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Key indicators

Single-crystal X-ray study
T = 130 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
R factor = 0.049
wR factor = 0.088
Data-to-parameter ratio = 15.1

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Brucinium toluene-4-sulfonate trihydrate at 130 K

The low-temperature (130 K) structure of the 1:1 proton-transfer compound of brucine with toluene-4-sulfonic acid (systematic name: 2,3-dimethoxy-10-oxostrychnidinium toluene-4-sulfonate trihydrate), $\text{C}_{23}\text{H}_{27}\text{N}_2\text{O}_4^+ \cdot \text{C}_7\text{H}_7\text{O}_3\text{S}^- \cdot 3\text{H}_2\text{O}$, has been determined. The asymmetric unit contains two cations, two anions and six molecules of water. Brucinium cations form the familiar undulating head-to-tail ribbon structures, which associate with the toluene-4-sulfonate anions and the water molecules in the interstitial cavities through hydrogen-bonding associations involving all available donor and acceptor atoms on all species. The result is a framework polymer structure.

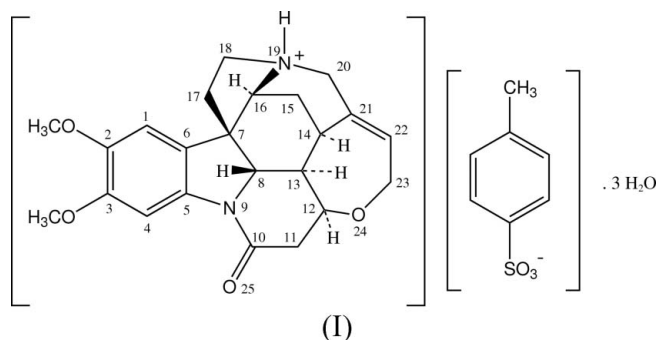
Comment

The crystal structures of the proton-transfer compounds of strychnine and brucine with chiral carboxylic acids are numerous, the particular utility being the resolution and subsequent absolute configuration analysis afforded by these alkaloids. The compounds include the strychninium and brucinium salts of N-protected amino acids (Gould & Walkinshaw, 1984; Gould *et al.*, 1984, 1985; Kuwata *et al.*, 1993; Białońska & Ciunik, 2004). Achiral organic acids similarly give complexes with strychnine and brucine, but the number of structures of these compared with the chiral acids is much smaller. Examples include fumaric and maleic acids (Dijksma, Gould, Parsons & Walkinshaw, 1998), 4-hydroxybenzoic acid (Sada *et al.*, 1998), 3-nitrobenzoic acid (Oshikawa *et al.*, 2002), 2,2'-dimethoxy-1-oxonaphthalene-4-carboxylic acid (Cheung *et al.*, 1999), 3-nitrophthalic acid (Smith, Wermuth, Young & Healy, 2005), and 5-nitrosalicylic, 3,5-dinitrosalicylic and 5-sulfosalicylic acids (Smith, Wermuth & Healy, 2005) (all with brucine). We have also completed the structure determinations of the strychnine salts with 5-nitrosalicylic and 3,5-dinitrosalicylic acids (Smith, Wermuth & White, 2005), as well as of that with 8-aminonaphthalene-2-sulfonic acid [the first reported example of a zwitterion–strychnine complex (Smith, Wermuth, Healy & Young, 2005)].

With the brucine compounds generally, the brucine species commonly form regular undulating parallel-chain host structures built from partially overlapping head-to-tail molecular associations (Gould & Walkinshaw, 1984; Dijksma, Gould, Parsons, Taylor & Walkinshaw, 1998; Białońska *et al.*, 2005). Compatible guest species, often including water molecules of solvation, occupy the interstitial cavities and associate with the host structures through hydrogen-bonding interactions. With strychnine, this structural regularity is not found, and this is probably the reason for the smaller number of reported structures of organic strychnine compared to brucine compounds.

Received 7 July 2005
Accepted 15 July 2005
Online 23 July 2005

The title compound, brucinium toluene-4-sulfonate trihydrate, (I), was obtained from the reaction of brucine with toluene-4-sulfonic acid (*p*-toluenesulfonic acid, PTSA) in 50% ethanol–water, and its structure is reported here. Initial room-temperature data were collected on a conventional four-circle diffractometer and afforded the basic structure, but this clearly indicated rotational disorder in one of the PTSA sulfonate groups [anion *C* in (I)], together with significant lability in a number of the molecules of solvent water, although physical crystal deterioration was not apparent. Low-temperature [130 (2) K] data were therefore collected using a CCD-detector diffractometer and these results are now presented.



The structure of (I) shows the presence of two independent brucinium cations (*A* and *B*), two toluene-4-sulfonate anions (*C* and *D*), and six molecules of solvent water in the asymmetric unit (Fig. 1). Atom numbering for the brucinium species follows the original Robinson convention (Holmes, 1952). In (I), all evidence of lability in the molecules of solvation has been removed, but some residual unmodelled disorder remains in the sulfonate group of the PTSA *C* anion.

