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Hydrogen bonding in (2R,3R)-(+)-2,3-dimethoxybutanedioic acid [(+)-tartaric acid dimethyl ether]

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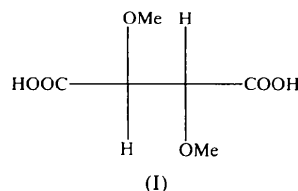
Abstract

The title acid, $C_6H_{10}O_6$, crystallized in the noncentrosymmetric space group $I2$, with half a molecule in the asymmetric unit (the molecular symmetry is 2). In the single type of hydrogen bond, the carboxylic H atom is ordered, and the $O_D \cdots O_A$ distance is 2.665(2) Å. Each molecule is linked to four others by hydrogen bonds and to two others by C—H$\cdots$O interactions. The dihedral angle between intramolecular carboxyl-group planes is 85.2(1)°.

Comment

This report on (2R,3R)-(+)-dimethoxybutanedioic acid, (I), is one of a series on hydrogen bonding in carboxylic acids. Compound (I) crystallized in the non-

(I)

centrosymmetric space group $I2$, with half a molecule in the asymmetric unit (the molecular symmetry is 2). The refined asymmetric unit and its symmetry-related partner, which together constitute a molecule, are shown in Fig. 1, together with the numbering scheme. A single hydrogen bond occurs in this structure, and in it the H atom is ordered. Geometric details are given in Table 2. Hydrogen-bond graph-set analysis (Bernstein *et al.*, 1995) gives the basic first-level descriptor as $C(4)[R_4^4(22)]$; there are no higher-level graphs. The one type of hydrogen bond links a central molecule to four other molecules. In addition, there is an intermolecular C—H$\cdots$O interaction for which the H$\cdots$O distance is less than the sum of the corresponding Bondi (1964) van der Waals radii, whose geometrical details are also given in Table 2. This latter interaction links a central molecule to two additional neighbors. Both the basic hydrogen-bond chain, which propagates along **b**, and the ring are apparent in Fig. 2, as are the C—H$\cdots$O interactions. The dihedral angle between the planes of the intramolecular carboxyl groups is 85.2(1)°.

For structural comparisons, the structure of (+)-tartaric acid as determined at 295 K by Albertsson *et al.* (1979) is appropriate. For the four bonds (not involving H atoms) in the half-molecule and the C2—C2^i bond [symmetry code: (i) $-x$, y, $2 - z$], the r.m.s. difference within corresponding pairs of values from
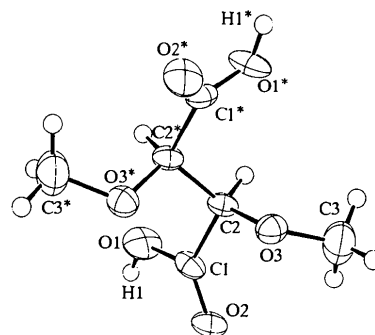

Fig. 1. *ORTEPII* (Johnson, 1976) drawing of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for all atoms except H, for which they have been set artificially small.
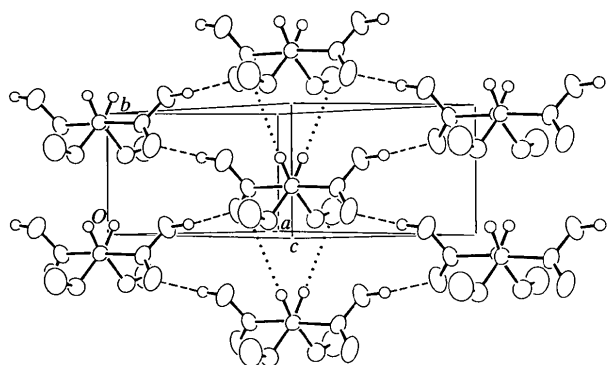
Fig. 2. *ORTEP*II (Johnson, 1976) packing diagram of (I). Displacement ellipsoids are drawn at the 50% probability level for all atoms except H, for which they have been set artificially small. For clarity, methyl group H atoms have been omitted. Hydrogen bonds are depicted by dashed lines and C—H···O interactions by dotted lines.

