Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

The diprotonated 2,2-(propane-1,3-diyl)bis(1,1,3,3-tetramethylguanidinium) cation: packing and conformational changes

Ulrich Flörke,* Sonja Herres-Pawlis, Andreas Heuwing, Adam Neuba, Oliver Seewald and Gerald Henkel

Department Chemie, Fakultät für Naturwissenschaften, Universität Paderborn, Warburgerstraße 100, D-33098 Paderborn, Germany
Correspondence e-mail: ulrich.floerke@upb.de

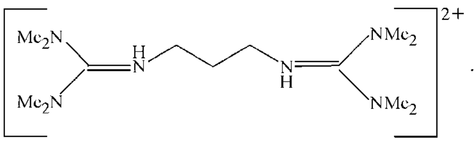
Received 16 March 2006
Accepted 20 April 2006
Online 16 May 2006

Subject to packing with different anions, the title cation undergoes various conformational changes with significantly different N—C—C—C torsion angles, as well as different angles between the NCN_2 guanidine planes. The 2,2-(propane-1,3-diyl)bis(1,1,3,3-tetramethylguanidinium) salts reported here, *viz.* the dibromide, $C_{13}H_{32}N_6^{2+}\cdot 2Br^-$, the tetraphenylborate chloride, $C_{13}H_{32}N_6^{2+}\cdot C_{24}H_{20}B^-\cdot Cl^-$, the tetrachloromercurate, $(C_{13}H_{32}N_6)[HgCl_4]$, and the bis(trifluoromethanesulfonate), $C_{13}H_{32}N_6^{2+}\cdot 2CF_3SO_3^-$, are dominated by strong intermolecular N—H⋯*X* hydrogen bonds, which form different packing patterns.

Comment

The series of four structures presented here consists of 2,2-(propane-1,3-diyl)bis(1,1,3,3-tetramethylguanidinium) cations, $[btmgpH_2]^{2+}$, crystallized with different anions, *viz.* (I) with Br^- (Fig. 1), (II) with BPh_4^- and Cl^- (Fig. 2), (III) with $[HgCl_4]^{2-}$ (Fig. 3), and (IV) with $CF_3SO_3^-$ (triflate; Fig. 4). Already known from earlier work is an initial member of this series, namely the structure (V) with Cl^- (Pohl *et al.*, 2000). Although isomolecular with (V), the structure of (I) is not isotypic but exhibits two independent molecules, (I*A*) and (I*B*), with different conformations in the asymmetric unit. As expected, the bond lengths for the $[btmgpH_2]^{2+}$ cations of all four structures are very similar [C—C = 1.504 (2)–1.536 (7) Å, N—C(propyl) = 1.455 (6)–1.477 (6) Å, N═C = 1.326 (7)–1.341 (6) Å and C—N(guanidyl) = 1.331 (2)–1.343 (3) Å]. The N—C—C and C—C—C angles are in the ranges 109.1 (2)–111.9 (2) and 109.1 (3)–114.1 (2)°, respectively.

Significant geometric differences, however, associated with the different packing patterns, are noted for the N—C—C—C torsion angles, which are given in Table 1. Fig. 5 depicts these different conformations. Likewise, the angles between the two NCN_2 guanidine planes of each cation differ markedly, being 15.5 (3)° for (I*A*), 24.7 (3)° for (I*B*), 67.00 (7)° for (II), 74.1 (1)° for (III), 67.23 (7)° for (IV) and 82.60 (6)° for (V). The relative orientations of the pairs of $CNMe_2$ planes, on the other hand, are again very similar for all structures and their corresponding dihedral angles lie in the narrow range 52.1 (1)–56.1 (1)°. Only the conformation of the cation in (III) shows approximate C_s symmetry, with a non-crystallographic mirror plane running through atom C2 and the attached H atoms; the other cations have C_1 point-group symmetry.



