# organic compounds

# 2,3-Dimethoxy-10-oxostrychnidinium 2-(2,4,6-trinitroanilino)benzoate monohydrate: a 1:1 proton-transfer salt of brucine with o-picraminobenzoic acid

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In the structure of the title 1:1 proton-transfer compound of brucine with 2-(2,4,6-trinitroanilino)benzoic acid, $C_{23}H_{27}N_2O_4^+ \cdot C_{13}H_7N_4O_8^- \cdot H_2O$, the brucinium cations form classic undulating ribbon substructures through overlapping head-to-tail interactions, while the anions and the three related partial solvent water molecules (having occupancies of 0.73, 0.17 and 0.10) occupy the interstitial regions of the structure. The cations are linked to the anions directly through N—H···$O_{COO^-}$ hydrogen bonds and indirectly by the three water molecules, which form similar conjoint cyclic bridging units [graph set $R_4^2(8)$] through O—H···$O_{C=O}$ and O—H···$O_{COO^-}$ hydrogen bonds, giving a two-dimensional layered structure. Within the anion, intramolecular N—H···$O_{COO^-}$ and N—H···$O_{nitro}$ hydrogen bonds result in the benzoate and picrate rings being rotated slightly out of coplanarity [inter-ring dihedral angle = 32.50 (14)°]. This work provides another example of the molecular selectivity of brucine in forming stable crystal structures, and also represents the first reported structure of any form of the guest compound 2-(2,4,6-trinitroanilino)benzoic acid.

## Comment

Although brucine has been used largely for the resolution of certain chiral compounds (Wilen, 1972), it has proven utility in the formation of crystalline adducts and salts with achiral carboxylic acids. In particular, the benzoic acid analogues have provided a number of brucinium salt structures, many of which are solvated, *e.g.* benzoic acid (a trihydrate) (Białońska & Ciunik, 2006*b*), 3-nitrobenzoic acid (methanol monosolvate) (Oshikawa *et al.*, 2002), 4-nitrobenzoic acid (isomorphous dihydrate and methanol monosolvate) (Białońska & Ciunik, 2007), 4-hydroxybenzoic acid (isopropyl alcohol monosolvate) (Sada *et al.*, 1998), 3,5-dinitrobenzoic acid (trihydrate,

methanol monosolvate and disolvate) (Białońska & Ciunik, 2006*a*) and the anhydrous example with 5-nitrosalicylic acid (Smith, Wermuth, Healy & White, 2006). Three 1:1 salts are also known, *viz.* with 5-nitrophthalic acid (a dihydrate) (Smith *et al.*, 2005), isophthalic acid (a trihydrate) (Smith, Wermuth, Young & White, 2006) and 4,5-dichlorophthalic acid (anhydrous) (Smith *et al.*, 2007*a*). However, with these acids, formation is certainly a hit-or-miss process, the selectivity being dependent upon guest molecule compatibility with the interstitial cavities in the brucinium cation substructures which are present in a large number of brucine adduct and brucinium proton-transfer compounds (Gould & Walkinshaw, 1984; Dijksma *et al.*, 1998; Oshikawa *et al.*, 2002; Białońska & Ciunik, 2004; Smith, Wermuth, Healy & White, 2006). In these substructures, the brucine species form undulating ribbons comprising overlapping head-to-tail molecules, this host structure then accomodating the compatible guest molecule or molecules and interacting with them through hydrogen-bonding associations. This phenomenon accounts for the presence in many of the structures of various polar solvent molecules. It has also been noted that the two-molecule brucine repeat period will be *ca* 12.5 Å (the cell dimension) in the direction of a $2_1$ screw axis, of which there is a high incidence among the small number of space groups into which brucine and its compounds and adducts fall (Smith, Wermuth, Healy & White, 2006).

The isomeric picraminobenzoic acids [2-, 3- and 4-(2,4,6-trinitroanilino)benzoic acid] were first synthesized by the reaction of the corresponding monoaminobenzoic acid with picryl chloride in 1911 (Crocker & Matthews, 1911). We have synthesized these three compounds using picrylsulfonic acid rather than picryl chloride, reporting the crystal structure of the *para* isomer (Smith *et al.*, 2007*b*). However, the uncompromising crystal morphology of the *ortho* and *meta* isomers precluded the structure determinations of these. The 1:1 stoichiometric reaction of 2-(2,4,6-trinitroanilino)benzoic acid with brucine in aqueous ethanol gave good crystals of the orange–red hydrated title salt, (I), and the structure is reported here. No suitable crystals resulted from the reactions of brucine with the *meta* and *para* isomers.



