Acta Crystallographica Section C
**Crystal Structure
Communications**
ISSN 0108-2701

Secondary interactions in 4-bromo-*N*,*N*-dimethylanilinium bromide

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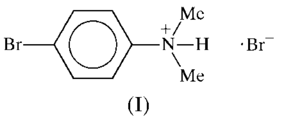
Received 6 March 2002
Accepted 15 March 2002
Online 19 April 2002

The crystal packing of the title compound, $C_8H_{11}BrN^+\cdot Br^-$, involves three types of secondary interaction: a classical N—H···Br⁻ hydrogen bond, a 'weak' but short C—H···Br⁻ interaction (normalized H···Br distance of 2.66 Å) and a cation–anion Br···Br contact of 3.6331 (4) Å. The hydrogen bonds connect two cations and two anions to form rings of graph set $R_4^2(14)$. The Br···Br contacts link these rings to form layers parallel to the *bc* plane.

Comment

We are interested in the variety of secondary interactions in halopyridinium and haloanilinium halides, and have published the structures of 4-halopyridinium halides (Jones *et al.*, 1999), 2-, 3- and various dihalopyridinium halides (Jones & Freytag, 2001), haloanilinium halides (Gray & Jones, 2002*a*) and dichloroanilinium chlorides (Gray & Jones, 2002*b*). These series of structures involve halogen–halogen contacts, classical N—H···halide hydrogen bonds and, in some cases, weak C—H···halide hydrogen bonds. The anilinium derivatives generally form structures with hydrophilic layers, and these consist of hydrogen-bonded rings of graph set $R_{2n}^n(4n)$, in which two of the three H atoms from each of n NH_3^+ groups are the donors and n halide ions are the acceptors (n = 2–4). We then wished to investigate the effect of blocking some of the hydrogen-bond donors, and so present here the structure of 4-bromo-*N*,*N*-dimethylanilinium bromide, (I).



(I)

The bond lengths and angles of (I) (Fig. 1) may be considered normal. The conformation of the dimethylamino group is such that the C2—C1—N—C8 grouping is approximately antiperiplanar [torsion angle 173.51 (13)°]. The ring is planar (the r.m.s. deviation of the six C atoms is 0.008 Å) and the Br and N substituents are slightly displaced to one side of the plane by 0.098 (2) and 0.150 (2) Å, respectively.

There are three predominant secondary interactions that determine the packing of (I). First, a classical, approximately linear, N—H···Br⁻ hydrogen bond is observed (Table 2). Secondly, the 'weak' C3—H3···Br⁻ hydrogen bond is by far the shortest of several such interactions (Table 2); if the C—H bond length is set to 1.08 Å, then the normalized H···Br distance (Steiner, 1998) is only 2.66 Å. Finally, a Br1···Br2($1 - x, y - \frac{1}{2}, \frac{1}{2} - z$) contact of 3.6331 (4) Å (*cf.* sum of van der Waals radii 3.70 Å; Bondi, 1964) connects cation and anion; as usual (see *e.g.* Jones *et al.*, 1999), the C—Br···Br⁻ angle is approximately linear, at 169.54 (4)°.

The combined effect of the two hydrogen bonds is to link two cations and two anions to form inversion-symmetric rings of graph set $R_4^2(14)$ (Fig. 2). These are linked by Br···Br interactions to form layers parallel to the *bc* plane.

The blocking of two hydrogen-bond donors by methyl groups in (I) has thus reduced the dimensionality of the hydrogen-bonding pattern from a two-dimensional array of classical hydrogen bonds to a zero-dimensional pattern of one classical and one 'weak' hydrogen bond. An intermediate type of system might be expected for an aniline derivative bearing the $-N^+(CH_3)H_2$ group. Corresponding studies are in progress.

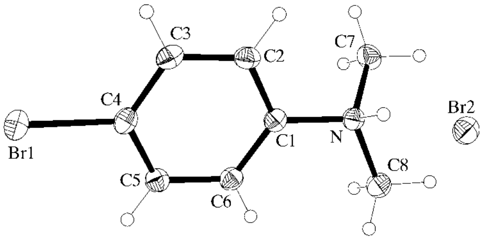


Figure 1
A view of the formula unit of (I) in the crystal. Displacement ellipsoids are drawn at the 50% probability level and H-atom radii are arbitrary.

