(1)	2006 (1)	1177 (13)	391 (6)	1873 (21)	-12(7)	418 (13)	- 98 (9)
H(31)	-1160(3)	-4224(2)	2162 (5)	1233 (31)	790 (20)	4723 (88)	-172 (19)	701 (42)	168 (32)
H(41)	-273(5)	-4057(2)	579 (4)	3911 (77)	905 (22)	2191 (56)	467 (32)	939 (51)	-250 (26)
O(21)	1320 (1)	-4442(1)	3356 (2)	1056 (15)	440 (8)	2390 (27)	50 (8)	581 (16)	119 (11)
H(21)	2229 (3)	-4363 (2)	3001 (4)	1411 (32)	789 (18)	3800 (70)	-17 (20)	1205 (40)	49 (27)
C(12)	4975 (1)	-4339 (1)	2248 (1)	932 (11)	520 (6)	1715 (19)	27 (7)	477 (12)	92 (9)
O(12)	6296 (1)	- 4919 (1)	2330 (2)	1149 (16)	572 (9)	2675 (30)	109 (9)	843 (18)	170 (13)
H(12)	6320 (3)	- 5819 (2)	2742 (3)	1462 (31)	682 (17)	2873 (53)	110 (17)	797 (33)	153 (23)
O(32)	3906 (1)	- 4858 (1)	2526 (3)	1486 (20)	741 (11)	4434 (47)	162 (12)	1647 (27)	524 (18)
C(22)	4954 (1)	- 2964 (1)	1734 (1)	1152 (13)	497 (7)	1847 (21)	9 (8)	532 (13)	69 (19)
H(32)	6055 (3)	- 2521 (2)	2773 (4)	1300 (32)	848 (20)	3974 (74)	-134(20)	481 (39)	-253(31)
H(42)	5031 (4)	-2910(3)	392 (4)	3704 (70)	1110 (25)	3037 (70)	448 (35)	2150 (59)	581 (33)
O(22)	3568 (1)	-2324(1)	1703 (2)	1092 (16)	538 (8)	2104 (26)	112 (9)	192 (17)	-85(12)
H(22)	2623 (3)	- 2508 (2)	525 (3)	1267 (30)	804 (19)	2632 (53)	- 31 (18)	160 (33)	64 (25)
			С	0	Н				
Conttanin		10-15	((1	677 (2)	2(0, 0)				

Scattering amplitudes (cm \times 10⁻¹⁵) 661

577 (2) - 369 (2)

(Amplitudes of atoms of the same chemical element were constrained to be equal. That of carbon was not varied.)

* Coefficients in the expression $\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl$.

H(11)–O(11)–C(11)–O(31)	$-3.0(3)^{\circ}$
H(12)-O(12)-C(12)-O(32)	-4.0(2)
O(21) - C(21) - C(11) - O(31)	-5.6(2)
O(22) - C(22) - C(12) - O(32)	-2.9(2)

The manner in which the molecules are linked by hydrogen bonds is shown in stereo in Fig. 3 (the aliphatic hydrogen atoms have been omitted for clarity). The shortest, strongest links are from the carboxyl groups as donors to the α -hydroxy oxygen atoms of the same type of molecule, O(11)-H(11)... O(21) and O(12)-H(12)...O(22), forming infinite strings of hydrogen-bonded equivalent molecules along the screw axes. These strings are cross-linked by somewhat weaker hydrogen bonds from the α -hydroxy groups as donors to carbonyl type oxygen atoms of the carboxyl group of the other molecular type as acceptor, O(21)-H(21)...O(32) and O(22)-H(22)...O(31). The result



Fig. 1. Stereoscopic drawings of the two crystallographically distinct molecules of glycolic acid and the atoms (unshaded in the drawing) of neighboring molecules to which they are hydrogen bonded. Atoms are represented by ellipsoids enclosing 50% of normally distributed thermal displacements. The viewing direction is 25° from the normal to the plane of the carboxyl group.



Fig. 2. Bond angles (degrees) in glycolic acid. The least-squares standard errors (degrees × 10⁻²) are given in parenthesis.



