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

Graham Smith* and Urs D. Wermuth

Faculty of Science and Technology, Queensland University of Technology, GPO Box 2434, Brisbane, Qld. 4001, Australia

Correspondence email: g.smith@qut.edu.au

In the structure of the 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 the classic undulating ribbon substructures through overlapping head-to-tail interactions while the anions and the three related partial water molecules of solvation (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···$O_{carboxyl}$ hydrogen bonds and indirectly by the three water molecules which form similar conjoint cyclic bridging units [graph set $R^2_4(8)$] through O—H···$O_{carbonyl}$ and $O_{carboxyl}$ hydrogen bonds, giving a two-dimensional layered structure. Within the anion, intramolecular N—H···$O_{carboxyl}$ 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) (Bialońska, A. & Ciunik, 2006*b*), 3-nitrobenzoic acid (methanol monosolvate) (Oshikawa *et al.*, 2002), 4-nitrobenzoic acid (isomorphous dihydrate and methanol monosolvate (Bialońska & Ciunik, 2007), 4-hydroxybenzoic acid (isopropyl alcohol monosolvate) (Sada *et al.*, 1998), 3,5-dinitrobenzoic acid (trihydrate, methanol monosolvate and disolvate) (Bialońska & Ciunik, 2007) and the anhydrous example with 5-nitrosalicylic acid (Smith, Wermuth, Healy & White, 2006). Three 1:1 salts are also known: 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; Bialońska & 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 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 $C_{23}H_{27}N_2O_4^+$ $C_{13}H_7N_4O_8^-$. H_2O (I) and the structure is reported here. No suitable crystals resulted from the reactions of brucine with the *meta*- and *para*-isomers.

In (I), protonation has occurred as expected at N19 of the brucine cage (Fig. 1), the invoked Peerdeman (1953) absolute configuration giving C7(*S*), C8(*S*), C12(*S*), C13(*R*), C14(*R*), C16(*S*), N19(*S*) for the 7 chiral centres for the brucinium cation. These cations form the the previously described undulating ribbon host substructures which have a dimeric repeat period in (I) of 12.4407 (3) Å along the direction of 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 water molecules of solvation [O1*W* (S.O.F = 0.73, O2*W* (S.O.F. = 0.17) and O3*W* (S.O.F = 0.10)] occupy the interstitial areas between the brucine substructures and are hydrogen-bonded to them. Brucinium cations form an N^+—H···O hydrogen bond with a carboxyl O acceptor of the anion while the water linkages are unusual, the three partial molecules forming a set of similar conjoint cyclic associations [graph set $R^2_4(8)$] involving two O-acceptor atoms (the brucinium carbonyl O25 and the carboxyl O3A of the anion) (Table 1) (see Fig. 2), giving a two-dimensional structure which layers down the *c*-cell direction (Fig. 3). Within the anion, intramolecular N—H···O$_{carboxyl}$ 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*- carboxyl group of the benzoate ring is rotated slightly out of the plane of the benzene ring [torsion angle 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 [torsion angles C11*A*–C21*A*–N21*A*–O22*A*, 151.7 (3)°; 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 [torsion angle 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* not unexpectedly is involved in some short intramolecular non-bonded interactions [O21*A*···C1*A*, 2.852 (4) Å; ···N1*A*, 2.892 (4) Å].

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

Experimental

The title compound (I) was synthesized by heating together under reflux for 10 min, 1 mmol quantities of brucine tetrahydrate and 2-(2,4,6-trinitroanilino)benzoic acid (*o*-picraminobenzoic acid) in 50 mL of 50% ethanol-water. After concentration to *ca.* 30 mL, partial room-temperature evaporation of 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, $\lambda = 0.71073$ Å
$\mu = 0.11$ mm^{-1}
$T = 173$ K
$0.35 \times 0.15 \times 0.12$ mm

Data collection

Oxford Diffraction Gemini-S CCD-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

0 restraints
H-atom parameters not refined
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}

Table 1

Hydrogen-bond geometry (Å, °)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N19—H19$\cdots$O2A	0.91	1.94	2.708 (4)	141
N1A—H1$A\cdots$O2A	0.90	1.90	2.662 (3)	141
N1A—H1$A\cdots$O62A	0.90	2.10	2.653 (4)	118
O1W—H11$W\cdots$O3A	0.89	1.80	2.695 (4)	177
O1W—H12$W\cdots$O25^i	0.90	2.19	3.091 (4)	178
O2W—H21$W\cdots$O3A	0.91	2.17	3.079 (14)	179
O2W—H22$W\cdots$O25^i	0.91	2.11	3.020 (14)	179
O3W—H31$W\cdots$O3A	0.90	2.17	3.08 (2)	179
O3W—H32$W\cdots$O25^i	0.91	1.73	2.65 (2)	179

Symmetry code: (i) $x-1/2, -y+3/2, -z$.

