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A second polymorph of 2,5-dibromoanilinium bromide

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All atoms of the title compound, $C_6H_6Br_2N^+\cdot Br^-$, except for two H atoms of the NH_3^+ group, lie in a crystallographic mirror plane. The packing within the plane is determined by hydrogen bonds $N^+—H\cdots Br^-$ and $C—H\cdots Br^-$, and by $Br\cdots Br$ contacts. Planes are linked by hydrogen bonds $N^+—H\cdots Br^-$. The packing is completely different from that of the previously known form [López–Duplá, Jones & Vancea (2003). *Z. Naturforsch. Teil B*, **58**, 191–200].

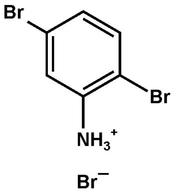
Key indicators

Single-crystal X-ray study
T = 133 K
Mean σ(C–C) = 0.005 Å
R factor = 0.030
wR factor = 0.074
Data-to-parameter ratio = 20.7

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

Comment

We are interested in secondary bonding contacts (classical and 'weak' hydrogen bonds, halogen–halogen contacts) in structures of haloanilinium halides (López-Duplá *et al.*, 2003; Gray & Jones, 2002*a*,*b*). We have already reported the synthesis and structure of 2,5-dibromoanilinium bromide (López-Duplá *et al.*, 2003), which crystallized from ethanol/diisopropyl ether in space group $P2_1/c$ with the usual type of packing for these compounds; this involves hydrophilic layers with rings of $N—H\cdots$halide hydrogen bonds, generally supported by halogen–halogen interactions. We have now, by chance, determined the structure of a second form of the same compound, crystallized from the very similar solvent system ethanol/diethyl ether.



(I)

The formula unit, which lies completely in the crystallographic mirror plane $y = \frac{1}{4}$, except for two H atoms of the NH_3^+ group, is presented in Fig. 1. Bond lengths and angles are normal.

The packing is completely different from that of the previously known form, being largely restricted to interactions within the mirror plane. One layer is presented in Fig. 2. A classical $N^+—H\cdots Br^-$ hydrogen bond is observed, as are two 'weak' hydrogen bonds, forming a bifurcated system of the form $(C—H\cdots)_2Br^-$ (Table 1). There are also two bromine–bromine contacts to the bromide anion, namely $Br1\cdots Br3(1 + x, y, z)$ = 3.3379 (6) Å and $Br2\cdots Br3(x, y, 1 + z)$ = 3.6977 (6) Å; both are approximately linear at the central bromine [$C—Br\cdots Br$ = 173.42 (11) and 176.47 (10)°].

The layers are connected by the second classical hydrogen bond, which is longer than the first and distinctly non-linear

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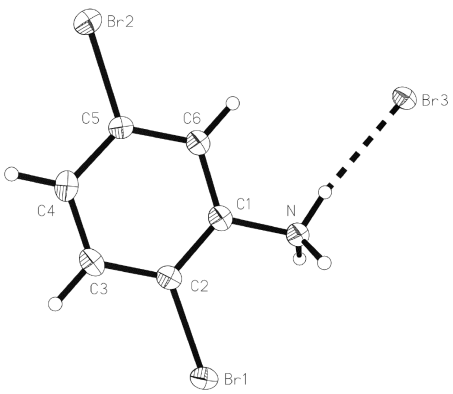

Figure 1
The formula unit of the title compound in the crystal. Displacement ellipsoids are drawn at the 50% probability level. The H-atom radii are arbitrary.

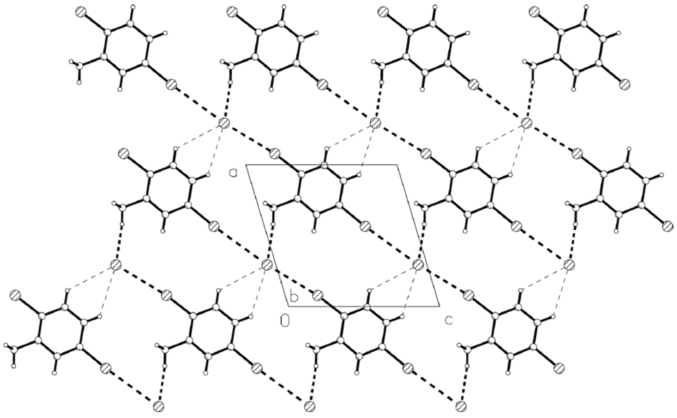

Figure 2
Packing diagram of one layer of the title compound (at $y = \frac{1}{4}$), projected along the *b* axis. Secondary interactions are indicated by dashed lines (thick, classical hydrogen bonds and Br$\cdots$Br; thin, 'weak' hydrogen bonds).

