organic papers

Michelle O. Fletcher Claville,[a]* **Roosevelt J. Payne**[a] **and Frank R. Fronczek**[b]

[a]Department of Chemistry, Southern University, Baton Rouge, LA 70813, USA, and [b]Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804, USA

Correspondence e-mail: michelle_claville@subr.edu

(Bromomethyl)trimethylammonium tetrafluoroborate

In the title compound, $C_4H_{11}BrN^+\cdot BF_4^-$, both ions lie on crystallographic mirror planes, and the compound is isomorphous with the chloromethyl analog. The C—Br distance is 1.927 (2) Å.

Comment

Halomethyltrimethyl ammonium salts have been shown to perform some interesting chemistry. They are precursors to alpha distonic radical cations (*i.e.* species with separate radical and charged sites) (Yates *et al.*, 1984; Rios *et al.*, 1996). Distonic radical cations are important central intermediates in dissociation reactions of many ionized molecules and have been produced from certain X- and γ-ray irradiated amino acids (Budzinski & Box, 1971; Minegishi, 1977). These species have been studied extensively in the gas phase (Stirk & Kenttamaa, 1991; Stirk *et al.*, 1992; Chyall & Kenttamaa, 1994) and to a smaller extent in the solution phase (Rios *et al.*, 1996). Studies of the species continue, with the expectation of gaining a better understanding of the biological consequences of ionizing irradiation. A study of the reactivity of the unusual radical cations that derive from these salts may also serve to formulate synthetic methodology towards elusive N-containing compounds (Della & Smith, 2000) and provide information regarding the stability of various amines and ammonium salts. Such information will allow for the design optimization of said compounds, which may serve as phase-transfer catalysts, household, industrial and institutional cleaners, pharmaceuticals, wood treatment chemicals, personal care items, oilfield chemicals, water treatment chemicals, *etc.* In order to achieve that ultimate goal, we wish to gain a fundamental understanding of the structures of precursory ammonium salts and present here the crystal structure of the title compound, (I).
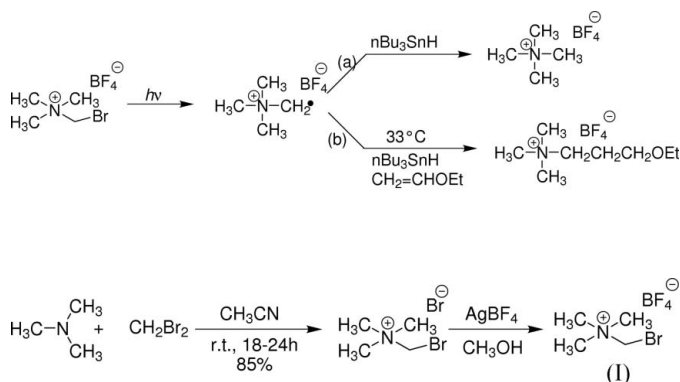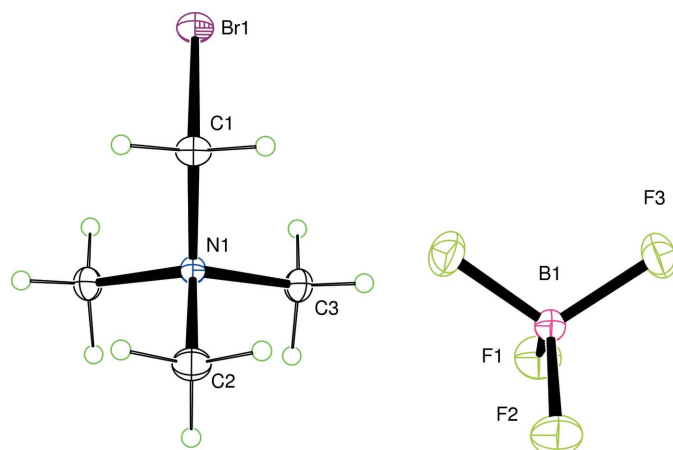
Figure 1
The structure of (I), showing the atom-numbering scheme and with displacement ellipsoids at the 50% probability level.
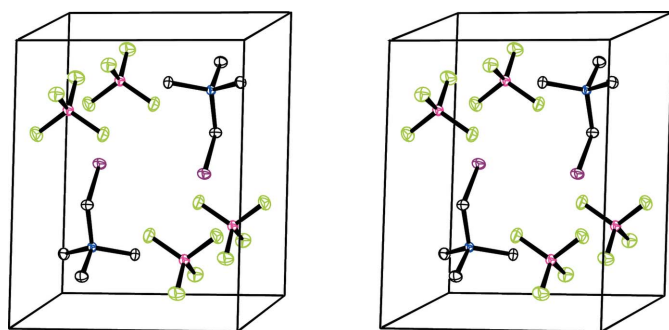
Figure 2
Stereopair of the unit cell contents, viewed approximately down the *a* axis. The origin is at the upper left (foreground) and **b** is horizontal. H atoms are not shown.

The structure of (I) is isomorphous with that of (chloromethyl)trimethylammonium tetrafluoroborate (Blake *et al.*, 1991), and 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 4.8 (2)°, with the in-plane angle, *anti* to Br, being smaller (Table 1).

