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p-Bromoanilinium chloride

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Key indicators

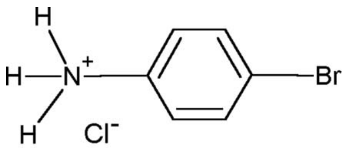
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.008 Å
R factor = 0.028
wR factor = 0.072
Data-to-parameter ratio = 9.5

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

Molecules of *p*-bromoanilinium chloride, $C_6H_7BrN^+\cdot Cl^-$ or $[BRANH]^+\cdot Cl^-$, are linked *via* $N^+—H\cdots Cl^-$ hydrogen bonds to form $R_4^2(8)$ supramolecular synthons parallel to the *bc* plane.

Comment

Owing to the paramount importance of the hydrogen bond in chemical, physical and biochemical processes, in recent decades the number of reports on this interaction has grown enormously. In addition, much attention has been devoted to non-classical hydrogen bonds and their role in crystal engineering and design, and this has been extensively reviewed (*e.g.* Desiraju, 1989). This interest has subsequently been extended to a specific class of compounds, namely solvent-free 4-halopyridinium halides and (mono)haloanilinium halides, and the interplay between hydrogen bonds and halogen–halogen contacts has been investigated (Freytag *et al.*, 1999; Gray & Jones, 2002). More recently, comparison of the crystal structures of solvent-free 4-*X*-substituted anilines (*X* is C≡C—H, Cl, Br or I; Dey *et al.*, 2003) has shown that ethynyl, chloro and bromo, but not iodo, substituents exert exactly the same role on crystal packing. To date, the crystal structures of *p*-fluoro- and *p*-chloroanilinium hydrochlorides have been reported in the literature (Colapietro *et al.*, 1981; Ploug-Sørensen & Andersen, 1985). Accordingly, in order to ascertain any topological similarities between *p*-haloanilinium hydrochlorides, this paper reports the crystal structure of *p*-bromoaniline hydrochloride or $[BRANH]^+\cdot Cl^-$, (I).



(I)

The asymmetric unit of (I) comprises a planar monoprotonated *p*-bromoanilinium cation and a Cl^- anion (Fig. 1). With regard to the aromatic ring, the bond lengths and angles agree, within experimental error, with the axial symmetry observed in most *para*-disubstituted benzene derivatives (Table 1). The Br substituent is displaced out of the least-squares plane of the aromatic ring by only 0.021 (5) Å and the C4—Br bond length of 1.892 (5) Å is experimentally the same as those observed in *p*-bromoanilinium bromide hemihydrate [1.901 (4) Å; Gray & Jones, 2002] and *p*-dibromobenzene [1.890 (3) Å; Schultz *et al.*, 1988].

In the NH_3^+ group, the C1—N distance of 1.463 (6) Å agrees with the values reported for *p*-substituted halo-

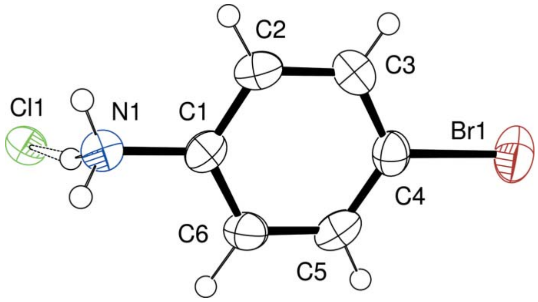


Figure 1
A drawing of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

anilinium cations [1.457 (3)–1.468 (3) Å] (Colapietro *et al.*, 1981; Ploug-Sørenson & Andersen, 1985; Gray & Jones, 2002). A comparison of the molecular geometry of (I) with that of the free base (Dey *et al.*, 2003) shows that the C1—N bond is lengthened by ~0.07 Å and the ring angle is widened by ~4.2°, results that are ascribed to protonation in the former. Consistent with previous cases, one of the H atoms of the NH_3^+ group is almost eclipsed with the benzene ring (Colapietro *et al.*, 1980, 1981, 1982; Ploug-Sørenson & Andersen, 1985; Gray & Jones, 2002).