Albertsson *et al.* (1979) (two values averaged for each bond, except C2—C2^i) and from (I) is 0.009 Å. A similar comparison involving the protonated carboxyl-group portion of the hydrogen tartrate ion in ammonium hydrogen tartrate (van Bommel & Bijvoet, 1958) and (I) also gives an r.m.s. difference, within the five corresponding pairs of values, of 0.009 Å. For the six angular values similarly specified, which range over ~16°, the r.m.s. difference within pairs of corresponding values is 1.4° for Albertsson *et al.* (1979) and (I), and 0.9° for van Bommel & Bijvoet (1958) and (I). From the published atomic coordinates of (+)-tartaric acid determined by Hope & de la Camp (1972) [whose results are in good agreement with those of Albertsson *et al.* (1979)], the magnitude of that torsion angle which is the analog of C1—C2—C2^i—C1^i in (I) is 175.4 (1)° (my calculation); the C1—C2—C2^i—C1^i torsion angle in (I) is 175.8 (2)°. Thus, the backbone torsion is little affected by the derivatization.

Distances and angles of special interest are given in Table 1. All distances and angles fall within normal ranges. Excluding pairs of atoms in hydrogen-bonded groups or involved in C—H···O interactions, no intermolecular approach is less than the corresponding Bondi (1964) van der Waals radius sum.

Experimental

(2*R*,3*R*)-(+)-2,3-Dimethoxybutanedioic acid was obtained as a colorless prism from a crystalline sample in Dr D. J. Hart's chemical collection. This prism was cut to provide the experimental sample. Purdie & Irvine (1901) describe a synthesis of this compound, and report that $[\alpha]_D^{20}$ = +95.8° (*c* 0.0178, acetone). Optical polarimetry on material from our sample gave $[\alpha]_D^{20}$ = +85.3° (*c* 0.0156, acetone). Thus, the dextrorotation of the sample is confirmed. The estimated uncertainty in *c* (the dominant uncertainty in the measurement) is ~6%, due approximately equally to mass (31.2 mg) and

volume (2 ml) measurements; this is consistent with an upper limit for $[\alpha]_D^{20}$ of +90.5°.

Crystal data

$C_6H_{10}O_6$	Mo $K\alpha$ radiation
M_r = 178.14	λ = 0.71073 Å
Monoclinic	Cell parameters from 25
*I*2	reflections
a = 7.0863 (5) Å	θ = 14.5–17.5°
b = 4.3394 (6) Å	μ = 0.133 mm^{-1}
c = 13.2126 (6) Å	*T* = 296 K
β = 90.147 (5)°	Cut prism
V = 406.29 (6) Å^3	0.35 × 0.27 × 0.12 mm
Z = 2	Colorless
D_x = 1.456 Mg m^{-3}	
D_m not measured	

Data collection

AFC-5S diffractometer	*h* = 0 → 9
$\omega/2\theta$ scans	*k* = 0 → 6
Absorption correction: none	*l* = −18 → 18
706 measured reflections	6 standard reflections
659 independent reflections	every 150 reflections
569 reflections with	intensity variation: ±0.8%
$I > 2\sigma(I)$	(average maximum
R_{int} = 0.010	relative intensity)
θ_{max} = 30.03°	

Refinement

Refinement on F^2	$w = 1/\sigma^2(F^2)$
$R(F)$ = 0.031	$(\Delta/\sigma)_{max} < 0.01$
$wR(F^2)$ = 0.056	$\Delta\rho_{max}$ = 0.21 e Å^{-3}
S = 1.90	$\Delta\rho_{min}$ = −0.16 e Å^{-3}
659 reflections	Extinction correction: none
62 parameters	Scattering factors from
H atoms treated by a	Stewart *et al.* (1965) (H)
mixture of independent	and Creagh & McAuley
and constrained refinement	(1992) (C, O)

