The structure was solved and refined using the *SHELXTL-Plus* (Sheldrick, 1990) software package on a MicroVAX 3500 computer. Refinement was by full-matrix least-squares methods, minimizing $\Sigma w(|F_o|-|F_c|)^2$. All non-H atoms were located on an E map and refined anisotropically. H atoms were assigned positions that were consistent with minor peaks on an intermediate difference Fourier map and were considered as riding atoms in the subsequent refinement cycle. Their isotropic displacement parameters were fixed at 0.08 Å^2.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and torsion angles have been deposited with the IUCr (Reference: CR1149). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). **C51**, 1407–1411

$(H_4$-Hexaaza-18-crown-6$)^{4+}.4CF_3SO_3^-$ and its Hydrated Form

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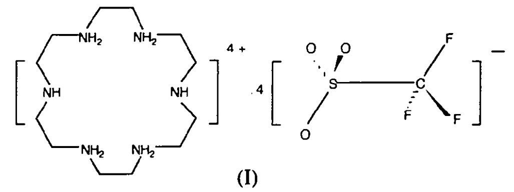
(*Received* 13 *April* 1994; *accepted* 6 *December* 1994)

Abstract

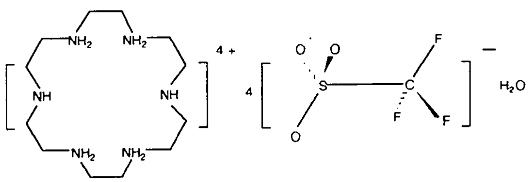
The structures of the two compounds reported here involve the tetraprotonated form of the macrocycle 1,4,7,10,13,16-hexaazacyclooctadecane (hexaaza-18-crown-6 = $C_{12}H_{30}N_6$): (H_4-hexaaza-18-crown-6).4(trifluoromethanesulfonate), $C_{12}H_{34}N_6^{4+}.4CF_3SO_3^-$, and the hydrated form (H_4-hexaaza-18-crown-6).4(trifluoromethanesulfonate).H_2O, $C_{12}H_{34}N_6^{4+}.4CF_3SO_3^-.H_2O$. In both compounds, the conformation of the macrocycle is $g^+g^-g^+g^-g^+g^-$. The counterions and the water molecule are hydrogen bonded to protonated N atoms.

Comment

In the course of our work on inclusion complexes between the uranyl ion and macrocycles, we have reported recently the structures of the inclusion complexes obtained with hexaaza-18-crown-6 (Nierlich, Sabattié, Keller, Lance & Vigner, 1994) and diaza-18-crown-6 (Thuéry, Keller, Lance, Sabattié, Vigner & Nierlich, 1995) with trifluoromethanesulfonate $CF_3SO_3^-$ as counterion. In the latter compound, one of the two amine functional groups is deprotonated, which is uncommon for this ligand. In the present paper, we report the structures of two compounds, (I) and (II), containing (H_4-hexaaza-18-crown-6)$^{4+}$ and $CF_3SO_3^-$. The binding properties of protonated hexaaza-18-crown-6 with the anions Cl^-, NO_3^-, Br^-, ClO_4^-, $C_6H_5SO_3^-$, CF_3COO^- and IO_3^- have already been investigated by pH-potentiometry, conductometry and X-ray diffraction (Margulis & Zompa, 1981; Cullinane, Gelb, Margulis & Zompa, 1982; Gelb, Lee & Zompa, 1985), and with biologically important polyanions such as polycarboxylates and phosphates by polarography and NMR experiments (Kimura, Sakonaka, Yatsunami & Kodama, 1981; Kimura, Kodama & Yatsunami, 1982). In all cases, the ion-pair formation arises from electrostatic and/or ionic hydrogen bonding of the form $N^+—H\cdots X^-$, as evidenced in the structures of (H_6-hexaaza-18-crown-6)$(NO_3)_4Cl_2$ (Margulis & Zompa, 1981) and (H_4-hexaaza-18-crown-6)$(NO_3)_2Cl_2.2H_2O$ (Cullinane *et al.*, 1982).



