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N-Benzyl-4-(hydroxyiminomethyl)pyridinium bromide

Renata Odžak,[a] Ivan Halasz,[a]* Sranka Tomić[a] and Dubravka Matković Čalogović[b]

[a]Laboratory of Organic Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, 10000 Zagreb, Croatia, and [b]Laboratory of General and Inorganic Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, 10000 Zagreb, Croatia

Correspondence e-mail: ihalasz@chem.pmf.hr

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Key indicators

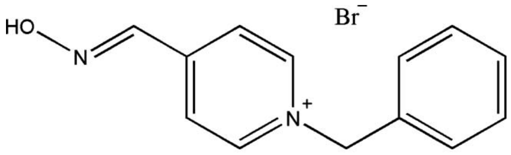
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
R factor = 0.032
wR factor = 0.080
Data-to-parameter ratio = 16.3

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

The title compound, $C_{13}H_{13}N_2O^+\cdot Br^-$, is a quaternary derivative of 4-(hydroxyiminomethyl)pyridine. The oxime adopts the *E* configuration and is involved in an O—H···Br hydrogen bond. Cations are linked by C—H···π interactions into dimers.

Comment

Many classes of heterocyclic oximes have been synthesized and tested as reactivators of acethylcholinesterase (AChE) inhibited by organophosphorus (OP) compounds used as pesticides and warfare agents (Primožič *et al.*, 2004; Sterling *et al.*, 1993; Bedford *et al.*, 1989). Unfortunately, only four of them are used or considered for use as antidotes against intoxication with OP compounds (toxogonin, PAM-2, HI-6 and TMB-4). The arrangement of substituents around the C═N bond of oximes, designated as the *E* or *Z* isomers (in the earlier literature indicated as the *syn* or *anti* isomers, respectively) may influence their reactivating potency. It has been shown that the *Z* isomer of *N*-methyl-4-(hydroxyiminomethyl)pyridinium iodide has inferior reactivating potency in comparison with the *E* isomer (Poziomek *et al.*, 1961). Furthermore, the toxicity of isomers can be different as shown for the more toxic *Z*,*Z* isomer of toxogonine (Leitis *et al.*, 1969). The arrangement of substituents around the C═N bond in *N*-benzyl-4-(hydroxyiminomethyl)pyridinum bromide, (I), shows that the oxime has the *E* configuration (Fig. 1).



(I)

Due to benzylations in (I), the N atom of pyridine can no longer act as an acceptor in a hydrogen bond, as was shown for (*E*)-4-(hydroxyiminomethyl)pyridine (Martinez-Ripoll & Lorenz, 1976). Instead, an O—H···Br hydrogen bond is formed, as expected (Table 1). Other interactions governing the packing of (I) are generally considered to be weak. The bromide ion is surrounded by either phenyl or pyridine rings from adjacent cations forming C—H···Br contacts. Additionally, C—H···π^i [symmetry code: (i) $1 - x$, $2 - y$, $1 - z$] interactions are formed between the methylene group and the benzyl group. The neighbouring benzylated N atom probably increases the proton-donor capabilities of the CH_2 group. The C—H···π interaction links cations into dimers (Fig. 2), with atom H7*B* 2.65 Å from the mean plane of the benzene ring.

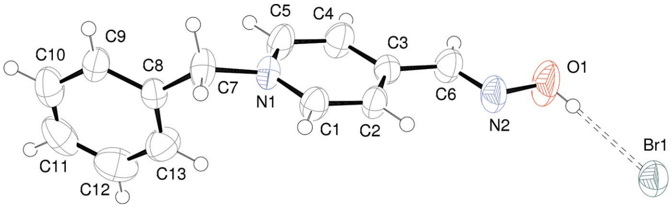


Figure 1
The formula unit of (I), showing the atom-labelling scheme and O—H···Br hydrogen bond (dashed line). Displacement ellipsoids are drawn at the 50% probability level.

Experimental

The title compound was prepared by a method similar to that decribed by De Jong *et al.* (1981) by addition of an equimolar amount of benzyl bromide (97.4 ml, 0.82 mmol, Aldrich) to a solution of (*E*)-4-(hydroxyiminomethyl)pyridine (100 mg, 0.82 mmol, Aldrich) in dry acetone (2 ml). The reaction mixture was left to stand in the dark at room temperature without stirring for 3 d. The title compound spontaneously crystallized from the reaction mixture as transparent crystals. A single crystal suitable for X-ray analysis was chosen directly from the reaction mixture.

Crystal data

$C_{13}H_{13}N_2O^+\cdot Br^-$
$M_r = 293.16$
Monoclinic, $P2_1/c$
$a = 10.365$ (2) Å
$b = 9.556$ (2) Å
$c = 13.297$ (3) Å
$\beta = 90.918$ (16)°
$V = 1316.9$ (5) Å^3
$Z = 4$
$D_x = 1.479$ Mg m$^{-3$}
Mo $K\alpha$ radiation
$\mu = 3.11$ mm^{-1}
$T = 295$ (2) K
Rounded block, colourless
0.65 × 0.45 × 0.30 mm

Data collection

Oxford Diffraction Xcalibur CCD diffractometer
ω scans
Absorption correction: analytical (Alcock, 1970)
$T_{\min} = 0.356$, $T_{\max} = 0.569$
4817 measured reflections
2571 independent reflections
1851 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.021$
$\theta_{\max} = 26.1°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.081$
$S = 0.98$
2571 reflections
158 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.43$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···Br1	0.80 (4)	2.37 (4)	3.153 (3)	166 (4)

H atoms of the aromatic rings and the methylene group positioned geometrically, with C—H = 0.93 and 0.97 Å, respectively, and refined as riding with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. The oxime H atom was found in a difference Fourier map and refined isotropically with no restraints.

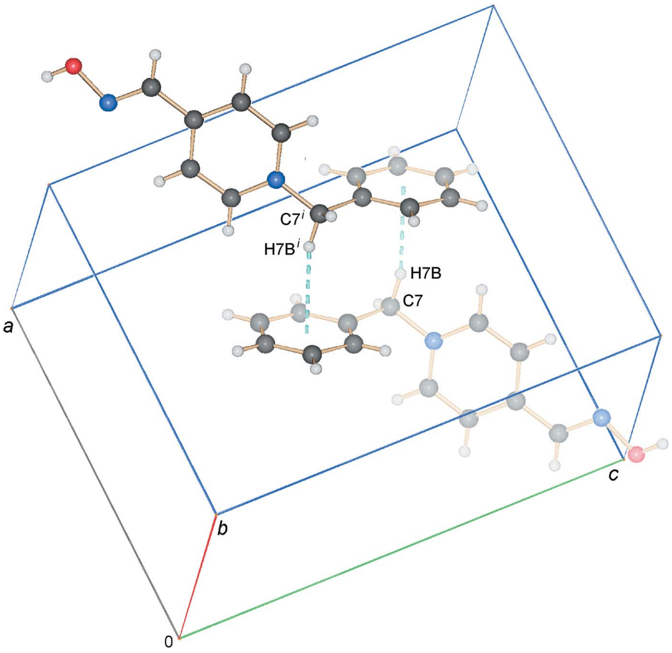


Figure 2
A dimer of cations formed by C—H···π interactions (dashed lines). [Symmetry code: (i) $1 - x, 2 - y, 1 - z$.]

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *SCHAKAL99* (Keller, 1999); software used to prepare material for publication: *SHELXL97*.

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