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(±)-Tartaric acid

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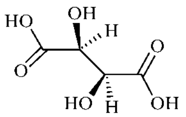
(±)-Tartaric acid, $C_4H_6O_6$, crystallized from ethanol in space group $P\bar{1}$. The structure is characterized by five hydrogen bonds, including the formation of a centrosymmetric carboxylic acid dimer which forms infinite chains along the body diagonal. These chains form sheets *via* hydrogen bonding between α-hydroxyl groups. The sheets are connected through a bifurcated hydrogen bond. Structural comparisons are made with homochiral (2*R*,3*R*)-(+)-tartaric acid.

Comment

Tartaric acid is an important additive in foods and pharmaceuticals. The structures of its various forms are of historical interest, dating back to the work of Pasteur (1848, 1850). The study of the molecular packing and hydrogen bonding in tartaric acid and its derivatives is relevant to the development of approaches for crystal engineering (Aakeröy *et al.*, 1992; Rychlewska & Warzajtis, 2000). Furthermore, tartaric acid has often been cited as a case satisfying Wallach's rule [see references in Brock *et al.* (1991)], which states that racemic crystals tend to be denser than their chiral counterparts (Wallach, 1895). The structure of the title compound, (I) (also known as DL-tartaric or racemic acid), has not been reported previously, although the structures of the homochiral [(+)-L-tartaric acid or (2*R*,3*R*)-(+)-tartaric acid, (II)] and *meso* forms have been determined (Stern & Beevers, 1950; Okaya *et al.*, 1966; Bootsma & Schoone, 1967). Anhydrous (I) can be recrystallized from water above 346 K; however, the crystals obtained were of too poor quality for structure determination (Parry, 1951). Consequently, Parry (1951) reported the structure of the hydrate. Very early reports of the structure of (I) were incomplete (Astbury, 1923; Gerstäker *et al.*, 1927). An appropriate comparison of the crystallographic features of the homochiral and heterochiral crystal forms requires the structures of both anhydrous forms. As part of our investigation of the molecular basis for differences between the near-IR spectra of (I) and (II) (Patel *et al.*, 2000), we have isolated a single crystal of (I) from absolute ethanol and determined its crystal structure. We report here the crystal structure of (I) and also compare its hydrogen-bonding features to those of (II).



(I)

The refined molecule and labeling scheme for (I) are shown in Fig. 1. The structure is characterized by five hydrogen bonds (Table 2). Unique to the structure of (I), relative to (II), is the hydrogen-bonding pattern associated with the carboxylic acid groups and the formation of centrosymmetric dimers in the former (Fig. 2). Graph-set analysis (Bernstein *et al.*, 1995) of the hydrogen bonds reveals four separate centrosymmetric rings between adjacent enantiomers, formed by four of the hydrogen-bond motifs. The fifth motif is a helical *C*(5) chain formed between molecules of like chirality, propagating along the *c* axis. A combination of the two unique motifs associated with the carboxylic acid dimers (O4—H4···O3 and O1—H1···O2) forms a chain of rings, *i.e.* $C_2^2(14)[R_2^2(8)R_2^2(8)]$. These twisted chains are crosslinked into sheets by the *C*(5) motif. Rings $R_2^2(12)$ and $R_2^2(10)$ result from O5—H5···O3 and O5—H5···O6 hydrogen bonds, respectively. Other binary graph sets form a variety of ladder and rail configurations with rings.

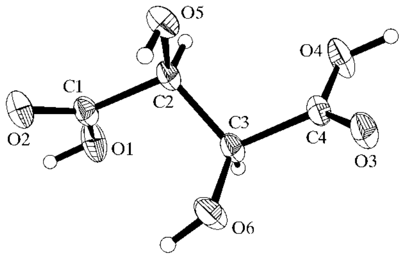


Figure 1
The molecular structure of (I), showing displacement ellipsoids at the 50% probability level.

