Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
O1	0.8696 (2)	0.8299 (2)	0.5653 (2)	0.0499 (5)
C1	0.8565 (3)	0.7482 (2)	0.4122 (3)	0.0445 (7)
C2	0.8927 (2)	0.8044 (2)	0.3114 (3)	0.0333 (6)
C3	0.9079 (2)	0.7166 (2)	0.1543 (3)	0.0305 (5)
C4	0.9607 (2)	0.7862 (2)	0.0807 (3)	0.0307 (5)
C5	0.8680 (2)	0.7864 (2)	−0.0560 (3)	0.0317 (5)
C6	0.7561 (2)	0.7132 (2)	−0.0938 (3)	0.0309 (5)
C7	0.7802 (2)	0.6653 (2)	0.0230 (3)	0.0306 (5)
C8	0.7446 (2)	0.5550 (2)	0.0294 (3)	0.0319 (5)
C9	0.6392 (2)	0.4767 (2)	−0.0439 (3)	0.0376 (6)
C10	0.6462 (3)	0.3703 (2)	−0.0190 (3)	0.0450 (7)
C11	0.7537 (3)	0.3418 (2)	0.0756 (3)	0.0450 (7)
C12	0.9825 (3)	0.4015 (2)	0.2480 (3)	0.0486 (7)
C13	1.0819 (3)	0.4828 (2)	0.3074 (4)	0.0522 (7)
C14	1.0719 (2)	0.5884 (2)	0.2806 (3)	0.0446 (7)
C15	0.9587 (2)	0.6106 (2)	0.1915 (3)	0.0339 (6)
C16	0.8564 (2)	0.5250 (2)	0.1265 (3)	0.0330 (5)
C17	0.8642 (2)	0.4198 (2)	0.1523 (3)	0.0392 (6)
C18	1.1720 (2)	0.8587 (2)	0.3050 (3)	0.0362 (6)
C19	1.2881 (2)	0.9210 (2)	0.3702 (3)	0.0433 (6)
C20	1.3221 (2)	0.9795 (2)	0.2871 (3)	0.0441 (7)
C21	1.2384 (2)	0.9737 (2)	0.1352 (3)	0.0414 (6)
C22	1.1222 (2)	0.9115 (2)	0.0701 (3)	0.0373 (6)
C23	1.0849 (2)	0.8524 (2)	0.1528 (3)	0.0311 (5)
C24	0.5271 (2)	0.6638 (2)	−0.2419 (3)	0.0389 (6)
C25	0.4209 (2)	0.6398 (2)	−0.3822 (3)	0.0472 (7)
C26	0.4293 (3)	0.6451 (3)	−0.5210 (3)	0.0521 (7)
C27	0.5429 (3)	0.6751 (2)	−0.5206 (3)	0.0503 (7)
C28	0.6492 (2)	0.6977 (2)	−0.3819 (3)	0.0402 (6)
C29	0.6428 (2)	0.6907 (2)	−0.2409 (3)	0.0332 (5)
C30	0.6797 (3)	0.8678 (3)	0.2113 (3)	0.0489 (7)
C31	0.6040 (3)	0.9501 (3)	0.1789 (3)	0.0656 (10)
C32	0.6548 (4)	1.0583 (3)	0.2105 (4)	0.0778 (12)
C33	0.7839 (4)	1.0845 (3)	0.2714 (4)	0.0639 (10)
C34	0.8573 (3)	1.0009 (2)	0.2994 (3)	0.0450 (7)
C35	0.8073 (2)	0.8923 (2)	0.2715 (3)	0.0356 (6)

