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

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Glycolic acid (hydroxyacetic acid) crystallizes in $P2_1/c$ with $a = 8.9649$, $b = 10.5634$, $c = 7.8261$ Å, $\beta = 115.083°$, at $24 \pm 1°C$, 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,

1960); these investigators found that the asymmetric unit contains 2 independent molecules. We have re-determined the unit-cell parameters with greater accuracy from the diffractometer settings of 12 Bragg reflections in the 2θ-range 87–156° (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 $B = 3.11$ Å^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

$$\varepsilon_h'^2 = 1 + (\beta_2^2 \beta_4^{-1} - 1) \frac{<(\varepsilon_k^2 - 1)(\varepsilon_{h-k}^2 - 1)>_k}{<(\varepsilon_k^2 - 1)^2>_k}, \quad (1)$$

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 ε_h yielded a set of 239 values of $\varepsilon_h' > 1$; of these 215 had also $\varepsilon_h > 1$. 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

$$\tanh(|F_o| \, |F_c|/32 f_H^2)$$

in which f_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

$$\sigma_{statistical}^2 + (0 \cdot 03 \, F^2)^2 ,$$

$\sigma_{statistical}^2$ 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

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

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)

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

Table 1. *Calculated and observed structure amplitudes*

The columns contain the Miller index h, the quantity $100 F_{calc}$, 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 $1 \cdot 05$. The reflection 641, flagged X, was deemed to have a gross error in measurement, and was omitted from consideration.

Table 1 (cont.)

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

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

is made, and terms of higher order in Q are ignored. Thus our form assumes that $\bar{T}$ 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 $\sigma(F^2_{obs})/2F_{obs}$ except for the weakest reflections, flagged with the symbol W, for which $\sigma(F^2_{obs})$ is listed instead; $\sigma(F^2_{obs})$ 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 $\sigma_1 \equiv \sum w(F^2_{obs} - S^2 F^2_{calc})^2/(N-P)$ where N is the number 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).

* One reflection, 641, judged to be a gross error in measurement, has been omitted; see Table 1.

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 $C-C{\Large{<}}^O_O$ 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. *Parameters of the structure of glycolic acid*

Least-squares standard errors are given in parenthesis.

	Fractional position parameter $\times 10^4$			Thermal parameter* $\times 10^5$					
	x	y	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)

	C	O	H
Scattering amplitudes (cm × 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)°
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
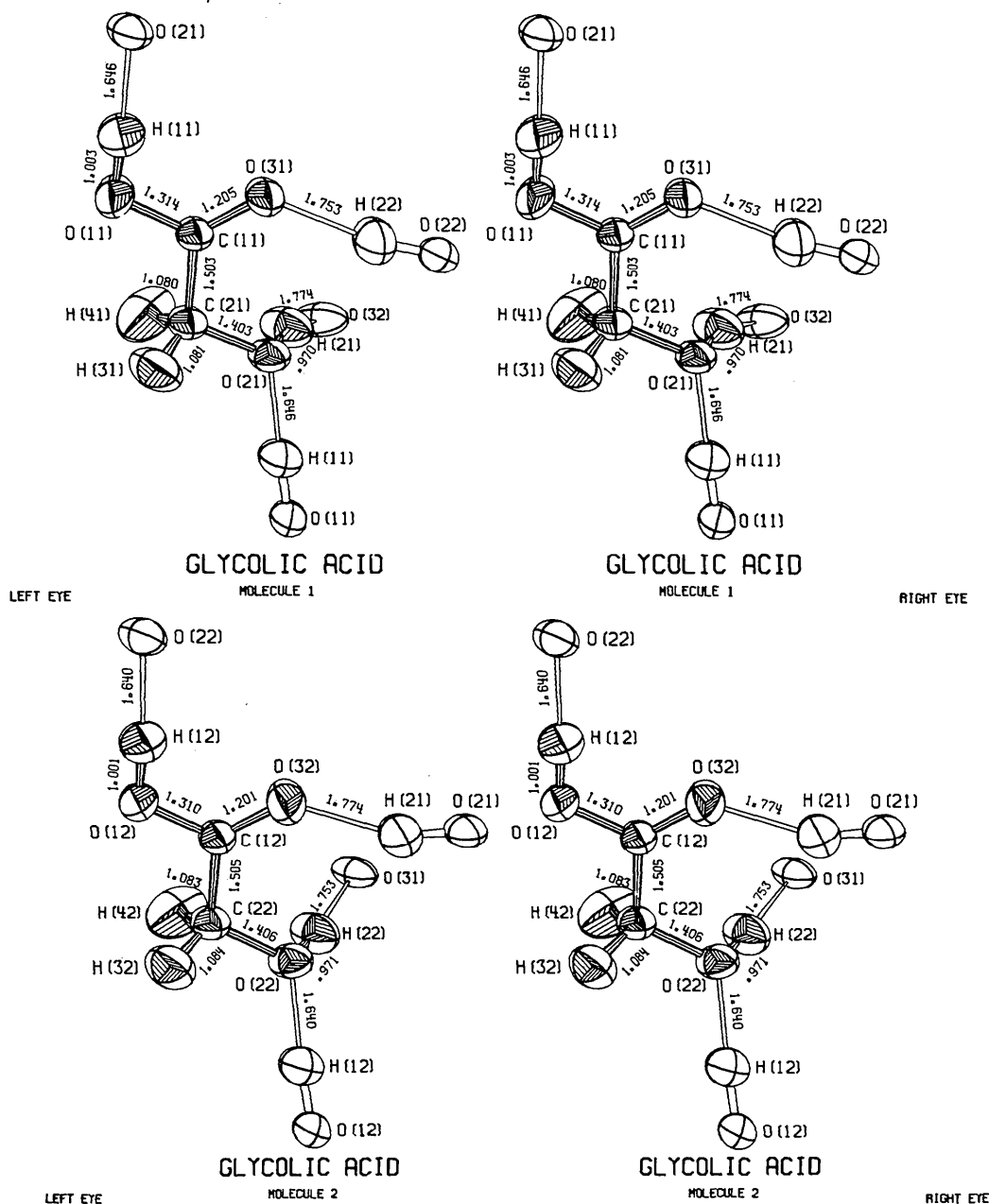

