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Quininium Hydrogen (*S,S*)-Tartrate Hemihydrate, a Salt with a Unique Conformation of the Hydrogen Tartrate Ion

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Abstract

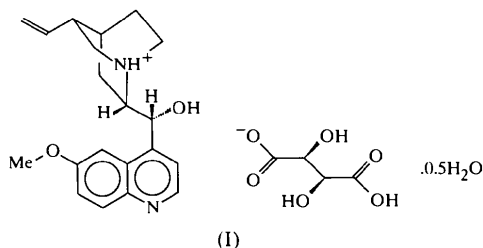
Two independent ion pairs [(6-methoxy-4-quinoly)(5-vinyl-1-azoniabicyclo[2.2.2]octan-2-yl)methanol hydrogen 2,3-dihydroxybutanedioate] and a water molecule are found in the asymmetric unit of 2C₂₀H₂₅N₂O₂⁺·2C₄H₅O₆⁻·H₂O. The two cations are virtually identical, but the two anions have markedly different stereochemistries. One of these anions adopts a unique conformation not observed previously for hydrogen tartrate ions. The packing resembles the arrangement in cinchonidinium (*S*)-mandelate, with hydrogen-bonded chains of alternating cations and anions. The herringbone stacking of the quinoline ring systems of the cations resembles the pattern seen in other cinchona structures.

Comment

A traditional method used to isolate the pure enantiomers from a racemic mixture is through the formation of diastereomeric compounds. The racemate is reacted with a suitable resolving agent, *i.e.* an optically active

compound with which it can form diastereomeric salts. The resulting salts may differ so much in their solubility that separation of the enantiomers can be achieved.

As part of our investigations of the factors that influence the suitability of a resolving agent, we are investigating the diastereomeric salts formed by the cinchona alkaloids and optically active tartaric acid. Both the cinchona alkaloid quinine and tartaric acid are frequently used as resolving agents for racemic acids and bases, respectively, and the salt, (I), formed by the reaction of quinine with optically pure (*S,S*)-tartaric acid was an obvious candidate for structure determination.



Two independent ion pairs (*A* and *D*) are found in the asymmetric unit. Like the free base, protonated quinine is a rather rigid molecule. In accordance with this, the two cations have almost identical geometry and stereochemistry (Fig. 1), and compare well with the geometry of the quininium ion in its mandelate salt (Gjerløv & Larsen, 1997*b*). The only significant variation of the stereochemistry involves the vinyl group, which is the most flexible part of the cation. In the present structure, the C24–C25–C26–C27 torsion angles are 127.5(2) and 116.0(2)° (for the ions labelled *A* and *D*, respectively), close to the average value found in a comparison of different compounds of cinchona alkaloids (Gjerløv & Larsen, 1997*a*). In the quininium mandelate salt, the corresponding torsion angle is 114.2(2)° (Gjerløv & Larsen, 1997*b*).

The two anions adopt significantly different conformations in the crystal, as shown in Fig. 1. A search in the Cambridge Structural Database (Allen & Kennard, 1993) for hydrogen tartrate ions resulted in 89 salts of organic cations. In all these compounds, the hydrogen tartrate ions have an extended conformation with the backbone torsion angles (C1–C2–C3–C4) in a narrow range of ±16° around 180°. The *A* anion conforms well with this picture, with a torsion angle of 172.80(13)°, whereas the equivalent angle in the *D* anion is –48.5(2)°. This first example of a hydrogen tartrate ion in a quite unique conformation is likely to be an effect of the crystal packing.