(I) X=$2Br^-$ (III) X=$[HgCl_4]^{2-}$
(II) X=$BPh_4^-\cdot Cl^-$ (IV) X=$2CF_3SO_3^-$

Compounds (II) and (III) each pack with two intermolecular cation–anion N—H⋯Cl hydrogen bonds of similar

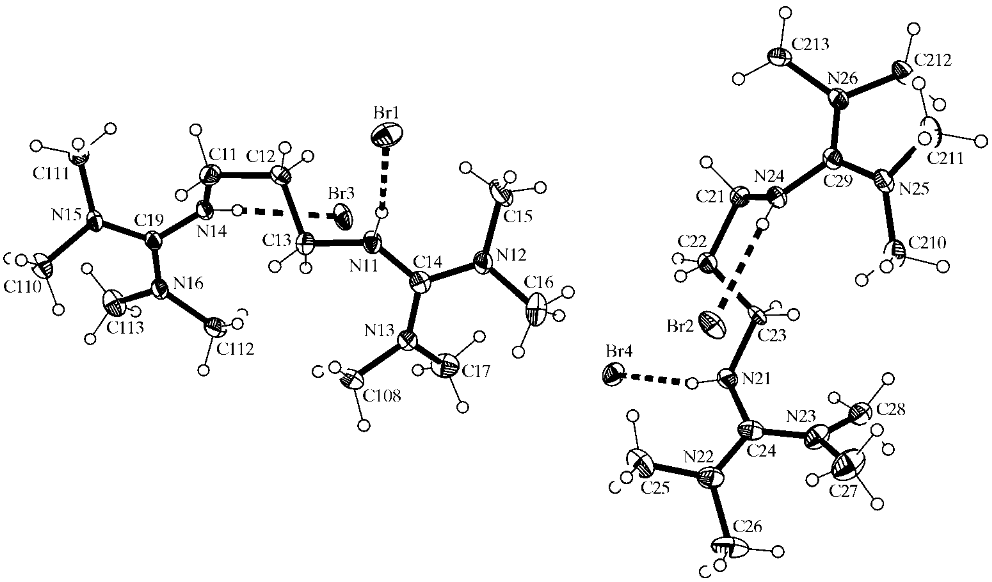


Figure 1
The molecular structure of (I), with broken lines indicating the bridging hydrogen bonds. Displacement ellipsoids are drawn at the 50% probability level.

DOI: 10.1107/S0108270106014429

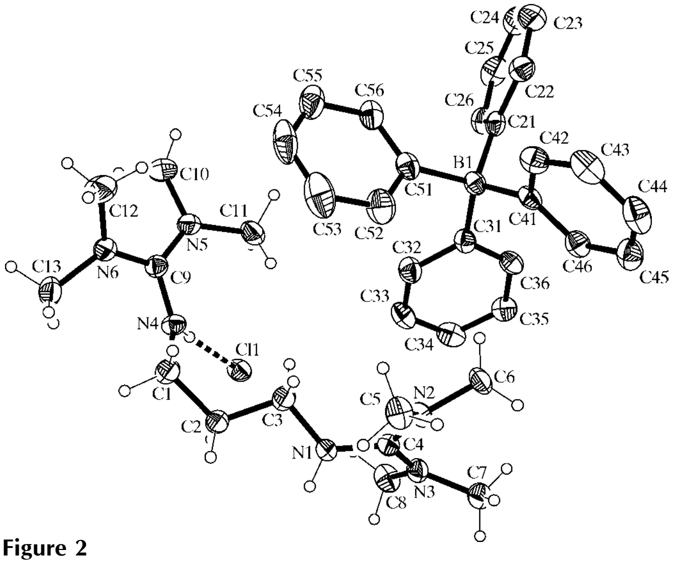


Figure 2
The molecular structure of (II), with broken lines indicating the bridging hydrogen bonds. H atoms of the BPh_4^- cations have been omitted and displacement ellipsoids are drawn at the 50% probability level.

