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Brucinium 3,5-dinitrobenzoate methanol solvate, methanol disolvate and trihydrate

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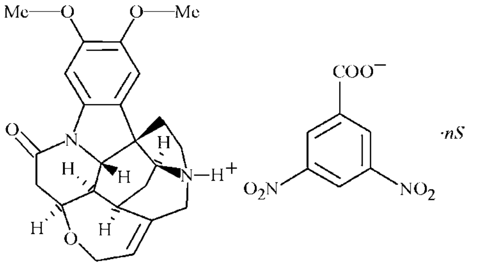
Crystals of brucinium 3,5-dinitrobenzoate methanol solvate, $C_{23}H_{27}N_2O_4^+ \cdot C_7H_3N_2O_6^- \cdot CH_3OH$, (I), brucinium 3,5-dinitrobenzoate methanol disolvate, $C_{23}H_{27}N_2O_4^+ \cdot C_7H_3N_2O_6^- \cdot 2CH_3OH$, (II), and brucinium 3,5-dinitrobenzoate trihydrate, $C_{23}H_{27}N_2O_4^+ \cdot C_7H_3N_2O_6^- \cdot 3H_2O$, (III), were obtained from methanol [for (I) and (II)] or ethanol solutions [for (III)]. The brucinium cations and 3,5-dinitrobenzoate anions are linked by ionic $N-H^+\cdots O^-$ hydrogen bonds. In the crystals of (I), (II) and (III), the brucinium cations exhibit different modes of packing, *viz*. corrugated ribbons, pillars and corrugated monolayer sheets, respectively. While in (III), the amide O atom of the brucinium cation participates in $O-H\cdots O$ hydrogen bonds, in which water molecules are the donors, in (I) and (II), the amide O atom of the brucinium cation is involved in weak $C-H\cdots O$ hydrogen bonds and other brucinium cations are the donors.

Comment

Brucine is one of the most often used resolving agents for separation of racemic acids (Jacques *et al.*, 1991). The racemic resolution by fractional crystallization of brucinium diastereomeric salts is usually performed from water, methanol or ethanol solution. In a recent paper concerning common brucine corrugated monolayer sheets, we showed that, in such cases, the amide O atoms of brucine molecules or brucinium cations reveal a great tendency to participate in hydrogen bonds in which solvent molecules, usually water molecules, are the donors (Białonska & Ciunik, 2006). The crystallization of brucinium 3,5-dinitrobenzoate from methanol and ethanol solutions has been performed. Crystals of brucinium 3,5-dinitrobenzoate methanol solvate, (I), were grown from methanol solution. As a result of a recrystallization of (I) from methanol solution, crystals of brucinium 3,5-dinitrobenzoate methanol disolvate, (II), were obtained. Crystals of brucinium 3,5-dinitrobenzoate trihydrate, (III), were grown from ethanol solution.

Selected views of (I)–(III) with the atom-numbering schemes employed are presented in Figs. 1–3. The geometry of the brucinium cations in the crystal structures of (I)–(III) is comparable to that found in related compounds (Cambridge Structural Database, Version 5.27 of November 2005; Allen, 2002). In each of (I)–(III), the protonated tertiary amine N2 atom of the brucinium cation and atom O5 of the deprotonated carboxyl group of the 3,5-dinitrobenzoate anion are linked by ionic $N-H^+\cdots O^-$ hydrogen bonds (see also Tables 1, 3 and 4).



(I) nS=MeOH
(II) nS=2MeOH
(III) nS=3H_2O

In (I), the brucinium cations form corrugated ribbons stabilized by $C-H\cdots O$ and $C-H\cdots\pi$ hydrogen bonds and extended in the [010] direction (Fig. 4). The brucinium ribbons are separated by the anions, which together with brucinium cations form π–π interactions (Table 2). The methanol molecule is the donor of a hydrogen bond in which atom O5 of the carboxyl group of the anion is the acceptor (see Fig. 1 and Table 1).