Each cation has two hydrogen-bond donors (O18 and N2) and only one hydrogen-bond acceptor (O18), whereas each hydrogen tartrate ion has three potential hydrogen-bond donors and six acceptor atoms. One water molecule with two donor H atoms and one acceptor is also present in the structure. All potential

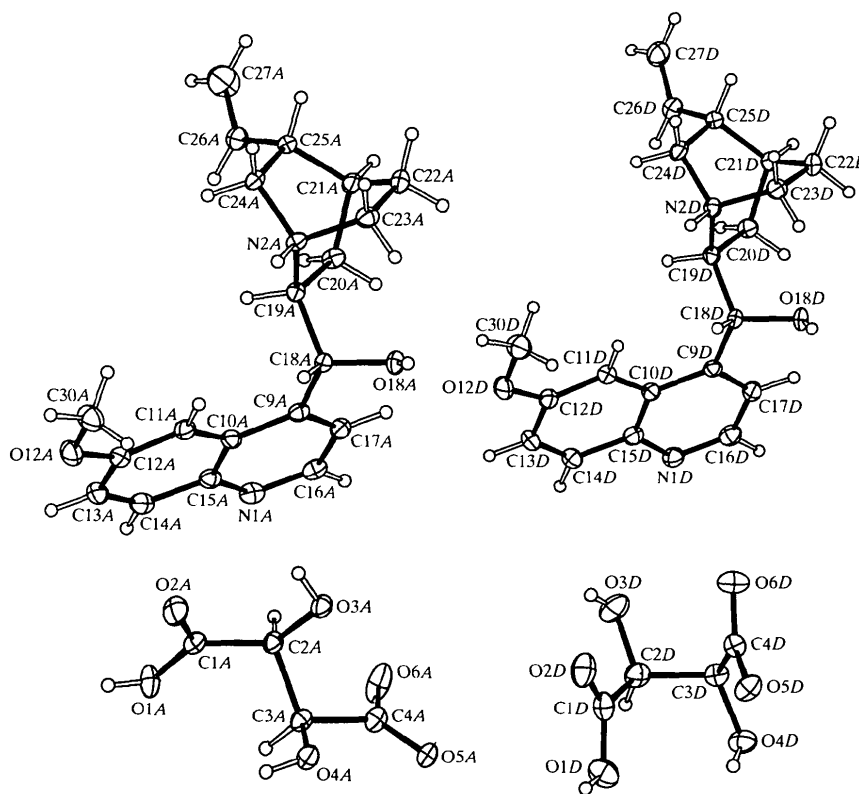


Fig. 1. ORTEPII (Johnson, 1976) drawing of the two ion pairs of (I). The displacement ellipsoids enclose 50% probability and the H atoms are drawn as spheres with a fixed radius.

hydrogen-bond donors take part in hydrogen bonds, with three of the H atoms (H43A, H48A and H52A) involved in three-centre or bifurcated hydrogen bonds. Another unique characteristic among the hydrogen bonds listed in Table 2 is the presence of three intramolecular hydrogen bonds in the hydrogen tartrate ions. Such intramolecular hydrogen bonds are frequently observed in other α -hydroxy acids like mandelic acid (Larsen & Lopez de Diego, 1993). Intermolecular hydrogen bonds link the hydrogen tartrate anions, water molecules and the hydrophilic parts of the cations into layers, as shown in the packing diagram (Fig. 2).

The arrangement of cations and anions is very similar to the packing in the cinchonidinium (*S*)-mandelate salt (Gjerløv & Larsen, 1997a). The only difference between quinine and cinchonidine is the lack of the methoxy group at C12 in the latter. The hydrogen (*S,S*)-tartrate ion and the (*S*)-mandelate ion each contain an α -hydroxycarboxylic acid moiety, but apart from this, they are not structurally similar and one would not have predicted that they could form salts so closely related structurally. Cinchonidinium (*S*)-mandelate crystallizes in the same space group as the present structure, with very similar values for the *a* and *b* axes [21.400 (2) and 6.2777 (6) Å, respectively]. The *c* axis of 17.853 (2) Å corresponds to half of the *c* axis in quininium hydrogen

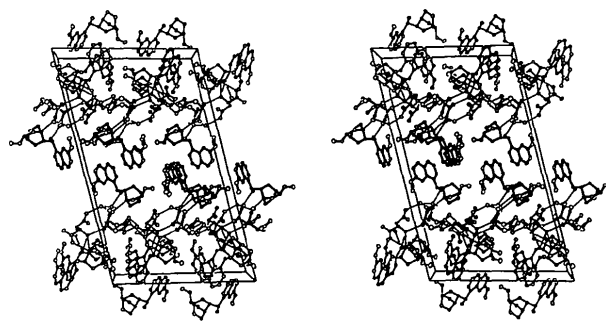


Fig. 2. A stereopair illustrating the crystal packing. The structure is viewed along the *b* axis with the *a* axis horizontal. The ion pair labelled *D* is drawn with open bonds. The intermolecular hydrogen bonds are shown as thin lines.

