Structure of D-Erythronic Acid 3,4-Carbonate (DEC)

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As part of the work on oxidation of ascorbic acids going on in our laboratory,¹⁻³ the crystal structure of D-erythronic acid 3,4-carbonate (DEC, C₅H₆O₆) has been determined by X-ray diffraction methods. The crystals were found together with crystals of D-erythrono-1,4-lactone obtained by oxidation of D-isoscorbic acid with H₂O₂ in water.³

The crystal belongs to the triclinic system with space group P1 and cell dimensions $a = 5.007(1)$ Å, $b = 5.492(1)$ Å, $c = 6.358(1)$ Å, $\alpha = 68.20(2)^\circ$, $\beta = 82.76(2)^\circ$, $\gamma = 68.37(2)^\circ$, $Z = 1$. The density was calculated to be $D_x = 1.78$ g/cm³.

1782 independent reflections were measured on an automatic four-circle diffractometer at -150°C with MoK α -radiation up to 2θ max = 80° . Of these, 1737 reflections were recorded as observed using an observed unobserved cutoff at 3.0σ (I). No corrections for absorption or secondary extinction were applied because the molecule consists of only

light atoms and the crystal-size ($0.5 \times 0.3 \times 0.1$ mm) is small.

The structure was solved by direct methods,⁴ successive use of Fourier-syntheses and finally refined by full-matrix least squares technique.⁵ Hydrogen atom positions were refined with isotropic temperature factors while anisotropic temperature factors were introduced for non-hydrogen atoms.

The final ordinary R -value is 5.0% with $R_w = 4.3\%$. Final fractional coordinates with estimated standard deviations are given in Table 1. The principal thermal vibration ellipsoids for non-hydrogen atoms correspond to maximum r.m.s. amplitudes between 0.08 and 0.16 Å.

Table 2. Bond distances, angles and dihedral angles with estimated standard deviations in parentheses.

Distance	(Å)	Distance	(Å)
C1—O1	1.212 (2)	C1—C2	1.526 (2)
C1—O6	1.322 (2)	C2—C3	1.531 (2)
C2—O2	1.420 (2)	C3—C4	1.531 (2)
C3—O3	1.447 (2)	C5—O4	1.327 (2)
C4—O4	1.448 (2)	C5—O5	1.207 (2)
C5—O3	1.341 (2)		
Angle	(°)	Angle	(°)
O1—C1—O6	126.0 (1)	O1—C1—C2	122.9 (1)
O6—C1—C2	111.1 (1)	C1—C2—C3	109.2 (1)
C1—C2—O2	111.2 (1)	O2—C2—C3	108.6 (1)
C2—C2—O3	108.3 (1)	C2—C3—C4	113.7 (1)
O3—C3—C4	103.5 (1)	C3—C4—O4	103.9 (1)
C4—O4—C5	109.8 (1)	C3—O3—C5	109.8 (1)
O4—C5—O3	112.7 (1)	O4—C5—O5	124.2 (2)
O3—C5—O5	123.2 (2)		
Dihedral angle	(°)		
O1—C1—C2—O2	-2.2 (2)		
O1—C1—C2—C3	-122.0 (2)		
C1—C2—C3—O3	179.7 (1)		
C1—C2—C3—C4	65.2 (1)		
O6—C1—C2—O2	176.5 (1)		
O6—C1—C2—C3	56.8 (2)		
C2—C3—O3—C5	-118.4 (1)		
C2—C3—C4—O4	111.9 (1)		
C3—O3—C5—O5	-178.5 (1)		
C3—C4—O4—C5	6.7 (2)		
C4—C3—O3—C5	2.6 (2)		
O3—C3—C4—O4	-5.4 (2)		
C4—O4—C5—O3	-5.5 (2)		
C4—O4—C5—O5	174.6 (1)		
O2—C2—C3—O3	58.3 (2)		
O2—C2—C3—C4	-56.2 (2)		

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Table 1. Final fractional coordinates with estimated standard deviations in parentheses.

Atom	x	y	z
O1	0.1403 (4)	0.3315 (4)	0.5332 (4)
O2	-0.1823 (4)	0.8841 (4)	0.4106 (3)
O3	-0.0253 (4)	1.2342 (3)	0.0136 (3)
O4	-0.2904 (4)	1.0969 (4)	-0.1419 (3)
O5	-0.4080 (4)	1.5529 (4)	-0.2027 (3)
O6	0.5258 (4)	0.4266 (3)	0.3479 (3)
C1	0.2589 (4)	0.4942 (4)	0.4216 (3)
C2	0.1095 (4)	0.8112 (4)	0.3431 (3)
C3	0.1187 (4)	0.9341 (4)	0.0844 (3)
C4	-0.0532 (4)	0.8427 (4)	-0.0357 (3)
C5	-0.2537 (4)	1.3123 (4)	-0.1174 (3)
HO2	-0.228 (9)	0.764 (9)	0.504 (7)
HO6	0.595 (5)	0.255 (5)	0.390 (4)
HC2	0.199 (6)	0.880 (6)	0.403 (5)
HC3	0.304 (6)	0.913 (6)	0.018 (4)
H1C4	-0.117 (6)	0.709 (6)	0.054 (5)
H2C4	0.068 (6)	0.784 (6)	-0.158 (5)

Fig. 1. ORTEP drawing of DEC as seen along the C5—O5 bond.