Table 2. *Selected geometric parameters (Å, °)*

O1—C1	1.430 (3)	C4—C23	1.471 (3)
C1—C2	1.513 (3)	C5—C6	1.455 (3)
C2—C35	1.523 (3)	C6—C7	1.357 (3)
C2—C3	1.607 (3)	C6—C29	1.472 (3)
C3—C4	1.520 (3)	C7—C8	1.459 (3)
C3—C7	1.521 (3)	C8—C16	1.424 (3)
C3—C15	1.534 (3)	C15—C16	1.409 (3)
C4—C5	1.349 (3)		
O1—C1—C2	111.2 (2)	C4—C3—C15	125.0 (2)
C1—C2—C35	111.1 (2)	C7—C3—C15	101.6 (2)
C1—C2—C3	114.6 (2)	C4—C3—C2	107.7 (2)
C35—C2—C3	112.6 (2)	C7—C3—C2	109.3 (2)
C4—C3—C7	102.7 (2)	C15—C3—C2	109.4 (2)

The intensity data were corrected for Lorentz and polarization effects, and also for extinction. All non-H atoms were anisotropically refined. H atoms were refined on calculated positions with isotropic displacement parameters. The ethanolic H atom was allowed to rotate freely on its calculated position and although its final displacement parameter was large compared with the other H atoms, the refinement converged.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993*b*). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1261). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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cis-Aconitic Acid at 150 K

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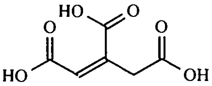
Abstract

cis-Aconitic acid (*cis*-1-propene-1,2,3-tricarboxylic acid, $C_6H_6O_6$) crystallizes with an intramolecular hydrogen bond between the two carboxylic acid groups linked by the C═C double bond and exhibits a complex intermolecular hydrogen-bond pattern. The two carboxylic acid groups involved in the intramolecular hydrogen bond are coplanar with the propene skeleton, while the third carboxylic group is twisted out of this plane with a dihedral angle of 66.21 (9)°.

Comment

Within the Krebs cycle, *cis*-aconitate originates from citrate catalyzed by the enzyme aconitase. The crystal structure of dipotassium *cis*-aconitate (Glusker, Orehowsky, Casciato & Carrell, 1972) has been determined in order to obtain information about a possible mechanism for this conversion. Our report, which is part of a project on the study of the formation of lipophilically wrapped polyion aggregates (Bock, John, Näther & Havlas, 1995; Bock, Dienelt, Schödel & Havlas, 1995), shows that the conformation of the dianion in the dipotassium salt and that in the crystal structure of the acid, (I), are similar.



(I)

All bond lengths and angles are within the usual range (Orpen *et al.*, 1994) (Fig. 1). The two carboxyl groups linked by the C═C double bond are in the plane of the propene skeleton and form a short intramolecular O—H···O hydrogen bond with distances O···O 2.443 (1) and H···O 1.43 (3) Å. This hydrogen bond is also present in the crystal structure of the dipotassium salt and, similarly, the third carboxyl group is considerably twisted out of the propene plane. The H3—O3—C5═O4 carboxyl group, acting as hydrogen donor in the intramolecular hydrogen bond, adopts an antiperiplanar arrangement, while the other two carboxyl groups are in the usual synperiplanar conformation. The H1—O1 hydroxyl group acts as a hydrogen-bond donor towards the O4 atom of a second molecule and O4 is, in turn, the hydrogen-bond acceptor from the H1—O1 hydroxyl group of a third molecule, with distances O1···O4 2.571 (1) and H1(O1)···O4 1.59 (2) Å. This arrangement results in a catemer motif (Leiserowitz, 1976; Berney, 1973) consisting of alternating intra- and intermolecular O—H···O hydrogen bonds (Fig. 2) and in which the connected molecules are related by the 2_1 screw axis parallel to the *b* axis.

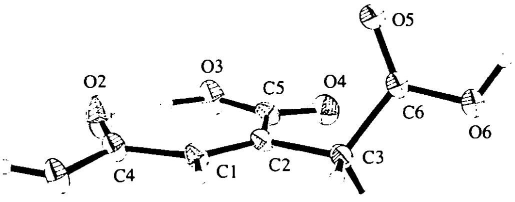


Fig. 1. The asymmetric unit of (I) showing the numbering scheme, with anisotropic displacement ellipsoids at the 50% probability level.