Fig. 1. Stereoscopic drawings of the two crystallographically distinct molecules of glycolic acid and the atoms (unshaded in the drawing) of neighboring molecules to which they are hydrogen bonded. Atoms are represented by ellipsoids enclosing 50% of normally distributed thermal displacements. The viewing direction is 25° from the normal to the plane of the carboxyl group.
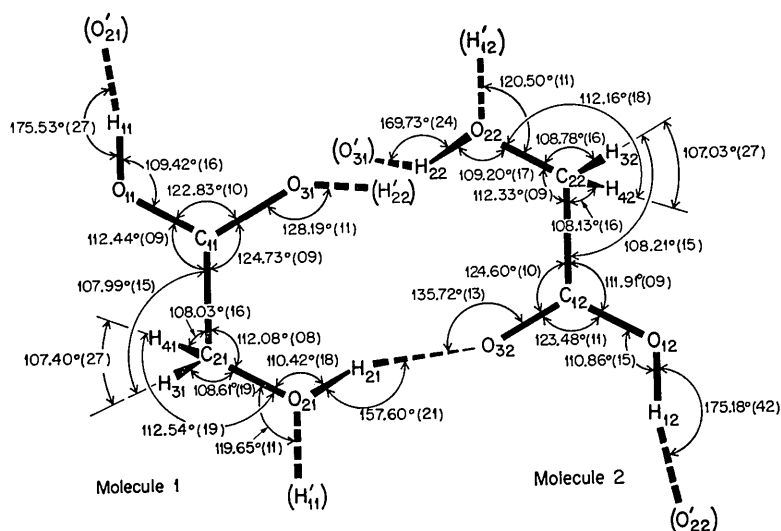
Fig. 2. Bond angles (degrees) in glycolic acid. The least-squares standard errors (degrees × 10⁻²) are given in parenthesis.