(I)



(II)

In the present work, two crystalline species were isolated: (H_4-hexaaza-18-crown-6)$^{4+}.4CF_3SO_3^-$, (I), and the hydrated form (H_4-hexaaza-18-crown-6)$^{4+}.4CF_3SO_3^-.H_2O$, (II). In agreement with protonation experiments (Bencini *et al.*, 1992), the only species present is (H_4-hexaaza-18-crown-6)$^{4+}$; the occurrence of this tetraprotonated species in anion complexation both in solution and in the solid state has already been indicated (Cullinane *et al.*, 1982; Gelb *et al.*, 1985). The geometric parameters of the $CF_3SO_3^-$ moieties, which are normal, are not reported here. *ORTEP*II (Johnson, 1976) drawings of the molecules are given in Figs. 1 and 2.

Acta Crystallographica Section C
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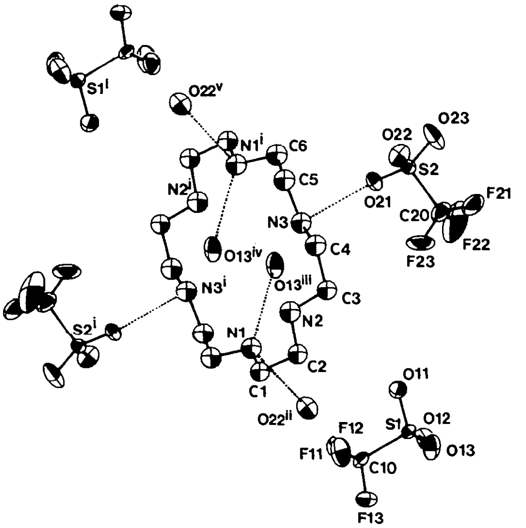

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (I) with atom labelling. Possible hydrogen bonds are indicated by dashed lines. Ellipsoids are drawn at the 40% probability level. Symmetry codes: (i) $2 - x, -y, 1 - z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (iv) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (v) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$.

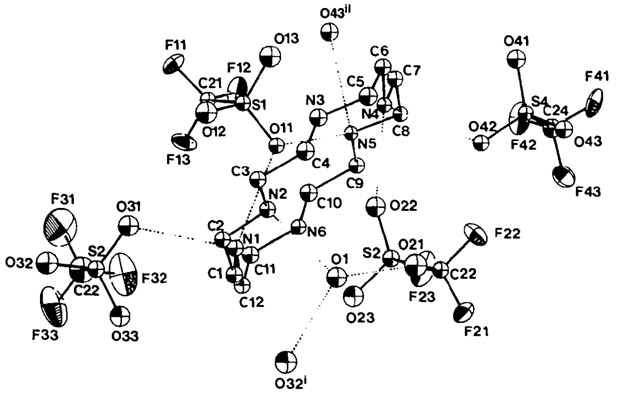

Fig. 2. *ORTEP*II (Johnson, 1976) drawing of (II) with atom labelling. Possible hydrogen bonds are indicated by dashed lines. Ellipsoids are drawn at the 40% probability level. Symmetry codes: (i) $-x, -y, 2 - z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

In both compounds, the polycationic macrocycle adopts the $g^+g^-g^+g^-g^+g^-$ conformation (distorted D_{3d} sequence), one of the most commonly found in 18-crown-6-type macrocycles (Fyles & Gandour, 1992), with only slight differences in the *gauche*-angle values between (I) and (II); the C—C—N—C torsion angles do not deviate much from the ideal *anti* value of 180°. Molecular-mechanics and semi-empirical quantum-mechanics calculations (Santos & Drew, 1991) have shown that this configuration is the more stable one in neutral hexaaza-18-crown-6, but not in $(H_3\text{-hexaaza-18-crown-6})^{3+}$ (it must be noted that, as already observed, the conformation in the solid state is not necessarily the lowest energy one in molecular-mechanics calculations). Our result concerning the macrocycle conformation differs from the results obtained from other anions (Cullinane *et al.*, 1982), which may be due to packing constraints depending on the anion's steric properties: in $(H_4\text{-hexaaza-18-crown-6})(NO_3)_2Cl_2.2H_2O$, the unusual conformation adopted by the protonated macrocycle ($g^+g^+g^+g^-g^-g^-$ and two *anti* torsion angles becoming *gauche* ones) is the same as in the previously reported structure of $(H_2\text{-diaza-18-crown-6})^{2+}.2CF_3SO_3^-$ (Thuéry *et al.*, 1995). This conformation is different from the one of the neutral diaza-18-crown-6 macrocycle ($g^+g^-g^+g^-g^+g^-$).

