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Structure of (−)-Malic Acid

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Abstract. $C_4H_6O_5$, $M_r = 134{\cdot}09$, monoclinic, $P2_1$, $a = 5{\cdot}041\,(1)$, $b = 9{\cdot}188\,(3)$, $c = 11{\cdot}792\,(4)$ Å, $\beta = 94{\cdot}06\,(2)^\circ$, $V = 544{\cdot}8\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}635$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu(\text{Mo } K\alpha) = 0{\cdot}15$ mm^{-1}, $F(000) = 280$, $T = 294$ K, $R = 0{\cdot}064$ for 667 unique observed diffractometer data $[I > \sigma(I)]$, $wR = 0{\cdot}071$. The carbon chains of the two independent molecules are in the extended form. The molecules form infinite chains being coupled *via* cyclic hydrogen-bonded carboxyl dimers. The chains are linked together in a sheet by hydrogen-bond interactions between aliphatic hydroxyl groups.

Introduction. "Die gewöhnliche links drehende Apfelsäure = COOH.CH(OH)CH$_2$.COOH krystallisiert nur schwierig in zerfließlichen Nadeln, von derem Form bisher keine brauchbare Bestimmung vorliegt" (Groth, 1910). Van Loock, van Havere & Lenstra (1981) confirm this problem in a paper in which the structure of α-(±)-malic acid is presented. We, however, were able by careful evaporation of an aqueous solution at room temperature to grow crystals of (−)-malic acid by means of which it was possible to elucidate the heavy-atom structure, the results of which are presented here.

Experimental. Crystal $0{\cdot}2 \times 0{\cdot}2 \times 0{\cdot}2$ mm, Enraf–Nonius CAD-4F diffractometer. Zr-filtered Mo $K\alpha$ radiation, unit cell determined using 23 reflexions ($7 < \theta < 10^\circ$). In one half of the reflexion sphere (h −5,5; k 0,10; l −16,16) 1757 reflexions measured, $\theta_{\max} = 23{\cdot}5^\circ$, $R_{\text{int}} = 0{\cdot}063$ for 864 independent reflexions, 667 unique observed reflexions $[I > \sigma(I)$, $\sigma^2(I) = \sigma^2(I)_{\text{cs}} + (pI)^2$ with $p = 0{\cdot}0063$ (McCandlish, Stout & Andrews, 1975)]. Intensities obtained by the $\omega/2\theta$-scan method with a scan width of $(1{\cdot}40 + 0{\cdot}35\tan\theta)^\circ$. For each reflection the scan speed was adjusted in order to obtain a minimum $I/\sigma(I)$ ratio of 100, provided that the scan time did not exceed 60 s. The 020 reflexion was used as an intensity and orientation check; decay during data collection 2·4%. Instability and Lp correction applied; no correction for absorption. Systematic absences $0k0$ with $k = 2n + 1$, indicating $P2_1$.

Applying direct methods using *MULTAN*80 (Main, Woolfson, Lessinger, Germain & Declercq, 1980) with a statistically weighted tangent refinement revealed, amongst several ghost peaks, the position of one cyclic carboxyl dimer. Using these six atoms, four subsequent difference Fourier syntheses (*SHELX*76, Sheldrick, 1976) resulted in the positions of all non-H atoms. After full-matrix isotropic and full-matrix anisotropic refinement a difference Fourier was calculated and unambiguous positions were found for the aliphatic H atoms, but no accurate positions could be assigned to the hydroxyl

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H atoms. The aliphatic H atoms were introduced at calculated positions and refined in the riding mode (C—H = 0·98 Å) with one common isotropic temperature parameter [$U = 0{\cdot}065\,(13)$ Å^2]. Final R = 0·064, wR = 0·071, $w = 1{\cdot}11/[\sigma^2(F) + 0{\cdot}00123F^2]$, S = 0·74, $(\Delta/\sigma)_{\max}$ = 0·18. Maximal and minimal residual density 0·33, −0·33 e Å^{-3}. The atomic coordinates are in accordance with the configuration as determined by Kryger & Rasmussen (1972) of cobalt(II) (−)-malate trihydrate. Scattering factors from Cromer & Mann (1968) and anomalous dispersions from Cromer & Liberman (1970). The program package *EUCLID* (Spek, 1982) was used for geometrical calculations and illustrations.

Discussion. Refined atomic coordinates and equivalent isotropic thermal parameters of the non-H atoms are given in Table 1. Bond lengths, bond angles and selected torsion angles are listed in Table 2.* Short intermolecular O—O distances are given in Table 3. The atomic labeling and conformation are shown in Fig. 1. A view perpendicular to the hydrogen-bonded sheet is depicted in Fig. 2. The conformation of the carbon chains of both independent molecules is in the extended form, which was also found for α-(±)-malic acid (van Loock, van Havere & Lenstra, 1981) and β-(±)-malic acid (van der Sluis & Kroon, 1985).

