

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1292). Services for accessing these data are described at the back of the journal.

References

- Blessing, R. H. (1987). *Crystallogr. Rev.* **1**, 3–58.
 Collet, A. (1998). Unpublished results.
 DeTitta, G. (1985). *J. Appl. Cryst.* **18**, 75–79.
 Enraf-Nonius (1994). *CAD-4 EXPRESS*. Version 5.1/1.2 Enraf-Nonius, Delft, The Netherlands.
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
 Gabard, J. & Collet, A. (1986). *Nouv. J. Chim.* **10**, 685–690.
 Jacques, J., Collet, A. & Wilen, S. H. (1994). *Enantiomers, Racemates and Resolutions*, pp. 94–95. Florida: Krieger Publishing Company.
 Jacques, J., Leclercq, M. & Brienne, M. J. (1981). *Tetrahedron*, **37**, 1727–1733.
 Johnson, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 Kennard, C. H. L., Smith, G. & White, A. H. (1982). *Acta Cryst.* **B38**, 868–875.
 Larsen, S. & Marthi, K. (1997). *Acta Cryst.* **B53**, 280–292, 803–811.
 Leiserowitz, L. (1976). *Acta Cryst.* **B32**, 775–802.
 Raghunathan, S., Chandrasekhar, K. & Pattabhi, V. (1982). *Acta Cryst.* **B38**, 2536–2538.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1999). **C55**, 956–958

(S)-2-Amino-3-methyl-1-butanol (2S,3S)-hydrogen tartrate monohydrate†

RIKKE MATSSON BRUUN AND SINE LARSEN

Centre for Crystallographic Studies, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark. E-mail: sine@xray.ki.ku.dk

(Received 16 September 1998; accepted 22 February 1999)

Abstract

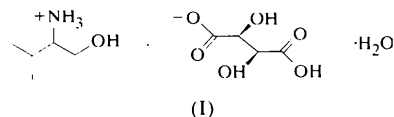
In the title compound, C₅H₁₄NO⁺·C₄H₅O₆⁻·H₂O, the hydrogen-bond system created by the chains of head-to-tail linked hydrogen tartrate ions and water molecules forms a V-shaped layer that is effective in discriminating between the two enantiomers of protonated 2-amino-3-methyl-1-butanol. The cation adopts a conformation that isolates its hydrophilic and hydrophobic parts, which is

† Alternative name: (S)-1-hydroxy-3-methylbut-2-ylammonium hydrogen (2S,3S)-tartrate monohydrate.

common for other cations containing the same N—C—C—O fragment.

Comment

Optically active tartaric acid is widely used as a resolving agent for racemic amines. The naturally occurring (2R,3R) enantiomer is most frequently used for the resolutions performed with the acid and base in equimolar amounts. It is a characteristic feature of the resulting diastereomeric salts that the crystal structures contain infinite chains of hydrogen tartrate ions. The carboxylic acid group from one anion is connected by a short hydrogen bond to the carboxylate group from another anion related by a translational period between 7 and 8 Å. Another property of the diastereomeric hydrogen tartrate salts is that they often form hydrates. A survey of hydrogen tartrate salts with chiral cations (Ryttersgaard & Larsen, 1999) showed that about half of the salts are solvated. The water molecules are well integrated into the hydrogen-bond system functioning as links between different chains of hydrogen-bonded hydrogen tartrate ions leading to the formation of V-shaped layers of hydrogen tartrate ions. The chiral environment created by these layers seems to be well suited to discriminate between the two enantiomers of a protonated amine which, by hydrogen bonds, can form links to the hydrogen tartrate layers. The survey also showed that smaller cations seem to fit best between the layers explaining the suitability of tartaric acid for such systems (Ryttersgaard & Larsen, 1999). To evaluate these results we undertook a structure determination of the diastereomeric salt, (I), formed between (S)-2-amino-3-methyl-1-butanol and (2S,3S)-tartaric acid to investigate how well it would conform with these observations.



