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(Bromomethyl)trimethylammonium bromide

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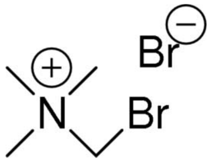
Key indicators: single-crystal X-ray study; T = 115 K; mean σ(N–C) = 0.005 Å; R factor = 0.038; wR factor = 0.114; data-to-parameter ratio = 23.5.

In the title compound, $C_4H_{11}BrN^+\cdot Br^-$, both ions lie on crystallographic mirror planes. The C$\cdots$Br distance is 1.943 (4) Å.

Related literature

For related literature, see: Budzinski & Box (1971); Chyall & Kenttamaa (1994); Della & Smith (2000); Fletcher *et al.* (1999); Fletcher Claville *et al.* (2006); Johnson *et al.* (1993); Minegishi (1977); Rios *et al.* (1996); Sieker *et al.* (1996); Stirk & Kenttamaa (1991); Stirk *et al.* (1992); Willey *et al.* (1991); Yates *et al.* (1984).



Experimental

Crystal data

$C_4H_{11}BrN^+\cdot Br^-$
M_r = 232.96
Orthorhombic, *Pnma*
a = 19.674 (3) Å
b = 6.9319 (11) Å
c = 5.7038 (10) Å
V = 777.9 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 10.32 mm^{-1}
T = 115 K
0.30 × 0.20 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer with an Oxford Cryosystems Cryostream cooler
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor 1997)
T_{min} = 0.148, T_{max} = 0.626
14337 measured reflections
1363 independent reflections
1149 reflections with $I > 2\sigma(I)$
R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.114
S = 1.04
1363 reflections
58 parameters
Only H-atom coordinates refined
$\Delta\rho_{max}$ = 1.73 e Å^{-3}
$\Delta\rho_{min}$ = −1.34 e Å^{-3}

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2016).

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supplementary materials

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(Bromomethyl)trimethylammonium bromide

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Comment

Recently, we reported our interest in the fundamental structure of halomethyltrimethyl ammonium salts (Fletcher Claville *et al.*, 2006), due to our interest in potential radical reactivity of these and analagous salts (Yates *et al.*,1984; Rios *et al.*, 1996; Budzinski & Box, 1971; Minegishi, 1977; Stirk & Kenttamaa, 1991; Stirk *et al.*, 1992; Chyall & Kenttamaa, 1994; Della & Smith, 2000). Halomethyltrialkylammonium halides, a specific genre of these salts, are known to perform Grob-like fragmentation reactions (Fig. 1) to produce the corresponding iminium salt and the alkyl halide (Fletcher *et al.*,1999). These two very different types of reactions from similar types of salts further promote our continued interest in the fundamental structure of these quaternary ammonium salts. Accordingly, we now report the structure for (bromomethyl)trimethylammonium bromide.

Both cation and anion lie on mirror planes. Thus, the conformation of the cation is such that the bromo substituent is exactly anti to a methyl group. The two independent CH_2—N—CH_3 angles differ by 5.9 (4)°, with the in-plane angle, anti to Br, being smaller (Table 1). This effect was also seen in the structure of the BF_4^- salt of this cation (Fletcher Claville *et al.*, 2006), where the difference was 4.8 (2)°.

The ionic packing is illustrated in Fig. 3. Of particular interest are the contacts between the bromide anion and the closest methyl group, due to the resulting demethylation and iminium formation that occurs with heating. Methyl group C3 has a C···Br distance 3.809 (3) Å to Br2 at x, 1/2-y, z. Methyl group C2 has C···Br distance 3.821 (2) Å to Br2 at x, 1/2-y, z and a distance of 3.862 (4) Å to Br2 at 1-x, 1-y, 1-z. There is also a short contact between the cation bromo atom and the bromide ion, Br1···Br2(3/2-x, 1-y, z-1/2), 3.369 (1) Å. These interactions are illustrated in Fig. 2.

Structures of three other salts of the (chloromethyl)trimethylammonium ion have been reported (Willey *et al.*, 1991; Johnson *et al.*, 1993; Sieker *et al.*, 1996), as well as the BF_4^- salt of (bromomethyl)trimethylammonium cation (Fletcher Claville *et al.*, 2006).

