

Fig. 1. A view of the molecular complex with atom labelling.

The bond lengths and angles in the tetrazole ring of molecule 3 are very close to those reported for anionic tetrazolide in hydrazinium 5-aminotetrazolide (Bryden, 1958), sodium tetrazolide monohydrate (Palenik, 1963) and dimethylammonium 5-(3-chlorobenzyl)tetrazolide (Ansell, 1975), thus suggesting the ionic form for the central molecule in the complex reported here; the negative charge on the ring is also in agreement with the presence of a surrounding network of hydrogen bonding and with *mm* symmetry of the ring: in sodium tetrazolide the *mm* symmetry is even imposed by crystallographic restrictions.

On the other hand, the *mm* symmetry is not present in the tetrazole rings of molecules 1 and 2.

The tetrazole and benzene rings are not coplanar in the three molecules, the angles between least-squares planes being  $10.2(5)^\circ$  in molecule 3 and  $15.1(6)$  and  $14.8(7)^\circ$  in molecules 1 and 2. This result was rather unexpected, since, in the absence of steric hindrance

between *ortho* positions, molecules containing two aromatic rings linked by a single bond are usually planar because of partial delocalization of  $\pi$  electrons and the packing influence, and suggests that  $\pi$  delocalization is negligible in the examined compounds; this is in agreement with the values of the C—C inter-ring bonds, av.  $1.476(5)$  Å, very close to the sum of C( $sp^2$ ) radii ( $1.48$  Å), and with insignificant effect from the *Y* substituent in the phenyl ring on the tetrazole reactivity, as evidenced by the kinetics results (Beltrame & Gelli, 1984).

As is also evident from Fig. 1, the two independent molecules 1 and 2 are related by a pseudo centre of symmetry, which is at *ca*  $x = 0.545$ ,  $y = 0.247$ ,  $z = -0.050$ ; therefore, by unit-cell symmetry, they are related by a pseudo translation of  $\mathbf{b}/2$  and this is the main feature of the crystal packing, which is regulated by normal van der Waals contacts.

#### References

- ANSELL, G. B. (1975). *J. Chem. Soc. Perkin Trans. 2*, pp. 1200–1202.  
 BELTRAME, P. & GELLI, G. (1984). *J. Chem. Soc. Perkin Trans. 2*. Submitted.  
 BRYDEN, J. H. (1958). *Acta Cryst.* **11**, 31–37.  
 IMMIRZI, A. (1967). *Ric. Sci.* **37**, 743–749.  
 IMMIRZI, A. (1973). *J. Appl. Cryst.* **6**, 246–249.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.  
 MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.  
 PALENIK, G. J. (1963). *Acta Cryst.* **16**, 596–600.

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## The Structure of ( $\pm$ )-Malic Acid, ( $\pm$ )- $C_4H_6O_5$ ,

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**Abstract.**  $M_r = 134.09$ , monoclinic,  $P2_1/c$ ,  $a = 4.889(1)$ ,  $b = 8.815(1)$ ,  $c = 13.036(2)$  Å,  $\beta = 102.93(1)^\circ$ ,  $V = 547.6$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.626$  Mg m<sup>-3</sup>,  $Mo K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 0.11$  mm<sup>-1</sup>,  $F(000) = 280$ ,  $T = 294$  K, final  $R = 0.049$

for 774 unique observed diffractometer data [ $I \geq 2.5\sigma(I)$ ]. The carbon chain of the molecule is in the extended form. The molecular conformation is compared with data from other malate crystal structures, with evidence from NMR experiments and with results obtained by molecular-mechanics calculations. The molecules form infinite chains in which they are coupled

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via cyclic H-bonded carboxyl dimers. The aliphatic hydroxyl groups link these chains together by H-bond interactions, so that layers are formed parallel to (101).

**Introduction.** (–)-Malic acid, in its ionized form, is one of the four-carbon compounds that constitute the last stage of the citric acid cycle. Until lately no crystal-structure determination of the free acid was reported, presumably because of the difficulty in getting crystals suitable for X-ray analysis (Groth, 1910; van Loock, van Havere & Lenstra, 1981); van Loock *et al.* (1981) were the first to obtain single, albeit unstable, crystals of (±)-malic acid.

Recently we obtained good quality crystals of a second, stable, modification of (±)-malic acid, whose structure is presented here. Since it appeared to be different from the crystal structure studied by van Loock *et al.*, we refer to it as the  $\beta$  form in order to distinguish it from the crystal structure ( $\alpha$  form) reported by the Belgian group.

