O(4)	0.4438 (2)	0.2821 (1)	0.3122 (2)	4.20 (6)
N(1)	0.2688 (2)	0.1063 (1)	0.1354 (2)	2.59 (6)
C(1)	0.2554 (3)	−0.0105 (2)	0.3573 (3)	3.9 (1)
C(2)	0.1764 (2)	0.0612 (2)	0.2256 (2)	2.52 (7)
C(3)	0.0092 (2)	0.0823 (2)	0.1917 (2)	2.37 (6)
C(4)	−0.0639 (2)	0.1513 (2)	0.0681 (2)	2.61 (7)
C(5)	0.0364 (2)	0.1958 (2)	−0.0190 (2)	3.27 (8)
C(6)	0.1994 (2)	0.1722 (2)	0.0154 (2)	3.24 (8)
C(7)	0.4479 (2)	0.0942 (2)	0.1705 (2)	2.83 (7)
C(8)	0.5259 (2)	0.1937 (2)	0.2821 (2)	2.67 (7)

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

O(1)—C(3)	1.352 (2)	C(1)—C(2)	1.489 (3)
O(2)—C(4)	1.321 (2)	C(2)—C(3)	1.384 (2)
O(3)—C(8)	1.273 (2)	C(3)—C(4)	1.404 (2)
O(4)—C(8)	1.226 (2)	C(4)—C(5)	1.387 (3)
N(1)—C(2)	1.364 (2)	C(5)—C(6)	1.355 (3)
N(1)—C(6)	1.355 (2)	C(7)—C(8)	1.529 (3)
N(1)—C(7)	1.469 (2)		
C(2)—N(1)—C(6)	120.9 (1)	O(2)—C(4)—C(3)	118.0 (2)
C(2)—N(1)—C(7)	121.4 (2)	O(2)—C(4)—C(5)	124.1 (2)
C(6)—N(1)—C(7)	117.6 (2)	C(3)—C(4)—C(5)	117.9 (2)
N(1)—C(2)—C(1)	120.0 (2)	C(4)—C(5)—C(6)	120.4 (2)
N(1)—C(2)—C(3)	118.9 (2)	N(1)—C(6)—C(5)	121.3 (2)
C(1)—C(2)—C(3)	121.1 (2)	N(1)—C(7)—C(8)	111.0 (1)
O(1)—C(3)—C(2)	117.8 (2)	O(3)—C(8)—O(4)	125.3 (2)
O(1)—C(3)—C(4)	121.5 (1)	O(3)—C(8)—C(7)	114.5 (2)
C(2)—C(3)—C(4)	120.6 (2)	O(4)—C(8)—C(7)	120.2 (2)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D	H	*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O(1)	H(1)	O(3^{i})	0.96 (2)	1.75 (2)	2.677 (2)	160 (2)
O(1)	H(1)	O(2)	0.96 (2)	2.40 (3)	2.732 (2)	100 (2)
O(2)	H(2)	O(3^{ii})	1.05 (3)	1.49 (3)	2.545 (2)	176 (3)
C(1)	H(3)	O(1)	0.91 (2)	2.32 (2)	2.786 (3)	112 (2)
C(6)	H(7)	O(4^{iii})	1.00 (2)	2.18 (2)	3.155 (3)	165 (2)
C(7)	H(8)	O(4^{iv})	0.99 (2)	2.46 (2)	3.387 (3)	156 (1)

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

Data collection and cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1985*a*). Data reduction, structure solution, refinement and preparation of material for publication: *TEXSAN* (Molecular Structure Corporation, 1985*b*). Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving H atoms, least-squares-planes data and torsion angles, and a stereoview of the molecular packing have been deposited with the IUCr (Reference: CD1062). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structures of Trimethyloxosulfonium Salts. VIII. New Refinement of the Perchlorate $(CH_3)_3SO^+.ClO_4^-$

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Abstract

The trimethyloxosulfonium cations, $(CH_3)_3SO^+$, have the same geometry as in the other salts reported previously. The ClO_4^- anions occupy two different sites of tetrahedral geometry. The first type is regular [Cl—O bonds 1.402 (2) Å], while the second has an irregular form [Cl—O bonds from 1.379 (5) to 1.417 (3) Å]; two kinds of tetrahedra are located at the site having *m* symmetry with occupation factors of 0.5. The structure of this compound has been solved previously [Coulder, Gantzel & McCullough, (1963). *Acta Cryst.* **16**, 676–681] but the old data required refinement.