The structure determination verified that the diastereomeric salt is hydrated – it contains one water molecule per ion pair. Fig. 1 illustrates the cation and anion found in the asymmetric unit. The bond lengths and angles for the hydrogen tartrate ion listed in Table 1 conform well with the geometry of hydrogen tartrate ions found in other crystal structures and it also adopts the conformation that is common for hydrogen tartrate salts (Ryttersgaard & Larsen, 1999). The torsion angles listed for the cation in Table 1 show that it has an extended conformation – the angle O7—C21—C22—N9, $-61.70(13)^\circ$, shows that the two hydrophilic groups are close. Fig. 1 illustrates how the cation can be considered composed of a hydrophilic moiety N9, C22, C21, O7 and a hydrophobic fragment comprised of the isopropyl group. A search in the Cambridge Structural

Database (Allen & Kennard, 1993) was conducted to investigate if this was a common feature for other cations containing the same O—C—C—N moiety. In the resulting 40 structures, the absolute value of the torsion angle N—C—C—O is found in a narrow range around 60° for the majority (33) of these with an average of 60.2°. In the remaining seven structures, the fragment is part of a ring system which imposes an eclipsed conformation on the N—C—C—O moiety.

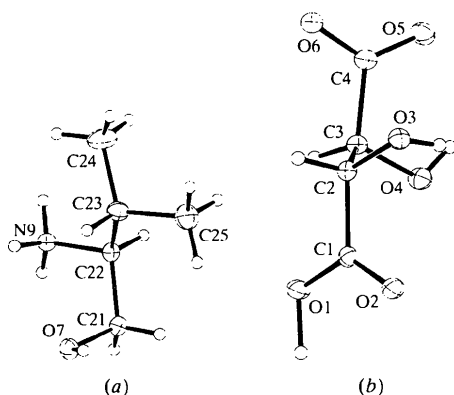


Fig. 1. (a) Molecular drawing of protonated (*S*)-2-amino-3-methyl-1-butanol and (b) (*2S,3S*)-hydrogen tartrate, showing the labelling of the atoms. The displacement ellipsoids are shown at the 50% probability level. H atoms are drawn as spheres of fixed radii.

The hydrogen tartrate ions form infinite chains along the *a* axis connected by the short hydrogen bond O1—H10··O6. The interactions between anions related by the translational symmetry is supported by the water molecule which is a hydrogen-bond donor to O2 and O3 and thereby bridges the anions as shown in the stereopair in Fig. 2. Another function of the water molecule

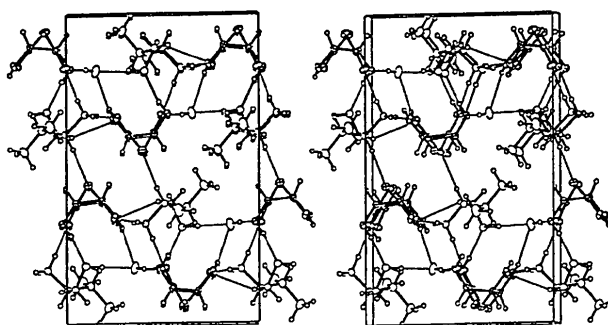


Fig. 2. Stereoscopic view of the crystal packing viewed along the *a* axis, with the *b* axis horizontal. The cation is drawn with open spheres. Hydrogen bonds are drawn as thin lines.

is to connect the chains of hydrogen tartrate ions by accepting a proton from O4 from a molecule related by translational symmetry along the *b* axis. The chiral environment created by the hydrogen-bonded anions and

water molecules accommodates the cation. Each cation is interacting with three different anions and a water molecule through hydrogen bonds and Fig. 2 shows how the cations are incorporated between V-shaped layers of hydrogen tartrate ions. The closest neighbour to the hydrophobic part of the cation is the equivalent part from another cation related by the twofold screw axis.