Table 1. *Final coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$(Å^2)
O(1)	0·090 (1)	0·301 (2)	0·4310 (6)	0·042 (2)
O(2)	0·184 (1)	0·520 (2)	0·3622 (6)	0·046 (3)
O(3)	−0·620 (1)	0·618 (2)	0·0977 (6)	0·057 (3)
O(4)	−0·477 (2)	0·398 (2)	0·0558 (7)	0·068 (3)
O(5)	−0·364 (1)	0·288 (2)	0·2920 (7)	0·065 (3)
C(1)	0·054 (2)	0·3961	0·3593 (8)	0·034 (3)
C(2)	−0·152 (2)	0·378 (2)	0·2595 (8)	0·035 (3)
C(3)	−0·262 (2)	0·523 (2)	0·2149 (7)	0·034 (3)
C(4)	−0·469 (2)	0·507 (2)	0·1160 (9)	0·036 (3)
O(11)	0·500 (1)	0·295 (2)	0·5874 (5)	0·042 (2)
O(12)	0·604 (1)	0·509 (2)	0·5124 (5)	0·040 (2)
O(13)	1·013 (2)	0·589 (2)	0·9306 (7)	0·063 (3)
O(14)	1·130 (2)	0·363 (2)	0·8969 (6)	0·054 (3)
O(15)	1·063 (1)	0·522 (2)	0·6419 (5)	0·039 (2)
C(11)	0·645 (2)	0·411 (2)	0·5818 (9)	0·036 (3)
C(12)	0·871 (2)	0·419 (2)	0·6708 (8)	0·032 (3)
C(13)	0·761 (2)	0·458 (2)	0·7857 (8)	0·041 (4)
C(14)	0·978 (2)	0·475 (2)	0·8820 (9)	0·038 (4)

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°) *for the non-*H *atoms with e.s.d.'s in parentheses*

O(1)—C(1)	1·22 (1)	O(11)—C(11)	1·30 (2)
O(2)—C(1)	1·31 (1)	O(12)—C(11)	1·22 (2)
O(3)—C(4)	1·29 (2)	O(13)—C(14)	1·20 (2)
O(4)—C(4)	1·23 (2)	O(14)—C(14)	1·29 (2)
O(5)—C(2)	1·42 (1)	O(15)—C(12)	1·41 (1)
C(1)—C(2)	1·52 (1)	C(11)—C(12)	1·49 (1)
C(2)—C(3)	1·52 (2)	C(12)—C(13)	1·54 (1)
C(3)—C(4)	1·52 (1)	C(13)—C(14)	1·53 (1)
O(1)—C(1)—O(2)	123·3 (9)	O(11)—C(11)—O(12)	125 (1)
O(1)—C(1)—C(2)	121·5 (8)	O(11)—C(11)—C(12)	114 (1)
O(2)—C(1)—C(2)	115·2 (8)	O(12)—C(11)—C(12)	122 (1)
O(5)—C(2)—C(1)	109·6 (8)	O(15)—C(12)—C(11)	111·2 (9)
O(5)—C(2)—C(3)	109·8 (8)	O(15)—C(12)—C(13)	111 (1)
C(1)—C(2)—C(3)	113 (1)	C(11)—C(12)—C(13)	109·1 (7)
C(2)—C(3)—C(4)	113 (1)	C(12)—C(13)—C(14)	113·3 (7)
O(3)—C(4)—O(4)	124 (1)	O(13)—C(14)—O(14)	125 (1)
O(3)—C(4)—C(3)	115 (1)	O(13)—C(14)—C(13)	121 (1)
O(4)—C(4)—C(3)	121 (1)	O(14)—C(14)—C(13)	114 (1)
O(1)—C(1)—C(2)—O(5)	30 (1)	O(12)—C(11)—C(12)—O(15)	−18 (2)
C(1)—C(2)—C(3)—C(4)	−179·4 (8)	C(11)—C(12)—C(13)—C(14)	−178 (1)
C(2)—C(3)—C(4)—O(4)	−23 (1)	C(12)—C(13)—C(14)—O(14)	−56 (2)

Table 3. *Short intermolecular* O—O *contacts*

O′ is a hydrogen-bond acceptor.

O···O′	Distance (Å)	Symmetry code O′
O(2)···O(12)	2·663 (9)	x, y, z
O(3)···O(13)	2·618 (11)	$x-2, y, z-1$
O(5)···O(15)	2·955 (18)	$1-x, y-0{\cdot}5, 1-z$
O(11)···O(1)	2·670 (9)	x, y, z
O(14)···O(4)	2·648 (11)	$x+2, y, z+1$
O(15)···O(1)	2·797 (18)	$1-x, 0{\cdot}5+y, 1-z$

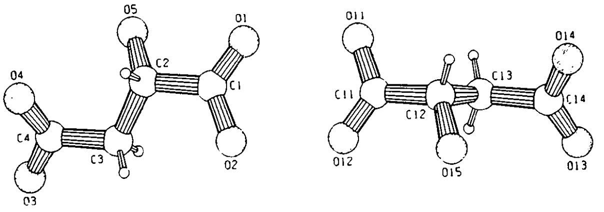

Fig. 1. Atomic labeling and conformation of the two crystallographically independent malic acid molecules.

