Fig. 3. Stereoscopic view of molecule 2. Thermal ellipsoids enclose 35% probability for non-H atoms.

C(11)—N(11) and S(12)—C(72)—C(12)—N(12): −3·7 (3)° for the former and −7·5 (3)° for the latter. The steric strain between H(21) [or H(22)] and the methyl group is somewhat relieved by the slight clockwise rotation of the whole five-membered ring around the C(11)—C(71) [or C(12)—C(72)] bond (to an extent not to interfere with the partial π character of this bond). The H(2)···C(8) separations are 2·53 (3) and 2·53 (4) Å in molecules 1 and 2. To achieve further the energy minimum, the methyl H atoms have rotated to positions which permit relatively facile interpenetration by the neighboring H(2), resulting in H(21)···H(8b1) and H(21)···H(8c1) distances of 2·24 (4) and 2·16 (4) Å in molecule 1; the corresponding values are 2·26 (5) and 2·12 (5) Å in molecule 2. Fig. 3 shows a stereoscopic view of molecule 2.

Relatively large deviations from the corresponding five-membered rings for the methyl carbons, C(81) and C(82) [−0·077 (5) and −0·028 (4) Å, respectively], can also be regarded as a consequence of the molecules alleviating the intramolecular strain. Despite the differences in molecular conformation arising also in part from possible packing effects, differences in the intramolecular contacts S(3)···C(8), N(1)···S(1) and C(2)···C(8) are 0·011 (3), 0·004 (3) and 0·018 (5) Å − not large enough to be significant.

References

BROWN, G. M., FREEMAN, G. R. & WALTER, R. I. (1977). *J. Am. Chem. Soc.* **99**, 6910–6915.
BUEDING, E., DOLAN, P. & LEROY, J. P. (1982). *Res. Commun. Chem. Path. Pharmacol.* **37**, 293–303.
BUEDING, E., FISHER, J. & BRUCE, J. (1973). *J. Pharmacol. Exp. Ther.* **186**, 403–407.
BUSING, W. R., ELLISON, R. D., LEVY, H. A., KING, S. P. & ROSEBERRY, R. T. (1968). *The Oak Ridge Computer-Controlled X-ray Diffractometer.* Report ORNL-4143. Oak Ridge National Laboratory, Tennessee.
BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180–182.
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS.* Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE.* Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.
CROMER, D. T. (1974). *International Tables for X-ray Crystallography,* Vol. IV, p. 149, Table 2.3.1. Birmingham: Kynoch Press.
CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography,* Vol. IV, pp. 72–75, Table 2.2A. Birmingham: Kynoch Press.
ENGLER, R., DRÄGER, M. & GATTOW, G. (1974). *Z. Anorg. Allg. Chem.* **403**, 81–86.
FOSS, O. & TJOMSLAND, O. (1958a). *Acta Chem. Scand.* **12**, 44–51.
FOSS, O. & TJOMSLAND, O. (1958b). *Acta Chem. Scand.* **12**, 1799–1809.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
HARDGROVE, G. L. JR, EINSTEIN, J. R. & WEI, C. H. (1983). *Acta Cryst.* **C39**, 616–620.
JEFFREY, G. A. & SHIONO, R. (1959). *Acta Cryst.* **12**, 447–454.
JOHNSON, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
KARLE, I. L., ESTLIN, J. A. & BRITTS, K. (1967). *Acta Cryst.* **22**, 273–280.
KARLE, I. L. & KARLE, J. (1965). *Acta Cryst.* **19**, 92–99.
KEHL, W. L. & JEFFREY, G. A. (1958). *Acta Cryst.* **11**, 807.
MITCHELL, D. J. (1969). *Acta Cryst.* **B25**, 998–1001.
PAULING, L. (1960). *The Nature of the Chemical Bond,* 3rd ed., pp. 224–239. Ithaca: Cornell Univ. Press.
POWER, L. F. & JONES, R. D. (1971). *Acta Cryst.* **B27**, 181–184.
SHIONO, R. (1971). *Crystallographic Computing Program for IBM 1130.* Tech. Rep. No. 49. Department of Crystallography, Univ. of Pittsburgh, Pennsylvania.
WEI, C. H. (1982). *Acta Cryst.* **B38**, 548–553.
WEI, C. H. & EINSTEIN, J. R. (1978). *Acta Cryst.* **B34**, 205–212.
WHEATLEY, P. J. (1957). *Acta Cryst.* **10**, 182–187.
WHEATLEY, P. J. (1960). *Acta Cryst.* **13**, 80–85.