LEFT EYE

RIGHT EYE

Fig. 3. Stereoscopic drawings showing the linking of molecules in glycolic acid by hydrogen bonds. The aliphatic hydrogen atoms have been omitted for clarity.

is a loose three-dimensional hydrogen-bonded network, in which the smallest closed loops involve parts of six molecules.

The usual inverse correlation between the O-H and the $H \cdots O$ or $O-H \cdots O$ distances is clearly evident, and the shorter $O \cdots H$ distances occur in the more nearly linear links. Table 3 shows these correlations.

Atherton & Whiffen (1960) have pointed out that there is simulated orthorhombic symmetry in the electron spin resonance (e.s.r.) spectrum ascribed to glycolyl radicals produced by γ -irradiation of glycolic acid. The origin of this 'extra' symmetry is illustrated in Fig. 4, which shows a projection along **b** of the *B*-centered cell in which **b** and **c** are common to the quoted monoclinic cell and new **A** is $2\mathbf{a} + \mathbf{c}$; the length of *A* is 16.24 Å and the angle to c is $89\cdot21^{\circ}$. It is clear that some pairs of molecules of the two types may be approximately interconverted as though by the operation of screw axes, and others as though by the operation of glide planes, parallel to the pseudo-orthorhombic directions. For example, the molecule designated in the Figure (2, -0.37) is related approximately to molecule (1, -0.32) as though there were a twofold screw axis parallel to c. However, this operator does not convert molecule (1, -0.32) into (2', -0.13); these latter are approximately related as though there were a glide plane parallel to the *bc* plane.

The presence of pseudo-symmetry led Atherton & Whiffen to conclude that the planes of the $O-C \cdot (H)-C$ part of the glycolyl radicals of both crystallographic

types are parallel or antiparallel to each other and perpendicular to **c**, and that the same description would hold for the corresponding parts of the host molecules. This erroneous conclusion arose, apparently, because in all the e.s.r. measurements the direction of the magnetic field lay in the symmetry plane or in one of the pseudo-symmetry planes; hence the spectra of at least two radicals were observed throughout as coincident.

Thermal motion

In the drawings of Fig. 1, the atoms are represented by ellipsoids enclosing 50% of normally distributed thermal displacements. These drawings suggest that the molecules undergo oscillation and libration as nearly rigid bodies restrained by the hydrogen bonds. A computer program written by Johnson (1967) was used to analyze the motion on the basis of the theory of rigid-body motion of Schomaker & Trueblood (1968), in which the motion is described in terms of three tensors of the second rank: T, describing translational motion, L, describing librational motion, and S describing the interaction of translation and libra-

tion. The two hydrogen atoms attached to oxygen atoms were excluded from the rigid bodies, since their displacements are substantially affected by internal rotation about the C-O single bonds. The thermal parameters of the aliphatic hydrogen atoms were first reduced by estimated values of their internal vibrational mean-square amplitudes, deduced from the normal modes (Shimanouchi & Suzuki, 1962) of the methylene chloride molecule; these are* 0.00578 Å² along, and 0.01369 Å² perpendicular to, the C-H bond. The fit of the rigid-body model to the observed thermal displacements is considered to be quite satisfactory for both molecules: the standard errors of fit are 0.0015 and 0.0016 Å² for molecules 1 and 2 respectively, considering only the seven atoms included in the rigid bodies. The largest principal-axis components of the residual tensors are 0.0037 and 0.0031 Å² respectively.

As shown by Schomaker & Trueblood (1968), the result of the rigid-body analysis may be visualized as

* Computed with a program by M. D. Danford of this Laboratory. The program is a modification of one reported by Schachtschneider (1962).

Table 3. Distances and angles for the hydrogen bonds

Errors in the least-significant digits appear in parenthesis. No thermal-motion corrections have been made.