The third carboxyl group (H6—O6—C6═O5) exhibits the cyclic hydrogen-bonded dimer motif (Leiserowitz, 1976) around a crystallographic centre of inversion (Wyckoff letter *a*), with longer contact distances [O5···O6 2.663 (1) and H6(O6)···O5 1.79 (3) Å] between the molecules (Fig. 2). In addition, the molecules are connected by pairs of weak C1—H1···O1 hydrogen bonds (Desiraju, 1991; Desiraju & Pedireddi, 1992; Desiraju, Kashino, Coombs & Glusker, 1993) around a centre of inversion (Wyckoff letter *b*), with intermolecular contact distances C1···O1 3.477 (1) and H1(C1)···O1 2.52 (2) Å (Fig. 2). All these hydrogen bonds connect the molecules into undulated layers perpendicular to the *a* axis. No hydrogen bonds are found between these layers. The three carboxyl groups exhibit different degrees of carbonyl/hydroxyl disorder, as detectable by examination of the differences in bond lengths and angles around the carboxyl groups (Desiraju, 1989; Leiserowitz, 1976; Dieterich, Paul & Curtin, 1974). The differences between the C—O bond lengths within a carboxyl group, *i.e.* *d*[C—O(H)] − *d*(C═O), range from 0.072 (3) and 0.078 (4) to only 0.047 (3) Å for the carboxyl groups at C1, C2 and C3, respectively. These data imply that the carboxyl groups involved in the catemer motif of hydrogen bonds show no significant carbonyl/hydroxyl disorder, whereas the carboxyl group at C3, which participates in the hydrogen-bonded dimer motif, is partly disordered. This result is reasonable, since carbonyl/hydroxyl disorder within the dimer motif is facilitated by the fact that the crystal environment is usually not severely affected (Dunitz & Strickler, 1968), whereas the catemer motif should be more prohibitive towards this type of disorder. The values of the refined isotropic displacement parameters of the hydroxy H atoms increase in the order H1O < H3O < H6O, but the enlarged displacement parameter of H6O is caused by the discussed carbonyl/hydroxyl disorder, whereas the enlarged displacement parameter of H3O is more likely to originate from thermal motion along the O2···O3 axis of the short intramolecular hydrogen bond.

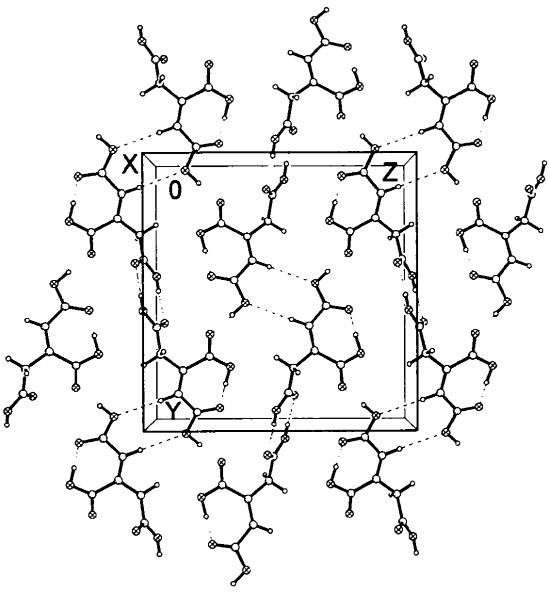


Fig. 2. Crystal packing viewed along the *a* axis. Dotted lines represent O—H···O hydrogen bonds and dashed lines represent C—H···O contacts.

Experimental

cis-Aconitic acid is commercially available. Crystals were obtained by isothermal distillation of petrol ether in a saturated solution of *cis*-aconitic acid in diethyl ether.