Structure of Dihydroxyacetic Acid (Glyoxylic Acid Monohydrate), C₂H₄O₄

BY T. LIS

Institute of Chemistry, The University, 50-383 Wrocław, Poland

Abstract. $M_r = 92·0$, triclinic, $P\bar{1}$, $a = 5·833$ (4), $b = 5·397$ (5), $c = 6·586$ (6) Å, $\alpha = 97·95$ (7), $\beta = 94·71$ (7), $\gamma = 118·26$ (6)°, $V = 178·3$ Å³, $Z = 2$, $D_m = 1·70$, $D_x = 1·72$ Mg m⁻³, μ(Mo $K\alpha$, $\lambda = 0·71069$ Å) $= 0·19$ mm⁻¹, $F(000) = 96$, $T = 296 \pm 2$ K, final $R = 0·040$ and $R_w = 0·045$ for 690 non-zero reflexions. The X-ray analysis showed that glyoxylic acid monohydrate (CHOCOOH.H₂O)

crystallized from aqueous solution exists in the solid state as dihydroxyacetic acid. The C—C bond length is 1·522 (3) Å and the C—O(alcoholic) distances are 1·400 (3) and 1·404 (3) Å. The (H)O—C—O(H) bond angle is 112·4 (2)°. All O bonded H atoms are involved in hydrogen bonds.

Introduction. Work on Mn carboxylates (Lis, 1982) showed that Mn^{II} glyoxylate crystallizes from water as the dihydroxyacetate. A similar result has been reported (Mattes & Uckelmann, 1981) for the Na salt. To extend our knowledge of this acid some of its other compounds are being examined. Here we report a study of glyoxylic acid monohydrate, $OCH—CO_2H.H_2O$, which is found to crystallize as dihydroxyacetic acid, $(HO)_2CH—CO_2H$.

Experimental. Single crystals of dihydroxyacetic acid were grown at room temperature by slow evaporation of an aqueous solution of commercial glyoxylic acid monohydrate (Ferak Berlin). The irregularly shaped crystals deliquesce rapidly and form a syrup on exposure to air. D_m measured pycnometrically in 1,2-dibromoethane/CCl_4. A specimen 0·26 × 0·18 × 0·12 mm was cut from a large crystal and sealed in a capillary; Weissenberg photographs showed the triclinic system. Syntex $P2_1$ diffractometer, Mo $K\alpha$ radiation for lattice-parameter (15 reflexions, $18 \le 2\theta \le 30°$) and intensity measurements; $2\theta-\omega$ scan technique; 1043 intensities measured below $\theta = 30°$; h 0 to 8, k −7 to 6, l −9 to 8; two standards, variation ±3%; no absorption correction; all calculations performed on a NOVA 1200 computer with programs supplied by Syntex (1976); neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); structure solved by direct methods assuming space group $P\bar{1}$; refinement on F[C, O anisotropic, H (from difference map) isotropic] gave $R = 0·040$ and $R_w = 0·045$ for 690 reflexions with $I > 2\sigma(I)$; $w = 1/\sigma^2(F_o)$; maximum least-squares shift to error 0·01. The residual peaks in the final difference Fourier map were confined to the molecular bonds; the higher peaks, 0·3 e Å⁻³, were on the C—C bonds. No correction for secondary extinction.

Discussion. Final atomic parameters are listed in Table 1,* hydrogen-bonding data and bond distances and bond and torsion angles in Table 2. Fig. 1 is an *ORTEP* diagram (Johnson, 1976) of one acid molecule, and also gives the atom-numbering scheme. The C—COO group is planar. The acid [H(1)] atom is also situated in this plane. There is also a tendency for one [O(3)] of the two *gem*-hydroxylic O atoms to lie in this plane as indicated by the conformational angles. Thus the configuration of

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38559 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the acid molecule having point symmetry 1 is different from that of the $C(OH)_2COO^-$ ion in the sodium salt, where point symmetry m was found. The molecular structure of crystalline dihydroxyacetic acid is probably influenced by H bonds. All O-bonded H atoms are involved in H bonds (Fig. 2). The strongest links are from the carboxyl groups as donors to the O(3) atoms, forming infinite strings along **a**. The O(4) atoms (as donors) form with the carbonyl O(2) atoms infinite chains along the **a** + **b** vector. The two-dimensional nets so formed are connected by H bonds between O(3) (donor) and O(4) (acceptor) atoms giving a double-layer structure.

