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# Low temperature crystal structure and molecular conformation of L-(+)-lactic acid

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## Abstract

L-(+)-Lactic acid,  $C_3H_6O_3$ ,  $M_r = 90.08$ , orthorhombic,  $P2_12_12_1$ ,  $a = 5.4896(3)$ ,  $b = 8.4221(3)$ ,  $c = 9.3453(5)$  Å,  $V = 432.07(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.385$  g cm<sup>-3</sup>,  $\lambda(\text{MoK}\alpha) = 0.71073$  Å,  $\mu = 1.2$  cm<sup>-1</sup>,  $F(000) = 192$ .

Diffraction data have been collected at 100 K and the structure has been solved by direct methods to  $R = 0.030$  for 976 unique observed data. The hydroxyacetic acid moiety of the molecule is almost planar with the aliphatic hydroxy-group oxygen atom at the side of the carbonyl oxygen atom of the carboxy group. The two hydroxy groups are involved in intermolecular hydrogen bonding. The aliphatic hydroxy group forms a bifurcate planar hydrogen-bond configuration in which the aliphatic hydroxy and acid carbonyl oxygen atoms of a symmetry-related molecule participate as acceptors. The acidic hydroxy group donates an intermolecular hydrogen bond to the aliphatic hydroxy-group oxygen atom.

## 1. Introduction

L-(+)-Lactic acid is a biologically important substance and the history of its study by the early chemists is closely linked to the development of the concept of optical activity [1]. L-(+)-Lactic acid is also an important end product of the anaerobic metabolism of many micro-organisms and animals such as molluscs and vertebrates.

It is curious that in spite of its well-established and important role, so far no crystal structure has been reported for this simple metabolite. The absence of crystal structure data of L-(+)-lactic acid is certainly related to the problems inherent in obtaining single crystals. The preparation

of such crystals is seriously hampered by the formation on prolonged standing of lactic acid oligomers by condensation polymerization. However, we have succeeded in obtaining single crystals of good quality by cooling an aqueous solution. We now report the crystal structure of L-(+)-lactic acid.

## 2. Experimental

A colourless crystal with dimensions  $0.75 \times 0.35 \times 0.35$  mm was used for data collection on an Enraf-Nonius CAD-4 diffractometer with Zr-filtered MoK $\alpha$  radiation. As the crystals of the compound are very hygroscopic, the structure analysis was carried out at low temperature by placing the crystal in a stream of gaseous nitrogen

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with a temperature of about 100 K. This procedure proved to be excellent for the prevention of deterioration of the crystal by uptake of water. Lattice parameters were determined from the setting angles of 25 reflections in the range  $12.20 \leq \theta \leq 19.58^\circ$ . The diffracted intensities of 1508 reflections were collected with the  $\omega - 2\theta$  scan mode,  $\Delta\omega = (0.62 + 0.35 \tan \theta)^\circ$ ,  $2\theta_{\max} = 55^\circ$ , and  $-7 \leq h < 7$ ,  $0 \leq k \leq 10$ ,  $-12 \leq l \leq 0$ , of which 976 were unique ( $R_{\text{int}} = 0.012$ ). Three periodically measured standard reflections ( $-2\ 1\ -2$ ,  $-3\ 2\ 0$  and  $0\ 2\ -2$ ), measured every 20 min, showed an average deviation of less than 2% during 11 h of X-ray exposure. Intensities were corrected for Lp (Lorentz polarization) effects but not for absorption. The structure was solved in space group  $P2_12_12_1$  by direct methods using the program SHELXS86 [2].

Hydrogen atoms were located from difference Fourier maps and treated with an overall isotropic thermal parameter which refined to  $0.026(2)\text{Å}^2$ . Anisotropic full-matrix least-squares refinement based on  $F^2$  of 74 parameters converged to  $R$  (on  $F$ ) = 0.030 and  $wR$  (on  $F^2$ ) = 0.074 for all data, with  $w = [\sigma^2(F_o^2) + (0.0435p)^2 + 0.0562p]^{-1}$  where  $p = (F_o^2 + 2F_c^2)/3$ ,  $S = 1.09$  and  $(\Delta/\sigma)_{\max} = -0.001$ . Maximum and minimum residual densities in the final difference map were 0.28 and  $-0.15\text{eÅ}^{-3}$ , respectively. The atomic scattering factors were taken from International Tables for

X-ray Crystallography [3]. The refinements were performed with the SHELXL92 program [4] and the EUCLID package [5] was used for the calculation of geometries and preparation of the illustration. All calculations were carried out on an ULTRIX DEC system-5000.