Atc	m numbe	rs in		Distance		$O-H\cdots O$
0	-H···O 1	ink	O-H	$H \cdots O$	O-H···O	angle
(11)	(11)	(21')	1·003 (2) Å	1·646 (2) Å	2·647 (2) Å	175·5 (3)°
(12)	(12)	(22')	1.001 (2)	1.640(2)	2.638 (2)	$175 \cdot 2(2)$
(21)	(21)	(32')	0.970 (3)	1.774 (3)	2.696(2)	157.6 (2)
(22)	(22)	(31')	0.971 (3)	1.753 (3)	2.714 (2)	169.7 (2)



Fig. 4. Projection along B of the pseudo-orthorhombic B-centered cell for which A = 2a + c of the monoclinic cell and B = b, C = c. The molecules are labeled in parenthesis by molecule type and z coordinate.

Table 4. Interpretation of the rigid-body thermal motion of glycolic acid in terms of independent simple motions

		Molecule 1			Molecule 2			
			Axis K			Axis K		
Helical motions (about non-intersecting axes)		1	2	3	1	2	3	
R.m.s. amplitude (radians) Pitch, ^a (Å.radian ⁻¹)		0·187 0·000	0.091 - 0.192	0·046 0·768	0·186 0·075	0.087 - 0.528	0·047 0·636	
Direction ^b	J = 1 2 3	-0.251 0.940 -0.231	-0.612 -0.339 -0.714	0·750 0·038 0·661	0·437 - 0·894 0·095	0·793 0·433 0·427	-0.423 - 0.112 0.899	
Center of reaction, ^c (Å)		0.168	-0.652	0.332	-0.027	0.667	-0.075	
Axis displacements, ^a (Å)	J = 1 2 3	0·011 0·072	-0.146 -0.305	0·579 0·179	0·025 0·025	0.057	-0.197 - 0.385	
Reduced translation ^e	-				0.020	• • • •		
R.m.s. amplitude (Å)		0.199	0.167	0.151	0.201	0.178	0.169	
Direction ^b	J = 1 2 3	0·246 0·034 0·969	0·968 0·036 0·247	0·044 0·999 0·025	0·661 0·096 0·744	0.666 0.532 0.523	0·346 -0·841 0·416	

a Based on the arbitrary constraint trace S=0.

b Columns are direction cosines of principal axis K with respect to Cartesian axes J parallel to a, b and c^* respectively.

c Referred to the Cartesian system of (b) with origins at atom C(11) for molecule 1 and C(22) for molecule 2. The term 'center of reaction' is defined by Brenner (1967).

d Columns are components of displacement of helical axis K along helical axes J from center of reaction.

e Defined in equation (20) of Schomaker & Trueblood (1968).

the superposition of six independent simple motions: three helical librations about a set of unique nonintersecting axes parallel to the principal axes of libration, and three translations. Parameters of these six independent motions are listed in Table 4 and are presented pictorially in Figs. 5 and 6. The wedge-cut cylinders in Fig. 6 have angles proportional to the respective principal root-mean-square librational amplitudes $L_{II}^{1/2}$ and lengths proportional to the associated screw-translations $S_{II}/L_{II}^{1/2}$. Also shown is the reduced translation ellipsoid⁺ (50% probability surface) in correct orientation with respect to the molecule. For comparison, the observed atomic displacement ellipsoids for C(11) and C(12) are shown.

It is of interest to examine the characteristics of the helical motions in relation to the inertial parameters of the molecules and the disposition of restraining hydrogen bonds. Helical axis No. 1, of largest angular amplitude, lies about 9 and 4° from the line connecting the α -hydroxyl oxygen atom to the carboxyl carbon atom [the O(2)...C(1) directions] of the two molecules. This direction appears to be one of low moment of inertia; the corresponding libration only slightly distorts the two strong hydrogen bonds O(1*n*)-H(1*n*)

[†] For the purpose of illustration, the reduced translation tensor is taken as

$${}^{r}\mathbf{T}'_{IJ} = \mathbf{T}_{IJ} - \sum_{K=1}^{3} S_{KI}S_{KJ}/L_{KK}, \quad I, J = 1, 2, 3$$