(I)
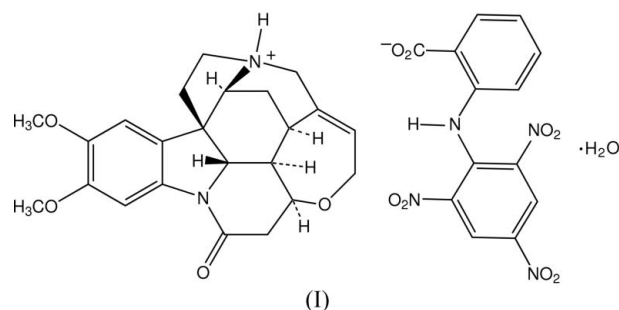
In (I), protonation has occurred, as expected, at N19 of the brucine cage (Fig. 1), the absolute configuration of the seven chiral centres of the brucinium cation being invoked (Peerdeman, 1956). These cations form the previously described undulating ribbon host substructures, which have a dimeric repeat period in (I) of 12.4407 (3) Å along the direction of
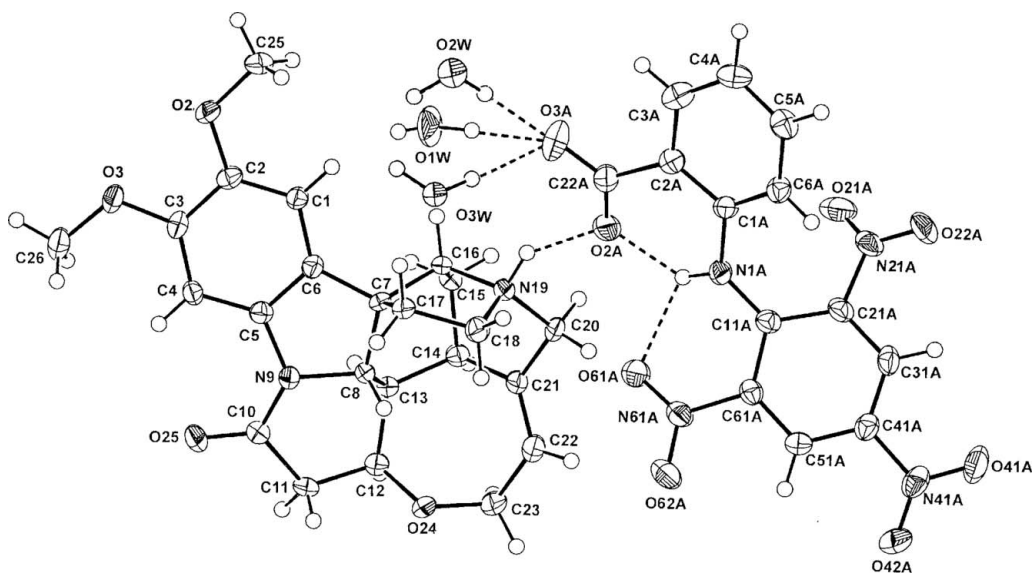
**Figure 1**
The molecular configuration and atom-numbering scheme for the brucinium cation, the *o*-picraminobenzoate anion and the partial solvent water molecules (O1*W*–O3*W*) in (I). Displacement ellipsoids are drawn at the 50% probability level. Inter-species hydrogen bonds are shown as dashed lines.

propagation [a $2_1$ screw axis, the *a* cell dimension] (Fig. 2). This value for the dimeric repeat in (I) is consistent with those for similarly structured brucine compounds (Gould & Walkinshaw, 1984; Smith, Wermuth, Healy & White, 2006). There is a molecule offset of *ca* 120° in the repeat unit of (I).