The six N atoms are in a puckered plane with maximum deviations of ±0.29 and ±0.34 Å in (I) and (II), respectively, the two neutral amine functional groups being located on the diameter of the macrocycle. The C—N distances seem to be somewhat shorter for neutral [1.45–1.47 (2) Å] than for protonated [1.49–1.52 (2) Å] N atoms. In both compounds, as well as in anion complexes of protonated hexaaza-18-crown-6 previously described (Margulis & Zompa, 1981; Cullinane *et al.*, 1982), hydrogen bonds are involved in the ion pairing: the possible hydrogen bonds in (I) and (II), with O···O or O···N < 3 Å (Hamilton & Ibers, 1968) are listed in Tables 2 and 4. In (I), only direct hydrogen bonds between the macrocyclic ammonium functions and the O atoms of the anions can be formed; but in (II), both direct and H_2O-mediated hydrogen bonds occur, the water molecule being involved in hydrogen bonds with one ammonium group and two anionic O atoms. A similar situation has been described in the case of $(H_4\text{-hexaaza-18-crown-6})(NO_3)_2Cl_2.2H_2O$ (Cullinane *et al.*, 1982), with the difference that, in the latter case, NO_3^- is not directly bonded to the macrocycle. The hydrogen bonds formed by the protonated macrocycle with $CF_3SO_3^-$ [N···O distances 2.83–2.92 (1) in (I), 2.82–2.96 (1) Å in (II)] are of the same order as those found in $(H_2\text{-diaza-18-crown-6})^{2+}.2CF_3SO_3^-$ [2.83 (1) Å; Thuéry *et al.*, 1995] and weaker than the direct ones with NO_3^-, as observed in $(H_6\text{-hexaaza-18-crown-6})(NO_3)_4Cl_2$ (2.77–2.88 Å; Margulis & Zompa, 1981). The hydrogen bond involving the water molecule in (II) appears particularly strong [N···O 2.72 (2) Å].

Experimental

The crystals were obtained from solutions of hexaaza-18-crown-6 (purchased from Fluka and used without further purification) and trifluoromethanesulfonic acid in water/acetonitrile, with a pH of ~3–4 (no crystals suitable for X-ray measurements were obtained from more acidic solutions).

Compound (I)

Crystal data

$C_{12}H_{34}N_6^{4+}.4CF_3SO_3^-$	Mo $K\alpha$ radiation
$M_r = 858.72$	$\lambda = 0.71073$ Å

Monoclinic
$P2_1/n$
$a = 8.919\,(4)$ Å
$b = 14.128\,(3)$ Å
$c = 14.079\,(6)$ Å
$\beta = 104.58\,(5)°$
$V = 1717\,(1)$ Å^3
$Z = 2$
$D_x = 1.661$ Mg m^{-3}

Cell parameters from 25 reflections
$\theta = 8–12°$
$\mu = 0.386$ mm^{-1}
$T = 243$ K
Irregular
0.50 × 0.45 × 0.30 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2473 measured reflections
2102 independent reflections
1409 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.023$
$\theta_{\rm max} = 22°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 14$
$l = -14 \rightarrow 14$
3 standard reflections frequency: 60 min intensity decay: insignificant