 $\cdots O'(2n)$ and $O(2n) \cdots H'(1n) - O'(1n)$ (n=1,2 refers to the molecule number) which lie in chains parallel to **b**, and produces mostly bending distortion of the two remaining, weaker, cross-linking hydrogen bonds. This placement is thus consistent with the relatively large angular amplitudes and small screw components of this libration mode. In contrast, rotations about axes No. 2 and No. 3, with larger moments of inertia, produce marked distortions of all hydrogen bonds, and the corresponding libration amplitudes are smaller. Rotation about axis 2 produces marked stretching of hydrogen bonds $O(2n)-H(2n)\cdots O'(3m)$ and $O(3n)\cdots$ H'(2m)-O'(2m) $(n \neq m = 1,2)$; this distortion in both bonds is reduced by the left-handed helical component. Rotation about axis 3 appears to produce some stretching distortion of all four hydrogen bonds formed by each molecule, and the distortion of each seems to be relieved by the right-handed helical component.*

Since the rigid-body analysis of thermal motion gives a satisfactory fit and has a reasonable interpretation, the libration tensors were judged to be sufficiently reliable to be the basis for estimating bond length corrections. These corrections were computed from the expression

$$\bar{S} = |S_0| \{ 1 + (4\pi^2)^{-1} [\text{trace } (2\pi^2 \mathbf{Lg}) \\ - \mathbf{S}'_0 \mathbf{g} (2\pi^2 \mathbf{L}) \mathbf{g} \mathbf{S}_0 / \mathbf{S}'_0 \mathbf{g} \mathbf{S}_0] \}$$

where \bar{S} represents the mean separation of two atoms, S₀ is the interatomic distance vector, expressed in

which differs from equation (20) of Schomaker & Trueblood (1968) by subtraction of the quantities S_{II}^2/L_{II} from the diagonal elements, in keeping with the notion of screw motion. In evaluating these quantities, the recommended constraint trace S=0 was applied.

^{*} Although the screw components are undetermined to the extent of the arbitrary constraint trace S=0, it is interesting that they appear to make sense in relation to the structure.

terms of oblique crystal coordinates (contravariant components), \mathbf{L} is the matrix of the libration tensor, also expressed in contravariant components⁺ and \mathbf{g} is

[†] The expression of L in terms of crystal oblique coordinates was chosen for ease in programming the correction, since now $2\pi^2 L$ enters computationally as β does in the riding correction (Busing & Levy, 1964). The components of L in the crystal oblique coordinates have formal dimensions radians².Å⁻². the matrix of the metric tensor whose elements are $\mathbf{a}_i \cdot \mathbf{a}_j$, the scalar products of the unit-cell translations. This expression is a generalization of one derived by Busing & Levy (1964) and equivalent to the diadic expression, equation (22), of Schomaker & Trueblood (1968). In the case of the bonds from carbon to aliphatic hydrogen atoms, an additional correction was made for the internal motion, considering that in each



Fig. 5. Stereoscopic drawings of the molecules in glycolic acid showing the non-intersecting axes of helical libration. The centers of reaction lie at the centers of the octagons.



Fig.6. Pictorial presentation of the results of the analysis of thermal displacement in terms of rigid-body motion. The nonintersecting libration axes are shown in the same orientation as in Fig. 5, but on an enlarged scale. The helical cut shows the angular and translational components of the helical libration, with the proper sense. The ellipsoids represent the reduced translation tensor and, for comparison, the thermal ellipsoids of C(11) and C(12).

Table 5.	Rigid hody	, and internal	vibration	narameters	for a	lvcolic	acia
Table J.	nigiu bouy	una inicinai	onoranon	purumerers	וטן צ	siycome.	uciu

ij	11	22	33	12	13	23
Libration tensor, $2\pi^2 L^{ij} \times 10^4$, crys	tal oblique co	oordinates				
Molecule 1 Molecule 2	30 38	57 52	28 14	19 24	25 15	-15 -5
Internal vibration, $\beta^{ij} \times 10^4$						
H(31) H(41) H(32) H(42)	25·90 40·57 24·87 40·91	22·45 23·70 21·60 24·18	53·46 26·50 39·42 29·79	- 5·16 - 0·46 - 6·49 - 0·06	22·12 16·54 4·69 21·28	0·76 - 3·76 - 6·13 0·97

Table 6. Intramolecular interatomic distances \hat{A} , in glycolic acid and their corrections for thermal motion