Crystal data

$C_6H_6O_6$
$M_r = 174.11$
Orthorhombic
Pbca
$a = 7.603\,(1)$ Å
$b = 13.634\,(2)$ Å
$c = 13.405\,(2)$ Å
$V = 1389.6\,(3)$ Å^3
$Z = 8$
$D_x = 1.664$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 80 reflections
$\theta = 10.2\text{–}19.4°$
$\mu = 0.154$ mm^{-1}
$T = 150\,(2)$ K
Block
$0.75 \times 0.65 \times 0.40$ mm
Colourless

Data collection

Siemens *P*4 four-circle diffractometer
ω-scans
Absorption correction: none
2623 measured reflections
2012 independent reflections
1637 observed reflections $[I > 2\sigma(I)]$

$R_{\text{int}} = 0.015$
$\theta_{\max} = 30°$
$h = -10 \rightarrow 1$
$k = -19 \rightarrow 1$
$l = -1 \rightarrow 18$
4 standard reflections monitored every 96 reflections intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0375$
$wR(F^2) = 0.0995$
$S = 1.029$
2012 reflections
125 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2 + 0.5385P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.414$ e Å^{-3}
$\Delta\rho_{\min} = -0.165$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	0.54701 (14)	0.53649 (6)	0.36507 (7)	0.0246 (2)
O2	0.5684 (2)	0.43688 (7)	0.23583 (8)	0.0379 (3)
O3	0.4600 (2)	0.27367 (7)	0.19233 (7)	0.0300 (2)
O4	0.32506 (14)	0.15268 (7)	0.26741 (7)	0.0281 (2)
O5	0.55895 (12)	0.11231 (6)	0.44784 (8)	0.0258 (2)
O6	0.30633 (13)	0.06452 (7)	0.51631 (9)	0.0316 (2)
C1	0.4475 (2)	0.37732 (8)	0.39085 (8)	0.0181 (2)
C2	0.39405 (15)	0.28554 (8)	0.37075 (8)	0.0165 (2)
C3	0.3146 (2)	0.22440 (8)	0.45253 (8)	0.0185 (2)
C4	0.5250 (2)	0.45155 (8)	0.32282 (9)	0.0211 (2)
C5	0.3923 (2)	0.23393 (8)	0.27156 (8)	0.0197 (2)
C6	0.4038 (2)	0.12713 (8)	0.47100 (8)	0.0184 (2)

Table 2. *Selected geometric parameters (Å, °)*

O1—C4	1.3001 (14)	C1—C2	1.343 (2)
O2—C4	1.228 (2)	C1—C4	1.484 (2)
O3—C5	1.2987 (15)	C2—C3	1.504 (2)
O4—C5	1.2214 (15)	C2—C5	1.504 (2)
O5—C6	1.2365 (15)	C3—C6	1.5099 (15)
O6—C6	1.2833 (14)		
C2—C1—C4	129.21 (11)	O4—C5—C2	117.91 (10)
C1—C2—C5	128.01 (10)	O3—C5—C2	121.61 (11)
O2—C4—O1	121.60 (11)	O5—C6—O6	124.13 (11)
O2—C4—C1	125.38 (11)	O5—C6—C3	122.06 (10)
O1—C4—C1	113.01 (10)	O6—C6—C3	113.75 (10)
O4—C5—O3	120.47 (11)		
C1—C2—C3—C6	−123.96 (12)	C2—C3—C6—O5	23.8 (2)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H3O$\cdots$O2	1.02 (3)	1.43 (3)	2.443 (1)	176 (2)
O1—H1O$\cdots$O4^{i}	0.98 (2)	1.59 (2)	2.571 (1)	177 (2)
O6—H6O$\cdots$O5^{ii}	0.89 (3)	1.79 (3)	2.663 (1)	170 (3)
C1—H1$\cdots$O1^{iii}	0.961 (17)	2.521 (17)	3.477 (1)	173 (1)

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

All C- and O-atom positions have been refined with anisotropic displacement parameters, while all H centres were located from the difference map. The positions and isotropic displacement parameters of the H1O, H3O, H6O and H1 atoms, which are involved in hydrogen bonds, were refined, while the others were placed in idealized positions and refined with fixed isotropic displacement parameters $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ using a riding model with C—H distances of 0.99 Å.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SK1040). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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N-[2-(1-Hydrazonoethyl)-3-benzofuranyl]-*p*-toluenesulfonamide

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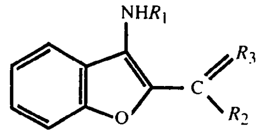
Abstract

The structure of the title compound, $C_{17}H_{17}N_3O_3S$, has been determined. It consists of two planar moieties, the benzofuran and *S*-aryl systems, which form an angle of 65.6 (1)° with one another.