In (II), the brucinium cations form pillars extending in the [100] direction (Fig. 5). The arene rings of the brucinium cations are directed inwards in the pillars, allowing the O atoms of the methoxy groups to participate in $C-H\cdots O$ hydrogen bonds. The anions are located in the channels formed by the four neighboring brucinium pillars. The brucinium cations and 3,5-dinitrobenzoate anions are linked, as mentioned above, by $N-H^+\cdots O^-$ hydrogen bonds, and also by $C-H\cdots O$ hydrogen bonds. Again, methanol molecules are

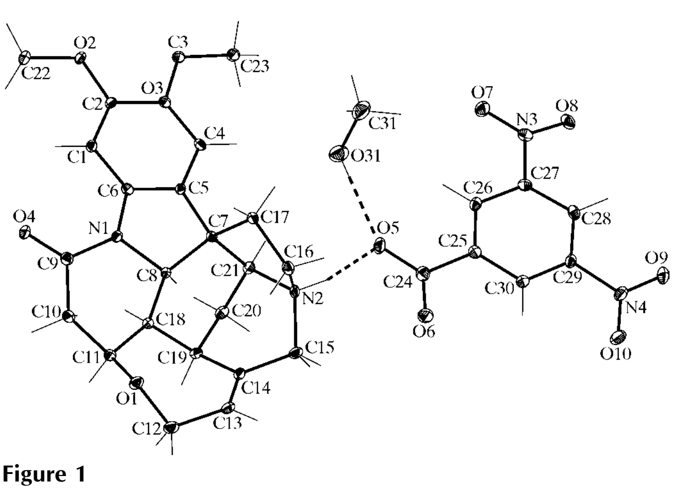


Figure 1
The molecular configuration and atom-numbering scheme in (I). Non-H atoms are shown as 30% probability displacement ellipsoids.

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donors of hydrogen bonds in which atoms O5 and O6 of the carboxylate group of the anion are the acceptors (see Fig. 2 and Table 3).

Similar to (I), in the crystal of (III), brucinium cations form corrugated ribbons. However, in (III), consecutive ribbons are directly linked by C—H···O and C—H···π hydrogen bonds, resulting in common brucinium corrugated monolayer sheets (Fig. 6). Neighboring brucinium corrugated sheets are separated by the anions and water molecules. As mentioned above, the cations and anions are linked by ionic $\mathrm{N—H^{+}\cdots O^{-}}$ hydrogen bonds. Water molecules O1*W*–O3*W*, linked by O—H···O hydrogen bonds, form discrete *D*3 chains (see Fig. 3 and Table 4) (Infantes & Motherwell, 2002). Additionally, the O1*W* water molecule is the donor of a hydrogen bond in which the carboxylate O6 atom of the anion and the amide O4($-x, y+\frac{1}{2}, -z+\frac{1}{2}$) atom of the cation are the acceptors (see Table 4). The O2*W* and O3*W* water molecules are donors of hydrogen bonds in which the O9($x-\frac{1}{2}, -y+\frac{5}{2}, -z+1$) atom of a nitro group and the O5($x-\frac{1}{2}, -y+\frac{3}{2}, -z+1$) atom of a carboxylate group of the anions are the acceptors, respectively.

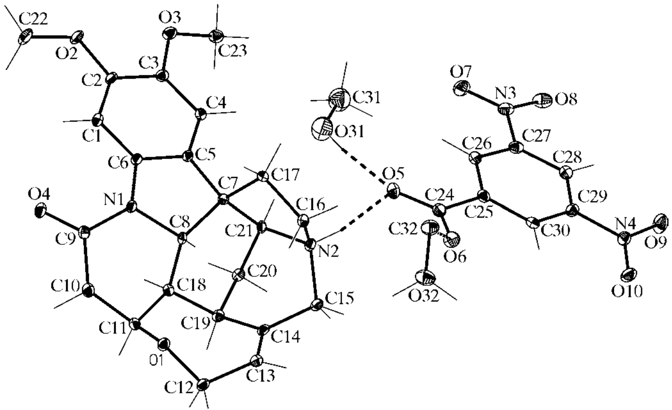

Figure 2
The molecular configuration and atom-numbering scheme in (II). Non-H atoms are shown as 30% probability displacement ellipsoids.