**Experimental.** Crystals of  $\beta$ -(±)-malic acid grown in standard way at room temperature by slow evaporation of aqueous solution. Irregular-shaped crystal, max. dimensions 0.5 × 0.5 × 0.6 mm. Enraf–Nonius CAD-4 diffractometer, Zr-filtered Mo K $\alpha$  radiation. Unit-cell dimensions determined using 19 reflections in range  $\theta = 5.4$  to  $\theta = 10.2^\circ$ . In one half of the reflection sphere ( $h -6/+5$ ,  $k 0/+11$ ,  $l -15/+15$ ) 2575 reflections measured,  $\theta_{\max} = 28^\circ$ ,  $R_{\text{int}} = 0.068$  for 1247 independent reflections, 772 unique observed reflections [ $I \geq 2.5\sigma(I)$ ].  $\omega/2\theta$  scan, scan width  $(1 + 0.35\tan\theta)^\circ$ . For each reflection scan speed adjusted to obtain min.  $I/\sigma(I)$  of 100, provided scan time did not exceed 60 s.  $\bar{1}15$  and  $1\bar{1}5$  reflections used as intensity check; intensity variation over period of data collection –19% for both reflections. Instability and Lp correction, no correction for absorption. Systematic absences  $0k0$  with  $k = 2n + 1$  and  $h0l$  with  $l = 2n + 1$ , indicating  $P2_1/c$ . Structure solution by direct methods using MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) failed, possibly due to pseudo symmetry ( $C2/c$ ). Approximate positions of all non-hydrogen atoms found by interpreting an  $E \times F$  Patterson map. After two cycles of isotropic refinement all hydrogen atoms located on difference Fourier map. Full-matrix least-squares refinement on  $F$  (C and O anisotropic, H isotropic) gave final  $R = 0.049$ ,  $wR = 0.055$  with  $w = 1.432/[\sigma^2(F) + 0.000903F^2]$  and  $S = 0.43$ . Final difference Fourier map showed no peaks above absolute level  $0.24 e \text{ \AA}^{-3}$ . Max.  $\Delta/\sigma 0.003$ . Scattering factors for C and O from Cromer & Mann (1968) and H from Stewart, Davidson & Simpson (1965). All calculations carried out with SHELX76 (Sheldrick, 1976), APOLLO (data reduction and correction by A. L. Spek) and EUCLID [calculations of geometrical data and illustrations (Spek, 1982)].

Table 1. Fractional atomic coordinates and isotropic thermal parameters ( $\text{\AA}^2$ ) with e.s.d.'s in parentheses

$U_{\text{eq}}$  is derived from the anisotropic parameters by  $U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$ .

	x	y	z	$U_{\text{eq}}$ or $U$
O(1)	0.2215 (4)	–0.0999 (2)	0.4482 (2)	0.0468 (7)
O(2)	0.0838 (4)	0.1384 (2)	0.4042 (2)	0.0469 (7)
O(3)	0.2703 (5)	–0.1139 (2)	0.0574 (2)	0.0619 (8)
O(4)	0.4625 (4)	0.1108 (2)	0.0977 (2)	0.0494 (7)
O(5)	0.5754 (4)	–0.0942 (3)	0.3154 (2)	0.0542 (8)
C(1)	0.2207 (5)	0.0128 (3)	0.3954 (2)	0.0371 (8)
C(2)	0.3745 (5)	0.0209 (3)	0.3065 (2)	0.0376 (9)
C(3)	0.1591 (6)	0.0123 (4)	0.2017 (2)	0.044 (1)
C(4)	0.3107 (5)	0.0076 (3)	0.1137 (2)	0.0385 (8)
H(1)	–0.018 (7)	0.143 (4)	0.462 (3)	0.063 (9)
H(2)	0.451 (6)	0.118 (3)	0.308 (2)	0.044 (8)
H(3)	0.488 (9)	–0.178 (6)	0.338 (4)	0.13 (2)
H(4)	0.056 (8)	–0.072 (4)	0.193 (3)	0.06 (1)
H(5)	0.057 (7)	0.103 (3)	0.196 (2)	0.051 (9)
H(6)	0.402 (8)	–0.123 (4)	0.001 (3)	0.09 (1)

Table 2. Bond distances ( $\text{\AA}$ ), bond angles ( $^\circ$ ) and hydrogen-bond geometry