Refinement

Refinement on F
$R = 0.058$
$wR = 0.060$
$S = 2.09$
1409 reflections
181 parameters
Unit weights applied
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.61$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.44$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2) *for* (I)

$B_{\rm iso}$ for N, C(1)—C(6); $B_{\rm eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$ for CF$_3$SO$_3$ atoms.

	x	y	z	$B_{\rm iso}/B_{\rm eq}$
S(1)	0.7349 (2)	0.3766 (1)	0.0562 (1)	2.66 (4)
S(2)	0.8084 (2)	0.3770 (1)	0.6749 (1)	2.86 (4)
F(11)	0.8439 (6)	0.2094 (3)	0.0350 (4)	5.7 (1)
F(12)	0.5994 (6)	0.2201 (4)	−0.0137 (5)	7.2 (2)
F(13)	0.7456 (8)	0.2792 (4)	−0.0977 (3)	8.5 (2)
F(21)	0.6957 (9)	0.5243 (4)	0.5710 (4)	10.8 (2)
F(22)	0.9265 (9)	0.4837 (6)	0.5690 (6)	20.9 (2)
F(23)	0.732 (1)	0.4043 (6)	0.4906 (4)	19.3 (3)
O(11)	0.7087 (8)	0.3507 (4)	0.1481 (4)	6.8 (2)
O(12)	0.8796 (6)	0.4174 (4)	0.0582 (5)	6.0 (2)
O(13)	0.6033 (7)	0.4280 (4)	−0.0012 (5)	5.6 (2)
O(21)	0.8995 (6)	0.2986 (4)	0.6556 (4)	4.0 (1)
O(22)	0.6543 (6)	0.3554 (5)	0.6759 (5)	5.8 (2)
O(23)	0.8843 (8)	0.4349 (5)	0.7561 (5)	7.0 (2)
N(1)	1.0145 (6)	0.0177 (4)	0.2928 (4)	2.6 (1)
N(2)	0.7489 (6)	0.1043 (4)	0.3354 (4)	2.6 (1)
N(3)	0.8023 (6)	0.1313 (4)	0.5462 (4)	2.4 (1)
C(1)	0.8686 (8)	0.0363 (5)	0.2151 (5)	3.1 (1)
C(2)	0.7920 (8)	0.1229 (6)	0.2431 (5)	3.3 (1)
C(3)	0.6985 (8)	0.1895 (5)	0.3771 (5)	3.1 (1)
C(4)	0.6586 (8)	0.1645 (5)	0.4724 (5)	3.0 (1)
C(5)	0.7660 (8)	0.0928 (5)	0.6373 (5)	2.9 (1)
C(6)	0.9121 (8)	0.0752 (5)	0.7179 (5)	2.9 (1)
C(10)	0.7281 (8)	0.2662 (6)	−0.0108 (5)	3.3 (2)
C(20)	0.788 (1)	0.4507 (7)	0.5697 (7)	9.0 (3)

Table 2. *Selected geometric parameters* (Å, °) *for* (I)

N(1)—C(1)	1.497 (9)	N(1)—C(6$^{\rm i}$)	1.49 (1)
N(2)—C(2)	1.468 (9)	N(2)—C(3)	1.460 (9)
N(3)—C(4)	1.507 (9)	N(3)—C(5)	1.501 (9)
C(1)—C(2)	1.50 (1)	C(3)—C(4)	1.51 (1)
C(5)—C(6)	1.52 (1)		
C(6$^{\rm i}$)—N(1)—C(1)	113.8 (5)	N(1)—C(1)—C(2)	108.7 (6)
C(1)—C(2)—N(2)	108.9 (6)	C(2)—N(2)—C(3)	112.6 (6)
N(2)—C(3)—C(4)	109.2 (6)	C(3)—C(4)—N(3)	109.6 (6)
C(4)—N(3)—C(5)	111.9 (5)	N(3)—C(5)—C(6)	111.6 (6)
C(5)—C(6)—N(1$^{\rm i}$)	112.6 (6)		
N(1)···O(22$^{\rm ii}$)	2.92 (1)	N(1)···O(13$^{\rm iii}$)	2.91 (1)
N(3)···O(21)	2.83 (1)		
O(13$^{\rm iii}$)···N(1)···O(22$^{\rm ii}$)	110.6 (3)		
C(6$^{\rm i}$)—N(1)—C(1)—C(2)	170.4 (6)		
C(1)—C(2)—N(2)—C(3)	169.9 (6)		
N(2)—C(3)—C(4)—N(3)	64.4 (7)		
C(4)—N(3)—C(5)—C(6)	−170.2 (5)		
C(5$^{\rm i}$)—C(6$^{\rm i}$)—N(1)—C(1)	−179.0 (5)		
N(1)—C(1)—C(2)—N(2)	−62.8 (7)		
C(2)—N(2)—C(3)—C(4)	−179.2 (6)		
C(3)—C(4)—N(3)—C(5)	−172.2 (6)		
N(3)—C(5)—C(6)—N(1$^{\rm i}$)	−83.0 (5)		

