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## Key indicators

Single-crystal X-ray study  
 $T = 100\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.008\text{ \AA}$   
 $R$  factor = 0.083  
 $wR$  factor = 0.134  
Data-to-parameter ratio = 8.0For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

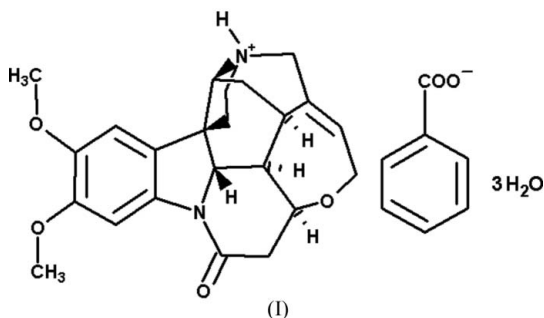
## Brucinium benzoate trihydrate

The title compound,  $\text{C}_{23}\text{H}_{27}\text{N}_2\text{O}_4^+ \cdot \text{C}_7\text{H}_5\text{O}_2^- \cdot 3\text{H}_2\text{O}$  contains two brucinium–benzoate ion pairs and six water molecules in the asymmetric unit. In the crystal structure of (I), corrugated layers of brucinium cations, stabilized by weak  $\text{C}-\text{H} \cdots \text{O}$  and  $\text{C}-\text{H} \cdots \pi$  interactions, are separated by anionic/water sheets. The cationic and the anionic/water layers are linked by  $\text{O}-\text{H} \cdots \text{O}$ ,  $\text{C}-\text{H} \cdots \text{O}$  and  $\text{N}-\text{H} \cdots \text{O}$  hydrogen bonds.

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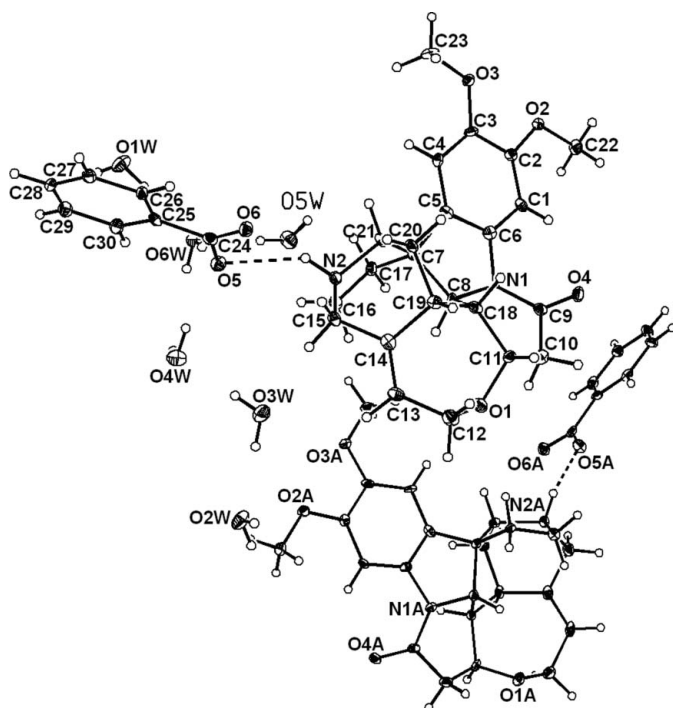
## Comment

Many molecular or salt-like crystal structures containing the chiral alkaloid brucine ( $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_4$ ), a resolving agent used for the separation of racemic acids (Jacques *et al.*, 1991), display corrugated layers of the alkaloid (CSD, Version 5.27 of November 2005; Allen, 2002). Such layers are present in the crystal structures of brucinium *N*-benzoyl-D-alaninate 4.5-hydrate (Gould & Walkinshaw, 1984), brucinium *N*-benzoyl-D-aspartate tetrahydrate, and brucinium *N*-benzoyl-D-asparaginate trihydrate (Białońska & Ciunik, 2006), independent of the resolved species. We obtained crystals of the title compound, (I), to determine the effect of the benzoate anion on the brucinium cation self-assembly process.