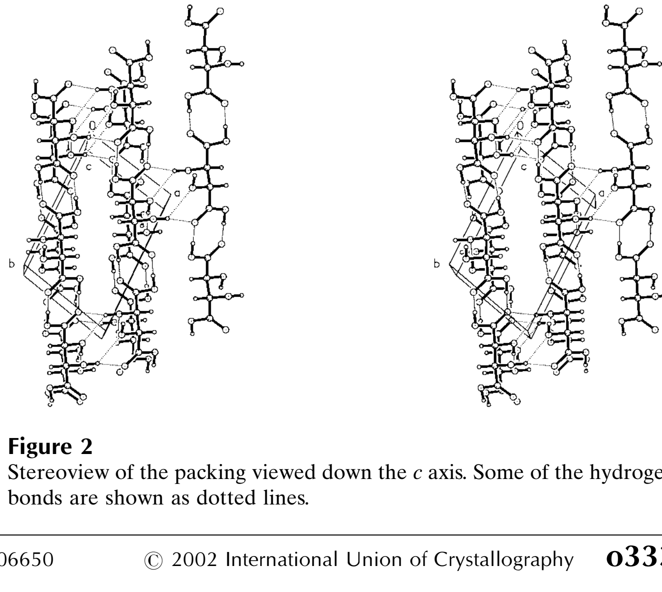


Figure 2
Stereoview of the packing viewed down the *c* axis. Some of the hydrogen bonds are shown as dotted lines.

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The angle between the two planes formed by the carboxyl groups is 55.9 (1)°. Carbonyl–carbonyl interactions of the antiparallel motif (Allen *et al.*, 1998) exist between C4—O3 carbonyl groups on adjacent molecules [O3···C4^{i} = 3.009 (1) Å; symmetry code: (i) 1 − *x*, −*y*, −*z*], and similarly between C1—O2 carbonyl groups [O2···C1^{ii} = 3.068 (1) Å; symmetry code: (ii) 2 − *x*, 1 − *y*, −*z*].

In constrast, for (II), carboxyl O atoms form hydrogen bonds with alcohol OH groups in addition to acidic OH groups on translationally related molecules in a head-to-tail arrangement along the *a* axis (Okaya *et al.*, 1966). Carboxylic acid dimers are not present despite their propensity to form (Leiserowitz, 1976). Both (I) and (II) contain binary graph-set $R_1^2(5)$, formed among two α-hydroxyl groups and a carboxyl O atom. However, (II) features $C(7)$ and $C_2^2(7)$ chains that form a ring with graph-set $R_3^3(12)$ (Rychlewska *et al.*, 1999; Rychlewska & Warzajtis, 2000). This feature links together three molecules and results in a more diffuse network in (II) than in (I). The impact of dimer formation and the altered hydrogen-bonding scheme in (I) is readily observed when comparing the splitting and shifting patterns of the ^{13}C CP/MAS (cross polarization/magic angle spinning) solid-state NMR and Raman spectra of the two forms (Patel *et al.*, 2000). There are other short O···O contacts [O4···O2^{iii} = 2.858 (1) Å, O4···O1^{iv} = 3.007 (1) Å and O6···O6^{v} = 2.930 (2) Å; symmetry codes: (iii) −1 + *x*, *y*, −1 + *z*; (iv) 1 − *x*, 1 − *y*, −*z*; (v) 2 −*x*, −*y*, 1 − *z*] that are not hydrogen-bonding contacts, as the associated H atoms are involved in hydrogen bonds with other O atoms.

The calculated value of Δ% (Brock *et al.*, 1991), a measure of the extent to which the racemate is denser than the homochiral form, was 2.2 for the tartaric acid pair. This value appears in the upper quartile for a wide range of structures examined by Brock *et al.* (1991) and is greater than the mean for pairs of chiral and racemic structures examined (0.92). The formation of dimers likely contributes to tighter packing in (I), as evidenced by its higher calculated density [1.796 *versus* 1.757 Mg m^{-3} for (II)]. Thus, the crystal pair reasonably satisfies Wallach's rule, provided the inherent bias in comparing resolvable racemic/chiral pairs is recognized (Brock *et al.*, 1991).