### 3. Discussion

The final atomic coordinates with equivalent isotropic thermal parameters for C and O atoms and a general isotropic thermal parameter for H atoms are listed in Table 1; the molecular geometry (distances, angles and selected torsion angles) are given in Table 2. A projection of part of the structure showing the hydrogen-bond network is portrayed in Fig. 1.

The carboxy-group geometry displays the characteristics of perfect ordering as follows from the C–O distances of 1.320(1) and 1.208(1) Å and C–C–O angles of 111.9(1) and 124.2(1)°, with the larger angle associated with the shorter C–O distance. The C1–C2 bond is short, 1.519(1) Å, which has often been observed in carboxylic acids [6,7], and the C2–C3 and C2–O3 bonds are normal with lengths of 1.521(2) Å and 1.425(1) Å respectively. The C–H distances average to 0.98 Å and the two O–H distances are shortened (0.79(2) and

Table 1

Fractional atomic coordinates and equivalent isotropic thermal parameters ( $\text{Å}^2$ ) of C and O atoms with esds in parentheses. The hydrogen atoms have an overall isotropic thermal parameter

	x	y	z	$U(\text{eq})^a$
O (1)	0.6162 (2)	0.4279 (1)	0.2898 (1)	0.0183 (3)
O (2)	0.8700 (2)	0.5956 (1)	0.1804 (1)	0.0222 (3)
O (3)	0.5535 (2)	0.6620 (1)	−0.02253 (9)	0.0150 (2)
C (1)	0.6735 (2)	0.5318 (1)	0.1895 (1)	0.0131 (3)
C (2)	0.4615 (2)	0.5635 (1)	0.0891 (1)	0.0131 (3)
C (3)	0.3492 (3)	0.4116 (2)	0.0307 (2)	0.0204 (3)
H (1)	0.727 (4)	0.411 (2)	0.342 (2)	0.026 (2)
H (2)	0.341 (3)	0.620 (2)	0.144 (2)	0.026 (2)
H (3)	0.451 (4)	0.727 (2)	−0.046 (2)	0.026 (2)
H (3A)	0.279 (3)	0.352 (2)	0.116 (2)	0.026 (2)
H (3B)	0.218 (3)	0.441 (2)	−0.032 (2)	0.026 (2)
H (3C)	0.470 (3)	0.352 (2)	−0.024 (2)	0.026 (2)

<sup>a</sup>  $U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$ .

Table 2

Bond distances (Å), bond angles (deg) and selected torsion angles (deg) with esds in parentheses

O(1)–C(1)	1.320(1)	O(3)–H(3)	0.82(2)
O(2)–C(1)	1.208(1)	C(2)–H(2)	0.96(2)
O(3)–C(2)	1.425(1)	C(3)–H(3A)	1.02(2)
C(1)–C(2)	1.519(1)	C(3)–H(3B)	0.96(2)
C(2)–C(3)	1.521(2)	C(3)–H(3C)	0.98(2)
O(1)–H(1)	0.79(2)		
O(1)–C(1)–O(2)	123.9(1)	C(1)–C(2)–H(2)	107(1)
O(1)–C(1)–C(2)	111.87(9)	C(3)–C(2)–H(2)	109(1)
O(2)–C(1)–C(2)	124.24(9)	C(2)–C(3)–H(3A)	107(1)
O(3)–C(2)–C(1)	106.44(9)	C(2)–C(3)–H(3B)	108 (1)
O(3)–C(2)–C(3)	111.7(1)	C(2)–C(3)–H(3C)	110(1)
C(1)–C(2)–C(3)	112.60(9)	H(3A)–C(3)–H(3B)	109(1)
C(1)–O(1)–H(1)	112(1)	H(3A)–C(3)–H(3C)	114(1)
C(2)–O(3)–H(3)	110(1)	H(3B)–C(3)–H(3C)	109(2)
O(3)–C(2)–H(2)	110(1)		
O(1)–C(1)–C(2)–O(3)	–173.49(8)		
O(1)–C(1)–C(2)–C(3)	–50.7(1)		
O(2)–C(1)–C(2)–O(3)	7.6(1)		
O(2)–C(1)–C(2)–C(3)	130.4(1)		

0.82(2) Å) as is typical for structures determined by X-ray diffraction.

