organic papers

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Key indicators

Single-crystal X-ray study

$T = 173$ K

Mean σ(C–C) = 0.004 Å

Disorder in solvent or counterion

R factor = 0.032

wR factor = 0.066

Data-to-parameter ratio = 11.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Strychninium (S)-2-(2-bromophenoxy)propanoate 1.4-hydrate

In the title molecular salt, $C_{21}H_{23}N_2O_2^+ \cdot C_9H_8BrO_3^- \cdot 1.4H_2O$, the components are linked by intermolecular $C-O^- \cdots H-{}^+N$ and $OW-H\cdots O$ interactions.

Comment

The quasiracemate approach to assembling supramolecular arrays involves the use of pairs of chemically unique compounds that, when cocrystallized, mimic the centrosymmetric packing tendencies of racemic compounds (Zhang & Curran, 2005; Jacques *et al.*, 1981; Fredga, 1973). Since quasiracemate design necessitates the use of molecules of opposite chirality, an important part of this work often initially includes preparing enantiopure building blocks. Our effort in this area over the last few years has explored several quasiracemate systems with fundamental components obtained by either standard stereoselective synthetic or resolution methods (Fomulu *et al.*, 2002a,b; Hendi *et al.*, 2001, 2004). As part of our current investigations, one such component, (S)-2-(2-bromophenoxy)propanoic acid, was isolated using the latter method, with strychnine as the resolving agent.

(I)
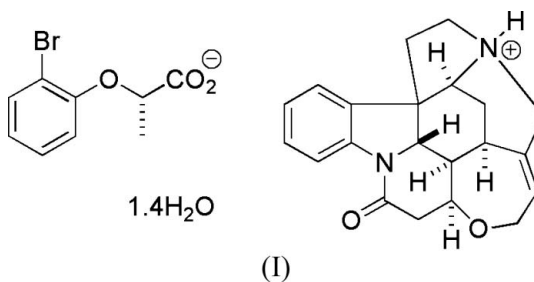
We report here the crystal structure of the title compound, (I), as part of an effort to confirm the stereochemical assignment of the phenoxypropionic acid, and also to understand the recognition behavior of this molecular salt. It is also expected that such structural information will provide insight into the hydrogen-bond and enantioselective preferences of this resolution process.

Inspection of Fig. 1 shows that the asymmetric unit of (I) contains a hydrated molecular salt consisting of (S)-2-(2-bromophenoxy)propanoate and strychninium ions. Two water molecules were located in the difference density map, with water atom O7 refined to 40% occupancy. The electron density of the carboxylate group is localized on O1, as evident from the difference between the C1—O1 and C1—O2 bond lengths [1.263 (3) and 1.240 (3) Å, respectively]. Other selected geometric parameters are given in Table 1. Each carboxylate group is linked to an adjacent strychninium N⁺—
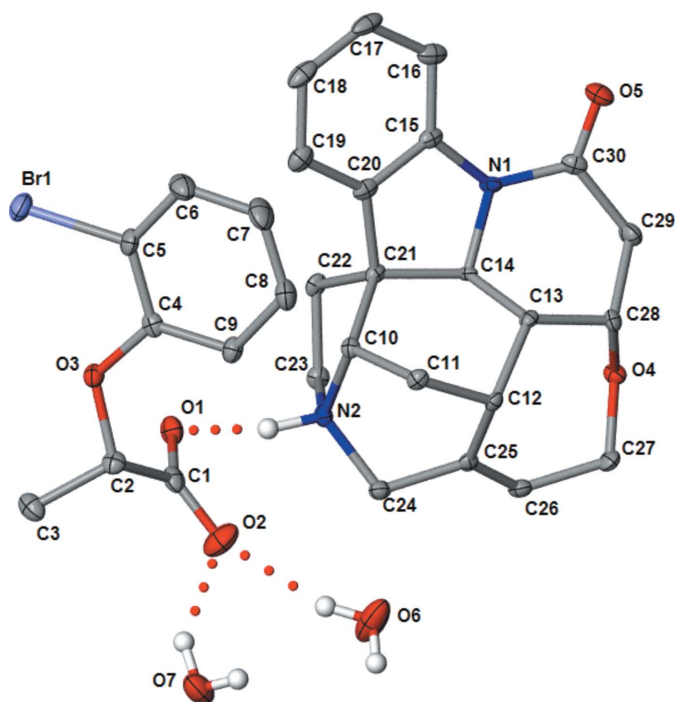
Figure 1
The asymmetric unit of (I), showing the atomic labeling scheme and with displacement ellipsoids drawn at the 50% probability level. Hydrogen bonds are shown as dotted lines; H atoms not involved in these interactions have been omitted for clarity.
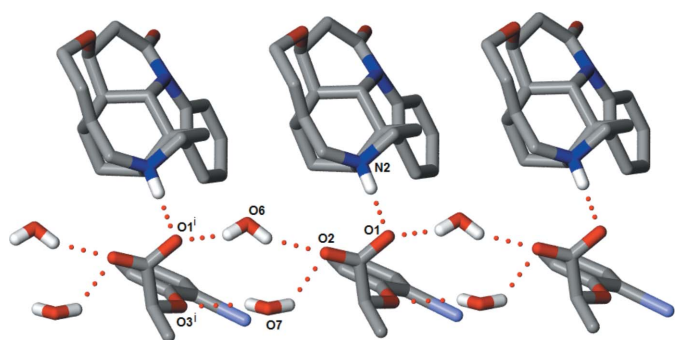

Figure 2
A view of the molecular packing of (I), showing the catemeric hydrogen-bond network (dotted lines). H atoms not involved in hydrogen bonding have been omitted. [Symmetry codes: (i) $x, y + 1, z$.]

we were somewhat surprised to discover that only two additional structures of this type exist in the Cambridge Structural Database (CSD, Version 5.27; Allen, 2002). Both N-benzoyl-alanine (CSD refcode CUXKIP10; Constante *et al.*, 1996) and bromochlorofluoroacetic acid (CSD refcode NUVPUP; Gould *et al.*, 1985) form molecular salts with strychine. In each case, including the present study of (I), the observed recognition behavior involves an (S)-carboxylate and the tertiary amminium group of strychnine *via* a $CO_2^-\cdots H\mathrm{-}^+N$ hydrogen bond, but the compounds vary in their degree of hydration: CUXKIP10 is a dihydrate and NUVPUP is anhydrous.