Symmetry codes: (i) $2 - x, -y, 1 - z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

Compound (II)

Crystal data

$C_{12}H_{34}N_6^{4+}.4CF_3SO_3^-.H_2O$
$M_r = 876.73$
Monoclinic
$P2_1/n$
$a = 8.984\,(5)$ Å
$b = 31.147\,(12)$ Å
$c = 13.357\,(3)$ Å
$\beta = 106.98\,(6)°$
$V = 3574\,(3)$ Å^3
$Z = 4$
$D_x = 1.629$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8–12°$
$\mu = 0.375$ mm^{-1}
$T = 295$ K
Irregular
0.5 × 0.35 × 0.15 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω/θ scans
Absorption correction: none
3500 measured reflections
3320 independent reflections
1807 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.025$
$\theta_{\rm max} = 20°$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 29$
$l = 0 \rightarrow 12$
3 standard reflections frequency: 60 min intensity decay: insignificant

Refinement

Refinement on F
$R = 0.074$
$wR = 0.077$
$S = 4.48$
1807 reflections
265 parameters
Unit weights applied
$(\Delta/\sigma)_{\rm max} = 0.02$

$\Delta\rho_{\rm max} = 0.61$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 3. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2) *for* (II)

$B_{\rm iso}$ for S, O, N, C; $B_{\rm eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$ for F atoms.

	x	y	z	$B_{\rm iso}/B_{\rm eq}$
S(1)	0.6764 (4)	0.0759 (1)	1.1349 (3)	3.12 (7)
S(2)	0.1895 (4)	0.1988 (1)	1.0677 (3)	3.90 (8)
S(3)	0.2303 (4)	−0.0437 (1)	1.2369 (3)	3.98 (8)
S(4)	0.5674 (4)	0.3062 (1)	0.9440 (3)	3.14 (7)