(Fig. 3). The distance between the layers is $b/2 = 3.274$ Å. The density of the current form is slightly lower than that of the previous form (2.465, *cf.* 2.480 Mg m^{-3}).

A similar layer structure involving crystallographic mirror planes in $P2_1/m$, though differing in detail, was observed for 3-iodoanilinium iodide (Gray & Jones, 2002*a*). These are the only two structures in the series that depart from the usual hydrophilic ring motif.

Experimental

During a study of tribromoacetates, small crystals of the title compound were obtained on attempting to crystallize 2,5-dibromoanilinium tribromoacetate from ethanol/diethyl ether.

Crystal data

$C_6H_6Br_2N^+\cdot Br^-$
$M_r = 331.85$
Monoclinic, $P2_1/m$
$a = 8.3640$ (12) Å
$b = 6.5476$ (11) Å
$c = 8.5472$ (12) Å
$\beta = 106.815$ (5)°
$V = 448.07$ (12) Å^3
$Z = 2$
$D_x = 2.460$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3592 reflections
$\theta = 2.5$–30.5°
$\mu = 13.43$ mm^{-1}
$T = 133$ (2) K
Prism, colourless
$0.16 \times 0.09 \times 0.06$ mm

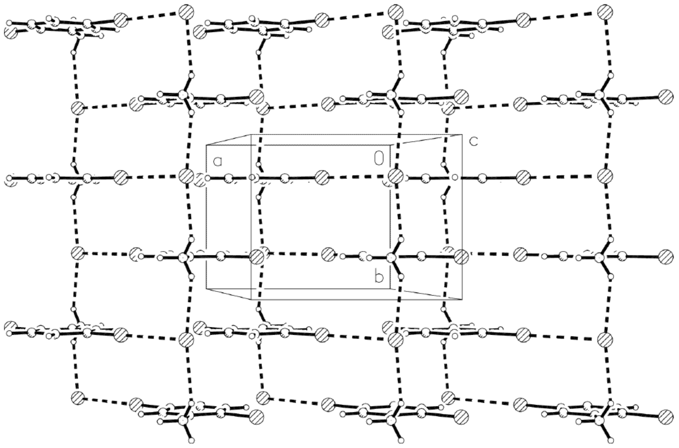

Figure 3
Side view of the layers of the title compound, viewed perpendicular to the *ab* plane. Secondary interactions are indicated by dashed lines.

Data collection

Bruker SMART 1000 CCD diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{\min} = 0.233$, $T_{\max} = 0.494$
7449 measured reflections
1408 independent reflections
1200 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\max} = 30.0°$
$h = -11 \rightarrow 11$
$k = -9 \rightarrow 9$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.074$
$S = 1.01$
1408 reflections
68 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0487P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.88$ e Å^{-3}
$\Delta\rho_{\min} = -1.27$ e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N—H01$\cdots$Br3	0.93 (3)	2.32 (3)	3.240 (3)	173 (4)
N—H02$\cdots$Br3$^{\rm i}$	0.92 (2)	2.54 (3)	3.2936 (6)	139 (2)
C3—H3$\cdots$Br3$^{\rm ii}$	0.95	3.11	3.757 (4)	127
C4—H4$\cdots$Br3$^{\rm ii}$	0.95	3.06	3.727 (4)	128

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $1 + x, y, 1 + z$.

H atoms bonded to nitrogen were refined freely but with N—H bond lengths restrained to be equal within a nominal s.u. of 0.02 Å. Other H atoms were included using a riding model with fixed C—H bond lengths of 0.95 Å; $U_{\rm iso}$(H) values were fixed at $1.2U_{\rm eq}$ of the parent atom. Main features of residual electron density lie close to the Br atoms.

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.

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