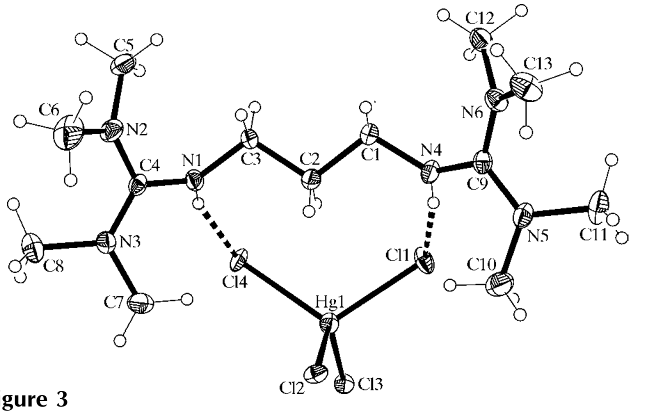


Figure 3
The molecular structure of (III), with broken lines indicating the bridging hydrogen bonds. Displacement ellipsoids are drawn at the 50% probability level.

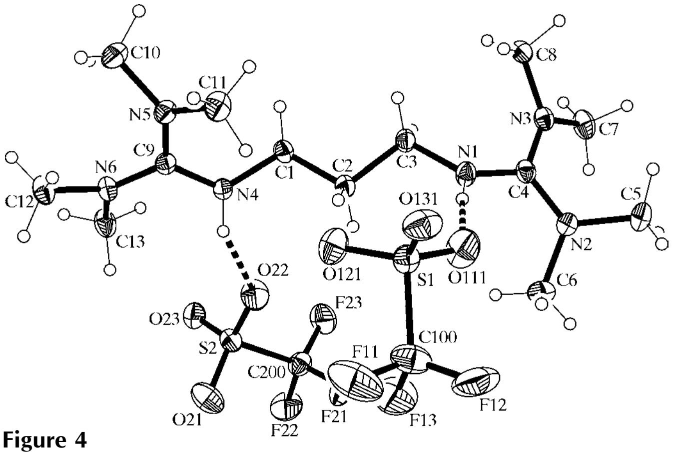


Figure 4
The molecular structure of (IV), with broken lines indicating the bridging hydrogen bonds. The minor component of the disordered triflate anion has been omitted and displacement ellipsoids are drawn at the 50% probability level.

geometries (Table 2). In (II) (Fig. 6), centrosymmetric dimeric units, each with two cations and anions, are formed; these units are stacked along [010]. In (III) (Fig. 7), the two chloride acceptors, Cl1 and Cl4, of each anion bridge to the two NH sites of a cation; additionally, a C—H···Cl interaction from atom Cl3 connects this cation–anion pair to another cation site. Compound (I) exhibits N—H···Br interactions with short (2.4–2.5 Å) H···Br distances and weaker C—H···Br interactions, with a H···Br distance of about 2.8 Å, which link cations (I*A*) and (I*B*) into a common network. In (IV), two strong N—H···O bridges link the cation to two triflate anions,

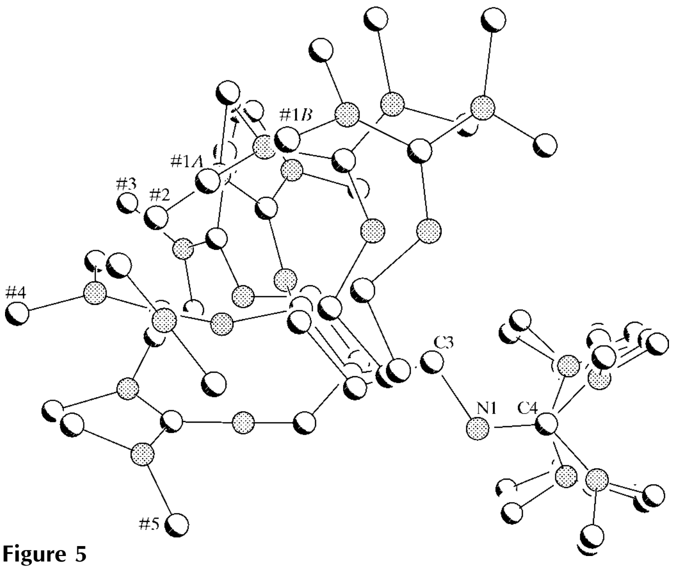


Figure 5
Cations of (I*A*)–(V) (labelled #1*A*–#5), showing different conformations with common N1, C3 and C4 positions.

