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A second polymorph of 3,5-dibromopyridinium bromide

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Key indicators

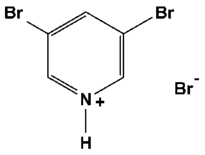
Single-crystal X-ray study
T = 133 K
Mean σ(C–C) = 0.004 Å
R factor = 0.020
wR factor = 0.052
Data-to-parameter ratio = 22.6

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

All atoms of the title compound, $C_5H_4Br_2N^+\cdot Br^-$, 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, but differs from that of the previous polymorph [Freytag & Jones (2001). *Z. Naturforsch. Teil B*, **56**, 889–869], which also lay completely in mirror planes.

Comment

We are interested in secondary bonding contacts (classical and 'weak' hydrogen bonds, halogen-halogen contacts) in structures of halopyridinium halides (see Freytag & Jones, 2001, and references therein). In that publication we had already reported the synthesis and structure of the compound 3,5-dibromopyridinium bromide, (I), which crystallized from acetonitrile/methanol/diethyl ether in space group $P4_2/mnm$. We have now by chance determined the structure of a second form of the same compound, crystallized from dichloromethane/diethyl ether.



(I)

The asymmetric unit, which lies completely in the crystallographic mirror plane $y = 0$, is shown in Fig. 1. Bond lengths and angles may be regarded as normal, in particular the widened bond angle at the protonated N atom.

The packing within one layer is presented in Fig. 2. A classical $N^+—H\cdots Br^-$ hydrogen bond is observed, as are two 'weak' hydrogen bonds of the form $C—H\cdots Br^-$ (Table 2). Only the shorter of these latter two interactions is shown explicitly in Fig. 2; it has a normalized $H\cdots Br$ distance of only 2.58 Å.

There are also several bromine-bromine contacts. The shortest of these, $Br1\cdots Br3(x, y, z - 1)$ = 3.4752 (5) and $Br2\cdots Br3(-x, -y, 1 - z)$ = 3.5117 (5) Å, involve the anion Br3 and are approximately linear at the central bromine [$C—Br\cdots Br$ = 158.35 (9) and 168.36 (9)°]. Such contacts are thought to be associated with a positive region of charge in the extension of the C—Br vector beyond Br. Two further $Br\cdots Br$ contacts are longer than the double van der Waals radius of 3.7 Å (Bondi, 1964), but may, nevertheless, be regarded as structurally significant; $Br1\cdots Br2(-x, -y, -z)$ = 3.9011 (5) Å and $Br1\cdots Br1(1 -x, -y, -z)$ = 3.8311 (7) Å. The latter, with $C—Br\cdots Br$ angles equal by symmetry at 119.39 (9)°, is a

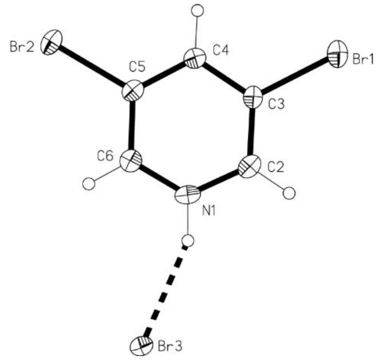


Figure 1
The formula unit of the title compound in the crystal. Ellipsoids are drawn at the 50% probability level and H-atom radii are arbitrary.