Comment

Heterocyclic compounds containing a benzofuran moiety have been studied because they are active on the central nervous system. 2-Acetyl-3-aminobenzofurans and their corresponding 3-*N*-*p*-toluenesulfonyl derivatives were allowed to react with hydrazines in order to prepare the related hydrazones as starting materials for the synthesis of compounds which were expected to have psychotropic activity. Since only the *N*-*p*-toluenesulfonylbenzofurans gave hydrazones in good yield, X-ray structural investigations on the starting compounds and products of this preliminary synthesis were carried out in order to gain a better understanding of the mechanism of the reaction with hydrazines. So far, the structures of the starting compounds (1) (Bachechi, Coiro, Gatta, Settimj & Delfini, 1988) and (2) (Bachechi, Coiro, Delfini & Settimj, 1988), and of the product (3) (Bachechi, Coiro, Delfini & Settimj, 1991) have been reported. The present work deals with the crystal structure of another product, *N*-[2-(1-hydrazonoethyl)-3-benzofuranyl)]-*p*-toluenesulfonamide, (4), which was easily prepared by treatment of the acetyl derivative (1) with hydrazine.



(1) $R_1 = SO_2C_6H_4CH_3$; $R_2 = CH_3$; $R_3 = O$
(2) $R_1 = H$; $R_2 = CH_3$; $R_3 = O$
(3) $R_1 = SO_2C_6H_4CH_3$; $R_2 = CH_6H_5$; $R_3 = N{-}NH_2$
(4) $R_1 = SO_2C_6H_4CH_3$; $R_2 = CH_3$; $R_3 = N{-}NH_2$

A perspective view of (4) with the atom-numbering scheme is shown in Fig. 1. Bond distances and angles are normal and compare well with those of the analogous compounds (1), (2) and (3).

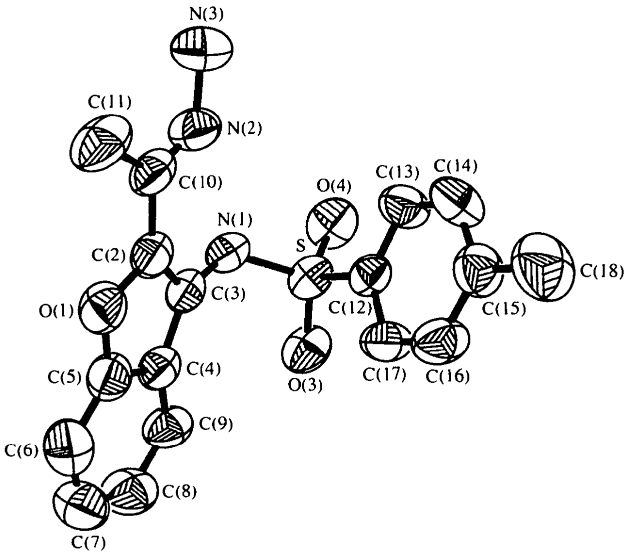


Fig. 1. A perspective view of the title molecule showing the labelling of the non-H atoms. Displacement ellipsoids are plotted at the 30% probability level.

The structure consists of two planar moieties, the benzofuran and the *S*-aryl systems, which form an angle of 65.6 (1)° with one another. The benzofuran moiety can be considered planar as is the case in the corresponding starting compound, (1). The mean plane through the benzofuran ring forms an angle of 3.5 (1)° with the plane through atoms C(10), C(11), N(2) and N(3) (Table 3). The C=N double bond thus lies in the plane of the benzofuran moiety.

An intramolecular hydrogen bond of 2.817 (4) Å is present between atoms N(1) and N(2). The hydrazone group assumes a *syn* configuration with respect to N(1) around the C(2)—C(10) bond and an *anti* configuration