F(11)	0.853 (1)	0.0263 (3)	1.2776 (7)	6.2 (3)
F(12)	0.796 (1)	0.0853 (3)	1.3350 (7)	6.7 (3)
F(13)	0.629 (1)	0.0366 (3)	1.2931 (7)	7.0 (3)
F(21)	0.054 (1)	0.2652 (3)	1.120 (1)	9.2 (4)
F(22)	0.287 (1)	0.2763 (3)	1.1276 (7)	6.9 (3)
F(23)	0.234 (2)	0.2391 (4)	1.2430 (8)	10.0 (4)
F(31)	0.425 (2)	−0.0618 (5)	1.414 (1)	16.7 (6)
F(32)	0.289 (2)	−0.0068 (4)	1.4166 (8)	13.0 (5)
F(33)	0.190 (2)	−0.0674 (4)	1.412 (1)	14.2 (5)
F(41)	0.650 (1)	0.3741 (3)	1.0638 (7)	7.0 (3)
F(42)	0.637 (1)	0.3158 (3)	1.1454 (7)	8.0 (3)
F(43)	0.430 (1)	0.3474 (3)	1.0602 (8)	7.6 (3)
O(1)	0.038 (1)	0.1357 (3)	0.8437 (8)	5.4 (3)
O(11)	0.552 (1)	0.1052 (3)	1.1391 (7)	3.5 (2)
O(12)	0.622 (1)	0.0399 (4)	1.0712 (8)	5.8 (3)
O(13)	0.807 (1)	0.0982 (4)	1.1217 (9)	6.5 (3)
O(21)	0.123 (1)	0.2126 (4)	0.9618 (9)	6.5 (3)
O(22)	0.352 (1)	0.1872 (3)	1.0963 (8)	4.9 (2)
O(23)	0.098 (1)	0.1695 (4)	1.1079 (8)	5.7 (3)
O(31)	0.348 (1)	−0.0173 (4)	1.2136 (8)	5.8 (3)
O(32)	0.234 (1)	−0.0879 (4)	1.2078 (9)	6.3 (3)
O(33)	0.080 (1)	−0.0249 (3)	1.2069 (8)	5.5 (3)
O(41)	0.727 (1)	0.2985 (3)	0.9519 (7)	4.4 (2)
O(42)	0.482 (1)	0.2683 (3)	0.9557 (7)	3.6 (2)
O(43)	0.483 (1)	0.3332 (3)	0.8601 (7)	4.1 (2)
N(1)	0.267 (1)	0.0722 (4)	1.1797 (8)	3.3 (2)
N(2)	0.277 (1)	0.0834 (4)	0.9440 (8)	3.5 (3)
N(3)	0.528 (1)	0.1235 (4)	0.8892 (9)	3.9 (3)
N(4)	0.632 (1)	0.1911 (3)	1.0394 (8)	2.9 (2)
N(5)	0.650 (1)	0.1794 (3)	1.2781 (8)	2.9 (2)
N(6)	0.395 (1)	0.1376 (3)	1.3305 (8)	2.9 (2)
C(1)	0.146 (2)	0.0635 (5)	1.079 (1)	3.9 (3)
C(2)	0.214 (2)	0.0482 (4)	0.995 (1)	3.5 (3)
C(3)	0.327 (2)	0.0685 (5)	0.852 (1)	4.2 (3)
C(4)	0.394 (2)	0.1056 (5)	0.809 (1)	4.7 (4)
C(5)	0.577 (2)	0.1648 (5)	0.860 (1)	4.4 (4)
C(6)	0.700 (2)	0.1830 (5)	0.950 (1)	3.9 (3)
C(7)	0.750 (1)	0.2073 (4)	1.134 (1)	3.4 (3)
C(8)	0.683 (2)	0.2181 (4)	1.222 (1)	3.6 (3)
C(9)	0.599 (2)	0.1911 (5)	1.373 (1)	4.0 (3)
C(10)	0.531 (1)	0.1525 (4)	1.412 (1)	3.4 (3)
C(11)	0.325 (2)	0.0990 (4)	1.361 (1)	3.8 (3)
C(12)	0.196 (1)	0.0838 (4)	1.265 (1)	3.5 (3)
C(21)	0.744 (2)	0.0546 (4)	1.267 (1)	3.7 (3)
C(22)	0.190 (2)	0.2474 (5)	1.143 (1)	3.7 (3)
C(23)	0.282 (2)	−0.0456 (7)	1.378 (2)	8.3 (5)
C(24)	0.574 (2)	0.3378 (5)	1.061 (1)	5.1 (4)

Table 4. *Selected geometric parameters* (Å, °) *for* (II)