Comment

In this series of papers, the iodide, bromide, chloride, nitrate, chromate, chlorocadmate and thiocyanate structures have been reported (Jannin, Puget, de Brauer & Perret, 1991*a*,*b*,*c*; de Brauer, Jannin, Puget

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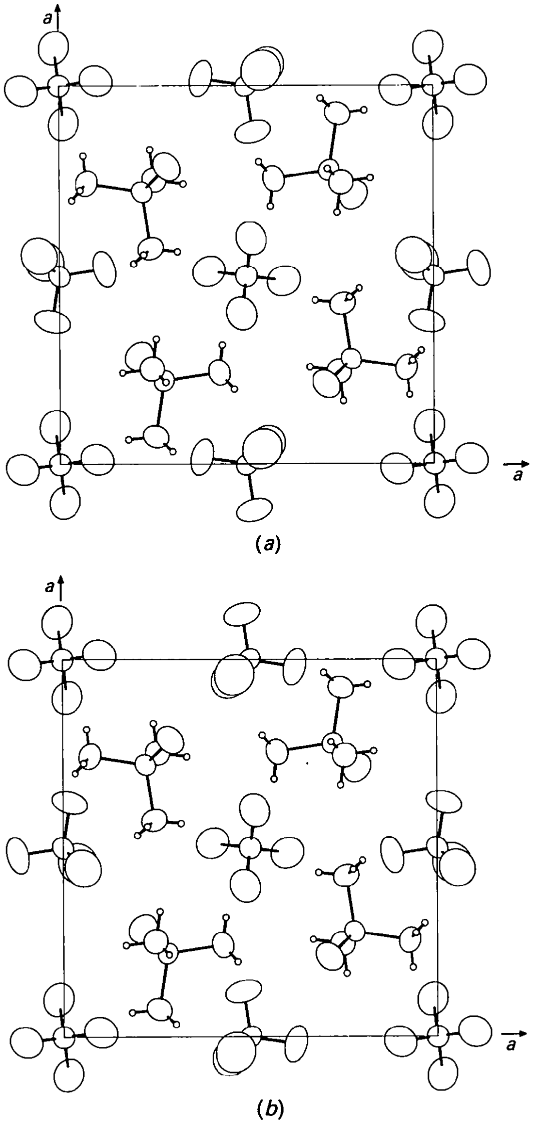
& Perret, 1991; Puget, Jannin, de Brauer & Perret, 1991; Puget, Jannin, Perret & de Brauer, 1991; Jannin, Puget, de Brauer & Perret, 1993).

The final atomic coordinates, interatomic distances and bond angles agree with those of previous work by Coulder, Gantzel & McCullough (1963). The pyramidal trimethyloxosulfonium cation, (CH$_3$)$_3$SO$^+$, possesses only one symmetry plane in which the S, O and C(1) atoms are located, but it closely approximates the $3m$ symmetry assigned to the free ion, as in the other salts reported previously. There are two types of perchorate ions. The ions of the first type have $\bar{4}$ symmetry; the Cl(1) atoms are located at the origin of the cell and at the centre of square faces, and the Cl(1)O$_4$ tetrahedra are only slightly deformed with Cl(1)—O(10) 1.402 (2) Å and O(10)—Cl(1)—O(10) 107.7 (1) and 113.0 (2)°. Ions of the second type are located at positions having $2mm$ symmetry, the coordinates of Cl(2) atoms being $(0,\frac{1}{2},z)$, $(\frac{1}{2},0,-z)$ with $z = 0.91$, approximately. The O(20) and O(21) atoms bound to Cl(2) have m symmetry and O(22) atoms are located at general positions; they form tetrahedra providing only half the expected sites are occupied. It was possible to carry out refinement by giving the three O atoms in equivalent positions an average occupation of 0.5. Fourier maps seemed to show a static disorder. The Cl(2)O$_4$ tetrahedra are also only slightly deformed: the interatomic distances Cl(2)—O range between 1.379 (5) and 1.417 (3) Å, the average value of 1.394 (4) Å being close to the interatomic distance Cl(1)—O(10); the bond angles O—Cl(2)—O range between 107.1 (2) and 112.1 (2)°.



(a)

(b)

Fig. 1. Projection along the c axis of the arrangement of (CH$_3$)$_3$SOClO$_4$. (a) and (b) show the two different positions of the perchlorate anions with $2mm$ symmetry.

Most of the perchlorate O atoms are mobile: for O(10) $B_{\rm eq} = 8.55$, for O(22) $B_{\rm eq} = 7.63$, and specially, for O(20) $B_{\rm eq} = 10.38$ and for O(21) $B_{\rm eq} = 11.7$ Å^2.

A projection of the structure along the c axis is presented in Fig. 1. Only half the equivalent sites of the O atoms surrounding Cl(2) are drawn in each part of Fig. 1 so as to distinguish the two different positions of the perchlorate anions with $2mm$ symmetry.

Experimental

The compound was prepared by the reaction of (CH$_3$)$_3$SOI and AgClO$_4$. Crystals were obtained by recrystallization from an aqueous solution.