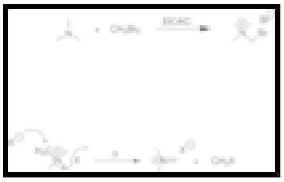
Experimental

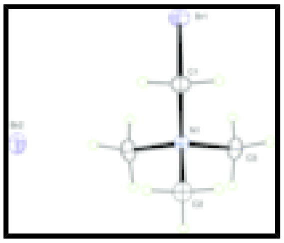
A 50 ml gas capturing flask that was first evacuated and cooled in a dry ice/isopropanol bath (-20°C), was charged with 1.89 g (0.032 mol) anhydrous trimethylamine gas. The trimethylamine gas was then dissolved with 10 ml of ethyl acetate. A 50 ml, 3 necked, round bottom flask that was fitted with a 25 ml-, pressure-equalizing addition funnel and a dry ice condenser, was charged with 10 ml dibromomethane. The flask was then cooled with a dry ice/isopropanol bath (-20°C). THe trimethylamine solution was added dropwise to the flask via the addition funnel over 10 min, with stirring. After allowing the reaction mixture to stir and warm over 24 hr, crude bromomethyltrimethyl ammonium bromide was produced and filtered from the product mixture using vacuum filtration. The pure product was obtained in 69.8% yield after recrystallization from ethanol. m.p. 161-3°C (decomp).

Refinement

H-atom positions were refined, resulting in C–H bond distances 0.94 (4) - 0.98 (3) Å. Displacement parameters for H atoms were assigned as either $U_{\rm iso}$ = 1.2Ueq (CH_2) or 1.5Ueq (CH_3) of the attached C. The largest difference map peak is 0.72 Å from Br2, while the deepest hole is 0.71 Å from Br2.

Figures





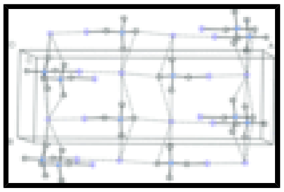


Figure 1. Preparation of bromomethyltrimethylammonium bromide.
Figure 2. Structure of (I), showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level.
Figure 3. The unit cell, viewed approximately down the c axis, showing closest contacts to the bromide ion. H atoms are not shown.
Scheme 1. Grob-like fragmentation/substitution reaction of bromomethyltrimethylammonium bromide.

(Bromomethyl)trimethylammonium bromide

Crystal data

$C_4H_{11}BrN^+\cdot Br^-$
F_{000} = 448
M_r = 232.96
D_x = 1.989 Mg m^{-3}
Orthorhombic, *Pnma*
Mo *K*α radiation
λ = 0.71073 Å
Hall symbol: -P 2ac 2n
Cell parameters from 1506 reflections
a = 19.674 (3) Å
θ = 2.5–31.5°
b = 6.9319 (11) Å
μ = 10.32 mm^{-1}
c = 5.7038 (10) Å
T = 115 K
V = 777.9 (2) Å^3
Plate, colorless
Z = 4
0.30 × 0.20 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer with an Oxford Cryosystems Cryostream cooler
1363 independent reflections
Radiation source: fine-focus sealed tube
1149 reflections with $I > 2\sigma(I)$

Monochromator: graphite	R_{int} = 0.029
T = 115 K	$\theta_{\max}$ = 31.5°
ω scans with κ offsets	$\theta_{\min}$ = 3.6°
Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor 1997)	$h = -28 \rightarrow 28$
$T_{\min}$ = 0.148, $T_{\max}$ = 0.626	$k = -10 \rightarrow 10$
14337 measured reflections	$l = -8 \rightarrow 8$

Refinement

Refinement on F^2	Only H-atom coordinates refined
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0802P)^2 + 0.1483P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.038$	$(\Delta/\sigma)_{\max}$ = 0.001
$wR(F^2)$ = 0.114	$\Delta\rho_{\max}$ = 1.73 e Å^{-3}
S = 1.04	$\Delta\rho_{\min}$ = −1.34 e Å^{-3}
1363 reflections	Extinction correction: SHELXL97, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
58 parameters	Extinction coefficient: 0.0071 (14)
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	
Hydrogen site location: inferred from neighbouring sites	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\mathrm{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Br1	0.75330 (2)	0.2500	0.55461 (9)	0.02202 (18)
Br2	0.58280 (2)	0.7500	0.88378 (7)	0.01593 (17)
N1	0.60677 (18)	0.2500	0.5040 (6)	0.0132 (6)
C1	0.6621 (2)	0.2500	0.6853 (8)	0.0167 (8)
H1A	0.658 (2)	0.131 (5)	0.775 (5)	0.020*
C2	0.5417 (2)	0.2500	0.6398 (8)	0.0177 (8)
H2A	0.538 (2)	0.360 (5)	0.737 (6)	0.027*
H2B	0.507 (3)	0.2500	0.527 (10)	0.027*

