

Isomorphous brucinium 4-nitrobenzoate methanol solvate and brucinium 4-nitrobenzoate dihydrate

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Received 29 November 2006

Accepted 19 December 2006

Online 23 January 2007

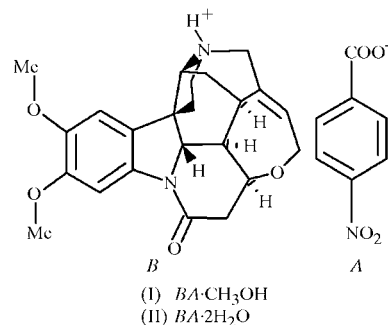
In isomorphous crystals of brucinium 4-nitrobenzoate methanol solvate, $C_{23}H_{27}N_2O_4^+ \cdot C_7H_4NO_4^- \cdot CH_3OH$, and brucinium 4-nitrobenzoate dihydrate, $C_{23}H_{27}N_2O_4^+ \cdot C_7H_4NO_4^- \cdot 2H_2O$, the brucinium cations form reverse corrugated layers, in which the amine N and amide O atoms of the brucinium cations are located in the grooves and at convex points of the layer surface, respectively. Similarly, as observed for the commonly occurring corrugated brucinium layers, the amide O atoms of the cations are involved in hydrogen bonds in which solvent molecules are the donors.

Comment

Brucine is a common resolving agent used for the separation of racemic acids by fractional crystallization of brucinium diastereomeric salts (Jacques *et al.*, 1991). In many crystals of brucinium salts, the cations form corrugated layers separated by guest anions and solvent molecules. A common feature of these layers is that the amine N and amide O atoms of the brucine molecules are located at convex and concave points of

the corrugated layer surface. The amide O atoms are involved in hydrogen bonds in which solvent molecules are usually the donors (Białońska & Ciunik, 2006a).

Crystallization and recrystallization of the brucinium salt of 3,5-dinitrobenzoic acid led to the formation of various pseudopolymorphic crystals of brucinium salts (Białońska & Ciunik, 2006b). Isomorphous crystals of brucinium 4-nitrobenzoate methanol solvate, (I), and brucinium 4-nitrobenzoate dihydrate, (II), were obtained from methanol solution.



In (I) and (II), the brucinium cation and the 4-nitrobenzoate anion are linked to each other by ionic hydrogen bonds. In the ionic $N-H^+ \cdots O^-$ hydrogen bond, the protonated amine N2 atom of the brucinium cation and atom O5 of the deprotonated carboxyl group of the 4-nitrobenzoate anion are the donor and acceptor, respectively (Fig. 1, and Tables 1 and 2). Amide atom O4 of the brucinium cation accepts an $O-H \cdots O$ hydrogen bond from methanol atom O31 or water molecule O2W in (I) and (II), respectively. In (II), the O2W molecule is also a donor to water atom O1W. Atom O1W in turn is a donor to atom O1 of the cation at $(-x, y + \frac{1}{2}, -z + 1)$ and to atom O6 of the anion at $(-x, y + \frac{1}{2}, -z)$ (Table 2).

In (I) and (II), the cations form corrugated layers (Fig. 2a). However, compared with the usual brucinium corrugated layers (Fig. 2b), the layers in (I) and (II) reveal a reverse corrugation. This means that the amine N2 and amide O4 atoms of the cations, which are located at convex points and in grooves, respectively, of a surface of the usual corrugated