Table 1. *The final atom coordinates and isotropic thermal parameters*

For non-H atoms $B_{eq} = \frac{1}{3}(B_{11} + B_{22} + B_{33})$.

	x	y	z	B_{eq} or B_{iso} (Å²)
O(1)	0·8488 (4)	0·2845 (4)	0·6825 (4)	3·34 (14)
O(2)	0·8970 (3)	0·7206 (4)	0·7744 (3)	2·74 (12)
O(3)	0·3713 (3)	0·5106 (4)	0·7254 (3)	2·21 (10)
O(4)	0·4083 (4)	0·1605 (4)	0·8736 (3)	2·13 (10)
C(1)	0·7617 (4)	0·4648 (5)	0·7268 (4)	1·67 (12)
C(2)	0·4629 (4)	0·3117 (5)	0·7114 (4)	1·63 (12)
H(1)	1·020 (7)	0·383 (7)	0·709 (5)	5·3 (8)
H(2)	0·377 (5)	0·180 (5)	0·583 (4)	1·9 (5)
H(3)	0·460 (7)	0·643 (8)	0·827 (6)	5·7 (9)
H(4)	0·253 (6)	0·037 (7)	0·842 (5)	3·9 (7)

Table 2. *Bond lengths (Å), bond angles (°), torsion angles (°), and H-bonding data*

O(1)—C(1)	1·306 (3)	O(3)—C(2)	1·404 (3)
O(2)—C(1)	1·198 (3)	O(4)—C(2)	1·400 (3)
C(1)—C(2)	1·522 (3)	C(2)—H(2)	0·95 (3)

O(1)—C(1)—O(2)	125·1 (2)	O(1)—C(1)—C(2)	111·9 (2)
O(2)—C(1)—C(2)	123·0 (2)	O(3)—C(2)—O(4)	112·4 (2)
O(3)—C(2)—C(1)	110·5 (2)	O(4)—C(2)—C(1)	105·9 (2)
H(1)—O(1)—C(1)	107 (3)	H(3)—O(3)—C(2)	110 (3)
H(4)—O(4)—C(2)	106 (3)		

H(1)—O(1)—C(1)—C(2)	−173 (3)	H(1)—O(1)—C(1)—O(2)	7 (2)
O(1)—C(1)—C(2)—O(3)	−170·1 (7)	O(2)—C(1)—C(2)—O(3)	9·9 (9)
O(1)—C(1)—C(2)—O(4)	67·9 (7)	O(2)—C(1)—C(2)—O(4)	−112·1 (9)
H(2)—C(2)—C(1)—O(1)	−51 (3)	H(2)—C(2)—C(1)—O(2)	129 (3)
H(2)—C(2)—O(3)—H(3)	−171 (3)	H(2)—C(2)—O(4)—H(4)	−40 (3)
H(3)—O(3)—C(2)—C(1)	−49 (3)	H(3)—O(3)—C(2)—O(4)	69 (3)
H(4)—O(4)—C(2)—O(3)	79 (3)	H(4)—O(4)—C(2)—C(1)	−160 (3)

H-bond distances (Å) and angles (°)

O—H···O	O···O	O—H	H···O	∠O—H···O
O(1)—H(1)···O(3ⁱ)	2·664 (3)	0·87 (4)	1·82 (5)	166 (4)
O(3)—H(3)···O(4ⁱⁱ)	2·786 (2)	0·83 (4)	2·00 (4)	158 (4)
O(4)—H(4)···O(2ⁱⁱⁱ)	2·739 (2)	0·82 (4)	1·92 (4)	175 (4)

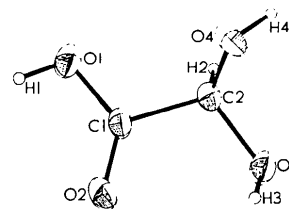Symmetry code: (i) $1+x,y,z$; (ii) $1-x, 1-y, 2-z$; (iii) $x-1, y-1, z$.

Fig. 1. *ORTEP* plot (Johnson, 1976) of dihydroxyacetic acid. The thermal ellipsoids are at 50% probability.
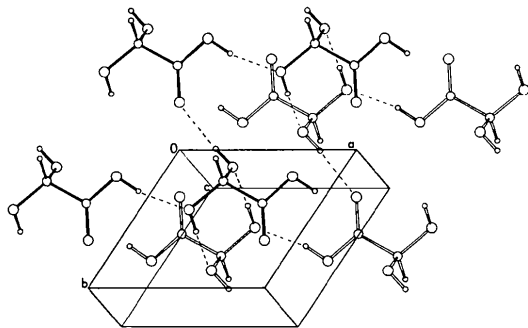
Fig. 2. Molecular packing and H-bonding scheme in the crystal structure of dihydroxyacetic acid.