Experimental

Compound (I) (Sigma, St. Louis, MO, USA) was recrystallized from absolute ethanol by slow evaporation followed by vacuum drying at 373 K for 12 h. The X-ray powder diffraction patterns (D5000, Bruker AXS Inc., Madison, WI, USA) of the recrystallized material, as well as of the commercial bulk material, matched the pattern found in the ICDD for (I) (listed as DL-tartaric acid; ICDD, 1989). The theoretically generated X-ray powder diffraction pattern (*Materials Studio* 2.0; Accelrys, 2002) from the structure reported here corresponded with the experimentally determined pattern of the commercial bulk sample, verifying the identity of the single-crystal form (pattern available in supplementary material). The true density of the commercial bulk sample was determined by helium pycnometry (MPY-2; Quantachrome, Boynton Beach, FL, USA).

Crystal data

$C_4H_6O_6$
M_r = 150.09
Triclinic, $P\overline{1}$
a = 6.580 (1) Å
b = 9.186 (1) Å
c = 4.8966 (7) Å
α = 91.52 (1)°
β = 103.52 (1)°
γ = 74.78 (1)°
V = 277.50 (7) Å^3
Z = 2

D_x = 1.796 Mg m^{-3}
D_m = 1.786 Mg m^{-3}
D_m measured by He pycnometry
Mo *K*α radiation
Cell parameters from 50 reflections
θ = 13.9–17.4°
μ = 0.18 mm^{-1}
T = 293 (2) K
Prism, colorless
0.31 × 0.21 × 0.17 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
θ–2θ scans
3193 measured reflections
1598 independent reflections
1363 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.015

$\theta_{\max}$ = 30.0°
h = −9 → 9
k = −12 → 12
l = −6 → 6
4 standard reflections
frequency: 120 min
intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.101
S = 1.06
1598 reflections
115 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2 + 0.0695P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.012
$\Delta\rho_{\max}$ = 0.46 e Å^{-3}
$\Delta\rho_{\min}$ = −0.19 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—O1	1.312 (1)	C3—C4	1.520 (1)
C1—O2	1.216 (1)	C3—O6	1.402 (1)
C1—C2	1.522 (1)	C4—O3	1.219 (1)
C2—C3	1.546 (1)	C4—O4	1.308 (1)
C2—O5	1.409 (1)		
O2—C1—O1	125.3 (1)	O6—C3—C4	107.3 (1)
O2—C1—C2	122.9 (1)	O6—C3—C2	112.3 (1)
O1—C1—C2	111.8 (1)	C4—C3—C2	107.6 (1)
O5—C2—C1	112.2 (1)	O3—C4—O4	124.8 (1)
O5—C2—C3	112.3 (1)	O3—C4—C3	123.3 (1)
C1—C2—C3	108.9 (1)	O4—C4—C3	112.0 (1)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4···O3^{i}	0.88 (2)	1.78 (2)	2.660 (1)	173 (2)
O1—H1···O2^{ii}	0.88 (2)	1.80 (2)	2.675 (1)	175 (2)
O6—H6···O5^{iii}	0.88 (2)	1.96 (2)	2.841 (1)	177 (2)
O5—H5···O3^{iv}	0.88 (2)	2.09 (2)	2.962 (1)	170 (2)
O5—H5···O6^{iv}	0.88 (2)	2.48 (2)	2.975 (1)	116 (1)

Symmetry codes: (i) 1 − *x*, −*y*, −1 − *z*; (ii) 2 − *x*, 1 − *y*, 1 − *z*; (iii) *x*, *y*, 1 + *z*; (iv) 2 − *x*, −*y*, −*z*.

All H atoms were refined with isotropic displacement parameters [C—H = 0.88 (2)–0.93 (1) Å].

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977); cell refinement: *CAD*-4 *Operations Manual*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1636). Services for accessing these data are described at the back of the journal.

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