Thus the present structure conforms well with the general crystal-structure pattern for diastereomeric hydrogen tartrate salts. Both diastereomeric salts could be obtained for the related amine 2-amino-1-butanol with (*2R,3R*)-tartaric acid and both compounds contain one water molecule per ion pair as the present structure (Andersen, 1987). We also attempted to grow crystals of the equivalent diastereomeric salt by mixing (*S*)-2-amino-3-methyl-1-butanol with (*2R,3R*)-tartaric acid in water, but despite considerable efforts we were unsuccessful in producing a crystalline material. In this hypothetical salt the same hydrogen-bond interactions can be formed as in the present structure, but this causes the position of isopropyl groups to be different and this makes it impossible for them to stack as in the present structure, which could explain why this salt was not formed.

Experimental

Optically active (*S*)-2-amino-3-methyl-1-butanol and (*2S,3S*)-tartaric acid in the molar ratio 1:1 were dissolved in the smallest possible amount of water. The colourless solution was boiled for a few minutes. Crystals suitable for X-ray diffraction were obtained after three hours storage at room temperature.

Crystal data

$C_5H_{14}NO^+ \cdot C_4H_5O_6^- \cdot H_2O$
 $M_r = 271.27$
 Orthorhombic
 $P2_12_12_1$
 $a = 7.2691(7) \text{ \AA}$
 $b = 10.4214(13) \text{ \AA}$
 $c = 16.868(2) \text{ \AA}$
 $V = 1277.9(3) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.410 \text{ Mg m}^{-3}$
 D_m not measured

Cu $K\alpha$ radiation
 $\lambda = 1.54184 \text{ \AA}$
 Cell parameters from 20 reflections
 $\theta = 39.47\text{--}42.19^\circ$
 $\mu = 1.073 \text{ mm}^{-1}$
 $T = 122.0(5) \text{ K}$
 Prism
 $0.44 \times 0.12 \times 0.10 \text{ mm}$
 Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω - 2θ scans
 Absorption correction: none
 4549 measured reflections
 1523 independent reflections (plus 2891 Friedel-related reflections)

2503 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.012$
 $\theta_{max} = 74.92^\circ$
 $h = 0 \rightarrow 9$
 $k = 0 \rightarrow 13$
 $l = -20 \rightarrow 21$
 5 standard reflections every 600 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.073$
 $S = 1.077$
 2549 reflections
 248 parameters
 H atoms treated by a
 mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0481P)^2$
 $+ 0.2260P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.006$

$\Delta\rho_{\max} = 0.224 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.166 \text{ e } \text{\AA}^{-3}$
 Extinction correction:
SHELXL97 (Sheldrick,
 1997)
 Extinction coefficient:
 0.0071 (5)
 Scattering factors from
International Tables for
Crystallography (Vol. C)
 Absolute structure:
 Flack (1983)
 Flack parameter = 0.09 (14)

Table 1. Selected geometric parameters (Å, °)

O1—C1	1.2853 (16)	C3—C4	1.5382 (18)
O2—C1	1.2299 (16)	N9—C22	1.5085 (16)
O3—C2	1.4063 (16)	O7—C21	1.4208 (16)
O4—C3	1.4193 (15)	C21—C22	1.5234 (18)
O5—C4	1.2356 (16)	C22—C23	1.5369 (18)
O6—C4	1.2781 (16)	C23—C24	1.524 (2)
C1—C2	1.5417 (18)	C23—C25	1.5289 (19)
C2—C3	1.5318 (17)		
O2—C1—C2—O3	-2.4 (2)	C2—C3—C4—O5	121.2 (1)
O1—C1—C2—O3	176.6 (1)	O4—C3—C4—O6	-179.5 (1)
O2—C1—C2—C3	122.9 (1)	C2—C3—C4—O6	-59.1 (1)
O1—C1—C2—C3	-58.1 (1)	O7—C21—C22—N9	-61.7 (1)
O3—C2—C3—O4	72.9 (1)	O7—C21—C22—C23	61.2 (1)
C1—C2—C3—O4	-51.8 (1)	N9—C22—C23—C24	-51.6 (2)
O3—C2—C3—C4	-47.9 (1)	C21—C22—C23—C24	-172.1 (1)
C1—C2—C3—C4	-172.6 (1)	N9—C22—C23—C25	-174 (1)
O4—C3—C4—O5	0.8 (2)	C21—C22—C23—C25	65.4 (2)

