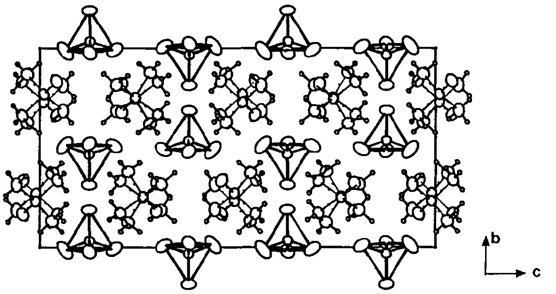

Fig. 1. Projection along the *a* axis of the atomic arrangement of $[(CH_3)_3SO]_2CrO_4$.

Table 1* reports the final atomic coordinates. The main interatomic distances and bond angles are given in Table 2. The CrO_4^{2-} anion, which has no symmetry element in this cell, is quasi-tetrahedral, as usual. The two pyramidal thiocations $(CH_3)SO^+$ also have neither symmetry plane nor axis; nevertheless, they closely approximate the $3m$ symmetry assumed for the free cation, as found in almost all the other salts studied. The projection of the atomic arrangement of $[(CH_3)_3SO]_2CrO_4$ along the *a* axis is given in Fig. 1.

Related literature. Very little is known about the structures of trimethyloxosulfonium salts: only the structures of the perchlorate (Coulder, Gantzel & McCullough, 1963) and the fluoroborate (Zimmermann, Barlow & McCullough, 1963) have been described at 293 K. We have reported the structure of some other trimethyloxosulfonium salts, *e.g.* iodide, bromide, chloride and nitrate (Jannin, Puget, de Brauer & Perret, 1991).

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* Lists of structure factors, anisotropic thermal parameters, bond angles, bond lengths and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53681 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structures of Trimethyloxosulfonium Salts. VI. The Thiocyanate

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Abstract. $[(CH_3)_3SO]SCN$, $M_r = 151{\cdot}25$, orthorhombic, $Pmn2_1$, $a = 7{\cdot}260\,(2)$, $b = 5{\cdot}951\,(2)$, $c = 8{\cdot}757\,(2)$ Å, $V = 378\,(1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}30$, $D_m = 1{\cdot}30\,(1)$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7173$ Å, $\mu(\text{Mo } K\alpha) = 5{\cdot}93$ cm^{-1}, $F(000) = 160$, $T = 293$ K, final $R = 0{\cdot}023$, $wR = 0{\cdot}033$ for 760 independent observed reflections. The structure contains linear anions SCN^- and pyramidal thiocations $[(CH_3)_3SO]^+$, which approximate to $3m$ symmetry: these cations possess only one symmetry plane ($x = 0{\cdot}500$) where the anions are also located. The H atoms were located.

Experimental. The preparation of the crystals will be described elsewhere (de Brauer & Perret, 1991). Prismatic colorless crystals, density measured by pycnometry in xylene, $D_m = 1{\cdot}30\,(1)$ Mg m^{-3}, crystal size $0{\cdot}21 \times 0{\cdot}23 \times 0{\cdot}24$ mm. Enraf–Nonius CAD-4 diffractometer, graphite monochromator. Unit-cell constants from least-squares refinement of 25 reflections with $5 < \theta < 13°$. Systematic absences $h0l$ ($h + l = 2n$). Space group $Pmn2_1$, $P2_1nm$ (No. 31) or $Pmnm$ (No. 59). $\omega/2\theta$ scan, scan width 1·2°. $1 < \theta < 33°$, $-10 < h < 10$, $-13 < k < 13$, $-9 < l < 9$. Four orientation reference reflections $(\bar{1}05, 1\bar{2}2, \bar{2}\bar{1}\bar{1}, \bar{2}00)$

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Table 1. *Final atomic coordinates for* $[(CH_3)_3SO]SCN$ *with e.s.d.'s in parentheses*

$B_{eq} = (4/3)\sum_i\sum_j a_i a_j \beta_{ij}$.

	x	y	z	B_{eq}(Å^2)
S(1)	0·500	0·14704 (7)	0·000	2·811 (6)
O(1)	0·500	−0·0153 (3)	−0·1217 (2)	4·86 (4)
C(11)	0·3080 (2)	0·1214 (3)	0·1196 (2)	3·83 (3)
C(12)	0·500	0·4265 (4)	−0·0640 (3)	4·29 (4)
S(2)	0·500	0·3549 (1)	0·5179 (1)	5·67 (2)
C(2)	0·500	0·250	0·3836 (3)	3·86 (4)
N(2)	0·500	0·3835 (4)	0·2940 (4)	5·61 (6)