O(1)–C(1)	1.208 (3)	O(2)–H(1)	0.99 (4)			
O(2)–C(1)	1.312 (3)	O(3)–H(6)	1.08 (4)			
O(3)–C(4)	1.288 (3)	O(5)–H(3)	0.93 (5)			
O(4)–C(4)	1.221 (3)	C(2)–H(2)	0.93 (3)			
O(5)–C(2)	1.399 (3)	C(3)–H(4)	0.89 (4)			
C(1)–C(2)	1.518 (4)	C(3)–H(5)	0.94 (3)			
C(2)–C(3)	1.529 (4)					
C(3)–C(4)	1.499 (4)					
O(1)–C(1)–O(2)	125.5 (3)	C(4)–O(3)–H(6)	114 (2)			
O(1)–C(1)–C(2)	122.3 (2)	C(2)–O(5)–H(3)	104 (3)			
O(2)–C(1)–C(2)	112.1 (2)	O(5)–C(2)–H(2)	113 (2)			
O(5)–C(2)–C(3)	111.6 (2)	C(3)–C(2)–H(2)	105 (2)			
C(1)–C(2)–C(3)	108.7 (2)	C(1)–C(2)–H(2)	107 (2)			
O(5)–C(2)–C(1)	111.2 (2)	C(2)–C(3)–H(5)	106 (2)			
C(2)–C(3)–C(4)	109.0 (2)	H(4)–C(3)–H(5)	115 (3)			
O(4)–C(4)–C(3)	122.2 (3)	C(4)–C(3)–H(4)	104 (3)			
O(3)–C(4)–C(3)	114.8 (3)	C(4)–C(3)–H(5)	108 (2)			
O(3)–C(4)–O(4)	122.9 (3)	C(2)–C(3)–H(4)	114 (3)			
C(1)–O(2)–H(1)	117 (2)					
No.*	O–H ( $\text{\AA}$ )	H...O ( $\text{\AA}$ )	O...O ( $\text{\AA}$ )	H...O ( $^\circ$ )		
1	O(2)–H(1)...	O(1)	0.99 (4)	1.74 (4)	2.707 (3)	164 (3)
2	O(3)–H(6)...	O(4 <sup>ii</sup> )	1.08 (4)	1.58 (4)	2.641 (4)	166 (3)
3	O(5)–H(3)...	O(4 <sup>iii</sup> )	0.93 (5)	2.03 (5)	2.859 (3)	147 (4)

Symmetry operations (performed on the acceptor atoms): (i)  $-x, -y, 1-z$ ; (ii)  $1-x, -y, -z$ ; (iii)  $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$ .

\* This number corresponds to the numbers used in Fig. 2.

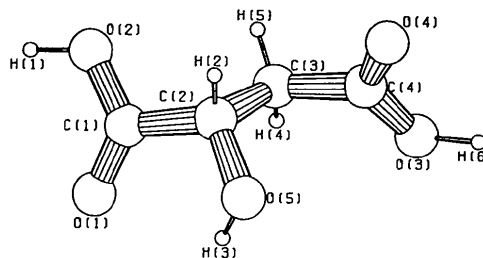


Fig. 1. Molecular conformation and atomic numbering of the molecule in  $\beta$ -(±)-malic acid.

**Discussion.** Refined parameters are listed in Table 1.\* Bond distances and bond angles are given in Table 2. The atomic numbering and molecular conformation are depicted in Fig. 1.

The conformation of the carbon skeleton is *anti* [ $\psi = -175.5(2)^\circ$ ], with the carboxyl group of the glycolic acid moiety roughly planar with C(2) and O(5) [ $\varphi_2 = -18.0(4)^\circ$ ].† The carboxyl-group conformation around the terminal C–C bond is anticlinal [ $\chi = -61.5(4)^\circ$ ].

In order to extend our conformational analysis we searched the Cambridge Crystallographic Database for malate fragments, added two not yet published structures and obtained structural data for 30 molecules.\* A wide variety of crystal packing types is thus involved. Whenever necessary each molecule was converted into its *S* configuration. Three torsion angles of interest for our conformational analysis were considered:

$$\begin{aligned}\psi &= \text{C}(1)\text{--C}(2)\text{--C}(3)\text{--C}(4); \\ \varphi_2 &= \text{O}(1)\text{--C}(1)\text{--C}(2)\text{--O}(5) \text{ or } \text{O}(2)\text{--C}(1)\text{--C}(2)\text{--O}(5) \\ &\quad \text{(the smaller of the two values);} \\ \chi &= \text{C}(2)\text{--C}(3)\text{--C}(4)\text{--O}(3) \text{ or } \text{C}(2)\text{--C}(3)\text{--C}(4)\text{--O}(4) \\ &\quad \text{(also depending on their absolute magnitudes).}\end{aligned}$$