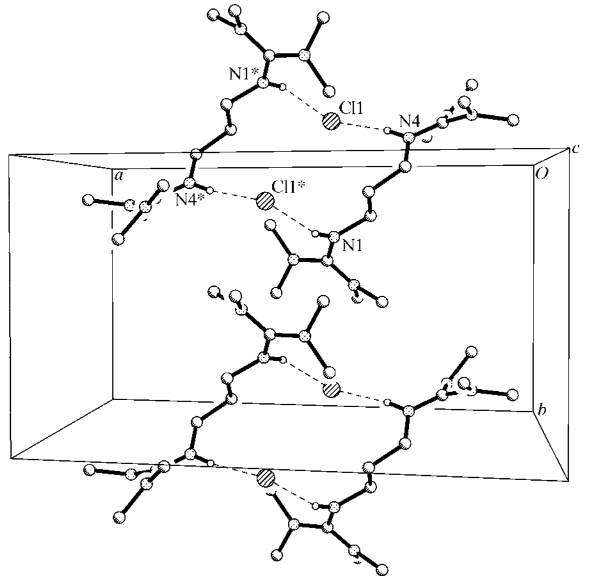


Figure 6
Part of the crystal packing of (II), with the hydrogen-bonding pattern indicated as dashed lines. BPh_4^- cations and H atoms not involved in the interactions shown have been omitted. Asterisks (*) denote the symmetry-equivalent position $(-x + 1, -y, -z + 1)$.

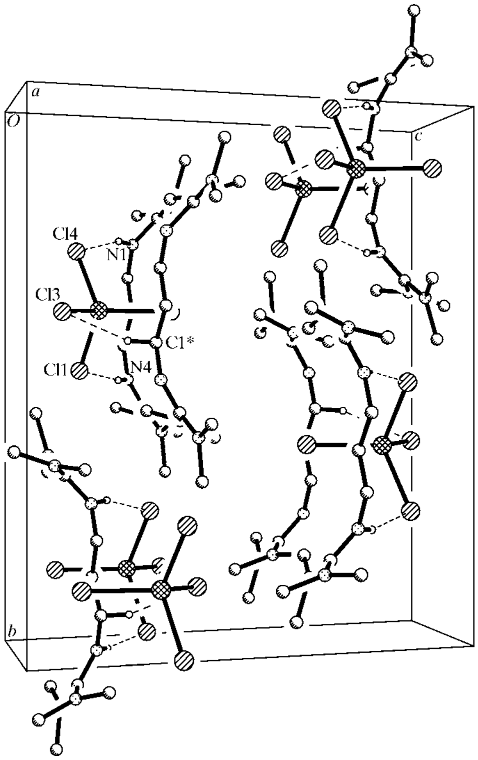


Figure 7
Part of crystal packing of (III), with the hydrogen-bonding pattern indicated by dashed lines. H atoms not involved in the interactions shown have been omitted. The asterisk (*) denotes the symmetry-equivalent position ($x - 1, y, z$).

thus forming 1:2 cation–anion units, which are then connected by C—H···O interactions in a zigzag manner along [001]. The BPh_4^- and $[HgCl_4]^{2-}$ anions of (II) and (III) exhibit no unusual features and need no further discussion. The SO_3 group of one of the triflate anions in (IV) is disordered around the C—S axis over two positions, with occupation factors of 0.919 (4) and 0.081 (4).