As expected, both brucine molecules in (I) have been protonated at N19, giving the overall Cahn–Ingold–Prelog absolute configuration (Eliel, 1962) of C7(*S*), C8(*S*), C12(*S*), C13(*R*), C14(*R*), C16(*S*), N19(*S*). The brucinium cations form the previously described undulating ribbon structures, which extend through the crystal structure along the *a*-axis direction (Figs. 2 and 3). However, the cations within the ribbons are not related by the 2_1 screw operation which is coincident with the direction of propagation of this basic structure in a large proportion of the brucine compounds.

The inter-ribbon cavities accommodate the PTSA anions and the six solvent water molecules, the overall structure being characterized by extensive hydrogen bonding involving all available H-atom donors and acceptors (Table 1). This includes direct $N^+ - H \cdots O(\text{sulfonate})$, $O - H(\text{water}) \cdots O(\text{brucine})$, $O - H(\text{water}) \cdots O(\text{sulfonate})$ and $O - H(\text{water}) \cdots O(\text{water})$ interactions. These create parallel two-dimensional secondary sheets within the cavities, giving an overall network polymer structure.

The two PTSA anions are arranged in an antiparallel fashion [dihedral angle between the planes of the aromatic

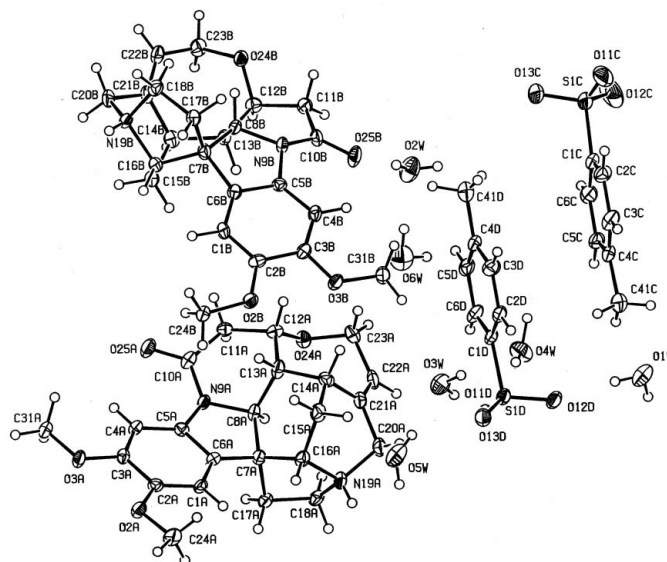


Figure 1

The molecular configurations and atom-numbering schemes for the two independent brucinium cations (*A* and *B*), the two PTSA anions (*C* and *D*) and the six solvent water molecules in the asymmetric unit of (I). Displacement ellipsoids are drawn at the 40% probability level.

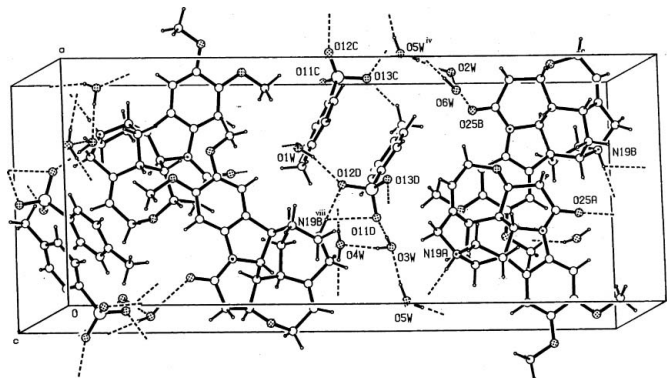


Figure 2

A perspective view of the packing of (I) in the unit cell, viewed approximately down the *c*-axis direction. Hydrogen-bonding associations are shown as broken lines. [Symmetry code: (viii) $1 - x, y - \frac{1}{2}, 1 - z$; for other codes, see Table 1.]

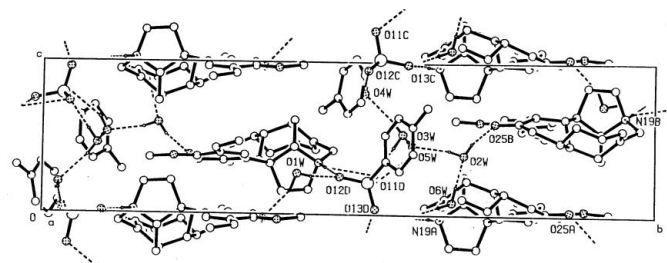


Figure 3

The packing of (I) in the unit cell, viewed down the *a* axis, showing the relationship between the brucinium *A* and *B* cations. Dashed lines indicate hydrogen bonds.

rings = $6.2 (1)^\circ$] and, although the perpendicular distance between these planes is *ca* 3.35 Å, the ring-centroid separation

[4.25 (1) Å] indicates no significant aromatic ring π - π interaction.