(*S,S*)-tartrate and therefore only one ion pair is found in the asymmetric unit of the cinchonidinium salt.

A characteristic feature of the crystal packing of the cinchona mandelates is their hydrogen-bonded chains of alternating cations and anions. Each cation interacts with two anions that are related by translational symmetry along a *ca* 6.2 Å axis. Similar chains of cations and anions parallel to the *b* axis are found in quininium hydrogen (*S,S*)-tartrate, but the cation–anion interactions are different in the two different ion-pair chains, as

shown in Fig. 2 and Table 2. In the *A* chain, the N2—H group forms three-centre hydrogen bonds to the hydroxy group (O4) and the O5 atom of the carboxylate group, and O18—H forms three-centre hydrogen bonds to the two hydroxy groups of an anion translated along the *b* axis. The interactions in the chain formed by the *D* ion pairs resemble the arrangement found in the mandelate salts. The N2—H group is hydrogen bonded to one of the O atoms (O6) of the carboxylate group and O18—H is hydrogen bonded to the other O atom (O5) of an anion related by translation along the *b* axis. This arrangement of hydrogen-bonded chains leads to the same herring-bone stacking of the quinoline ring systems of the cations as found in the cinchonidinium mandelate salts (Gjerløv & Larsen, 1997*a*). The quinoline systems related by the crystallographic twofold axis make interplanar angles of 63.8(1) and 65.7(1)° for the *A* and *D* cations, respectively.

It is particularly noteworthy that the hydrogen tartrate ions do not form the head-to-tail arrangement found in almost all hydrogen tartrate structures, where the anions are linked by short O—H...O hydrogen bonds between the carboxylic acid group of one molecule and the carboxylate group of another anion related by a translational period of *ca* 7 Å (Fogassy *et al.*, 1986). The two anions form an anion pair linked by one such hydrogen bond (O1D—H41D...O6A); its two terminal carboxy groups form hydrogen bonds with the cations and are part of the cation-anion chains. In the present structure, it appears that it is the interactions between the cinchona cations that exert the strongest effect on the crystal packing.

Experimental

Suitable crystals of (I) were obtained after slow evaporation of a solution prepared by mixing quinoline (0.4 mol) in ethanol (20 ml) with (*S,S*)-tartaric acid (0.4 mol) in an equivalent amount of ethanol.

Crystal data

$2C_{20}H_{25}N_2O_2^+ \cdot 2C_4H_5O_6^- \cdot H_2O$

$M_r = 967.02$

Monoclinic

*C*2

a = 21.198 (8) Å

b = 6.3283 (9) Å

c = 35.442 (9) Å

$\beta = 104.44(2)^\circ$

V = 4604 (2) Å³

Z = 4

$D_x = 1.395 \text{ Mg m}^{-3}$

D_m not measured

Cu *K*α radiation

$\lambda = 1.5418 \text{ Å}$

Cell parameters from 20 reflections

$\theta = 28.78\text{--}40.31^\circ$

$\mu = 0.888 \text{ mm}^{-1}$

T = 122.0 (5) K

Rod

0.6 × 0.1 × 0.1 mm

Transparent

Data collection

Enraf-Nonius CAD-4 diffractometer

ω -2 θ scans

Absorption correction: none

10 808 measured reflections

9338 independent reflections

8929 reflections with

$I > 2\sigma(I)$

$R_{int} = 0.021$

$\theta_{max} = 74.88^\circ$

h = 0 → 26

k = -7 → 7

l = -44 → 42

4 standard reflections

frequency: 167 min

intensity decay: none

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.098$

S = 1.036

9338 reflections

640 parameters

H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0601P)^2 + 1.5909P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.051$