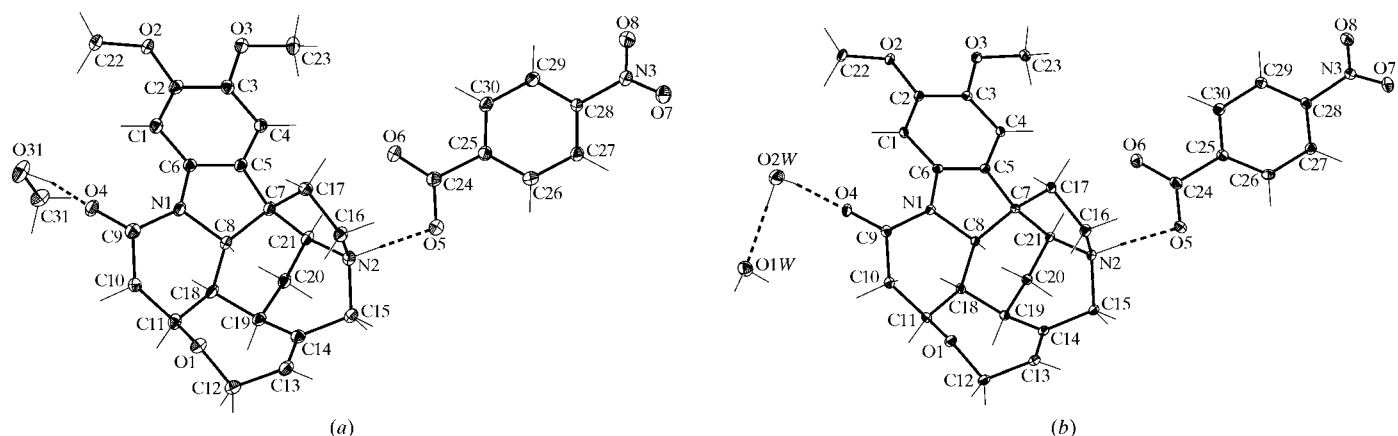
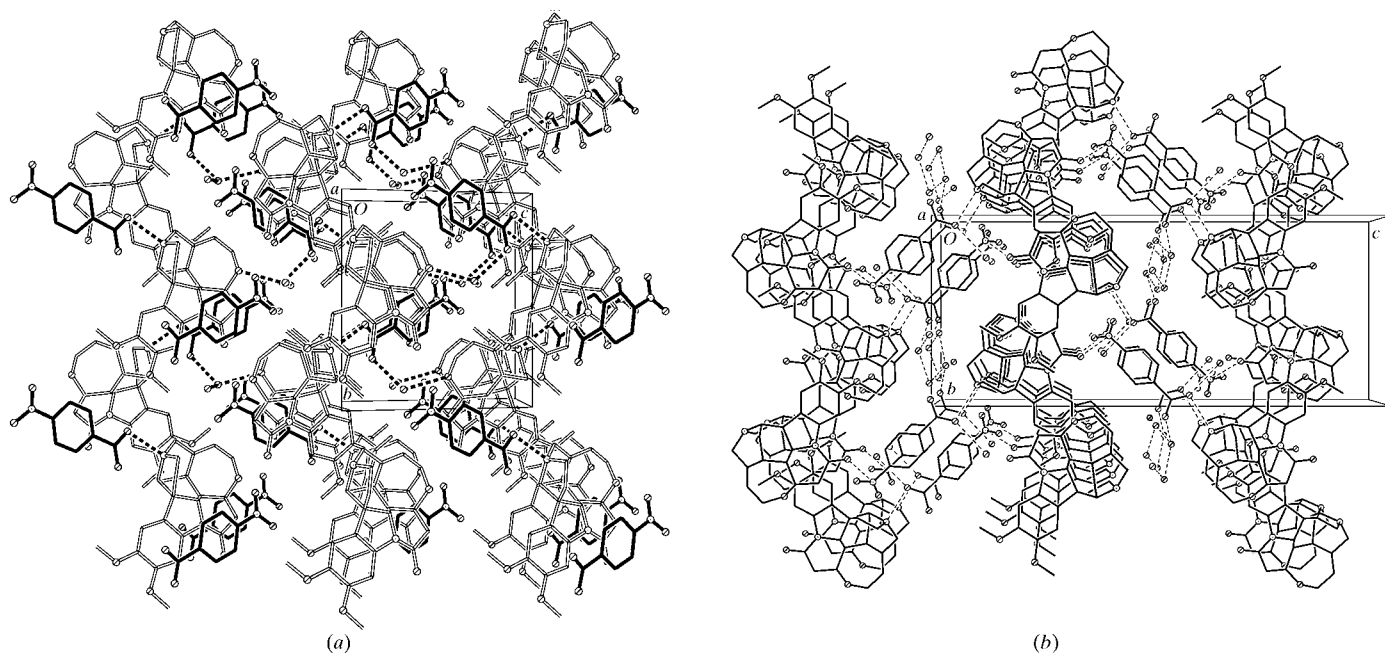


Figure 1

The molecular configuration and atom-numbering scheme in the crystal structure of (a) compound (I) and (b) compound (II). Non-H atoms are shown as 30% probability displacement ellipsoids.