N(1)—C(1)	1.49 (2)	N(1)—C(12)	1.51 (2)
N(2)—C(2)	1.49 (2)	N(2)—C(3)	1.51 (2)
N(3)—C(4)	1.47 (2)	N(3)—C(5)	1.45 (2)
N(4)—C(6)	1.52 (2)	N(4)—C(7)	1.48 (2)
N(5)—C(8)	1.49 (2)	N(5)—C(9)	1.51 (2)
N(6)—C(10)	1.45 (2)	N(6)—C(11)	1.47 (2)
C(1)—C(2)	1.50 (2)	C(3)—C(4)	1.49 (2)
C(5)—C(6)	1.49 (2)	C(7)—C(8)	1.50 (2)
C(9)—C(10)	1.51 (2)	C(11)—C(12)	1.53 (2)
N(1)—C(1)—C(2)	113 (1)	C(1)—C(2)—N(2)	113 (1)
C(2)—N(2)—C(3)	113 (1)	N(2)—C(3)—C(4)	109 (1)
C(3)—C(4)—N(3)	110 (1)	C(4)—N(3)—C(5)	113 (1)
N(3)—C(5)—C(6)	109 (1)	C(5)—C(6)—N(4)	109 (1)
C(6)—N(4)—C(7)	112 (1)	N(4)—C(7)—C(8)	113 (1)
C(7)—C(8)—N(5)	113 (1)	C(8)—N(5)—C(9)	112 (1)
N(5)—C(9)—C(10)	111 (1)	C(9)—C(10)—N(6)	109 (1)
C(10)—N(6)—C(11)	113 (1)	N(6)—C(11)—C(12)	108 (1)
C(11)—C(12)—N(1)	109 (1)	C(12)—N(1)—C(1)	112 (1)
N(1)···O(11)	2.96 (1)	N(1)···O(31)	2.88 (2)
N(4)···O(22)	2.83 (1)	N(4)···O(42)	2.82 (1)
N(5)···O(11)	2.93 (1)	N(5)···O(43^{ii})	2.89 (1)
N(2)···O(1)	2.72 (2)		
O(1)···O(21)	2.85 (2)	O(31)···O(32^{i})	2.77 (2)
O(31)···N(1)···O(11)	100.0 (4)	O(22)···N(4)···O(42)	77.5 (4)
O(11)···N(5)···O(43^{ii})	102.6 (4)	O(21)···O(1)···O(32^{i})	131.7 (5)
N(2)···O(1)···O(21)	100.6 (5)	N(2)···O(1)···O(32^{i})	108.2 (5)

N(1)—C(1)—C(2)—N(2)	−80 (1)
C(2)—N(2)—C(3)—C(4)	−178 (1)
C(3)—C(4)—N(3)—C(5)	−168 (1)
N(3)—C(5)—C(6)—N(4)	−63 (1)
C(6)—N(4)—C(7)—C(8)	176 (1)
C(7)—C(8)—N(5)—C(9)	174 (1)
N(5)—C(9)—C(10)—N(6)	−61 (1)
C(10)—N(6)—C(11)—C(12)	−174 (1)
C(11)—C(12)—N(1)—C(1)	−171 (1)
C(1)—C(2)—N(2)—C(3)	−173 (1)
N(2)—C(3)—C(4)—N(3)	59 (1)
C(4)—N(3)—C(5)—C(6)	173 (1)
C(5)—C(6)—N(4)—C(7)	177 (1)
N(4)—C(7)—C(8)—N(5)	77 (1)
C(8)—N(5)—C(9)—C(10)	166 (1)
C(9)—C(10)—N(6)—C(11)	178 (1)
N(6)—C(11)—C(12)—N(1)	62 (1)
C(12)—N(1)—C(1)—C(2)	−175 (1)

Symmetry codes: (i) $-x, -y, 2 - z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

For (I), Lorentz–polarization corrections were applied. The structure was solved by direct methods and refined by full-matrix least-squares procedures with anisotropic displacement parameters for the atoms of the $CF_3SO_3^-$ moiety. The H atoms bonded to the ammonium atoms were located on a difference Fourier map, then introduced, as were those bonded to C atoms, in calculated positions as riding atoms (C—H 0.95, N—H 1.05 Å, $B = 6$ Å^2). The ammonium N atoms appear to be hydrogen-bond donors to $CF_3SO_3^-$.