Table 1. *Selected geometric parameters (Å, °)*

O1—C1	1.315 (2)	O3—C3	1.421 (2)
O2—C1	1.205 (2)	C1—C2	1.525 (2)
O3—C2	1.403 (2)	C2—C2^i	1.527 (3)
O1—C1—O2	125.2 (1)	O2—C1—C2	123.1 (2)
O1—C1—C2	111.7 (1)	C1—C2—C2^i	110.3 (2)
C1—C2—C2^i—C1^i	175.8 (2)	C2—C2^i—O3^i—C3^i	−152.4 (1)
C1—C2—O3—C3	85.0 (2)	O3—C2—C2^i—O3^i	−71.2 (2)
O3—C2—C2^i—C1^i	52.3 (1)		

Symmetry code: (i) $-x, y, 2 - z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2^{ii}	0.84 (2)	1.84 (2)	2.665 (2)	172 (3)
C2—H2···O3^{iii}	1.01 (2)	2.41 (2)	3.386 (2)	162 (1)

Symmetry codes: (ii) $-\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (iii) $x, 1 + y, z$.

The absolute configuration is known from the work of Bijvoet and co-workers, *e.g.* van Bommel & Bijvoet (1958). Scan widths were (1.60 + 0.35tanθ)° in ω, with a background/scan time-ratio of 0.5. The data were corrected for Lorentz and

polarization effects. The Laue group assignment, systematic absences and non-centrosymmetric intensity statistics indicated space group *I*2 or *Im* (No. 5 or 8). Initial preference was given to *I*2, since it occurs more commonly and since the homochirality of the sample (incompatible with *Im*) had not yet been independently established. Refinement proceeded well and *I*2 was adopted. Difference Fourier methods were used to locate initial H-atom positions, and the H atoms were then refined isotropically. Refined C—H distances ranged from 0.99 (2) to 1.02 (4) Å, with a mean value of 1.00 (3) Å. Subsequently, the methyl group H atoms were made canonical, with C—H = 0.98 Å and U_{iso} = $1.2U_{eq}$ of the attached C atom. The refined O—H distance is given in Table 2. The extinction coefficient was predicted to be negative in the late stages of refinement, and was thus not included in the model. The maximum positive residual peak is located approximately midway between C1 and C2; the maximum negative peak is located ∼1.3 and 1.4 Å from O2 and C1, respectively.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

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3-(3-Indolyl)acrylamide

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Abstract

The title compound ($C_{11}H_{10}N_2O$) was isolated, together with other indole derivatives, from the acetone extract of the red algae *Chondria atropurpurea*. The acrylamide group deviates only slightly from the overall planarity of the entire molecule. The packing is stabilized by an intermolecular interaction between an amide H atom and the indole ring.

Comment

3-(3-Indolyl)acrylamide, (I), was isolated, together with other indole derivatives, from the acetone extract of the red algae *Chondria atropurpurea* Harvey (Rhodomelaceae). Chondriamide A, (II), is also found. The coexistence of both compounds in the above-mentioned extract favours the hypothesis of the biosynthetic mechanism proposed by Palermo *et al.* (1992) for (II). Further structural research on (II) and other derivatives will be carried out, based on the results presented in this report.
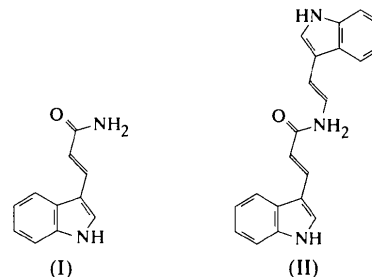
As can be expected from the chemical structural diagram, the title compound is a molecule with a marked planarity. The least-squares equation of the molecular plane is $-9.268\,(5) \times x + 11.182\,(7) \times y + 2.996\,(3) \times z = 3.500\,(3)$, and the maximum deviation is 0.143 (2) Å, for O14. Slight deviation from this planarity can be described through the relative orientations of the two main planar moieties, namely,