They are listed in Table 3, which shows that only two staggered conformations about the central C–C bond are found in crystals. In 20 cases the molecule adopts the antiperiplanar conformation (type I). The second conformation (ten cases) is anticlinal ( $\psi = ca -60^\circ$ ; type II), whereas the synclinal conformation ( $\psi = ca +60^\circ$ ; type III) is not met with at all. The distribution of these species in aqueous solution was determined by NMR studies by Mariano & Gil (1969). The populations they calculated (in %) are as follows: malic acid 42 (I), 51 (II) and 7 (III); sodium malate 60 (I), 37 (II) and 3 (III); Zn<sup>II</sup> malate complex 28 (I), 70 (II) and 2 (III). These figures are thus in good qualitative agreement with the relative abundances of the conformations in crystals.

Inspection of Table 3 shows that the well known tendency of the  $\alpha$ -hydroxyl group to be coplanar with the carboxyl group (Jeffrey & Parry, 1952; Kanters, Kroon, Peerdeman & Schoone, 1967; Newton & Jeffrey, 1977) exists in both types I and II. On the other hand, the torsion angle around the terminal C–C bond ( $\chi$ ) appears to be very sensitive to the carbon-chain conformation. In type II we encounter a fairly narrow distribution with the carboxyl group nearly coplanar

\* Lists of structure factors, anisotropic thermal parameters and a table of torsion angles found in crystal structures of malates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42071 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† The symbol  $\varphi_2$  for this torsion angle is chosen in accordance with the paper by Newton & Jeffrey (1977) dealing with model calculations on glycolic acid.

with the carbon chain of the propionic acid moiety. Because of the repulsive interaction between the carboxyl group and the hydroxyl group in its  $\beta$  position, this conformation cannot be realized in type I and in this case a broad distribution occurs. These findings are corroborated by preliminary molecular-mechanics calculations (Kroon-Batenburg, Kroon & de Vries, 1985). It appears that the molecular conformations in both crystal structures of the free acid fall within the distributions found.

The malic acid molecules are packed in layers parallel to (101). In these layers the molecules are arranged in infinite chains, coupled *via* centres of symmetry by cyclic H-bonded carboxyl-dimer formation. A two-dimensional H-bonded network, brought about by the aliphatic hydroxyl groups, links these chains into sheets (see Fig. 2).

Although the cell dimensions of the  $\alpha$ -(±)-malic acid crystal structure (van Loock *et al.*, 1981) are very similar to that of the title compound, the Belgian group found a different space group (*Aa*). Their crystal structure exhibits the same pattern of infinite chains of molecules. However, these chains are generated by a twofold screw axis. Van Loock *et al.* (1981) considers the aliphatic hydroxyl group in the  $\alpha$  structure to be free, so that the hydrogen-bond scheme is only one dimensional.

Table 3. Statistical analysis of torsion angles  $\tau$  ( $^\circ$ ) in malate molecules

Successive columns contain the mean values of the torsion angles, their standard deviations, and the minimum and maximum values found in the crystal-structure statistics.

	$\tau$	$\langle \tau \rangle$	$\sigma(\tau)$	$\tau_{\min}$	$\tau_{\max}$	$\alpha$ -(±)-Malic acid	$\beta$ -(±)-Malic acid
Type I	$\psi$	175.4	1.5	-173.7	163.7	-172.9	-175.5
	$\varphi_2$	-4	4	-37.2	29.3	-13.6	-18.0
	$\chi$	-42	5	-80.4	-9.8	-61.3	-61.5
Type II	$\psi$	-62.0	1.8	-70.7	-54.1		
	$\varphi_2$	-2	5	-27.3	15.6		
	$\chi$	4	5	-13.6	30.4		

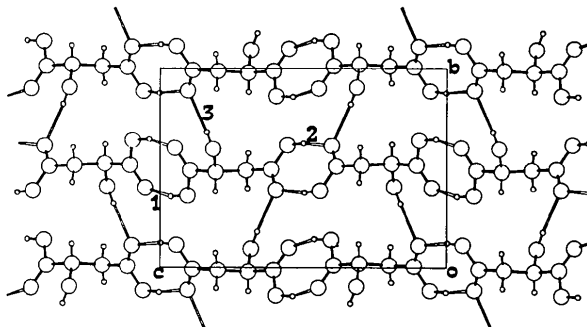


Fig. 2. Packing diagram viewed down *a*. The hydrogen bonds are indicated by open rods and labelled according to Table 2.