Crystal data

C$_3$H$_9$OS$^+$.ClO$_4^-$
$M_r = 192.62$
Tetragonal
$P\bar{4}2_1m$
$a = 11.605$ (2) Å
$c = 6.005$ (2) Å
$V = 808.7$ (5) Å^3
$Z = 4$
$D_x = 1.582$ Mg m^{-3}
$D_m = 1.55$ (5) Mg m^{-3}
D_m measured by pycnometry

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 5$–15°
$\mu = 0.6865$ mm^{-1}
$T = 293$ K
Prismatic
0.24 × 0.23 × 0.23 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans (width 1.2°)
Absorption correction: empirical (ψ scans)
$T_{\rm min} = 0.979$, $T_{\rm max} = 0.998$
6473 measured reflections
1072 independent reflections
1062 observed reflections [$I > 3.0\sigma(I)$]

$R_{\rm int} = 0.017$
$\theta_{\rm max} = 30°$
$h = -5 \rightarrow 13$
$k = -13 \rightarrow 13$
$l = -8 \rightarrow 8$
4 standard reflections frequency: 120 min intensity variation: −2.1% in 114 h

Refinement

Refinement on *F*
$R = 0.0249$
$wR = 0.0246$
$S = 0.333$
1062 reflections
112 parameters
Only coordinates of H atoms refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.005$
$\Delta\rho_{\max} = 0.575$ e Å^{-3}
$\Delta\rho_{\min} = -0.245$ e Å^{-3}
Extinction correction: Stout & Jensen (1968)
Extinction coefficient: 2.7496×10^{-6}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
S	0.27908 (7)	1/2−x	0.61369 (9)	3.187 (5)
O	0.2124 (1)	1/2−x	0.4577 (3)	5.82 (3)
C(1)	0.2467 (2)	1/2−x	0.8895 (5)	4.45 (3)
C(2)	0.4266 (2)	0.2439 (2)	0.5827 (3)	4.48 (4)
Cl(1)	0	0	0	3.709 (9)
Cl(2)	0	1/2	0.9136 (1)	3.67 (1)
O(10)	0.0999 (1)	0.0129 (2)	0.1289 (3)	8.55 (4)
O(20)	0.0534 (3)	1/2−x	1.0922 (9)	10.38 (9)
O(21)	0.0403 (4)	1/2−x	0.712 (1)	11.7 (1)
O(22)	−0.0188 (3)	0.3794 (2)	0.9165 (6)	7.63 (9)

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

Cl(1)—O(10)	1.402 (2)	S—O	1.439 (2)
Cl(2)—O(20)	1.385 (5)	S—C(1)	1.739 (3)
O(20)···O(21)	2.292 (8)	S—C(2)	1.742 (2)
O(20)···O(22)	2.314 (4)	O—C(1)	2.653 (3)
Cl(2)—O(21)	1.379 (5)	O—C(2)	2.646 (2)
Cl(2)—O(22)	1.417 (3)	C(1)···C(2)	2.786 (3)
O(21)···O(22)	2.249 (4)		
O(10)—Cl(1)—O(10)	113.0 (2)	O(21)—Cl(2)—O(22)	107.1 (2)
O(10)—Cl(1)—O(10)	107.7 (1)	O—S—C(1)	112.82 (9)
O(20)—Cl(2)—O(21)	112.1 (2)	O—S—C(2)	112.13 (9)
O(20)—Cl(2)—O(22)	111.3 (2)	C(1)—S—C(2)	106.34 (9)

Systematic absences, $0k0$ ($k = 2n$) and $h00$ ($h = 2n$), indicated space group $P\bar{4}2_1m$ (No. 113) or $P42_12$ (No. 90). Intensity data were corrected for decay and Lorentz–polarization effects. Direct methods (*MULTAN77*; Main, Lessinger, Woolfson, Germain & Declercq, 1977) were used for structure determination in $P\bar{4}2_1m$. H atoms were located by difference Fourier synthesis. Anisotropic full-matrix least-squares refinement was performed for non-H atoms, isotropic for H atoms. *SDP* (Enraf–Nonius, 1977) was used for all calculations on a VAX 730 computer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DU1067). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,4,6-Triphenylcyanobenzene and 2,4,6-Triphenylnitrobenzene

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Abstract

The structures of the title compounds, the cyano derivative $C_{25}H_{17}N$ (TPCB; 2,4,6-triphenylbenzonitrile) and the nitro derivative $C_{24}H_{17}NO_2$ (TPNB), have been determined. In the two symmetry independent molecules of TPNB the nitro group is twisted by almost the same amount, 64 and 65°.

Comment

In a continuation of our studies of sterically affected chemical species (Krygowski, Anulewicz, Daniluk & Drapala, 1990; Wozniak, Krygowski, Kariuki, Jones & Grech, 1990) we have investigated 2,4,6-triphenyl-