The hydroxyacetic acid moiety is almost planar as is indicated by the torsion angle O2–C1–C2–O3 of 7.6(1)° and  $\sigma_{\text{plane}}$  of 0.054 Å, and the O atom of the aliphatic hydroxy group is at the side of C=O

of the carboxy group which is usual in  $\alpha$ -hydroxy acids [8].

The two hydrogen-bond donors, O1–H1 and O3–H3, are involved in intermolecular hydrogen bonding. The acidic O1–H1 donor interacts strongly with O3 of a symmetry-related molecule

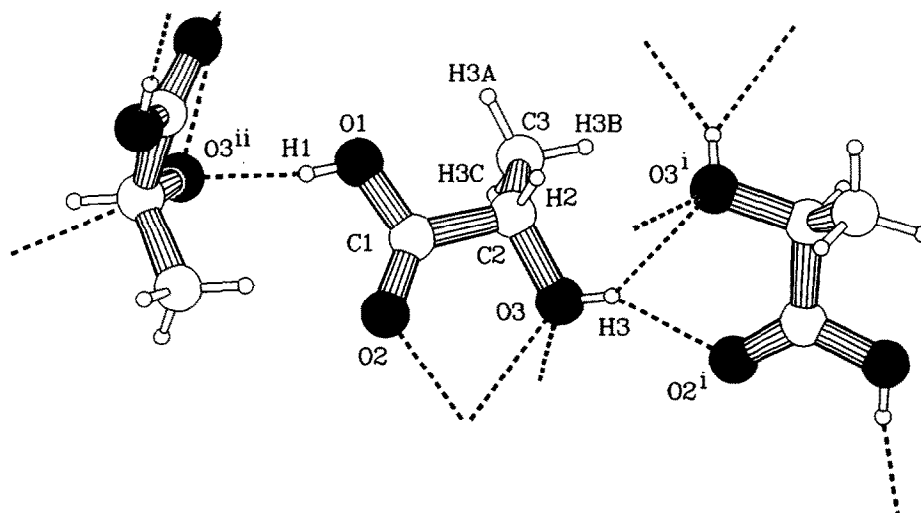


Fig. 1. Projection of part of the structure with atom numbering showing the hydrogen-bond network. Symmetry code: (i)  $\frac{1}{2} + x$ ,  $\frac{1}{2} - y$ ,  $-z$ ; (ii)  $\frac{1}{2} - x$ ,  $1 - y$ ,  $\frac{1}{2} + z$ .

at  $1\frac{1}{2} - x$ ,  $1 - y$ ,  $\frac{1}{2} + z$  with  $O1 \cdots O3$  2.634(1) Å,  $H3 \cdots O3$  1.85(2) Å and  $O1-H1 \cdots O3$  168(2)°. The aliphatic hydroxy group  $O3-H3$  participates in a symmetrical bifurcate (three centre) hydrogen bond by interaction with the carbonyl  $O2$  atom of the acid group and  $O3$  of the aliphatic  $OH$  group of a symmetry-related molecule at  $-\frac{1}{2} + x$ ,  $1\frac{1}{2} - y$ ,  $-z$ . The geometry of this four-atom configuration is as follows:  $O3 \cdots O2$  2.713(1) Å,  $H3 \cdots O2$  2.00(2) Å and  $O3-H3 \cdots O2$  145(2)°, and  $O3 \cdots O3$  3.148(1) Å,  $H3 \cdots O3$  2.46(2) Å and  $O3-H3 \cdots O3$  143(2)°. This configuration is planar as can be deduced from the sum of angles of 360(3)° around the hydrogen atom.

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