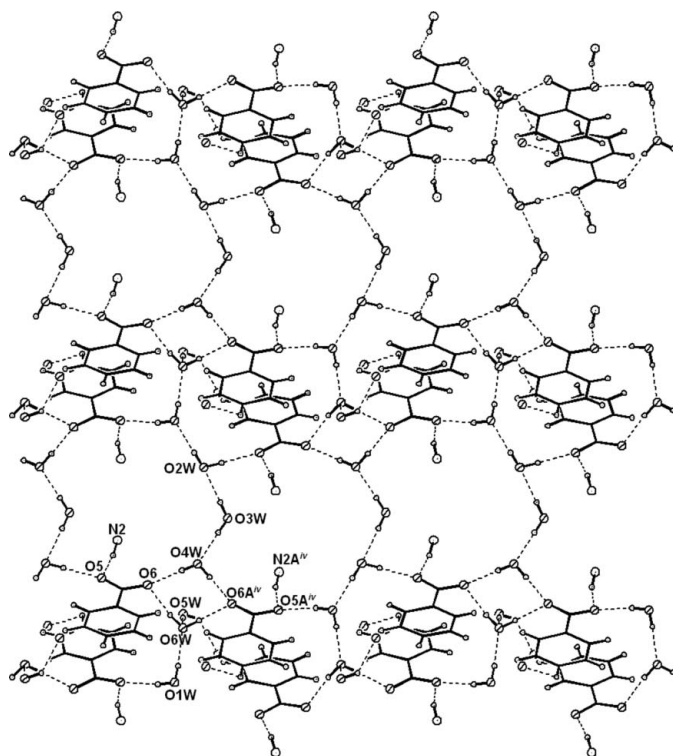


There are two brucinium–benzoate ion pairs and six water molecules in the asymmetric unit of (I) (Fig. 1). The brucinium cations and benzoate anions are linked by  $\text{N}-\text{H} \cdots \text{O}$  hydrogen bonds formed between the protonated amine  $\text{N}2$  and  $\text{N}2A$  atoms of the two brucinium cations and the  $\text{O}5$  and  $\text{O}5A$  atoms of the deprotonated carboxylate groups of the anions. The carboxylate groups of the anions and the water molecules,  $\text{O}1W-\text{O}6W$ , form hydrogen-bonded sheets consisting of four-, seven- and nine-membered edge-sharing rings (Fig. 2 and Table 1).

The anionic/water sheets are separated by corrugated layers of brucinium cations (Fig. 3). As seen in other crystal structures in which brucinium cations form corrugated layers, in (I) the amide  $\text{O}4$  atom of the brucinium cation, located at the bottom of a groove in the surface of the corrugated layer, is

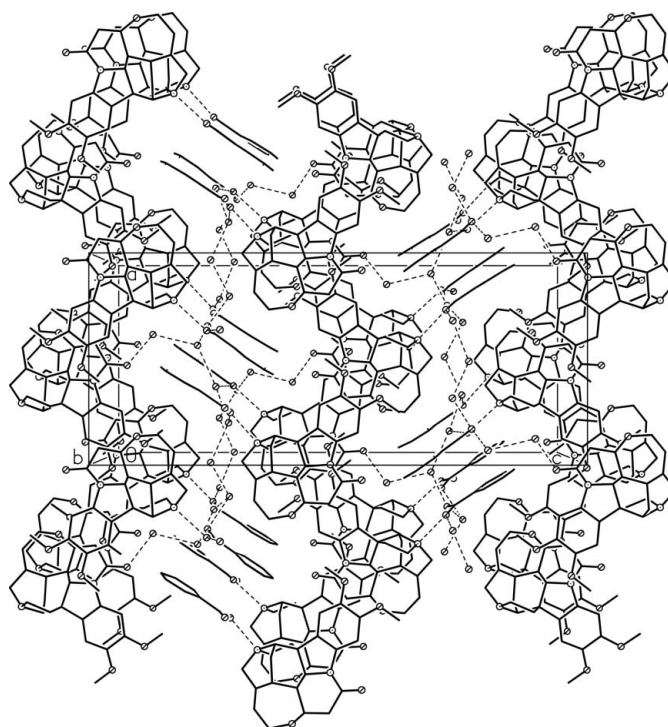


**Figure 1**  
The asymmetric unit of (I) with 30% probability displacement ellipsoids.



**Figure 2**  
Part of the packing of (I), showing the benzoate anions and water molecules forming hydrogen-bonded (dashed lines) sheets. [Symmetry code: (iv)  $x + \frac{1}{2}, \frac{3}{2} - y, 1 - z$ .]