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *for* $[(CH_3)_3SO]SCN$

Pyramidal trimethyloxosulfonium			
S(1)—O(1)	1·439 (2)	O(1)—S(1)—C(11)	112·6 (1)
S(1)—C(11)	1·750 (2)	O(1)—S(1)—C(12)	113·6 (1)
S(1)—C(12)	1·756 (3)	C(11)—S(1)—C(12)	105·6 (1)
		C(11)—S(1)—C(12)	105·9 (1)
Linear thiocyanate			
C(2)—N(2)	1·075 (5)	N(2)—C(2)—S(2)	180·1 (1)
C(2)—S(2)	1·613 (3)		

every 200 scans showed no significant variations. Four standard intensity reference reflections $(0\bar{2}7, \bar{1}05, 0\bar{2}1, \bar{2}1\bar{2})$ recorded every 2 h showed fading of 6·8% during 183·6 h; decay corrections. 5313 measured reflections, 4285 with $\sigma(I)/I < 0·3$. Lorentz and polarization corrections. Absorption corrections from ψ scans: relative transmission factor between 0·986 and 0·999. 767 reflections after averaging $R_{int} = 0·010$.

Structure solved by Patterson and Fourier methods in $Pmn2_1$. H atoms located by difference Fourier synthesis. Anisotropic full-matrix least-squares refinement (on F) for non-H atoms, isotropic for H atoms. Extinction coefficient refined: $g = 2·256 \times 10^{-6}$ (Stout & Jensen, 1968). Unit weights. 65 variables. Final refinement with 760 reflections (three rejected as unobserved, five as bad) gave $R = 0·023$, $wR = 0·033$ and $S = 0·897$. Maximum and minimum peak heights in final difference Fourier synthesis = 0·288 and $-0·324$ e Å^{-3}; maximum $\Delta/\sigma = 0·00$. Scattering factors for neutral atoms and f', f'' were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Enraf–Nonius (1977) *SDP* employed for all calculations. Computer: VAX 730.

Final positional and equivalent isotropic thermal parameters are given in Table 1. Table 2 reports the main interatomic distances and bond angles.* The thiocyanate anion is really linear S(2)C(2)N(2) = 180·1 (1)° with bond lengths C(2)—N(2) = 1·075 (5) Å and C(2)—S(2) = 1·613 (3) Å. The $(CH_3)_3SO$ ion is pyramidal and well individualized; if it possesses only one symmetry plane (for $x = 0·5$), as frequently observed in trimethyloxosulfonium salts, it approximates very closely to $3m$ symmetry. The distances S(1)—C(11) = 1·750 (2) Å and S(1)—C(12) = 1·756 (3) Å are equal and the angles C(11)—S(1)—C(11) = 105·6 (1)° and C(11)—S(1)—C(12) = 105·9 (1)° are not significantly different.

The projection along the b axis of the atomic arrangement of $[(CH_3)_3SO]SCN$ is shown in Fig. 1 and the crystal packing is shown in Fig. 2.

Related literature. Very little is known about the structures of trimethyloxosulfonium salts: only the structures of the perchlorate (Coulder, Gantzel & McCullough, 1963) and the fluoroborate (Zimmermann, Barlow & McCullough, 1963) have

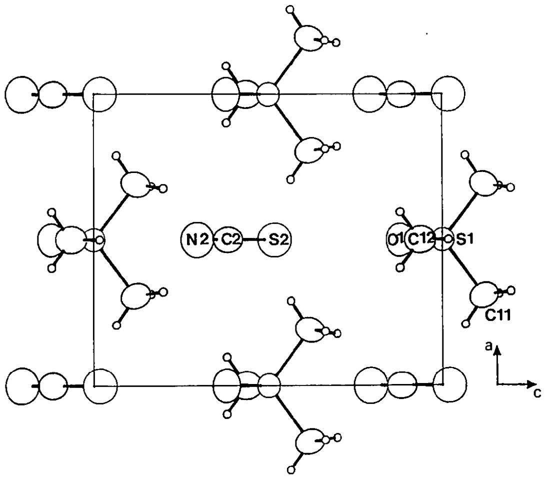

Fig. 1. Projection along b axis of the atomic arrangement of $[(CH_3)_3SO]SCN$.