C3	0.61043 (17)	0.0733 (5)	0.3522 (6)	0.0187 (6)
H3A	0.611 (2)	−0.039 (6)	0.455 (7)	0.028*
H3B	0.654 (2)	0.075 (7)	0.271 (5)	0.028*
H3C	0.573 (2)	0.084 (7)	0.251 (7)	0.028*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0145 (2)	0.0227 (3)	0.0289 (3)	0.000	−0.00021 (16)	0.000
Br2	0.0200 (3)	0.0131 (2)	0.0147 (2)	0.000	−0.00118 (14)	0.000
N1	0.0153 (16)	0.0114 (15)	0.0128 (15)	0.000	0.0016 (12)	0.000
C1	0.0155 (18)	0.020 (2)	0.0147 (17)	0.000	−0.0010 (15)	0.000
C2	0.0183 (19)	0.019 (2)	0.0159 (18)	0.000	0.0005 (16)	0.000
C3	0.0263 (15)	0.0138 (13)	0.0160 (12)	−0.0010 (12)	0.0035 (11)	−0.0042 (12)

Geometric parameters (Å, °)

Br1—C1	1.943 (4)	C2—H2A	0.95 (4)
N1—C2	1.496 (5)	C2—H2B	0.94 (6)
N1—C3^{i}	1.502 (4)	C3—H3A	0.97 (4)
N1—C3	1.502 (4)	C3—H3B	0.97 (4)
N1—C1	1.502 (5)	C3—H3C	0.94 (4)
C1—H1A	0.98 (3)		
C2—N1—C3^{i}	109.8 (2)	N1—C2—H2A	112 (3)
C2—N1—C3	109.8 (2)	N1—C2—H2B	105 (4)
C3^{i}—N1—C3	109.3 (3)	H2A—C2—H2B	110 (3)
C2—N1—C1	105.3 (3)	N1—C3—H3A	108 (2)
C3^{i}—N1—C1	111.2 (2)	N1—C3—H3B	108 (3)
C3—N1—C1	111.2 (2)	H3A—C3—H3B	107 (4)
N1—C1—Br1	113.9 (3)	N1—C3—H3C	105 (3)
N1—C1—H1A	107 (2)	H3A—C3—H3C	116 (4)
Br1—C1—H1A	106 (2)	H3B—C3—H3C	113 (3)
C2—N1—C1—Br1	180.0	C3—N1—C1—Br1	61.1 (2)
C3^{i}—N1—C1—Br1	−61.1 (2)		

Symmetry codes: (i) *x*, −*y*+1/2, *z*.