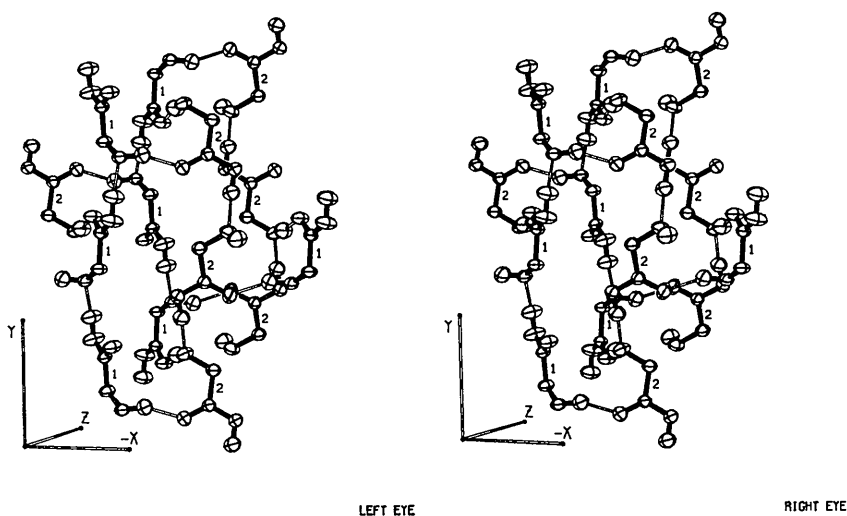LEFT EYE   RIGHT EYE

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···O or O–H···O distances is clearly evident, and the shorter O···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 $2a+c$; the length of A is 16·24

Å and the angle to **c** is 89·21°. 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 · (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 Å^2 along, and 0.01369 Å^2 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 Å^2 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 Å^2 respectively.

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

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* 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.

Atom numbers in O–H···O link			O–H	Distance H···O	O–H···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)	175·2 (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)
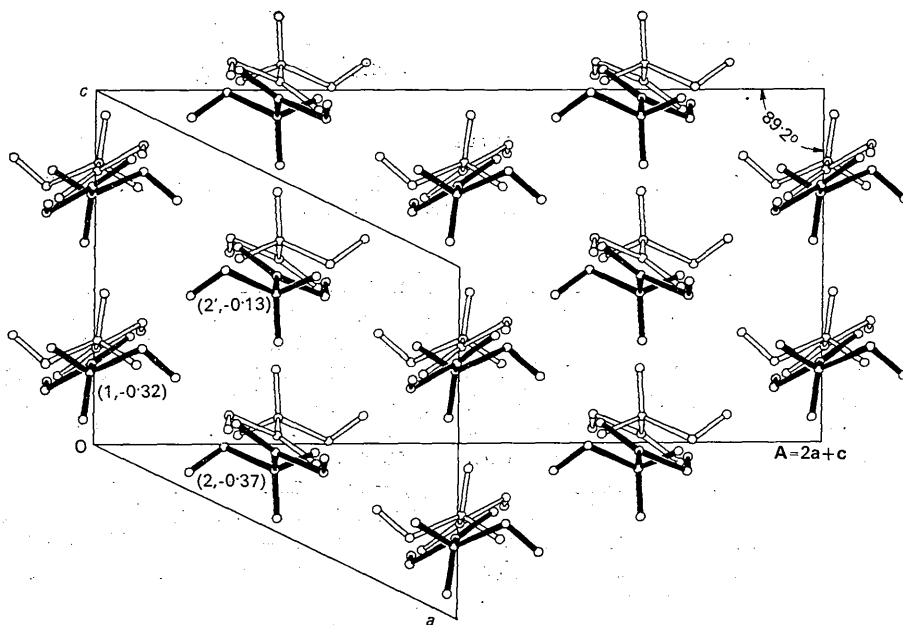
Fig. 4. Projection along **B** of the pseudo-orthorhombic B-centered cell for which **A** = 2**a** + **c** of the monoclinic cell and **B** = **b**, **C** = **c**. The molecules are labeled in parenthesis by molecule type and z coordinate.

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

		Molecule 1 Axis K			Molecule 2 Axis K		
		1	2	3	1	2	3
Helical motions (about non-intersecting axes)							
R.m.s. amplitude (radians)		0·187	0·091	0·046	0·186	0·087	0·047
Pitch,[a] (Å.radian⁻¹)		0·000	−0·192	0·768	0·075	−0·528	0·636
Direction[b]	$J=1$	−0·251	−0·612	−0·750	0·437	0·793	−0·423
	2	0·940	−0·339	−0·038	−0·894	0·433	−0·112
	3	−0·231	−0·714	0·661	0·095	0·427	0·899
Center of reaction,[c] (Å)		0·168	−0·652	0·332	−0·027	0·667	−0·075
Axis displacements,[d] (Å)	$J=1$		−0·146	0·579		0·057	−0·197
	2	0·011		−0·179	0·025		−0·385
	3	0·072	−0·305		0·025	−0·115	
Reduced translation[e]							
R.m.s. amplitude (Å)		0·199	0·167	0·151	0·201	0·178	0·169
Direction[b]	$J=1$	0·246	0·968	0·044	0·661	0·666	0·346
	2	0·034	0·036	−0·999	−0·096	0·532	−0·841
	3	−0·969	0·247	−0·025	−0·744	0·523	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 non-intersecting 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 $O(2)\cdots C(1)$ 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 $O(1n)-H(1n)$