**Figure 2**

(a) The packing in (II), where brucinium cations (open bonds) form reverse corrugated layers. (b) The packing in brucinium 4-nitrobenzoate 2.6-hydrate (see supplementary material), where brucinium cations form common corrugated layers separated by anion/water sheets. Water molecules and 4-nitrobenzoate anions with occupancy equal to 0.4 have been omitted. Crystals of brucinium 4-nitrobenzoate 2.6-hydrate were grown from ethanol solution. For clarity, H atoms have been omitted.

layers, are found in grooves and at convex points of the layer surface in (I) and (II). The reverse corrugated layers in (I) and (II) are stabilized by C—H...O and C—H... π hydrogen bonds. Among them, the shortest intermolecular contacts between brucinium cations are found for C17—H17A...O2(1 - x, - $\frac{1}{2}$ + y, -z) and C15—H15A...Cg1(-x, - $\frac{1}{2}$ + y, -z) hydrogen bonds (Cg1 is the centroid of the C1—C6 arene ring).

Experimental

Crystals of (I) were grown from a methanol solution containing equimolar amounts of brucine (commercially available) and 4-nitrobenzoic acid. Crystals of (II) were obtained from a sample containing crystals of (I) dissolved in methanol by heating. The crystallizations and recrystallizations were performed at room temperature by slow evaporation of the solvent.

Isomorph (I)

Crystal data

$C_{23}H_{27}N_2O_4^+ \cdot C_7H_4NO_4^- \cdot CH_4O$	$Z = 2$
$M_r = 593.62$	$D_x = 1.441 \text{ Mg m}^{-3}$
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 9.830$ (2) Å	$\mu = 0.11 \text{ mm}^{-1}$
$b = 12.364$ (3) Å	$T = 100$ (2) K
$c = 11.560$ (3) Å	Block, yellow
$\beta = 103.09$ (3)°	$0.25 \times 0.25 \times 0.20 \text{ mm}$
$V = 1368.5$ (6) Å ³	

Data collection

Kuma KM-4-CCD diffractometer	2492 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.063$
9166 measured reflections	$\theta_{\text{max}} = 27.0^\circ$
3078 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0734P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.055$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.130$	$(\Delta/\sigma)_{\text{max}} = 0.004$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$
3078 reflections	$\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$
388 parameters	Absolute structure: Toda <i>et al.</i>
H-atom parameters constrained	(1985)

Table 1

Hydrogen-bond geometry (Å, °) for (I).

D—H...A	D—H	H...A	D...A	D—H...A
N2—H2...O5	0.93	1.62	2.552 (4)	177
O31—H31...O4	0.82	2.00	2.815 (4)	172

Isomorph (II)

Crystal data

$C_{23}H_{27}N_2O_4^+ \cdot C_7H_4NO_4^- \cdot 2H_2O$	$Z = 2$
$M_r = 597.61$	$D_x = 1.449 \text{ Mg m}^{-3}$
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 10.085$ (2) Å	$\mu = 0.11 \text{ mm}^{-1}$
$b = 12.338$ (3) Å	$T = 100$ (2) K
$c = 11.615$ (3) Å	Block, yellow
$\beta = 108.61$ (3)°	$0.30 \times 0.30 \times 0.30 \text{ mm}$
$V = 1369.7$ (6) Å ³	

Data collection

Kuma KM-4-CCD diffractometer	2925 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.028$
9184 measured reflections	$\theta_{\text{max}} = 27.0^\circ$
3110 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0521P)^2 + 0.1159P]$
$R[F^2 > 2\sigma(F^2)] = 0.030$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.078$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.05$	$\Delta\rho_{\max} = 0.23 \text{ e } \text{Å}^{-3}$
3110 reflections	$\Delta\rho_{\min} = -0.20 \text{ e } \text{Å}^{-3}$
388 parameters	Absolute structure: Toda <i>et al.</i> (1985)
H-atom parameters constrained	

Table 2

Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H2\cdots O5$	0.93	1.74	2.653 (2)	169
$O2W-H22W\cdots O4$	0.88	2.05	2.924 (2)	172
$O2W-H21W\cdots O1W$	0.88	1.93	2.807 (2)	177
$O1W-H11W\cdots O6^i$	0.88	1.84	2.715 (3)	178
$O1W-H12W\cdots O1^{ii}$	0.88	1.96	2.843 (2)	178

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

All H atoms bonded to C atoms were treated as riding atoms, with C—H distances of 0.95–1.00 Å. The remaining H atoms were located in difference maps and then refined with isotropic displacement parameters before being fixed prior to the final cycles of refinement. Friedel pairs were merged before the final refinement (MERG 4). The absolute configurations of (I) and (II) were chosen on the basis of the known absolute configuration of brucine (Toda *et al.*, 1985).

For both isomorphs, 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, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Bruker, 1999); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3069). Services for accessing these data are described at the back of the journal.

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