the acceptor for an O—H...O hydrogen bond, and the O5W water molecule is its donor (see Table 1). However, the amide atom O4A of the other brucinium cation, also located at a



**Figure 3**  
The packing of (I). For clarity, H atoms have been omitted.

bottom of the grooves in the surface of the brucinium sheet, is involved in accepting a weak C—H...O hydrogen bond arising from a benzoate anion.

### Experimental

The crystals of (I) were grown from ethanol solutions containing equimolar amounts of brucine and benzoic acid. The crystallization was performed at room temperature by slow evaporation of the solvent.

#### Crystal data

$C_{23}H_{27}N_2O_4^+ \cdot C_7H_5O_2^- \cdot 3H_2O$   
 $M_r = 570.62$   
 Orthorhombic,  $P2_12_12_1$   
 $a = 12.479(2) \text{ \AA}$   
 $b = 14.978(2) \text{ \AA}$   
 $c = 29.272(3) \text{ \AA}$   
 $V = 5471.2(13) \text{ \AA}^3$

$Z = 8$   
 $D_x = 1.385 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.10 \text{ mm}^{-1}$   
 $T = 100(2) \text{ K}$   
 Plate, colourless  
 $0.30 \times 0.25 \times 0.10 \text{ mm}$

#### Data collection

Kuma KM4CCD diffractometer  
 $\omega$  scan  
 Absorption correction: none  
 34091 measured reflections

5934 independent reflections  
 4492 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.109$   
 $\theta_{max} = 26.0^\circ$

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.083$   
 $wR(F^2) = 0.134$   
 $S = 1.19$   
 5934 reflections  
 739 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0431P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.26 \text{ e \AA}^{-3}$   
 $\Delta\rho_{min} = -0.27 \text{ e \AA}^{-3}$

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2···O5	0.93	1.80	2.693 (6)	160
N2A—H2A···O5A	0.93	1.68	2.595 (6)	168
O1W—H11W···O5 <sup>i</sup>	0.88	1.88	2.748 (6)	169
O1W—H12W···O6W	0.88	1.98	2.857 (6)	176
O2W—H21W···O5A <sup>ii</sup>	0.88	1.87	2.752 (6)	179
O2W—H22W···O1W <sup>iii</sup>	0.88	1.88	2.764 (6)	179
O3W—H31W···O2W	0.88	1.98	2.864 (6)	179
O3W—H32W···O4W	0.88	1.94	2.822 (6)	179
O4W—H41W···O6	0.88	1.92	2.784 (6)	165
O4W—H42W···O6A <sup>iv</sup>	0.88	1.93	2.813 (6)	179
O5W—H51W···O4 <sup>v</sup>	0.88	2.19	2.915 (6)	140
O5W—H52W···O6W	0.88	1.99	2.872 (6)	178
O6W—H61W···O6A <sup>iv</sup>	0.88	1.93	2.798 (6)	168
O6W—H62W···O6	0.88	1.83	2.707 (6)	179
C28—H28···O4A <sup>vi</sup>	0.95	2.48	3.118 (7)	125

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

Anomalous diffraction effects were very small and Friedel pairs were merged before the final refinement. The absolute configuration of (**1**) was chosen on the basis of the known absolute configuration of brucine (Toda *et al.*, 1985). The C-bound H atoms were placed in idealized locations ( $C-H = 0.95-0.99$  Å) and refined as riding with

$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}(\text{methyl C})$ . The remaining H atoms were located in difference maps, repositioned in idealized locations ( $N-H = 0.93$ ,  $O-H = 0.88$  Å) and refined as riding, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$ .

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2001); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2001); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Bruker 1999); software used to prepare material for publication: *SHELXL97*.

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