$\Delta\rho_{max} = 0.200 \text{ e Å}^{-3}$

$\Delta\rho_{min} = -0.386 \text{ e Å}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Absolute structure: Flack (1983)

Flack parameter = 0.09 (10)

Table 1. Selected geometric parameters (Å, °)

C1A—O2A	1.215 (2)	C1D—O2D	1.213 (2)
C1A—O1A	1.318 (2)	C1D—O1D	1.304 (3)
C1A—C2A	1.521 (2)	C1D—C2D	1.528 (3)
C2A—O3A	1.4163 (19)	C2D—O3D	1.410 (2)
C2A—C3A	1.527 (2)	C2D—C3D	1.555 (3)
C3A—O4A	1.4183 (19)	C3D—O4D	1.421 (2)
C3A—C4A	1.527 (2)	C3D—C4D	1.531 (2)
C4A—O5A	1.247 (2)	C4D—O5D	1.247 (2)
C4A—O6A	1.272 (2)	C4D—O6D	1.263 (2)
C9A—C18A	1.520 (2)	C9D—C18D	1.522 (2)
C15A—N1A	1.364 (2)	C15D—N1D	1.372 (2)
N1A—C16A	1.317 (2)	N1D—C16D	1.319 (2)
C18A—O18A	1.424 (2)	C18D—O18D	1.420 (2)
C18A—C19A	1.542 (2)	C18D—C19D	1.543 (2)
C19A—N2A	1.520 (2)	C19D—N2D	1.515 (2)
C23A—N2A	1.505 (2)	C23D—N2D	1.510 (2)
N2A—C24A	1.507 (2)	N2D—C24D	1.504 (2)
C25A—C26A	1.506 (2)	C25D—C26D	1.501 (2)
C26A—C27A	1.309 (3)	C26D—C27D	1.316 (3)
O2A—C1A—O1A	124.10 (16)	O2D—C1D—O1D	126.92 (19)
O3A—C2A—C1A	111.58 (14)	O3D—C2D—C1D	111.66 (16)
O4A—C3A—C4A	108.87 (13)	O4D—C3D—C4D	112.32 (15)
O5A—C4A—O6A	125.45 (17)	O5D—C4D—O6D	125.88 (15)
C9A—C18A—C19A	106.88 (12)	C9D—C18D—C19D	109.09 (13)
N2A—C19A—C18A	113.35 (12)	N2D—C19D—C18D	111.90 (13)
C27A—C26A—C25A	123.42 (18)	C27D—C26D—C25D	124.38 (17)
O1A—C1A—C2A—O3A	−175.11 (13)		
O3A—C2A—C3A—O4A	56.47 (17)		
C1A—C2A—C3A—C4A	172.80 (13)		
O4A—C3A—C4A—O6A	−174.49 (16)		
C17A—C9A—C18A—O18A	−25.2 (2)		
C17A—C9A—C18A—C19A	95.96 (17)		
C18A—C19A—C20A—C21A	−133.24 (14)		
C20A—C21A—C22A—C23A	−58.42 (18)		
C22A—C23A—N2A—C19A	59.65 (17)		
N2A—C24A—C25A—C26A	124.23 (15)		
C24A—C25A—C26A—C27A	127.5 (2)		
O1D—C1D—C2D—O3D	156.38 (16)		
O3D—C2D—C3D—O4D	−161.34 (14)		
C1D—C2D—C3D—C4D	−48.5 (2)		
O4D—C3D—C4D—O6D	−23.7 (2)		
C17D—C9D—C18D—O18D	−20.5 (2)		
C17D—C9D—C18D—C19D	100.56 (18)		
C18D—C19D—C20D—C21D	−127.58 (15)		
C20D—C21D—C22D—C23D	−62.20 (18)		