The C—C bond length of 1·522 (3) Å is 0·015 Å shorter than in Na[C(OH)₂COO] and 0·020 Å longer than in hydroxyacetic acid (Pijper, 1971; Ellison, Johnson & Levy, 1971). The C—O(alcoholic) bond

lengths and (H)O—C—O(H) bond angles are similar to the values found in other geminal diols (Mattes & Uckelmann, 1981). The electrostatic repulsion between O(2) and O(3), which are *syn*, results in the O(3)—C(2)—C(1) bond angle being larger than O(4)—C(2)—C(1).

References

Ellison, R. D., Johnson, C. K. & Levy, H. A. (1971). *Acta Cryst.* B27, 333–344.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
Johnson, C. K. (1976). *ORTEP*-II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
Lis, T. (1982). Collect. Abstr. 4th Symp. Org. Cryst. Chem., Poznań-Kiekrz, Poland, p. 44.
Mattes, R. & Uckelmann, G. (1981). *Acta Cryst.* B37, 2071–2072.
Pijper, W. P. (1971). *Acta Cryst.* B27, 344–348.
Syntex (1976). *XTL/XTLE Structure Determination System.* Syntex Analytical Instruments, Cupertino, California.

Détermination Structurale du Monomère Bis(butoxycarbonylméthylcarbamate) de Hexadiyne-2,4 Diyle-1,6, C₂₀H₂₈N₂O₈

Par P. Spinat, A. Whuler et C. Brouty

Laboratoire de Minéralogie–Cristallographie des Universités Pierre et Marie Curie et Paris VII, associé au CNRS (LA 09), 4 place Jussieu, 75230 Paris CEDEX 05, France

Abstract. $M_r = 424$, m.p. = 336 K, triclinic, $P\bar{1}$, $a = 25\cdot753$ (8), $b = 13\cdot966$ (2), $c = 4\cdot940$ (1) Å, $\alpha = 85\cdot19$ (1), $\beta = 90\cdot38$ (2), $\gamma = 84\cdot52$ (2)°, $V = 1762$ (1) Å³, $Z = 3$, $D_x = 1\cdot20$ Mg m⁻³, $F(000) = 678$, $\lambda(Cu\,K\alpha) = 1\cdot5418$ Å, $\mu = 0\cdot79$ mm⁻¹, room temperature, $R = 0\cdot095$ for 1540 hkl with $F_o \geq 0\cdot02F_o$max. The monomer crystal is not polymerizable under X-radiation. The structure is described as stacks of monomer-molecule ribbons based on a repeated pattern of three consecutive molecules; H bonds maintain the intermolecular cohesion within these ribbons. The structural results can explain how neither polymerization nor trimerization is possible.

Introduction. Dans le cadre de l'étude cristallographique des composés diacétyléniques R—C≡C—C≡C—R des séries carbamates (ou uréthanes) [$R = (CH_2)_n$—COONH—Y] (Brouty, Spinat & Whuler, 1983; Spinat, Brouty & Whuler, 1983), nous abordons ici l'étude structurale de l'un des dérivés du type butoxycarbonylméthyluréthane pour lesquels $Y = CH_2COOC_4H_9$. Comme les composés de type phényluréthane (PU), les composés diacétyléniques

butoxycarbonylméthyluréthane (BCMU) ont la propriété de se polymériser à l'état cristallin par irradiation X, UV ou γ (Patel & Miller, 1981). L'arrangement structural des monomères conditionne l'activité des monocristaux (Baughman, 1974), qui restent incolores s'ils sont inactifs, tandis qu'ils acquièrent diverses couleurs s'ils sont polymérisables.

Dans la série BCMU ($n = 1,2,3,4$), seul le composé étudié ici [$n = 1$, appelé 1 BCMU ou HDBCMU en référence à la nomenclature généralement utilisée par les auteurs, à savoir (en anglais), 2,4-hexadiyne-1,6-diyl bis(butoxycarbonylméthyluréthane)], est inactif, ses cristaux restant incolores sous irradiation X. Le présent travail a pour but d'expliquer l'inactivité du HDBCMU à partir de ses caractéristiques structurales.

Partie expérimentale. Cristaux préparés par G. N. Patel,* recristallisation dans anisole, cristaux monomères incolores inactifs sans inclusion de solvant (contrôle par ATG); plaquette 0,7 × 0,3 × 0,06 mm,

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* Allied Chemical Corporation Chemical Company, PO Box 6, Solvay, New York 13209, E-U.