The hydrogen-bonding scheme of (I) involves all H atoms of the NH_3^+ group (Fig. 2 and Table 2) and consists entirely of $N^+—H\cdots Cl^-$ interactions; the average $N^+\cdots Cl^-$ distance is 3.147 (5) Å. The NH_3^+ and Cl^- ions are connected through $N^+—H\cdots Cl^-$ hydrogen bonds parallel to *bc*, forming just one $R^2_4(8)$ supramolecular synthon (Etter *et al.*, 1990). Roughly perpendicular to the *bc* plane, there is one Cl···Br contact of 3.587 (4) Å per molecule. A similar topology has been found in *p*-chloroaniline hydrochloride (Ploug-Sørenson & Andersen, 1985) and in *p*-toluidine hydrochloride (Colapietro *et al.*, 1982), while the network of hydrogen bonds is different from that occurring in the *p*-fluoro-, *p*-cyano- (Colapietro *et al.*, 1981) and *p*-aminoaniline hydrochlorides (Colapietro *et al.*, 1980). This study supports the observed supramolecular similarity for 4-haloanilines (Dey *et al.*, 2003), because the replacement of Cl with Br causes no significant change in their crystal structure.

Experimental

p-Bromoaniline hydrochloride was obtained as a white powder by adding concentrated HCl to an ethanol solution of the free base (Sigma–Aldrich, 99% purity, 0.001 mol), and this was recrystallized by slow evaporation of an aqueous solution of (I).

Crystal data

$C_6H_7BrN^+\cdot Cl^-$
$M_r = 208.49$
Monoclinic, $P2_1/c$
$a = 8.629$ (2) Å
$b = 9.784$ (2) Å
$c = 9.863$ (9) Å
$\beta = 105.61$ (5)°
$V = 802.0$ (8) Å^3
$Z = 4$
$D_x = 1.727$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12 reflections
$\theta = 15$–20°
$\mu = 5.37$ mm^{-1}
$T = 298$ (2) K
Prism, colourless
0.18 × 0.18 × 0.15 mm

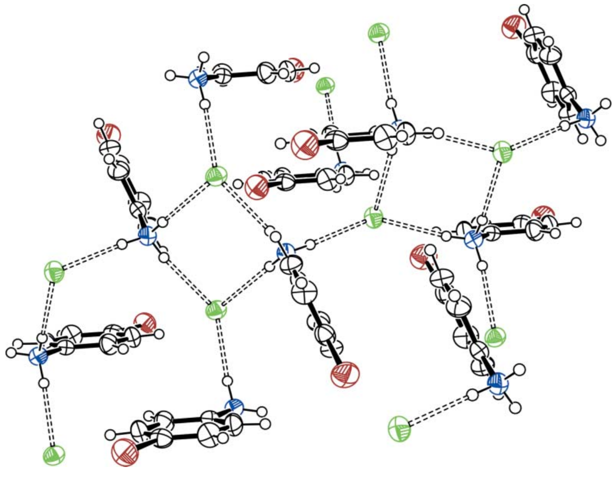


Figure 2
A packing diagram for (I), viewed down the *a* axis. Hydrogen bonds are indicated by dashed lines.

Data collection

Enraf–Nonius CAD-4F diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.396$, $T_{max} = 0.450$
3628 measured reflections
1113 independent reflections
781 reflections with $I > 2\sigma(I)$
$R_{int} = 0.011$
$\theta_{max} = 23.5°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 11$
3 standard reflections
frequency: 33 min
intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.072$
$S = 1.10$
781 reflections
82 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0331P)^2 + 2.5739P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.57$ e Å^{-3}
$\Delta\rho_{min} = -0.56$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Br1—C4	1.892 (5)	C2—C3	1.385 (8)
N1—C1	1.463 (6)	C3—C4	1.376 (8)
C1—C2	1.372 (7)	C4—C5	1.367 (8)
C1—C6	1.371 (7)	C5—C6	1.373 (7)
N1—C1—C2	119.5 (5)	Br1—C4—C5	120.3 (4)
N1—C1—C6	119.0 (5)	Br1—C4—C3	119.4 (4)
C2—C1—C6	121.5 (5)	C3—C4—C5	120.3 (5)
C1—C2—C3	119.3 (5)	C4—C5—C6	120.9 (5)
C2—C3—C4	119.4 (5)	C1—C6—C5	118.7 (5)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11···Cl1	0.93	2.24	3.143 (5)	164
N1—H12···Cl1^{i}	0.85	2.31	3.136 (5)	162
N1—H13···Cl1^{ii}	0.85	2.31	3.161 (4)	171

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

All H atoms were found in a difference map and kept fixed during the final refinement (C—H = 0.84–1.02 Å and N—H = 0.85–0.93 Å), with $U_{\rm iso}$(H) values equal to $1.2U_{\rm eq}$ of the parent atom.

Data collection: *XCS* (Colapietro *et al.*, 1992); cell refinement: *XCS*; data reduction: *XCS*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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