C22D—C23D—N2D—C19D	56.97 (18)
N2D—C24D—C25D—C26D	128.03 (15)
C24D—C25D—C26D—C27D	116.0 (2)

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N,N'-Bis(5-bromo-2-hydroxybenzylidene)-1,3-propanediamine

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

D—H...A	H...A	D...A	D—H...A
O3A—H43A...O2A	2.37	2.736 (2)	107
O3D—H43D...O2D	2.27	2.728 (2)	115
O4D—H44D...O6D	2.40	2.698 (2)	102
O1A—H41A...O61 ⁱ	1.74	2.564 (2)	165
O3A—H43A...O5A ⁱⁱ	2.07	2.861 (2)	158
O4A—H44A...O4D ⁱ	1.92	2.747 (2)	166
O1D—H41D...O6A	1.66	2.488 (2)	167
O18A—H48A...O3A ⁱⁱⁱ	2.12	2.872 (2)	149
O18A—H48A...O4A ⁱⁱⁱ	2.49	3.165 (2)	138
N2A—H52A...O4A	2.38	2.997 (2)	126
N2A—H52A...O5A	1.95	2.817 (2)	160
N2D—H52D...O6D	1.80	2.740 (2)	162
O18D—H48D...O5D ⁱ	1.83	2.657 (2)	171
O61—H61A...O5D ⁱⁱ	1.93 (3)	2.720 (2)	156 (3)
O61—H61B...O6D	1.86 (3)	2.725 (2)	166 (3)

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

The data reduction was performed with the *DREDD* programs (Blessing, 1989). Direct methods failed to provide a solution and Patterson search methods (*PATSEE*; Egert & Sheldrick, 1985) were employed instead. Cinchonidine without substituents was used as a search model and gave the positions of the cations. The refinement of the structure was performed with *SHELXL93* (Sheldrick, 1993) and in the final stages with *SHELXL97* (Sheldrick, 1997). The H atoms, shown clearly in the difference electron-density map, were fixed in idealized positions, each with an isotropic displacement parameter of $1.5U_{eq}$ of the attached atom.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1012). Services for accessing these data are described at the back of the journal.

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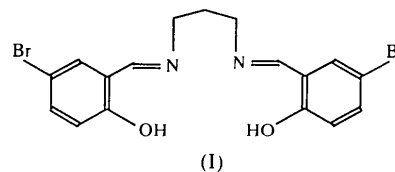
Abstract

The title compound {alternative name for this Schiff base: 4,4'-dibromo-2,2'-[propanediylbis(nitrilomethylidene)]diphenol; C₁₇H₁₆Br₂N₂O₂} displays two strong intramolecular N...H—O hydrogen bonds within each salicylideneimine unit. The molecule is not planar and the two aromatic rings are inclined at an angle of 69.8 (1)°.

Comment

Schiff bases and their biologically active complexes have been studied extensively over the past decade. Although numerous transition metal complexes of Schiff bases have been structurally characterized, relatively few free Schiff bases have been similarly characterized (Garnovskii *et al.*, 1993). *N*-Salicylideneaniline and its derivatives show photochromism and thermochromism in the solid state (Cohen *et al.*, 1964). These effects are produced by intramolecular proton transfer associated with a change in the π -electron configuration (Hadjoudis *et al.*, 1987).

In the course of a structural investigation of Schiff bases (Elerman *et al.*, 1991, 1992, 1994, 1995, 1997, 1998; Elmali *et al.*, 1995; Elmali & Elerman, 1997, 1998; Elmali, Elerman & Zeyrek, 1998), the structure of the tetradentate Schiff base ligand, (I), was determined.



Several non-planar tetradentate Schiff bases similar to (I) have been reported (Pahor *et al.*, 1976, 1978; Subrahmanyam *et al.*, 1982; Cimerman *et al.*, 1992; Senn & Nowacki, 1977; Elerman *et al.*, 1991, 1994; Corden *et al.*, 1996). The title molecule is also not planar. The