## References

- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.  
 GROTH, P. (1910). *Chem. Kristallogr.* **3**, 290.  
 JEFFREY, G. A. & PARRY, G. S. (1952). *Nature (London)*, **169**, 1105–1106.  
 KANTERS, J. A., KROON, J., PEERDEMAN, A. F. & SCHOONE, J. C. (1967). *Tetrahedron*, **23**, 4027–4033.  
 KROON, BATENBURG, L. M. J., KROON, J. & DE VRIES, A. (1985). In preparation.  
 LOOCK, J. F. J. VAN, VAN HAVERE, W. & LENSTRA, A. T. H. (1981). *Bull. Soc. Chim. Belg.* **90**, 161–166.  
 MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.  
 MARIANO, J. S. & GIL, V. M. S. (1969). *Mol. Phys.* **17**, 313–315.  
 NEWTON, M. D. & JEFFREY, G. A. (1977). *J. Am. Chem. Soc.* **99**, 2413–2421.  
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.  
 SPEK, A. L. (1982). *The EUCLID Package*. In *Computational Crystallography*, edited by D. SAYRE, p. 528. Oxford: Clarendon.  
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

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### 3,4,5-Triiodotoluene, C<sub>7</sub>H<sub>5</sub>I<sub>3</sub>

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**Abstract.**  $M_r = 469.83$ , tetragonal,  $P\bar{4}2_1m$ ,  $a = 15.407(4)$ ,  $c = 4.348(1)$  Å,  $V = 1032.3(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 3.02$  g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.7107$  Å,  $\mu = 84.4$  cm<sup>-1</sup>,  $F(000) = 824$ ,  $T = 298$  K,  $R = 0.033$  for 572 unique nonzero reflections. A crystallographic mirror plane, normal to the molecular plane, bisects the molecule. With the exception of the H atoms of the methyl group, the molecule is planar. A short intermolecular I...I contact of 3.746(1) Å involves I atoms only in the 3 and 5 positions and links molecules in sheets perpendicular to the  $c$  axis.

**Introduction.** Although 3,4,5-triiodotoluene has been known for some time (Wheeler & Liddle, 1909), its crystal structure has not been reported. Short intermolecular contacts are well known for halogen compounds, including simple organic halides such as *p*-iodotoluene (Ahn, Soled & Carpenter, 1972). Compounds such as hexaiodobenzene have been found to be planar, with short I...I intramolecular and intermolecular contacts (Steer, Watkins & Woodward, 1970).

**Experimental.** 2,6-Diiodo-4-methylaniline was treated with isoamyl nitrite and dimethyl disulfide at 353 K to produce small amounts of 3,4,5-triiodotoluene (1), as well as the main product 2,6-diiodo-4-methylthioanisole. Colorless parallelepiped of (1) 0.15 ×

0.2 × 0.42 mm;  $c$  axis approximately coaxial with fiber mount; Syntex  $P\bar{1}$  diffractometer; orientation matrix and unit-cell dimensions from 15 carefully centered reflections with  $2\theta < 27^\circ$ ; intensities measured for  $2\theta < 50^\circ$ ,  $k \geq h$  ( $h_{\max} = 12$ ,  $k_{\max} = 18$ ,  $l_{\max} = 5$ ), no indices negative;  $\theta$ - $2\theta$  scan from 1.0° below Mo  $K\alpha_1$  to 1.0° above Mo  $K\alpha_2$ ; scan rate 12.0° min<sup>-1</sup>; intensities of three standard reflections measured every 97 reflections showed no significant change during data collection; total of 581 independent reflections; 572 independent nonzero reflections used in structure solution and refinement; absorption corrections were made, range of transmission factors 0.515–0.546, ave. 0.532 (applied to  $F$ ); correction for extinction [ $F^* = F_c(1 - 0.0001kF_c^2/\sin 2\theta)$ ,  $k = 0.0020(1)$  (Sheldrick, 1976)]; structure determined by heavy-atom methods and refined by least squares on  $F$  (Busing, Martin & Levy, 1962); scattering factors and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974); all H atoms were located approximately and fixed in position (C–H = 1.0 Å; for H on ring C 360° –  $\angle C-C-C = 2$   $\angle C-C-H$ ; for H on methyl group  $\angle H-C-H = 109.5^\circ$ , but methyl not constrained to be in ordered position bisected by the mirror plane through the molecule); refinement completed with anisotropic displacement parameters† for nonhydrogen atoms, isotropic displacement parameters for H atoms (for H of

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† More commonly, but misleadingly, called 'vibration parameters' or 'temperature factor parameters'.