		Molecu	ile 1	Molecu	Model for	
From	То	Uncorrected*	Corrected	Uncorrected*	Corrected	correction [†]
C(1)	O(1)	1.314 (1)	1.329	1.310 (1)	1.323	ML
	C(2)	1.205(1) 1.503(1)	1.227	1.202(2) 1.505(1)	1.225	ML ML
C(2)	O(2)	1.403 (1)	1.420	1.406 (2)	1.420	
	H(3) H(4)	1.081(3) 1.080(3)	1.115	1.084(2) 1.083(3)	1.117	ML + IV ML + IV
O(1)	H(1)	1.003 (2)	1.007	1.001 (2)	1.011	RM
O(2)	H(2)	0.970 (3)	0.998	0.971(3)	0.988	KM

* Least-squares standard error in least-significant digit given in parentheses.

† ML = molecular libration; IV = internal vibration; RM = riding model.

case the hydrogen atom rides on a carbon atom; the expression for the corrected value is

$$S' = S + (4\pi^2)^{-1} |\mathbf{S}_0| [\text{trace} (\boldsymbol{\beta} \mathbf{g}) - \mathbf{S}_0^t \mathbf{g} \boldsymbol{\beta} \mathbf{g} \mathbf{S}_0 / \mathbf{S}_0^T \mathbf{g} \mathbf{S}_0]$$

where β is the tensor for the internal motion, again expressed in doubly contravariant components relative to the axes. The tensors involved are listed in Table 5. In the case of the O-H bonds, which are influenced by internal rotations about C-O, the empirical ridingmodel correction (Busing & Levy, 1964) seems to be the best available. The corrected distances are listed in Table 6.

Computations for this work were carried out on

IBM 360/75 and CDC 1604A electronic computers. Of the programs used, those included in the *World List of Crystallographic Computer Programs* (Shoemaker, 1966) and their accession numbers are as follows:

	523 (a)
ORSTAT	496
XFOUR(b)	391
XFLS	389
EDIT	393
ORTEP	387
ORFFE (c)	363
	ORSTAT XFOUR (b) XFLS EDIT ORTEP ORFFE (c)

(a) Modified for the CDC 1604A by the authors.(b) Modified for the IBM 360/75 by G. Brunton of this Laboratory.

(c) Modified for the IBM 360/75 by C. K. Johnson.

The multiple implication and superposition diagrams were prepared using programs written during a previous study; the functions evaluated are described in the report of that work (Ellison & Levy, 1965). Pseudc normalized structure factor magnitudes for the 'squared scattering amplitude' structure were calculated using programs written by the authors for this investigation. Analysis of the thermal motion made extensive use of a program written by Johnson (1967).

References

- AMMON, H. L. (1964). A System of Programs (PHASER and SIGNIE) for the IBM 709-7090-7094 for Application of the Symbolic Addition Procedure. Unpublished work.
- AMMON, H. L. & JENSEN, L. H. (1967). Acta Cryst. 23, 805. ATHERTON, N. M. & WHIFFEN, D. H. (1960). Mol. Physics,
- 3, 1.
- BRENNER, H. (1967). J. Colloid Interface Sci. 23, 407.
- BROWN, G. M. & LEVY, H. A. (1964). J. Phys. 25, 497.
- BUSING, W. R. & LEVY, H. A. (1964). Acta Cryst. 17, 142. BUSING, W. R., SMITH, H. G., PETERSON, S. W. & LEVY, H. A. (1964). J. Phys. 25, 495.
- ELLISON, R. D. & LEVY, H. A. (1965). Acta Cryst. 19, 260.
- ELLISON, R. D. & LEVY, H. A. (1967). Chemistry Division Annual Progress Report, Oak Ridge National Laboratory, Report No. ORNL-4164, p. 126.
- ELLISON, R. D. & LEVY, H. A. (1968). Chemistry Division Annual Progress Report, Oak Ridge National Laboratory, Report No. ORNL-4306, p. 151.
- GLUSKER, J. P., MINKIN, J. A. & PATTERSON, A. L. (1969). Acta Cryst. B25, 1066.