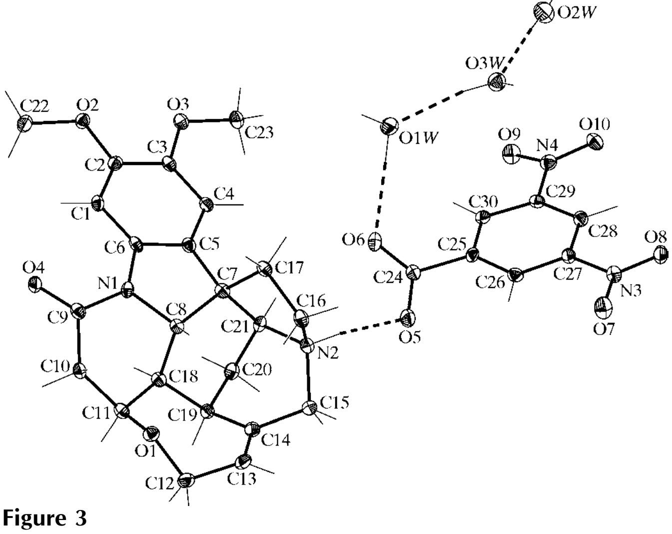

Figure 3
The molecular configuration and atom-numbering scheme in (III). Non-H atoms are shown as 30% probability displacement ellipsoids.

As described above, in (I) and (III), brucinium cations form similar corrugated ribbons. These results confirm our previous observations (Białonska & Ciunik, 2006), namely that in the crystals in which the brucinium ribbons form corrugated monolayer sheets, similar to those observed in (III), amide atom O4 of the brucinium cations reveals a tendency to participate in hydrogen bonds with solvent molecules as the donors. On the other hand, in the cases in which brucinium cations form separated corrugated ribbons, similar to those observed in (I), atom O4 does not exhibit the same behavior. However, the separated ribbons give the brucinium cations an opportunity to be involved in interactions, such as π–π interactions, with the anions. The formation of brucinium monolayer sheets does not allow brucinium cations to form such types of interaction with cocrystallizing guests. The interactions involving the amide O atom of the brucinium corrugated layers are specific for solvent molecules. In a similar way, weak interactions involving the arene rings of separated brucinium corrugated ribbons seem to be specific for guest molecules/anions. Simultaneously, it seems that such weak connections between the cations and anions resulting in cationic/anionic sheets decrease the ability of amide O atoms of brucinium cations to participate in hydrogen bonds with solvent molecules. Moreover, in (I), amide atom O4 of the brucinium cations seems to reveal similar properties to those of O atoms of nitro groups protruding out of the cationic/anionic sheet, which, generally, do not reveal a tendency to participate in strong hydrogen bonds.

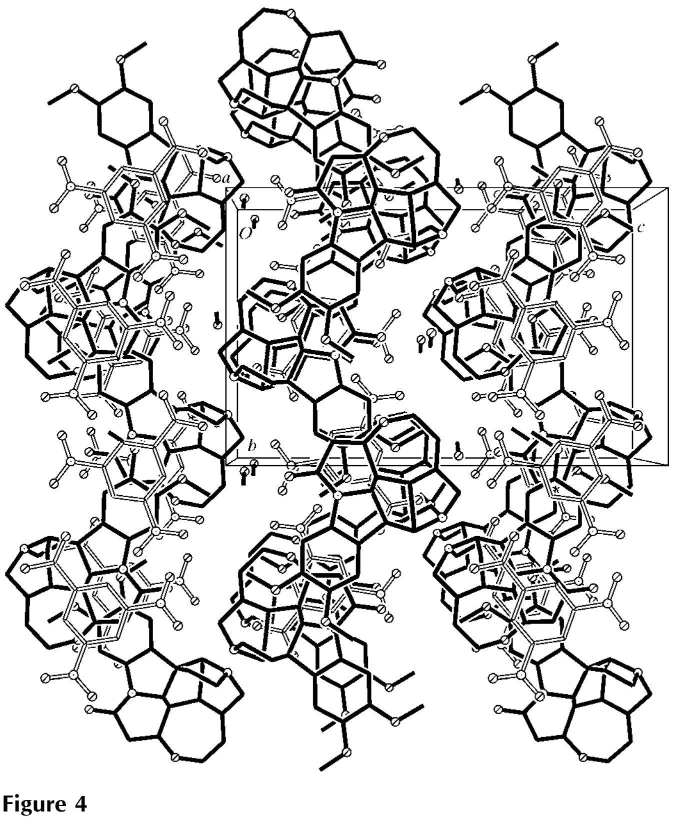

Figure 4
The packing of (I), showing the brucinium ribbons (solid lines) separated by the anions (open lines).

In summary, on the basis of the crystal structures described above, a different molecular recognition of 3,5-dinitrobenzoate anions by brucinium cations appears in various solutions (methanol or ethanol). A variety of packing motifs of brucinium cations and interactions with cocrystallizing 3,5-dinitrobenzoate anions are observed in the crystal structures of (I)–(III).