The monoanion and the three associated partial solvent water molecules [O1*W* (site-occupancy factor = 0.73), O2*W* (site-occupancy factor = 0.17) and O3*W* (site-occupancy factor = 0.10)] occupy the interstitial volumes between the brucine substructures and are hydrogen bonded to them. The brucinium cations form an $N^+$—H···O hydrogen bond with a carboxylate O-atom acceptor of the anion, while the water

linkages are unusual, the three partial molecules forming a set of similar conjoint cyclic associations [graph set $R_4^2(8)$; see Bernstein *et al.* (1995) for graph-set notation] involving two O-atom acceptor atoms (brucinium carbonyl atom O25 and carboxylate atom O3*A* of the anion) (Table 1) (see Fig. 2), giving a two-dimensional structure which forms layers down the *c* cell direction (Fig. 3). Within the anion, intramolecular N—H···$O_{COO^-}$ and O—H···$O_{nitro}$ hydrogen bonds result in moderate rotation of the benzoate and picrate ring systems out of coplanarity [inter-ring dihedral angle = 32.50 (14)°]. The *ortho*-carboxylate group of the benzoate ring is rotated slightly out of the plane of the benzene ring [C1*A*—C2*A*—C22*A*—O3*A* = 159.4 (3)°], while the two *ortho*-related nitro groups are similarly non-coplanar with the picrate ring [C11*A*—C21*A*—N21*A*—O22*A* = 151.7 (3)° and C11*A*—C61*A*—N61*A*—O61*A* = −165.2 (3)°]. The less sterically compromised *para*-nitro group is essentially coplanar with the picrate ring [C31*A*—C41*A*—N41*A*—O42*A* = −177.8 (3)°]. One of the O atoms of the *ortho*-related nitro group at C21*A* is
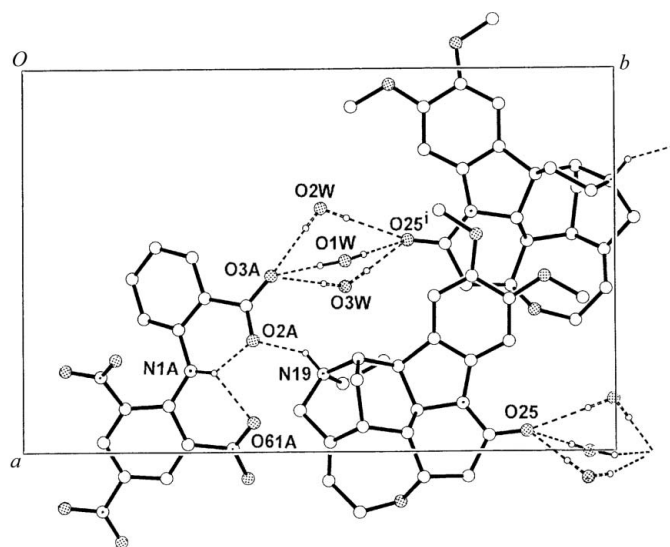


**Figure 2**
The cation–anion–water hydrogen-bonding environment in (I), showing the head-to-tail overlap of the brucinium cations which are part of the substructure extending along *a*. Hydrogen bonds are shown as dashed lines and non-associative H atoms have been omitted. [For symmetry code (i), see Table 1.]
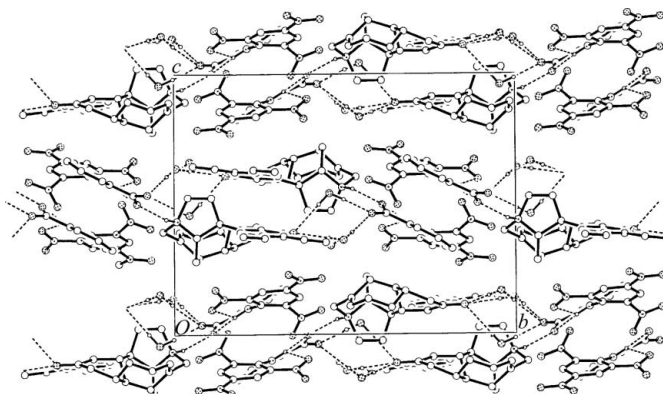


**Figure 3**
The layered structure of (I) in the unit cell, viewed down the *a* cell direction.

involved, not unexpectedly, in some short intramolecular nonbonded interactions [O21$A$···C1$A$ = 2.852 (4) Å and O21$A$···N1$A$ = 2.892 (4) Å].