Experimental

For the preparation of (I) and (III), btmgp (270 mg, 1 mmol) was added to a solution of $MnBr_2$ (215 mg, 1 mmol) or $HgCl_2$ (271.5 mg, 1 mmol), respectively, in acetonitrile (aqueous, 15 ml); the mixture was stirred for 15 min at room temperature and then refluxed for a further 15 min. Colourless crystals were obtained using the vapour pressure equalization method with this solution in the presence of isopropyl ether. For the preparation of (II), a solution of $PtCl_2$ (266 mg, 1 mmol) in acetonitrile (15 ml) was combined with btmgpg (270 mg, 1 mmol) and the mixture was stirred for 15 min at room temperature. $NaBPh_4$ (342 mg, 1 mmol) was then added and the mixture was stirred for a further 15 min. Colourless crystals were obtained using the vapour pressure equalization method with this solution in the presence of isopropyl ether. For the preparation of (IV), trifluoracetic acid (251 mg, 2.2 mmol) was added dropwise to a solution of btmgp (270 mg, 1 mmol) in MeCN (10 ml) and the reaction mixture was then refluxed for 1 h. Crystals were grown by slow diffusion of diethyl ether into the colourless reaction solution.

Salt (I)

Crystal data

$C_{13}H_{32}N_6^{2+}\cdot 2Br^-$
$M_r = 432.27$
Triclinic, $P\bar{1}$
$a = 12.4256$ (14) Å
$b = 12.5254$ (15) Å
$c = 12.6935$ (15) Å
$\alpha = 79.465$ (3)°
$\beta = 89.731$ (3)°
$\gamma = 89.361$ (2)°
$V = 1942.1$ (4) Å^3
$Z = 4$
$D_x = 1.478$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 4.18$ mm^{-1}
$T = 120$ (2) K
Prism, colourless
0.42 × 0.22 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{min} = 0.243$, $T_{max} = 0.435$
19556 measured reflections
9242 independent reflections
5769 reflections with $I > 2\sigma(I)$
$R_{int} = 0.065$
$\theta_{max} = 27.9°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.139$
$S = 0.99$
9242 reflections
387 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.044P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.95$ e Å^{-3}
$\Delta\rho_{min} = -0.89$ e Å^{-3}

Salt (II)

Crystal data

$C_{13}H_{32}N_6^{2+}\cdot BC_{24}H_{20}^-\cdot Cl^-$
$M_r = 627.11$
Monoclinic, $P2_1/c$
$a = 17.5770$ (8) Å
$b = 9.3797$ (4) Å
$c = 22.4953$ (10) Å
$\beta = 107.034$ (1)°
$V = 3546.0$ (3) Å^3
$Z = 4$
$D_x = 1.175$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.14$ mm^{-1}
$T = 150$ (2) K
Prism, colourless
0.20 × 0.20 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{min} = 0.962$, $T_{max} = 0.975$
39279 measured reflections
7800 independent reflections
4307 reflections with $I > 2\sigma(I)$
$R_{int} = 0.100$
$\theta_{max} = 27.1°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.072$
$S = 0.91$
7800 reflections
414 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.014P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

Salt (III)

Crystal data

$(C_{13}H_{32}N_6)[HgCl_4]$
$M_r = 614.84$
Monoclinic, $P2_1/c$
$a = 8.3199$ (4) Å
$b = 18.0809$ (9) Å
$c = 15.8086$ (8) Å
$\beta = 104.291$ (1)°
$V = 2304.5$ (2) Å^3
$Z = 4$
$D_x = 1.772$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 7.15$ mm^{-1}
$T = 120$ (2) K
Plate, colourless
0.45 × 0.20 × 0.08 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{\min} = 0.133$, $T_{\max} = 0.563$

23407 measured reflections
5049 independent reflections
4421 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$
$\theta_{\max} = 27.1^\circ$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.087$
$S = 1.07$
5049 reflections
225 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0523P)^2 + 4.0796P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.92$ e Å^{-3}
$\Delta\rho_{\min} = -0.55$ e Å^{-3}

Salt (IV)

Crystal data

$C_{13}H_{32}N_6^{2+}\cdot 2CF_3O_3S^-$
$M_r = 570.59$
Triclinic, $P\overline{1}$
$a = 8.8771$ (7) Å
$b = 12.3802$ (10) Å
$c = 12.5704$ (10) Å
$\alpha = 108.939$ (2)°
$\beta = 91.478$ (2)°
$\gamma = 97.775$ (2)°