- GOLIČ, L. & SPEAKMAN, J. C. (1965). J. Chem. Soc. p. 2521.
- GUPTA, M. P. & GUPTA, N. P. (1968). Acta Cryst. B24, 631. JACOBSON, R. A., WUNDERLICH, J. A. & LIPSCOMB, W. N. (1961). Acta Cryst. 14, 598.
- JOHNSON, C. K. (1966). Amer. Cryst. Assn. Program and Abstracts of Annual Meeting, Austin, Texas. Abstract K-9, p. 49; Chemistry Division Annual Progress Report, Oak Ridge National Laboratory, Report No. ORNL-3994, p. 125.
- JOHNSON, C. K. (1967). Chemistry Division Annual Progress Report, Oak Ridge National Laboratory, Report No. ORNL-4164, p. 127.
- KARLE, J. (1966). Acta Cryst. 20, 881.
- KARLE, J. & KARLE, I. L. (1966). Acta Cryst. 21, 849.
- LEVY, H. A. & ELLISON, R. D. (1967). Amer. Cryst. Assoc. Program and Abstracts of Winter Meeting, Atlanta, Georgia. Abstract A9, p. 21.
- OKAYA, Y., STEMPLE, N. R. & KAY, M. I. (1966). Acta Cryst. 21, 237.
- PIJPER, W. P. (1971). Acta Cryst. B20, 344.
- SCHACHTSCHNEIDER, J. H. (1962). Vibrational Analysis of Polyatomic Molecules. III. Vibrational Secular Equation Programs. Shell Development Co. Tech. Report 263-62.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). Acta Cryst. B24, 63.
- SHIMANOUCHI, T. & SUZUKI, I. (1962). J. Mol. Specty. 8, 222. SHOEMAKER, D. P. (1966). World List of Crystallographic
- Computer Programs, 2nd Edition. Utrecht: Oosthoek. VAN DER HELM, D., GLUSKER, J. P., JOHNSON, C. K.,
- VAN DER HELM, D., GLUSKER, J. F., JOHNSON, C. K., MINKIN, J. A., BUROW, N. E. & PATTERSON, A. L. (1968). Acta Cryst. B24, 578.
- VAN EIJCK, B. P., KANTERS, J. A. & KROON, J. (1965). Acta Cryst. 19, 435.
- WILSON, A. J. C. (1942). Nature, Lond. 150, 152.
- WOOLFSON, M. M. (1956). Acta Cryst. 9, 804.
- YAKEL, H. L. (1964). ORSTAT, A Fortran Program for the Statistical Analysis of Diffraction Data, Oak Ridge National Laboratory Report, ORNL-TM-750.
- ZACHARIASEN, W. H. (1965). Trans. Amer. Cryst. Assoc. 1, 33.

Acta Cryst. (1971). B27, 344

÷.

The Molecular and Crystal Structure of Glycollic Acid

By W.P.PLIPER

Laboratorium voor Kristalchemie, Rijksuniversiteit, Catharijnesingel 51, Utrecht, The Netherlands

(Received 3 March 1970)

The structure of glycollic acid has been determined by X-ray analysis, by a direct method. The structure crystallizes in the space group $P_{2_1/c}$ with unit-cell dimensions: a=9.061, b=10.562, c=7.828 Å and $\beta=116.41^{\circ}$, with Z=8. The structure refined to R=0.041. The carboxylic-hydroxylic hydrogen bonding, in which the alcoholic hydroxylic oxygen atom serves as an acceptor, is unusual; the expected dimers were not found.

Introduction

Glycollic acid has been examined as part of a programme of investigation of carboxylic acids. The problem was whether glycollic acid in the crystal structure was likely to form dimers, probably with non-hydrogen-bonded hydroxyl groups, or a structure with hydroxyl-carbonyl coupling. An infrared analysis gave no reason to assume that there might be non-hydrogen-bonded hydroxyl groups in the structure (Kanters, Kroon, Peerdeman & Vliegenthart, 1969), and the

Present address: Netherlands Foundation for Chemical Research, Laan van Meerdervoort 123 A, The Hague, Netherlands.