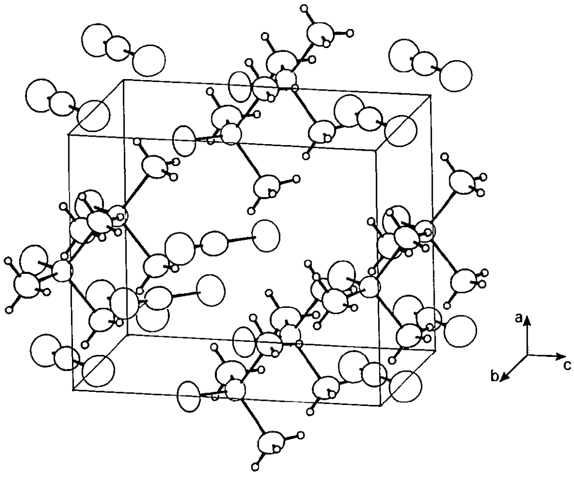

Fig. 2. Atomic packing of the unit cell of $[(CH_3)_3SO]SCN$.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and interatomic contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53825 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

been described at 293 K. In previous papers, we have reported the structures of trimethyloxosulfonium iodide, bromide, chloride, nitrate and chromate (Jannin, Puget, de Brauer & Perret, 1991 *a,b,c*; de Brauer, Jannin, Puget & Perret, 1991).

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Acta Cryst. (1991). C47, 2234–2236

Structures of (2*S*,3*R*)-*exo*-1,7,7-Trimethyl-3-propylsulfonylbicyclo[2.2.1]heptan-2-ol (I) and (2*S*,3*R*)-*exo*-1,3,7,7-Tetramethyl-3-propylsulfonylbicyclo[2.2.1]heptan-2-ol (II)

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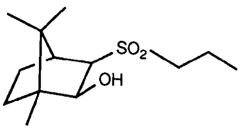
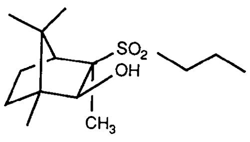
Abstract. (I), $C_{13}H_{24}O_3S$, M_r = 260·4, orthorhombic, $P2_12_12_1$, a = 11·737 (2), b = 21·244 (4), c = 22·932 (3) Å, V = 5717·9 (1·4) Å^3, Z = 16, D_x = 1·21 g cm^{-3}, Cu $K\alpha$, λ = 1·54178 Å, μ = 19·23 cm^{-1}, $F(000)$ = 2272, T = 291 K, R = 0·063 for 3245 observed reflections. (II), $C_{14}H_{26}O_3S$, M_r = 274·4, orthorhombic, $P2_12_12_1$, a = 8·651 (2), b = 11·920 (4), c = 14·256 (3) Å, V = 1470·1 (6) Å^3, Z = 4, D_x = 1·24 g cm^{-3}, Cu $K\alpha$, λ = 1·54178 Å, μ = 18·95 cm^{-1}, $F(000)$ = 600, T = 291K, R = 0·056 for 1491 observed reflections. Regio- and stereocontrolled three-carbon annulation is a valuable tool for the synthesis of natural products. In a previous communication [De Lombaert, Nemery, Roekens, Carretero, Kimmel & Ghosez (1986). *Tetrahedron Lett.* **27**, 5099-5102] we reported a novel two-step sequence yielding highly functionalized, fused cyclopentanes. The title compounds are being used to develop an enantioselective version, and were synthesized efficiently in optically pure, crystalline form from (+)-camphor. X-ray crystallography confirmed the stereochemistries shown for (I) and (II).

Experimental. D_m not measured. Crystal sizes: (I) 0·3 × 0·4 × 0·25 mm; (II) 0·3 × 0·3 × 0·2 mm. Lattice parameters refined using (I) 20, (II) 30 reflections in the range (I) $9 \leq 2\theta \leq 50°$, (II) $12 \leq 2\theta \leq 49°$. Huber four-circle diffractometer, graphite-monochromatized Cu $K\alpha$ radiation. For (I) 5735 independent reflections with $\sin\theta/\lambda \leq 0·69$ Å^{-1}; $0 \leq h \leq 14$, $0 \leq k \leq 25$, $0 \leq l \leq 27$, 3245 with $I \geq 2·5\sigma(I)$. For (II) 1567 independent reflections with $\sin\theta/\lambda \leq 0·69$ Å^{-1}; $0 \leq h \leq 10$, $0 \leq k \leq 14$, $0 \leq l \leq 17$, 1491 with $I \geq 2·5\sigma(I)$. Standard reflections (I): 303; (II): $02\bar{7}$ checked every 50 reflections, no significant deviation.



(I)



(II)

Structure solved by direct methods using *SHELXS*86 (Sheldrick, 1985). All H atoms in computed positions, except those of the hydroxyl groups [for (I) from difference Fourier synthesis, not found for (II)]. Anisotropic least-squares refinement (*SHELX*76; Sheldrick, 1976) using F; H atoms isotropic with common refined temperature factor [U = 0·0940 (I), 0·0926 (II) Å^2]. $w = 1/(\sigma^2 + gF^2)$; g =

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