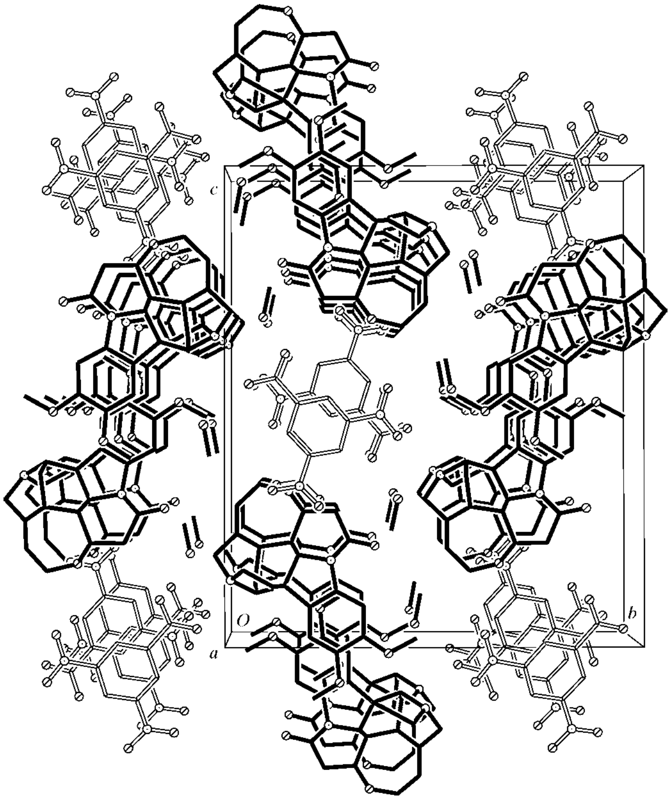

Figure 5
The packing of (II), showing the columnar packing of brucinium cations. Channels, formed between four neighboring columns, are occupied by the anions.

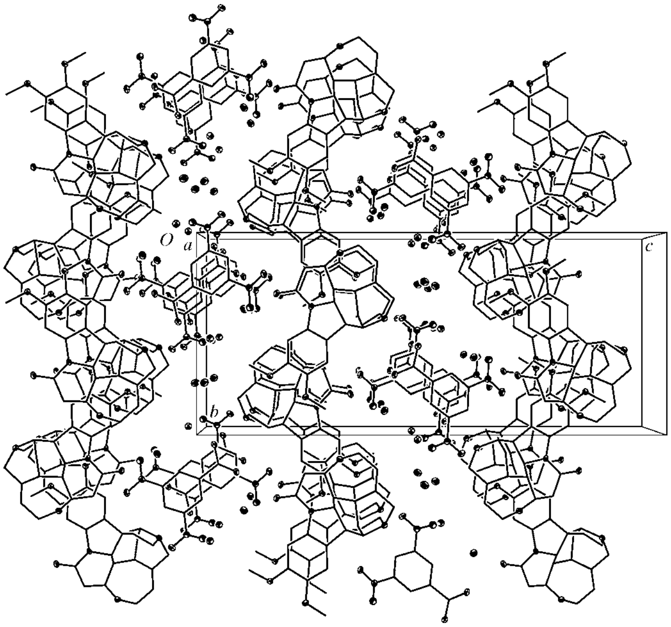

Figure 6
The packing of (III), showing common brucinium corrugated monolayer sheets separated by the anions and water molecules.

Experimental

Crystals of (I) and (III) were grown from methanol and ethanol solutions, respectively, containing equimolar amounts of brucine and 3,5-dinitrobenzoic acid. Crystals of (II) were obtained as a result of recrystallization of (I) from methanol solution. The crystallizations were performed at room temperature by slow evaporation of the solvent.

Compound (I)

Crystal data

$C_{23}H_{27}N_2O_4^+ \cdot C_7H_3N_2O_6^- \cdot CH_4O$
$M_r = 638.62$
Orthorhombic, $P2_12_12_1$
$a = 11.8539\ (18)$ Å
$b = 12.2726\ (18)$ Å
$c = 19.498\ (3)$ Å
$V = 2836.5\ (7)$ Å^3
$Z = 4$
$D_x = 1.495$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.12$ mm^{-1}
$T = 100\ (2)$ K
Block, orange
0.30 × 0.30 × 0.25 mm

Data collection

Kuma KM-4 CCD diffractometer
ω scan
18431 measured reflections
3470 independent reflections
2929 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.077$
$\theta_{\rm max} = 27.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.094$
$S = 1.08$
3470 reflections
415 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0408P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.21$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.26$ e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O5	0.93	1.73	2.643 (3)	166
O31—H31···O5	0.83	1.97	2.766 (3)	161

Table 2
π–π interactions (Å, °) in (I).