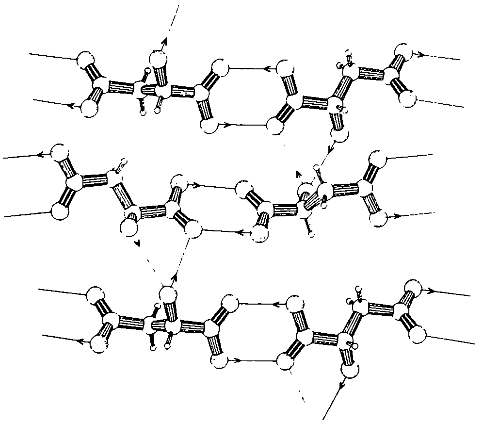

Fig. 2. View perpendicular to the hydrogen-bonded sheet. The orientation of the lowest two molecules corresponds to Fig. 1. Hydrogen bonds indicated with single lines, directionality with arrows.

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* Lists of anisotropic thermal parameters, calculated H-atom positions and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51934 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The geometry of the four carboxyl groups of the two independent molecules lies within the distribution reported earlier for carboxyl groups with no orientational disorder (Leiserowitz, 1976). From the asymmetry in the carboxyl groups, donor and acceptor atoms can clearly be assigned within the cyclic hydrogen-bonded dimers which form chains in the [$\bar{2}$01] direction. The carbonyl hydroxyl groups within both molecules are on the same side of the aliphatic chain. Chain formation, however, is still possible without inversion centers or twofold axes, because the carboxyl hydroxyl groups of the two independent molecules are on different sides of the polymeric chain. If the two independent molecules are regarded as one supramolecule, the two hydroxyl groups are on different sides of the aliphatic chain and chain formation is then possible by translation, which is the only possible mode in the absence of inversion centers and twofold axes as mentioned by Leiserowitz (1976). It is noteworthy that the carbonyl groups are appreciably rotated away from the α-hydroxyl group, whereas normally a planar situation is preferred (Kroon, 1982).

The chains are connected in the [010] direction by two hydrogen bonds formed by the two aliphatic hydroxyl groups and one carboxyl group, the directionality of which can be inferred from stereochemical considerations (Fig. 2).

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2,2′,3,4,4′,5′-Hexachlorodiphenyl Ether*

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Abstract. $C_{12}H_4Cl_6O$, $M_r = 376{\cdot}9$, triclinic, $P\bar{1}$, $a = 8{\cdot}363\,(2)$, $b = 9{\cdot}306\,(2)$, $c = 10{\cdot}655\,(3)$ Å, $\alpha = 103{\cdot}56\,(2)$, $\beta = 98{\cdot}50\,(2)$, $\gamma = 113{\cdot}81\,(2)^\circ$, $V = 709{\cdot}6\,(8)$ Å^3, $Z = 2$, $D_x = 1{\cdot}76$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 1{\cdot}20$ mm^{-1}, $F(000) = 372$, $T = 296$ K, final $R = 0{\cdot}032$ for 1650 unique observed reflections. The angle [C(1)—O(1)—C(1′)] between the phenyl rings is 117·2 (3)°. The molecule has a twist conformation, with a twist angle of 85·46 (8)° between the phenyl rings. The chlorine substituents deviate only slightly from the least-squares plane formed by the O and the benzene C atoms [max. deviations −0·089 (1) and 0·090 (1) Å for Cl(4) and Cl(4′), respectively].

Introduction. The relationship between the only moderately toxic or nontoxic polychlorinated diphenyl ethers and the acutely toxic polychlorinated dibenzofurans is attracting considerable interest because polychlorinated diphenyl ethers transform to polychlorinated dibenzofurans under UV light and during pyrolysis (Norström, Andersson & Rappe, 1976; Garå, Andersson, Nilsson & Norström, 1981). The presence of polychlorinated diphenyl ethers in various commercial chlorophenol preparations (Garå, Andersson, Nilsson & Norström, 1981) has forced environmental analysts to focus their attention on polychlorinated diphenyl ethers in the biosphere (Paasivirta, Tarhanen & Soikkeli, 1986; Paasivirta, Mäntykoski, Koistinen, Kuokkanen, Mannila & Rissanen, 1989). Diphenyl ethers have been suggested to have four different conformational

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* Structures of Chlorinated Diphenyl Ethers. II. Part I: Rissanen, Valkonen & Virkki (1988).

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