Experimental

2-(2-Bromophenoxy)propanoic acid was prepared and resolved according to the procedure described by Fredga & Andersson (1966). Suitable crystals for diffraction studies were obtained by slow evaporation of a 1:1 water–methanol solution.

Crystal data

$C_{21}H_{23}N_2O_2^+ \cdot C_9H_8BrO_3^- \cdot 1.4H_2O$	$Z = 2$
$M_r = 604.69$	$D_x = 1.493$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 11.8967 (7)$ Å	$\mu = 1.58$ mm^{-1}
$b = 7.3825 (4)$ Å	$T = 173 (2)$ K
$c = 15.6221 (9)$ Å	Blade, colorless
$\beta = 101.359 (3)°$	$0.24 \times 0.11 \times 0.04$ mm
$V = 1345.17 (13)$ Å^3	

Data collection

Bruker Kappa APEXII diffractometer	25259 measured reflections
φ and ω scans	4414 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)	3668 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.685, T_{\max} = 0.945$	$R_{\mathrm{int}} = 0.088$
	$\theta_{\max} = 30.6°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0275P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.032$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.066$	$(\Delta/\sigma)_{\max} = 0.002$
$S = 0.98$	$\Delta\rho_{\max} = 0.71$ e Å^{-3}
4414 reflections	$\Delta\rho_{\min} = -0.39$ e Å^{-3}
383 parameters	Absolute structure: Flack (1983), with 3478 Friedel pairs
H atoms treated by a mixture of independent and constrained refinement	Flack parameter: $-0.011 (5)$

H donor *via* $C\mathrm{-}O^-\cdots H\mathrm{-}^+N$ interactions (Fig. 2 and Table 2). This binary motif is further linked by two adjacent symmetry-independent water molecules to give a one-dimensional catemeric assemblage that propagates along the *b* axis. In the case of water atom O6, $O\mathrm{-}H\cdots O$ contacts are made to neighboring carboxylate groups, while atom O7 links adjacent carboxylate and phenoxy O3 atoms. Except for a possible close bromine$\cdots O_{\mathrm{ether}}$ interaction [Br1$\cdots$O4 = 3.209 (1) Å and C5$\mathrm{-}$Br1$\cdots$O4 = 161.15 (9)°], no other notable intermolecular contacts exist near van der Waals radii.

Since strychnine is a widely used alkaloid for Pasteurian resolutions of racemic carboxylic acids (Jacques *et al.*, 1981),

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.263 (3)	N1—C14	1.484 (3)
O2—C1	1.240 (4)	N2—C24	1.499 (4)
N1—C30	1.382 (3)	N2—C23	1.504 (3)
N1—C15	1.416 (3)	N2—C10	1.542 (3)
O2—C1—O1	125.1 (3)	C24—N2—C23	111.79 (19)
O2—C1—C2	116.9 (3)	C24—N2—C10	113.1 (2)
O1—C1—C2	118.0 (3)	C23—N2—C10	107.7 (2)
C30—N1—C15	123.1 (2)	C24—N2—HN2	114 (3)
C30—N1—C14	118.7 (2)	C23—N2—HN2	105 (3)
C15—N1—C14	109.4 (2)	C10—N2—HN2	104.4 (19)

Table 2
Hydrogen-bond geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
N2—HN2$\cdots$O1	0.95 (3)	1.73 (3)	2.656 (3)	164 (3)
O6—HO6A$\cdots$O2	0.74 (5)	2.16 (5)	2.845 (4)	156 (4)
O6—HO6B$\cdots$O1^{i}	0.79 (6)	2.05 (6)	2.806 (4)	160 (5)
O7—HO7A$\cdots$O2	0.87 (2)	2.37 (13)	2.905 (8)	120 (12)
O7—HO7B$\cdots$O3^{i}	0.87 (2)	2.45 (4)	3.255 (8)	155 (9)

Symmetry code: (i) $x, y + 1, z$.

Water molecules 06 and 07 were located in a difference density map and refined, resulting in unusually large anisotropic displacement parameters for O7. The occupancy factor for O7 and attached H atoms was refined to 0.397 and subsequently fixed at 0.40 for further data refinement.

Nitrogen- and oxygen-bound H atoms were located in a difference density map and refined isotropically. The H atoms on water atom O7 were fixed at O—H = 0.87 (2) Å. All other H atoms were treated as riding, with C—H distances of 0.95 (C_{Ar}—H), 0.98 (CH_3), 0.99 (CH_2) and 1.00 Å (CH), and with $U_{iso}(H) = 1.2U_{eq}(C)$ [$1.5U_{eq}$ for methyl H atoms]. Riding methyl H atoms were allowed to rotate freely during refinement.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT* and *XPREP* (Bruker, 2001); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *X-SEED* (Barbour, 2001).

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