*Cg*1 and *Cg*2 represent the centroids of the C1–C6 and C25–C30 rings. *Cg*···*Cg* is the distance between ring centroids. The interplanar angle is that between the planes of the rings *CgI* and *CgJ*. $CgI_{\rm perp}$ is the perpendicular distance of *CgI* from ring *J*. $CgJ_{\rm perp}$ is the perpendicular distance of *CgJ* from ring *I*.

CgI	*CgJ*	*Cg*···*Cg*	Interplanar angle	$CgI_{\rm perp}$	$CgJ_{\rm perp}$	Slippage
*Cg*1	$Cg2^{\rm i}$	3.690 (4)	3.25 (4)	3.310	3.271	1.71

Symmetry code: (i) $-x+\frac{3}{2}, -y, z+\frac{1}{2}$.

Compound (II)

Crystal data

$C_{23}H_{27}N_2O_4^+ \cdot C_7H_3N_2O_6^- \cdot 2CH_4O$
$M_r = 670.66$
Orthorhombic, $P2_12_12_1$
$a = 7.1733\ (18)$ Å
$b = 19.100\ (2)$ Å
$c = 21.955\ (2)$ Å
$V = 3008.0\ (9)$ Å^3
$Z = 4$
$D_x = 1.481$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.11$ mm^{-1}
$T = 100\ (2)$ K
Block, orange
0.30 × 0.30 × 0.30 mm

Data collection

Kuma KM-4 CCD diffractometer
ω scan
20084 measured reflections
3707 independent reflections
3407 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.085$
$\theta_{\rm max} = 27.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.124$
$S = 1.10$
3707 reflections
433 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.079P)^2 + 0.1302P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.31$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.44$ e Å^{-3}

Table 3
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O5	0.93	1.79	2.708 (3)	169
O31—H31···O5	0.83	2.03	2.852 (4)	172
O32—H32···O6	0.82	1.96	2.778 (3)	175

Compound (III)

Crystal data

$C_{23}H_{27}N_2O_4^+ \cdot C_7H_3N_2O_6^- \cdot 3H_2O$
$M_r = 660.63$
Orthorhombic, $P2_12_12_1$
$a = 8.2499$ (8) Å
$b = 12.5379$ (12) Å
$c = 29.109$ (3) Å
$V = 3010.9$ (5) Å^3
$Z = 4$
$D_x = 1.457$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.12$ mm^{-1}
$T = 100$ (2) K
Block, yellow
0.30 × 0.25 × 0.25 mm

Data collection

Kuma KM-4 CCD diffractometer
ω scan
20148 measured reflections
3700 independent reflections
3036 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.070$
$\theta_{\rm max} = 27.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.127$
$S = 1.12$
3700 reflections
424 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0633P)^2 + 0.1372P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.26$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.25$ e Å^{-3}

Table 4
Hydrogen-bond geometry (Å, °) for (III).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O5	0.93	1.72	2.632 (4)	168
O1W—H11W···O4$^{\rm i}$	0.88	1.94	2.817 (4)	175
O1W—H12W···O6	0.88	1.93	2.805 (4)	174
O2W—H21W···O9$^{\rm ii}$	0.88	2.35	3.163 (4)	154
O2W—H22W···O3W	0.88	1.99	2.850 (4)	166
O3W—H31W···O5$^{\rm iii}$	0.88	1.93	2.801 (4)	167
O3W—H32W···O1W	0.87	1.96	2.826 (4)	170

Symmetry codes: (i) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x-\frac{1}{2}, -y+\frac{5}{2}, -z+1$; (iii) $x-\frac{1}{2}, -y+\frac{3}{2}, -z+1$.

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 refined with isotropic displacements 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)–(III) were chosen on the basis of the known absolute configuration of brucine (Toda *et al.*, 1985).

For all compounds, 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*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3018). Services for accessing these data are described at the back of the journal.

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