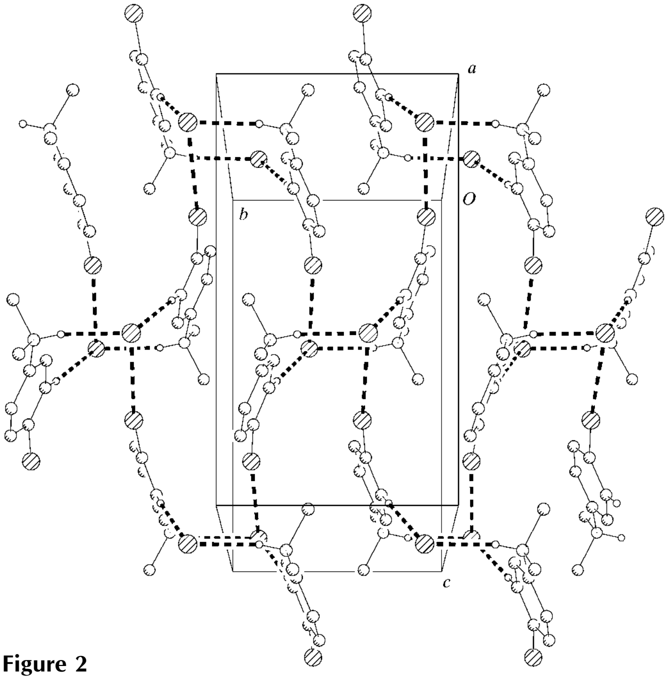


Figure 2
A packing diagram of (I) viewed perpendicular to the *bc* plane. H atoms not involved in hydrogen bonds have been omitted for clarity. Hydrogen bonds and Br···Br interactions are indicated by dashed lines. There is one such layer per *a*-axis repeat.

DOI: 10.1107/S0108270102004882

Experimental

4-Bromo-*N*,*N*-dimethylaniline (2.14 g, 7.62 mmol) was dissolved in ethanol (10 ml) and 48% hydrobromic acid (1.22 ml) was added slowly with stirring. Further ethanol (10 ml) was added and the solution stirred for 2 h. The solution was then evaporated to dryness and the residue taken up in the minimum amount of ethanol. Addition of diethyl ether (30 ml) precipitated the product as a white solid, which was filtered off, washed with diethyl ether and dried *in vacuo*. Analysis found: C 34.22, H 3.96, N 4.75%; calculated: C 34.20, H 3.95, N 4.98%. Single crystals of (I) were obtained from ethanol–diethyl ether.

Crystal data

$C_8H_{11}BrN^+\cdot Br^-$
$M_r = 281.00$
Monoclinic, $P2_1/c$
$a = 9.9511$ (12) Å
$b = 7.6156$ (10) Å
$c = 13.5616$ (16) Å
$\beta = 109.104$ (3)°
$V = 971.1$ (2) Å^3
$Z = 4$
$D_x = 1.922$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 11 315 reflections
$\theta = 2$–28°
$\mu = 8.29$ mm^{-1}
$T = 143$ (2) K
Square prism, colourless
0.40 × 0.16 × 0.13 mm

Data collection

Bruker SMART1000 CCD area-detector diffractometer
ω and φ scans
Absorption correction: numerical (*XPREP*; Siemens, 1994)
$T_{min} = 0.113$, $T_{max} = 0.379$
20 417 measured reflections
2837 independent reflections
2457 reflections with $I > 2\sigma(I)$
$R_{int} = 0.059$
$\theta_{max} = 30°$
$h = -14 \rightarrow 14$
$k = -10 \rightarrow 10$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.043$
$S = 1.04$
2837 reflections
106 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0195P)^2 + 0.1484P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.57$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—N	1.4805 (18)	N—C8	1.4942 (19)
C4—Br1	1.8992 (15)	N—C7	1.4998 (19)
C6—C1—C2	121.13 (13)	C1—N—C7	112.48 (11)
C3—C4—C5	121.39 (14)	C8—N—C7	109.46 (12)
C1—N—C8	115.20 (12)		
C2—C1—N—C8	173.51 (13)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N—H0···Br2	0.91 (2)	2.28 (2)	3.1716 (13)	167.3 (16)
C3—H3···Br2^{i}	0.95	2.79	3.7147 (15)	165
C6—H6···Br2^{ii}	0.95	3.04	3.9052 (15)	152
C7—H7*A*···Br2^{iii}	0.98	2.96	3.9216 (16)	168
C7—H7*B*···Br2^{iv}	0.98	3.04	3.9537 (16)	155
C8—H8*A*···Br2^{ii}	0.98	2.98	3.7043 (17)	132
C8—H8*B*···Br2^{iv}	0.98	3.02	3.9331 (16)	156

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

The following faces (with distances from a common point in mm) were indexed and used for a numerical absorption correction: 110 0.087, $\bar{1}\bar{1}0$ 0.070, 001 0.212, $00\bar{1}$ 0.178, $\bar{1}10$ 0.063 and $1\bar{1}0$ 0.080. H atoms were visible in difference syntheses. The H atom bonded to the N atom was refined freely. Methyl groups were idealized and refined as rigid groups allowed to rotate but not tip. Other H atoms were included using a riding model starting from calculated positions. Aromatic C—H distances were fixed to 0.95 Å and methyl C—H to 0.98 Å, and U_{iso}(H) values were set to $1.2U_{eq}$ of the parent atom.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

LG was financed under the Erasmus scheme. The authors thank the Fonds der Chemischen Industrie for financial support and Mr A. Weinkauf for technical assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1494). Services for accessing these data are described at the back of the journal.

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