The structure presented here provides another example of the molecular selectivity of brucine in forming stable complexes and is also the first reported structure of any form of the guest compound 2-(2,4,6-trinitroanilino)benzoic acid.

## Experimental

Compound (I) was synthesized by heating together brucine tetrahydrate (1 mmol) and 2-(2,4,6-trinitroanilino)benzoic acid (*o*-picraminobenzoic acid) (1 mmol) in ethanol–water (1:1 *v*/*v*, 50 ml) under reflux for 10 min. After concentration to *ca* 30 ml, partial room-temperature evaporation from the hot-filtered solution gave short orange–red prisms of (I) (m.p. 475 K).

*Crystal data*

$C_{23}H_{27}N_2O_4^+ \cdot C_{13}H_7N_4O_8^- \cdot H_2O$  
$M_r = 760.71$  
Orthorhombic, $P2_12_12_1$  
$a = 12.4407$ (3) Å  
$b = 19.1542$ (5) Å  
$c = 14.6744$ (4) Å  

$V = 3496.79$ (16) Å$^3$  
$Z = 4$  
Mo $K\alpha$ radiation  
$\mu = 0.11$ mm$^{-1}$  
$T = 173$ K  
$0.35 \times 0.15 \times 0.12$ mm  

*Data collection*

Oxford Gemini-S CCD area-detector diffractometer  
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2010)  
$T_{min} = 0.911$, $T_{max} = 0.980$  

12634 measured reflections  
4487 independent reflections  
3291 reflections with $I > 2\sigma(I)$  
$R_{int} = 0.031$  

*Refinement*

$R[F^2 > 2\sigma(F^2)] = 0.043$  
$wR(F^2) = 0.109$  
$S = 0.96$  
4487 reflections  

506 parameters  
H-atom parameters constrained  
$\Delta\rho_{max} = 0.58$ e Å$^{-3}$  
$\Delta\rho_{min} = -0.20$ e Å$^{-3}$  

A nonstandard orthorhombic axial setting was chosen for a better comparison with previous similar brucine structures. C-bound H atoms were included at calculated positions, with C—H = 0.93 (aromatic and $sp^2$) or 0.96–0.98 Å (aliphatic), and treated as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$. The H atom of the brucinium N$^+$—H group was located in a difference Fourier synthesis and its positional and isotropic displacement parameters were allowed to ride in the refinement [$U_{iso}(H) = 1.2U_{eq}(N)$]. The occupancies of the three partial solvent water molecules were determined as 0.73 (O1$W$), 0.17 (O2$W$) and 0.10 (O3$W$) from peak heights, and the O atoms of the two minor-occupancy components were refined isotropically. All three partial water molecules were found to be associated with the same two O-atom acceptors, and the H atoms on these were derived geometrically and also allowed to ride in the refinement [$U_{iso}(H) = 1.2U_{eq}(O)$]. The known absolute configuration of the parent strychnidin-10-one molecule (Peerdeman, 1956) was invoked and Friedel pairs were averaged for data used in the final cycles of refinement.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994);

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N19—H19···O2$A$ | 0.91 | 1.94 | 2.708 (4) | 141 |
| N1$A$—H1$A$···O2$A$ | 0.90 | 1.90 | 2.662 (3) | 141 |
| N1$A$—H1$A$···O62$A$ | 0.90 | 2.10 | 2.653 (4) | 118 |
| O1$W$—H11$W$···O3$A$ | 0.89 | 1.80 | 2.695 (4) | 177 |
| O1$W$—H12$W$···O25$^i$ | 0.90 | 2.19 | 3.091 (4) | 178 |
| O2$W$—H21$W$···O3$A$ | 0.91 | 2.17 | 3.079 (14) | 179 |
| O2$W$—H22$W$···O25$^i$ | 0.91 | 2.11 | 3.020 (14) | 179 |
| O3$W$—H31$W$···O3$A$ | 0.90 | 2.17 | 3.08 (2) | 179 |
| O3$W$—H32$W$···O25$^i$ | 0.91 | 1.73 | 2.65 (2) | 179 |

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

program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) within *WinGX* (Farrugia, 1999); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

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