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

$$^rT'_{IJ}=T_{IJ}-\sum_{K=1}^{3} S_{KI}S_{KJ}/L_{KK}, \quad I,J=1,2,3$$

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.

$\cdots O'(2n)$ 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

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

where $\bar{S}$ represents the mean separation of two atoms, S_0 is the interatomic distance vector, expressed in

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* 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), **L** is the matrix of the libration tensor,
also expressed in contravariant components† and **g** is

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† The expression of **L** in terms of crystal oblique coordinates
was chosen for ease in programming the correction, since now
$2\pi^2\mathbf{L}$ enters computationally as β does in the riding correction
(Busing & Levy, 1964). The components of **L** in the crystal
oblique coordinates have formal dimensions radians^2.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 ali-
phatic hydrogen atoms, an additional correction was
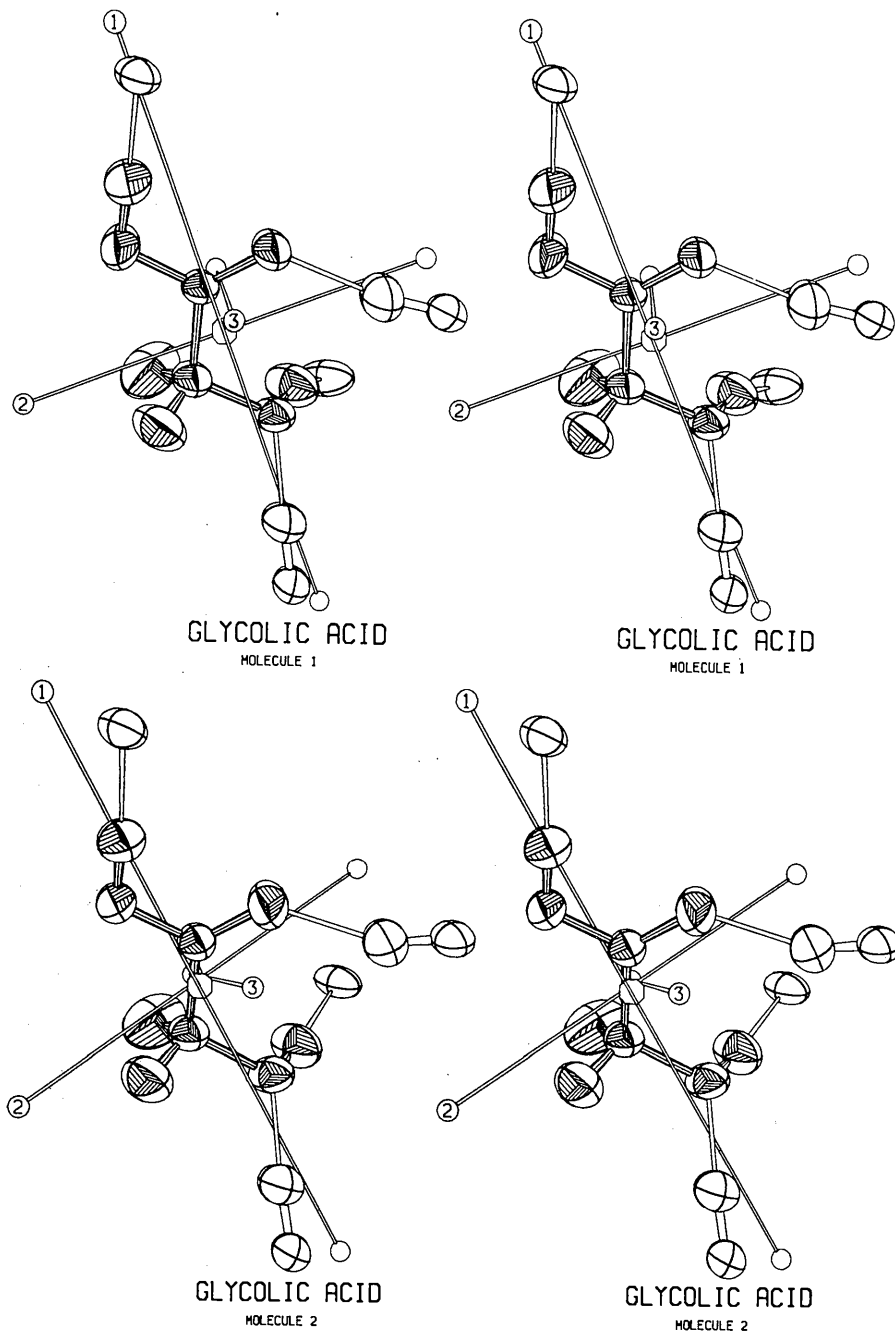made for the internal motion, considering that in each