Hydrogen atoms potentially involved in hydrogen-bonding interactions were located by difference-Fourier methods and their positional and isotropic displacement parameters were allowed to ride in the refinement. Other H atoms were included at calculated positions [C—H(aromatic) = 0.93 Å; C—H (aliphatic) = 0.96–0.98 Å] and treated as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. The known absolute configuration for the parent strychnidin-10-one molecule (Peerdeman, 1956) was invoked. The occupancy of the three partial water molecules of solvation were determined as 0.73 (1) (O1W), 0.17 (1) (O2W) and 0.10 (1) (O3W and the two minor occupancy components were subsequently fixed and the O atoms were refined isotropically. Friedel pairs were averaged for data used in the final cycles of refinement.

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

References

Altomare, A., Burla, M. C., Camalli, M., Cascarno, C., Giacovazzo, A., Guagliardi, A. & Polidori, G. (1994). *J. Appl. Cryst.* **27**, 435.

Bialońska, A. & Ciunik, Z. (2004). *CrystEngComm.* **6**, 276–279.

Bialońska, A. & Ciunik, Z. (2006*a*). *Acta Cryst.* C**62**, o450–o453.

Bialońska, A. & Ciunik, Z. (2006*b*). *Acta Cryst.* E**62**, o5817–o5819.

Bialońska, A. & Ciunik, Z. (2007). *Acta Cryst.* C**63**, o120–o122.

Bialońska, A., Ciunik, Z., Popek, T. & Lis, T. (2005). *Acta Cryst.* C**61**, o88–o91.

Crocker, J. C. & Matthews, F. (1911). *J. Chem. Soc. Trans.* **99**, 301–313.

Dijksma, F. J. J., Gould, R. O., Parsons, S., Taylor, P. & Walkinshaw, M. D. (1998). *Chem. Commun.*, pp. 745–746.

Farrugia, L. J. (1999). *J. Chem. Cryst.* **32**, 837–838.

Gould, R. O. & Walkinshaw, M. D. (1984). *J. Am. Chem. Soc.* **106**, 7840–7842.

Oshikawa, T., Pochamroen, S., Takai, N., Ide, N., Takemoto, T. & Yamashita, M. (2002). *Heterocycl. Commun.* **8**, 271–274.

Oxford Diffraction (2010). *CrysAlis PRO*. Oxford Diffraction Ltd., Yarnton, England.

Peerdeman, A. F. (1956). *Acta Cryst.* **9**, 824.

Sada, K., Yoshikawa, K. & Miyata, M. (1998). *Chem. Commun.* pp. 1763–1764.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Smith, G., Wermuth, U. D., Healy, P. C. & White, J. M. (2006). *Aust. J. Chem.* **59**, 320–328.

Smith, G., Wermuth, U. D. & White, J. M. (2007*a*). *Acta Cryst.* C**63**, o4276–o4277.

Smith, G., Wermuth, U. D. & White, J. M. (2007*b*). *Acta Cryst.* C**63**, o4803.

Smith, G., Wermuth, U. D., Young, D. J. & Healy, P. C. (2005). *Acta Cryst.* E**61**, o2008–o2011.

Smith, G., Wermuth, U. D., Young, D. J. & White, J. M. (2006). *Acta Cryst.* E**62**, o1553–o1555.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

Wilen, S. H. (1972). *Tables of Resolving Agents and Optical Resolutions*, edited by E. L. Eliel, pp. 68–75. London: University of Notre Dame Press.

Figure 1

Figure 1. Molecular configuration and atom numbering scheme for the brucinium cation, the *o*-picraminobenzoate anion and the partial water molecules of solvation [O1*W*–O3*W*] in (I). Inter-species hydrogen bonds are shown as dashed lines with non-H atoms shown as 50% probability displacement ellipsoids.

Figure 2

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 are omitted. For symmetry code (i), see Table 1.

Figure 3

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