For (II), Lorentz–polarization corrections were applied. The structure was solved by direct methods and refined by full-matrix least-squares procedures with anisotropic displacement parameters for F atoms. Ammonium N atoms were assumed to be hydrogen-bond donors as in compound (I). H atoms bonded to C atoms and to the ammonium N atoms [N(1), N(2), N(4) and N(5)] were introduced in calculated positions as riding atoms (C—H 0.95, N—H 1.05 Å, $B = 6$ Å^2).

For both compounds, data collection: Enraf–Nonius CAD-4 software; cell refinement: Enraf–Nonius CAD-4 software; data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structures: *MULTAN*11/82 (Main *et al.*, 1982) for (I); *SHELXS*86 (Sheldrick, 1985) for (II). For both compounds, program(s) used to refine structures: *MolEN*; molecular graphics: *ORTEP*II (Johnson, 1976). Computer: VAX 4200.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1089). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Homochiral Methyl (*S*)-2-Benzenesulfonyloxy-4-bromo-4-methylpentanoate

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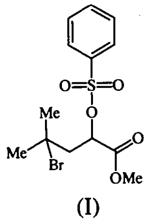
(*Received* 20 *December* 1994; *accepted* 7 *February* 1995)

Abstract

The stereochemistry at position 2 of the title compound, $C_{13}H_{17}BrO_5S$, has been confirmed as (*S*).

Comment

The title compound, (I), was investigated as part of a study into the regioselective bromination of 2-hydroxy-4-methylpentanoic acid derivatives. This structure determination was undertaken to confirm that the stereochemistry at the 2 position (*i.e.* C5) was unaffected by the bromination reaction. The compound crystallized in the monoclinic space group $P2_1$ and refinement of the structure showed the presence of only one enantiomer. The stereochemistry at C5 was found to be (*S*), with the correct choice of 'handedness' verified by the value of the Flack (1983) parameter [χ = 0.01 (2)]. Close intermolecular contacts occur between Br1 and H10($2 - x, y + 1/2, 2 - z$) [2.989 (7) Å], and O2 and H9($2 - x, y + 1/2, 2 - z$) [2.438 (8) Å]. A similar regioselective (and stereoselective) bromination of a cinnamate derivative has been reported previously (Shaw, Tan & Blackman, 1995).



(I)

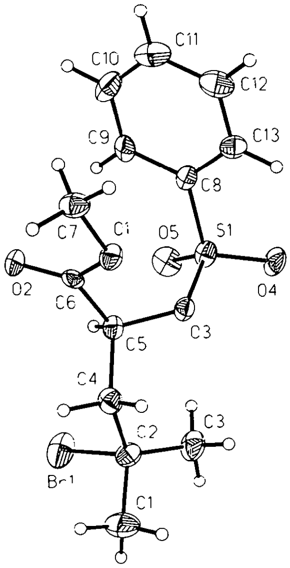


Fig. 1. *ORTEP* (Johnson, 1965) drawing of (I) showing displacement ellipsoids drawn at the 50% probability level.

Experimental

A mixture of methyl (*S*)-2-benzenesulfonyloxy-4-methylpentanoate (0.32 g, 1.1 mmol) and *N*-bromosuccinimide (0.24 g, 1.3 mmol) in CCl_4 (40 ml) was heated at reflux under nitrogen for 8 h, the reaction being initiated by irradiation with a 160 W mercury lamp. The reaction mixture was then cooled, filtered and evaporated under reduced pressure. The resulting solid was recrystallized from dichloromethane and hexane (Shaw & Tan, 1995). The compound crystallizes as large blocks which were used for the analysis, as smaller crystals could not be grown.

Crystal data

$C_{13}H_{17}BrO_5S$
M_r = 365.24
Monoclinic
$P2_1$
a = 10.352 (2) Å
b = 7.1190 (10) Å
c = 10.652 (2) Å
β = 104.89 (3)°
V = 758.6 (2) Å^3
Z = 2
D_x = 1.599 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 15 reflections
θ = 12–17°
μ = 2.862 mm^{-1}
T = 130 (2) K
Block
0.7 × 0.6 × 0.3 mm
Colourless