$V = 1291.10$ (18) Å^3
$Z = 2$
$D_x = 1.468$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.29$ mm^{-1}
$T = 120$ (2) K
Prism, colourless
$0.40 \times 0.20 \times 0.20$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{\min} = 0.893$, $T_{\max} = 0.944$

7636 measured reflections
5165 independent reflections
4404 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.012$
$\theta_{\max} = 26.4^\circ$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.121$
$S = 1.03$
5165 reflections
337 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0574P)^2 + 0.8973P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.76$ e Å^{-3}
$\Delta\rho_{\min} = -0.51$ e Å^{-3}

Table 1
Selected torsion angles (°) for compounds (I)–(V).

	(I)	(II)	(III)	(IV)	(V)
N4—C1—C2—C3	−62.8 (6)	63.4 (2)	−179.9 (3)	−169.8 (2)	69.8 (2)
C1—C2—C3—N1	−173.4 (4)	−177.6 (2)	175.5 (3)	177.7 (2)	−173.3 (1)

Table 2
Hydrogen-bond parameters (Å, °) for salts (I)–(IV).

Compound	D—H···A	D—H	H···A	D···A	D—H···A
(I*A*)	N11—H11···Br1	0.88	2.42	3.282 (4)	168
(I*B*)	N21—H21···Br4	0.88	2.43	3.283 (4)	165
(I*B*)	N24—H24···Br2	0.88	2.54	3.396 (4)	166
(I*A*)	N14—H14···Br3	0.88	2.52	3.373 (4)	165
(I*B*)	C28—H20*Q*···Br4^{i}	0.98	2.81	3.736 (6)	158
(I*B*)	C213—H21*M*···Br2^{ii}	0.98	2.82	3.764 (5)	163
(II)	N1—H1···Cl1^{iii}	0.88	2.41	3.2516 (18)	160
(II)	N4—H4···Cl1	0.88	2.29	3.1668 (17)	172
(III)	N1—H1···Cl4	0.88	2.50	3.349 (4)	164
(III)	N4—H4···Cl1	0.88	2.36	3.215 (4)	164
(III)	C1—H1*A*···Cl3^{iv}	0.99	2.65	3.597 (4)	161
(IV)	N4—H4···O22	0.88	2.03	2.796 (2)	144
(IV)	N1—H1···O111	0.88	1.98	2.855 (3)	172
(IV)	N1—H1···O112	0.88	2.05	2.883 (18)	157
(IV)	C2—H2*B*···O112	0.99	2.44	3.171 (19)	130
(IV)	C5—H5*C*···O21^{v}	0.98	2.49	3.448 (3)	166
(IV)	C7—H7*B*···O132^{vi}	0.98	2.25	3.111 (17)	145
(IV)	C8—H8*A*···O131^{vi}	0.98	2.46	3.245 (3)	137

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $-x+1, -y+2, -z+1$; (iii) $-x+1, -y, -z+1$; (iv) $x-1, y, z$; (v) $x, y, z+1$; (vi) $x-1, y, z$.

H atoms were placed at idealized positions and treated as riding on their C atoms, with $U_{\rm iso}$(H) values of 1.2 or 1.5 (for CH_3) times $U_{\rm eq}$(C). All CH_3 groups were allowed to rotate but not to tip. The S—O bond geometry of the disordered triflate group in (IV) was restrained with the SADI command of *SHELXTL* (Bruker, 2002), which restrains all S—O distances of this group to be equal. Atoms O112–O132 of the minor part [occupation factor = 0.081 (4)] were refined isotropically.

For all four salts, data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2002); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3012). Services for accessing these data are described at the back of the journal.

References

Bruker (2002). *SMART* (Version 5.62), *SAINT* (Version 6.02), *SHELXTL* (Version 6.10) and *SADABS* (Version 2.03). Bruker AXS Inc., Madison, Wisconsin, USA.

Pohl, S., Harmjanz, M., Schneider, J., Saak, W. & Henkel, G. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3473–3479.