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

D—H...A	D—H	H...A	D...A	D—H...A
O1—H10...O6 ⁱ	1.15 (3)	1.33 (3)	2.4622 (13)	169 (3)
O8—H81...O3 ⁱⁱ	0.93 (3)	1.77 (3)	2.6987 (14)	175 (2)
O8—H82...O2 ⁱⁱⁱ	0.78 (3)	2.01 (3)	2.7805 (15)	170 (2)
O3—H30...O7 ^{iv}	0.81 (2)	1.85 (2)	2.6493 (15)	170 (2)
O4—H40...O8 ^v	0.81 (2)	2.33 (2)	2.9007 (16)	128.9 (18)
O7—H7...O8 ^{vi}	0.85 (2)	1.80 (2)	2.6424 (15)	176 (2)
N9—H91...O4 ^{vii}	0.92 (2)	1.90 (2)	2.8183 (15)	174.0 (16)
N9—H92...O5 ^{viii}	0.91 (2)	1.97 (2)	2.8689 (15)	169.3 (19)
N9—H93...O2 ^{ix}	0.894 (17)	1.975 (18)	2.8358 (15)	161.0 (16)

Symmetry codes: (i) $x - 1, y, z$; (ii) $2 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $\frac{3}{2} - x, 1 - y, z - \frac{1}{2}$; (v) $x, 1 + y, z$; (vi) $\frac{3}{2} - x, -y, \frac{1}{2} + z$; (vii) $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$; (viii) $x - \frac{1}{2}, \frac{3}{2} - y, 1 - z$; (ix) $\frac{3}{2} - x, 1 - y, \frac{1}{2} + z$.

After anisotropic displacement parameters were introduced for all the non-H atoms, all H atoms were introduced in the positions calculated from the difference Fourier map. The hydrogen positional parameters were included in the refinement and given isotropic displacement parameters equal to $1.2U_{\text{eq}}$ or $1.5U_{\text{eq}}$ of the parent C or O atoms, respectively. The absolute configuration of the optically active diastereomer was determined by refinement of the absolute structure parameter (Flack, 1983).

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *DREADD* (Blessing, 1987). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEPII* (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1047). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
 Andersen, J. E. T. (1987). Masters thesis, University of Copenhagen, Denmark.
 Blessing, R. H. (1987). *Crystallogr. Rev.* **1**, 3–58.
 Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 Ryttersgaard, C. & Larsen, S. (1999). In preparation.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1999). **C55**, 958–960

1-D-3,4-Anhydro-1,2:5,6-di-O-isopropylidene-*allo*-inositol

ANDREW FALSHAW, GRAEME J. GAINSFORD AND CORNELIS LENSINK

Industrial Research Limited, PO Box 31-310, Lower Hutt, New Zealand. E-mail: g.gainsford@irl.cri.nz

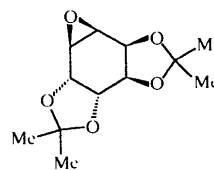
(Received 1 October 1998; accepted 9 February 1999)

Abstract

The title compound was isolated from the reaction of the 3,4-bis-*O*-mesylate of 1-D-1,2:5,6-di-*O*-isopropylidene-*chiro*-inositol with lithium diphenylphosphide in tetrahydrofuran. The structure consists of independent molecules of 1-D-3,4-anhydro-1,2:5,6-di-*O*-isopropylidene-*allo*-inositol, C₁₂H₁₈O₅. The two fused dioxolane rings adopt identical envelope conformations around the inositol ring.

Comment

The current interest in the use of carbohydrate molecules as asymmetric ligand fragments for homoge-



(I)