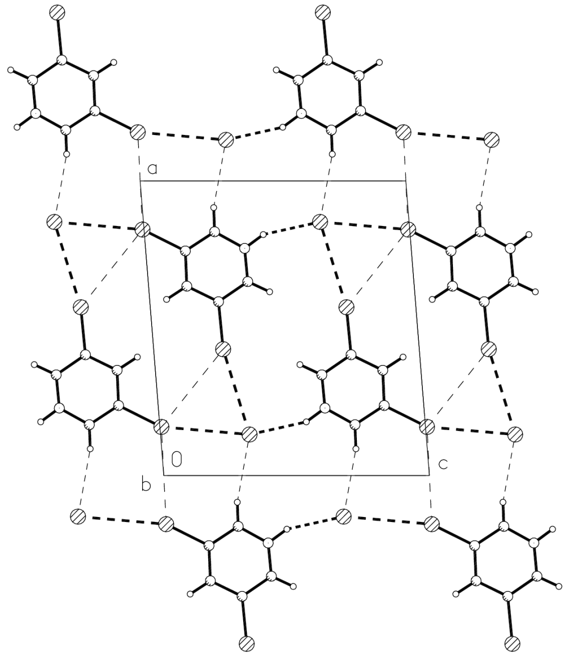


Figure 2
Packing diagram of one layer of the title compound (at $y = \frac{1}{2}$), projected along the *b* axis. Secondary interactions are indicated by dashed lines (thick, classical hydrogen bonds and short Br···Br; thin, 'weak' hydrogen bonds and long Br···Br).

typical 'type I' interaction as classified by Pedireddi *et al.* (1994); in contrast to type II interactions (one 90° and one 180° angle), these are not thought to represent significant electrostatic interactions, but nevertheless are observed so frequently that some stabilizing effect might be presumed. The former has angles of 101.84 (9) and 136.03 (9)° and lies between types I and II.

The packing of the previous modification, also involving layers in crystallographic mirror planes, differed from the pattern described here in one important respect; the higher symmetry of the layers (4/*mmm*), in which the N—H bonds of neighbouring rings are exactly antiparallel and 'share' two bromides *via* three-centre hydrogen bonds, thus forming units $N^+—H(\cdots Br^-\cdots)_2H—N^+$. In Fig. 2, the formal conversion of the lower to the higher symmetry form can be seen in terms of the $R_4^2(10)$ ring centred at $x = 1$, $z = \frac{1}{2}$; the pyridine rings to the upper right and lower left of the cell edge should both be rotated anticlockwise.

The distance between the layers is $b/2 = 3.419$ Å, *cf.* 3.442 Å in the previous modification; however, the latter has a significantly higher density, 2.631 *versus* 2.553 Mg m^{-3}, suggesting more efficient packing in its layers. One surmises that the energy balance between the two forms would be very delicate.

Experimental

During a study of tribromoacetates, small crystals of the title compound were obtained on attempting to crystallize 3,5-dibromopyridinium tribromoacetate from dichloromethane/diethyl ether. Presumably these arose from small quantities of bromine or bromide as a decomposition product.

Crystal data

$C_5H_4Br_2N^+\cdot Br^-$
$M_r = 317.82$
Monoclinic, $C2/m$
$a = 11.6270$ (8) Å
$b = 6.8372$ (4) Å
$c = 10.4344$ (6) Å
$\beta = 94.574$ (4)°
$V = 826.85$ (9) Å^3
$Z = 4$
$D_x = 2.553$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4877 reflections
$\theta = 3.5$–30.5°
$\mu = 14.55$ mm^{-1}
$T = 133$ (2) K
Prism, colourless
0.25 × 0.13 × 0.08 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{\min} = 0.253$, $T_{\max} = 0.462$
7962 measured reflections
1308 independent reflections
1138 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\max} = 30.0°$
$h = -16 \rightarrow 16$
$k = -9 \rightarrow 9$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.052$
$S = 1.06$
1308 reflections
58 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0338P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.55$ e Å^{-3}
$\Delta\rho_{\min} = -0.78$ e Å^{-3}

Table 1
Selected geometric parameters (°).

C6—N1—C2	124.4 (3)	N1—C6—C5	119.1 (3)
N1—C2—C3	117.7 (3)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H01···Br3	0.912 (19)	2.29 (2)	3.140 (2)	156 (4)
C6—H6···Br2$^{\rm i}$	0.95	3.08	4.006 (3)	166
C2—H2···Br3$^{\rm ii}$	0.95	2.71	3.641 (3)	168

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

The acidic H atom was refined freely but with an N—H bond length restraint. 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 1.2 times $U_{\rm eq}$ 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.

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