Experimental

The title compound, (I), was synthesized by heating 1 mmol quantities of brucine and toluene-4-sulfonic acid (*p*-toluenesulfonic acid, PTSA) in 50% ethanol-water (50 ml) for 10 min under reflux. After concentration to ca 30 ml, partial room-temperature evaporation of the hot-filtered solution gave large colourless prisms of (I) (m.p. 539.4–540.1 K).

Crystal data

$C_{23}H_{27}N_2O_4^+ \cdot C_7H_7O_3S^- \cdot 3H_2O$ $D_x = 1.411 \text{ Mg m}^{-3}$
 $M_r = 620.71$ $\text{Mo K}\alpha$ radiation
 Monoclinic, $P2_1$ Cell parameters from 3782 reflections
 $a = 12.1813 (9) \text{ \AA}$ $\theta = 2.6\text{--}22.4^\circ$
 $b = 30.862 (2) \text{ \AA}$ $\mu = 0.17 \text{ mm}^{-1}$
 $c = 7.7875 (6) \text{ \AA}$ $T = 130 (2) \text{ K}$
 $\beta = 93.400 (2)^\circ$ Plate, colourless
 $V = 2922.5 (4) \text{ \AA}^3$ $0.50 \times 0.30 \times 0.05 \text{ mm}$
 $Z = 4$

Data collection

Bruker SMART CCD area-detector 8427 reflections with $F^2 > 2\sigma(F^2)$
 diffractometer $R_{\text{int}} = 0.041$
 φ and ω scans $\theta_{\text{max}} = 27.6^\circ$
 Absorption correction: none $h = -15 \rightarrow 8$
 18490 measured reflections $k = -37 \rightarrow 39$
 12628 independent reflections $l = -10 \rightarrow 10$

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.0263P)^2]$
 $R[F^2 > 2\sigma(F^2)] = 0.050$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.088$ $(\Delta/\sigma)_{\text{max}} = 0.003$
 $S = 0.84$ $\Delta\rho_{\text{max}} = 0.53 \text{ e \AA}^{-3}$
 12628 reflections $\Delta\rho_{\text{min}} = -0.40 \text{ e \AA}^{-3}$
 837 parameters Absolute structure: Flack (1983),
 H atoms treated by a mixture of with 5742 Friedel pairs
 independent and constrained refinement Flack parameter: 0.00 (6)

Table 1 Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N19A—H19A \cdots O13C ^d	0.86 (3)	1.82 (3)	2.675 (3)	177 (2)
N19B—H19B \cdots O11D ⁱⁱ	0.88 (3)	2.38 (3)	3.012 (3)	129 (2)
N19B—H19B \cdots O12D ⁱⁱ	0.88 (3)	1.94 (3)	2.779 (3)	159 (3)
O1W—H11W \cdots O25A ⁱⁱⁱ	0.95 (5)	2.00 (5)	2.886 (4)	154 (4)
O1W—H12W \cdots O12D	0.84 (4)	2.04 (4)	2.856 (4)	166 (4)
O2W—H21W \cdots O25B	0.92 (5)	1.93 (5)	2.832 (4)	167 (5)
O2W—H22W \cdots O5W ^v	0.81 (4)	2.00 (4)	2.804 (5)	169 (4)
O3W—H31W \cdots O11D	0.90 (4)	1.92 (5)	2.819 (4)	180 (6)
O3W—H32W \cdots O4W	0.81 (4)	2.06 (4)	2.847 (4)	167 (4)
O4W—H41W \cdots O13D ^v	1.00 (4)	1.87 (4)	2.862 (4)	176 (3)
O4W—H42W \cdots O12C ^{vi}	0.78 (4)	2.03 (4)	2.814 (5)	175 (4)
O5W—H51W \cdots O3W	0.87 (4)	1.96 (4)	2.824 (4)	173 (4)
O5W—H52W \cdots O11C ^d	0.87 (4)	2.04 (5)	2.811 (5)	148 (4)
O6W—H61W \cdots O2W	0.90 (5)	1.85 (4)	2.746 (4)	180 (5)
O6W—H62W \cdots O13C ^{vii}	0.90 (4)	2.11 (4)	3.010 (4)	180 (6)

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

H atoms potentially involved in hydrogen-bonding interactions were located by difference methods and their positional and isotropic displacement parameters were refined. Other H atoms were included in the refinement at calculated positions [C—H(aromatic) = 0.95 Å and C—H(aliphatic) = 0.99 Å] and treated as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The atom-numbering scheme (Fig. 1) follows the original Robinson convention for strychnine (Holmes, 1952). The absolute configuration determined for the parent brucine (Peerdeman, 1956) was invoked and is consistent with the Flack parameter of 0.00 (6) (Flack, 1983) determined in this analysis.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Bruker, 1997); program(s) used to refine structure: SHELXTL; molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: PLATON.

The authors acknowledge financial support from the School of Physical and Chemical Sciences (Queensland University of Technology), the University of Melbourne and Griffith University.

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