Fig. 1

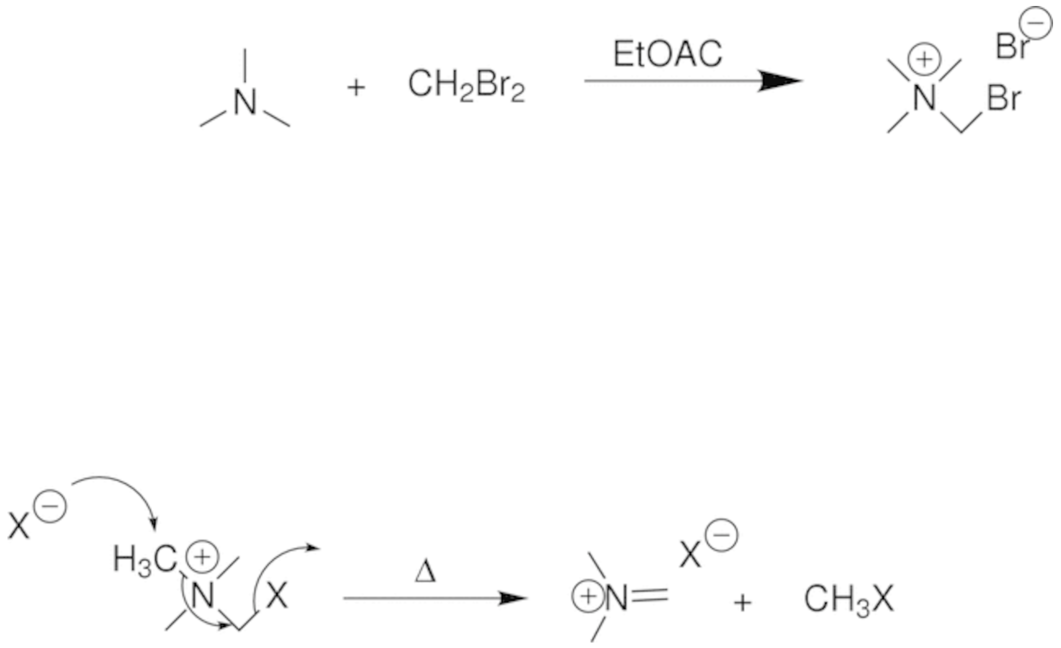


Fig. 2

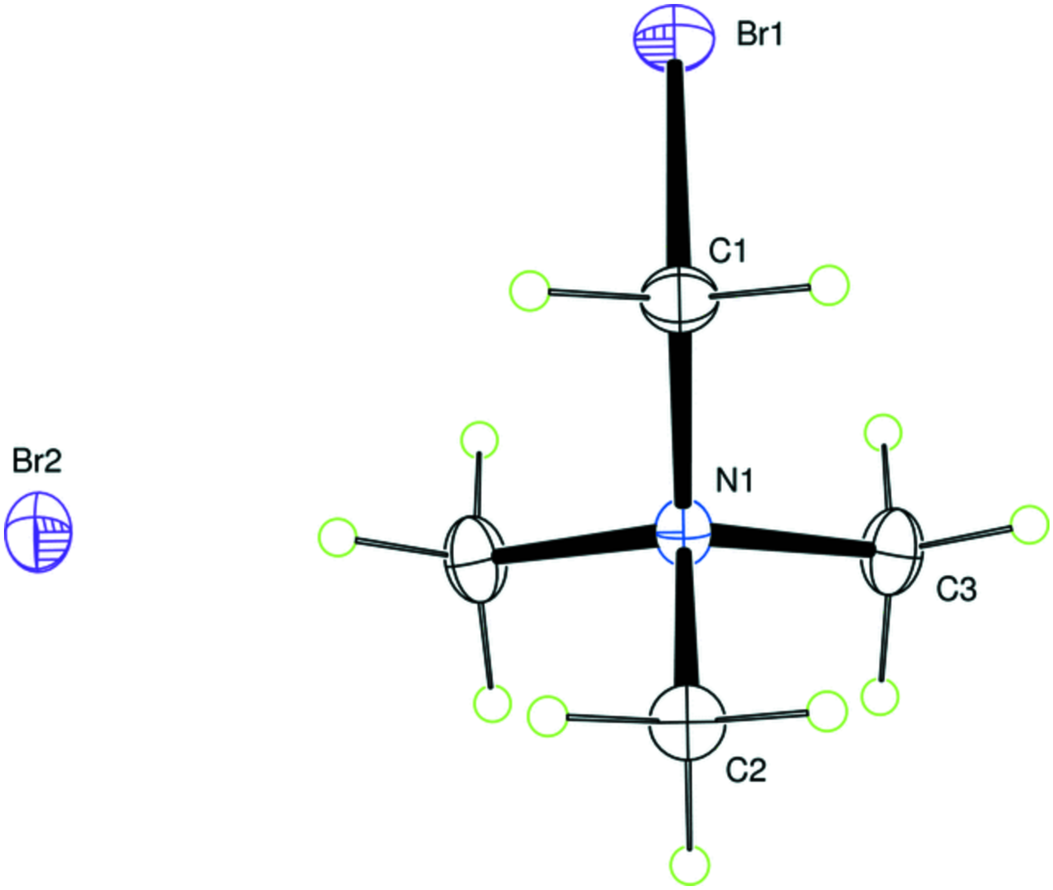


Fig. 3