Bond distances, bond angles and some dihedral angles for DEC are given in Table 2 with estimated standard deviations in parenthesis. These are calculated from the correlation matrix of the final least squares refinement cycle. Fig. 1 shows the molecule of DEC as seen along the C5—O5 bond.

The bond distances and angles of Table 2 are as expected, but differ slightly from those found in similar structures. Some selected bond distances of DEC compared with those of other structures are given in Table 3. The larger deviations seen from the carbonate group in BDPVC, bis(dimethylphosphatovinyl) carbonate ($C_9H_{16}P_2O_{11}$), might

be explained by the noncyclic arrangement of the carbonate group. We also observe the significant differences between bond distances C5—O3 (1.341 Å) and C5—O4 (1.327 Å) which generally are regarded as equal in cyclic carbonates.⁶ The bond distances C3—O3 and C4—O4 are greater than the similar distances in ethylene carbonate,⁶ but more equal to those of erythritol.¹⁰

The crystal structure consists of monomers, hydrogen bonded between O2 and HO6 and between O5 and HO2, as shown in Fig. 2. Table 4 gives data for the hydrogen bonding pattern. It is observed that DEC is not built up of dimers as the simple carboxylic acids.^{7,8}

The internal contact O2---O1 is 2.715 Å with the distance HO2---O1 being 2.37 Å which could imply a weak internal hydrogen bond, even though the angle O2—HO2—O1 is only 108°. This suggests the existence of a bifurcated hydrogen bond arrangement as earlier observed in 2,5-dihydroxy-1,4-benzoquinone¹² and β -L-lyxopyranose.¹³

The carboxylic acid group defined by O1, O6, C1 and C2, is planar within experimental error with C1 0.007 Å above the least squares plane as greatest deviation. The condensed carbonate-ring system, however, cannot be considered as planar. The best least squares plane is fitted through O3, O4, C5 and O5, with C3 and C4 0.04 and 0.13 Å beneath the plane. This is in agreement with the non-planarity found in the ethylene carbonate molecule.⁶ The angle between the best planes through O1, O6, C1, C2 and O3, O4, C5, O5 is calculated to 60.6°.

Fig. 2. The hydrogen bonding pattern of DEC as seen along the *a*-axis of the unit cell.

Table 3. Bond distances (Å) in some selected compounds.

Compound	C1—O1	C1—O6	C1—C2	C2—O2	C2—C3	C3—C4	C3—O3	C4—O4	C5—O3	C5—O4	C5—O5
DEC	1.212	1.322	1.526	1.420	1.531	1.531	1.447	1.448	1.341	1.327	1.207
Propionic acid ⁷	1.23	1.32	1.50		1.54						
Butyric acid ⁸	1.20	1.32	1.52		1.51	1.52					
BDPVC ^a							1.38	1.40	1.36	1.37	1.17
Erythritol ^b			1.523	1.433	1.539	1.523	1.433	1.425			
Ethylene carbonate ⁶						1.52	1.40	1.40	1.33	1.33	1.15
Vinylene carbonate ¹¹						1.236	1.349	1.396	1.284	1.335	1.160

^a Bis(dimethylphosphatovinyl) carbonate (C₉H₁₆P₂O₁₁); Ref. 9. ^b Neutron diffraction investigation; Ref. 10.

Table 4. Data for the hydrogen bonding in DEC.

Distance	(Å)	Angle	(°)
1 O2---O6	2.688 (2)	O2---HO6—O6	164 (2)
O2---HO6	1.89 (3)		
2 O5---O2	2.850 (2)	O5---HO2—O2	161 (4)
O5---HO2	2.09 (4)		
3 O1---O2 ^a	2.715 (2)	O1---HO2—O2	108 (4)
O1---HO2	2.37 (4)		

^a Intramolecular.

- Hvoslef, J. and Pedersen, B. *Acta Chem. Scand. B* 34 (1980) 285.
- Hvoslef, J. and Pedersen, B. *Carbohydr. Res.* 92 (1981) 9.
- Moen, T. O., Hvoslef, J. and Pedersen, B. *To be published.*
- Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr. A* 27 (1971) 368.
- Groth, P. *Acta Chem. Scand.* 27 (1973) 1837.
- Brown, C. J. *Acta Crystallogr.* 7 (1954) 92.
- Strieter, F. J., Templeton, D. H., Sheuerman, R. F. and Sass, R. L. *Acta Crystallogr.* 15 (1962) 1233.
- Strieter, F. J. and Templeton, D. H. *Acta Crystallogr.* 15 (1962) 1240.
- Ul-Haque, M., Caughlan, C. N., Smith, G. D., Ramirez, F. and Glaser, S. L. *J. Org. Chem.* 41 (1976) 1152.
- Ceccarelli, C., Jeffrey, G. A. and McMullan, R. K. *Acta Crystallogr. B* 36 (1980) 3079.
- Cser, F. *Acta Chim. Acad. Sci. Hung.* 80 (1974) 49.
- Semmingsen, D. *Acta Chem. Scand. B* 31 (1977) 11.
- Nordenson, D., Takagi, S. and Jeffrey, G. A. *Acta Crystallogr. B* 34 (1978) 3809.

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