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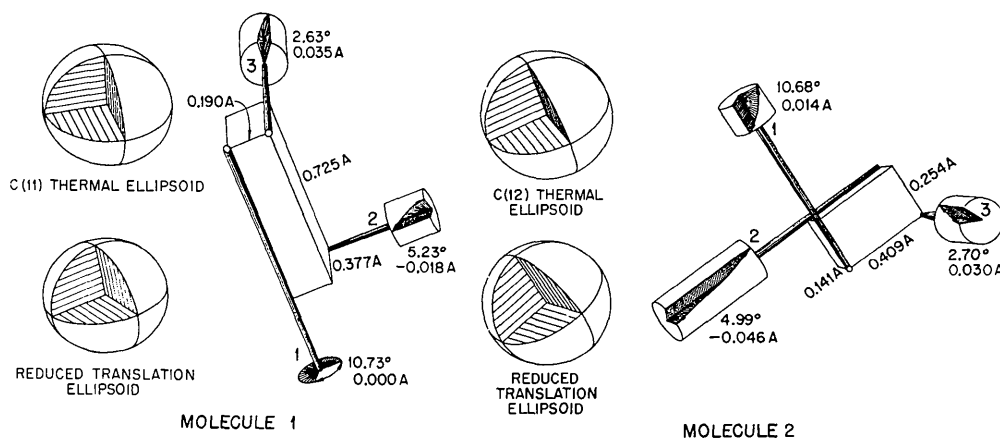of reaction lie at the centers of the octagons.

Fig. 6. Pictorial presentation of the results of the analysis of thermal displacement in terms of rigid-body motion. The non-intersecting 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 body and internal vibration parameters for glycolic acid*

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

Table 6. *Intramolecular interatomic distances Å, in glycolic acid and their corrections for thermal motion*

From	To	Molecule 1 Uncorrected*	Corrected	Molecule 2 Uncorrected*	Corrected	Model for correction†
C(1)	O(1)	1·314 (1)	1·329	1·310 (1)	1·323	ML
	O(3)	1·205 (1)	1·227	1·202 (2)	1·225	ML
	C(2)	1·503 (1)	1·514	1·505 (1)	1·519	ML
C(2)	O(2)	1·403 (1)	1·420	1·406 (2)	1·420	ML
	H(3)	1·081 (3)	1·115	1·084 (2)	1·117	ML+IV
	H(4)	1·080 (3)	1·115	1·083 (3)	1·118	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	RM

* 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

$$\bar{S}' = \bar{S} + (4\pi^2)^{-1}|S_0| \, [\text{trace } (\beta g) - S_0^t g \beta g S_0 / S_0^T g S_0]$$

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 riding-model 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:

Absorption correction		523 (*a*)
Statistical analysis of data	*ORSTAT*	496
Fourier synthesis	*XFOUR* (*b*)	391
Least-squares refinement	*XFLS*	389
Structure factor table	*EDIT*	393
Structure drawings	*ORTEP*	387
Distances and angles	*ORFFE* (*c*)	363

(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). Pseudo 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).

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The Molecular and Crystal Structure of Glycollic Acid

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The structure of glycollic acid has been determined by X-ray analysis, by a direct method. The structure crystallizes in the space group $P2_1/c$ with unit-cell dimensions: $a = 9.061$, $b = 10.562$, $c = 7.828$ Å and $\beta = 116.41°$, 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 prob-

lem 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