The ionic packing of (I) is illustrated in Fig. 2. Distances from the anion to the N atom and to the CH_2Br C atom are of interest with respect to potential crowding at the site of subsequent radical generation. Studies have shown that the trimethylammoniomethylene radical $[(CH_3)_3N^+CH_2]$ readily performs hydrogen-abstraction reactions but reluctantly performs intermolecular alkene addition (Rios *et al.*, 1996) This is especially peculiar as intramolecular alkene additions of analogous alkenyl-substituted ammonio distonic radicals $[CH_2=CH(CH_2)_n(CH_3)_2N^+CH_2]$ occur very readily. The shortest $N \cdots B$ distances are 4.567 (3) Å to B at $(1 - x, 1 - y, 2 - z)$, 4.584 (3) Å at (x, y, z), and 5.203 (3) Å at $(x + 1, y, z)$. The shortest $C1 \cdots B1$ distances are 3.779 (3) Å at $(-x, 1 - y, 1 - z)$ and 4.632 (3) Å at (x, y, z).

Structures of three other salts of the (chloromethyl)-trimethylammonium ion have been reported previosly (Willey

et al., 1991; Johnson *et al.*, 1993; Sieker *et al.*, 1996), but no other salts of (bromomethyl)trimethylammonium.

Experimental

Bromomethyltrimethylammonium bromide (5.006 g, 0.025 mol) was dissolved in methanol (25 ml) with stirring. AgBF$_4$ (4.185 g, 0.025 mol) was dissolved in methanol (30 ml) and added dropwise to the ammonium solution over a 20 min period, and the mixture was stirred at room temperature for 4 h. The AgBr precipitate which formed was removed by filtration, and the filtrate was concentrated to give the crude bromomethyltrimethylammonium tetrafluoroborate salt. After evaporation of the residual reaction solvent at ambient pressure overnight, recrystallization from ethyl acetate afforded pure bromomethyltrimethylammonium tetrafluoroborate in 85% yield.

Crystal data

$C_4H_{11}BrN^+ \cdot BF_4^-$	$Z = 2$
$M_r = 239.86$	$D_x = 1.897$ Mg m^{-3}
Monoclinic, $P2_1/m$	Mo $K\alpha$ radiation
$a = 5.9478$ (15) Å	$\mu = 4.90$ mm^{-1}
$b = 7.7276$ (12) Å	$T = 115$ K
$c = 9.428$ (2) Å	Lath, colorless
$\beta = 104.274$ (9)°	$0.22 \times 0.15 \times 0.02$ mm
$V = 419.95$ (15) Å^3	

Data collection

Nonius KappaCCD diffractometer with an Oxford Cryosystems Cryostream cooler	9258 measured reflections
	1519 independent reflections
ω scans with κ offsets	1307 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)	$R_{int} = 0.023$
	$\theta_{max} = 31.8°$
$T_{min} = 0.410$, $T_{max} = 0.908$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.019P)^2 + 0.2967P]$
$R[F^2 > 2\sigma(F^2)] = 0.027$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.056$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.05$	$\Delta\rho_{max} = 0.48$ e Å^{-3}
1519 reflections	$\Delta\rho_{min} = -0.63$ e Å^{-3}
79 parameters	Extinction correction: *SHELXL97* (Sheldrick, 1997)
Only H-atom coordinates refined	Extinction coefficient: 0.0090 (17)

Table 1
Selected geometric parameters (Å, °).

Br1—C1	1.927 (2)	N1—C2	1.506 (3)
N1—C3	1.5014 (19)	N1—C1	1.508 (3)
C3—N1—C1	111.15 (11)	N1—C1—Br1	112.14 (16)
C2—N1—C1	106.40 (18)		
C3—N1—C1—Br1	61.43 (12)		

H-atom positions were refined, resulting in C—H distances in the range 0.92 (3)–0.95 (2) Å. Displacement parameters for H atoms were assigned as $U_{iso}(H) = 1.2U_{eq}(C)$.

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);

organic papers

molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Blake, A. J., Ebsworth, E. A. V., Gould, R. O. & Roberton, N. (1991). *Z. Kristallogr.* **195**, 304–305.

Budzinski, E. E. & Box, H. C. (1971). *J. Phys. Chem.* **75**, 2564–2570.

Chyall, L. J. & Kenttamaa, H. I. (1994). *J. Am. Chem. Soc.* **116**, 3135–3136.

Della, E. W. & Smith, P. A. (2000). *J. Org. Chem.* **65**, 6627–6633.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Johnson, B. F. G., Sieker, A., Blake, A. J. & Winpenny, R. E. P. (1993). *J. Chem. Soc. Chem. Commun.* pp. 1345–1346.

Minegishi, A. (1977). *J. Phys. Chem.* **81**, 1688–1699.

Nonius (2000). *COLLECT.* Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Rios, L. A., Dolbier, W. R. Jr, Paredes, R., Lusztyk, J., Ingold, K. & Johnsson, M. (1996). *J. Am. Chem. Soc.* **118**, 11313–11315.

Sheldrick, G. M. (1997). *SHELXL97.* University of Göttingen, Germany.

Sieker, A., Blake, A. J. & Johnson, B. F. G. (1996). *J. Chem. Soc. Dalton Trans.* pp. 1419–1427.

Stirk, K. & Kenttamaa, H. I. (1991). *J. Am. Chem. Soc.* **113**, 5880–5881.

Stirk, K. M., Kiminkinen, L. K. & Kenttamaa, H. I. (1992). *Chem. Rev.* **92**, 1649–1665.

Willey, G. R., Ravindran, M. & Drew, M. G. B. (1991). *Inorg. Chim. Acta*, **188**, 159–162.

Yates, B. F., Bouma, W. J. & Radom, L. (1984). *J. Am. Chem. Soc.* **106**, 5805–5808.