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Structures of Trimethyloxosulfonium Salts. I. The Iodide and the Bromide

BY MICHEL JANNIN, RENÉ PUGET, CHRISTINE DE BRAUER AND RENÉ PERRET

Laboratoire de Physique du Solide, associé au CNRS (URA 785), Université de Bourgogne, BP 138, 21004 Dijon CEDEX, France

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Abstract. $[(CH_3)_3SO]I$, $M_r = 220{\cdot}07$, orthorhombic, *Pnma*, $a = 11{\cdot}289$ (3), $b = 7{\cdot}701$ (2), $c = 8{\cdot}298(2)$ Å, $V = 721{\cdot}5$ (5) Å^3, $Z = 4$, $D_x = 2{\cdot}026$, $D_m = 2{\cdot}0$ (1) Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ(Mo $K\alpha$) = 4·56 mm^{-1}, $F(000) = 416$, $T = 293$ K, final $R = 0{\cdot}018$, $wR = 0{\cdot}023$ for 528 independent observed reflections. $[(CH_3)_3SO]Br$, $M_r = 173{\cdot}08$, orthorhombic, *Pnma*, $a = 10{\cdot}978$ (2), $b = 7{\cdot}462$ (2), $c = 8{\cdot}062$ (2) Å, $V = 660{\cdot}5$ (5) Å^3, $Z = 4$, $D_x = 1{\cdot}740$, $D_m = 1{\cdot}71$ (5) Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073, μ(Mo $K\alpha$) = 6·35 mm^{-1}, $F(000) = 344$, $T = 293$ K, final $R = 0{\cdot}018$, $wR = 0{\cdot}019$ for 758 independent observed reflections. These two compounds have the same structure; a stacking of anions (I^- or Br^-) and pyramidal thiocations $(CH_3)_3SO^+$, which approximate closely to symmetry $3m$; the thiocation has only one symmetry plane (for $y = 0{\cdot}25$ or 0·75) where the halogen atoms are also located.

Introduction. Very little is know about the structures of the trimethyloxosulfonium salts: only the structures of the perchlorate (Coulder, Gantzel & McCullough, 1963) and the fluoborate (Zimmerman, Barlow & McCullough, 1963) have been described at 293 K. Many other salts exist and may be easily prepared. In this first paper, we describe the structures of the iodide and the bromide.

Experimental. *The iodide*. Crystal obtained by recrystallization of the commercial product (Aldrich) in water, prismatic colorless crystals, density measured by pycnometry in xylene, $D_m = 2{\cdot}0$ (1) Mg m^{-3}. Crystal size 0·18 × 0·20 × 0·21 mm. Enraf–Nonius CAD-4 diffractometer, graphite monochromator. Unit-cell constants from least-squares refinement of 25 reflections with $5 < \theta < 13°$. Systematic absences $0kl$ ($k + l = 2n$) and $hk0$ ($h = 2n$). Space group *Pnma* (No. 62) or $Pn2_1a$ (No. 33). $\omega/2\theta$ scan, scan width 1·2°. $1 < \theta < 30°$. $-4 < h < 15$, $-6 < k < 11$, $-6 < l < 12$. Four orientation reference reflections (331, 400, 411, 442) every 200 scans, no significant variations. Four intensity reference reflections (331, 400, 601, 250) recorded every 2 h varied by −2·2% during 50·0 h; decay correction. 2045 measured reflections, 1648 with $I > 3\sigma(I)$. Lorentz and polarization corrections. Absorption corrections from ψ scans: relative transmission factor between 0·820 and 0·998. 528 reflections after averaging: $R_{int} = 0{\cdot}017$. Crystal structure solved by direct methods with *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977), in *Pnma*. 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: $g = 1{\cdot}5085 \times 10^{-6}$ (Stout & Jensen, 1968). Unit weights. 54 variables. Final refinement with 528 reflections gave $R = 0{\cdot}018$, $wR = 0{\cdot}023$ and $S = 1{\cdot}109$. Maximum and minimum peak heights in final difference Fourier synthesis: 0·323 and −0·577 e Å^{-3}; $\Delta/\sigma_{max} = 0$.

The bromide. The crystals were obtained by using the preparative method described elsewhere (de Brauer & Perret, to be published), prismatic colorless crystals, density measured by pycnometry in xylene, $D_m = 1{\cdot}71$ (5) Mg m^{-3}. Crystal size 0·20 × 0·20 × 0·21 mm. Enraf–Nonius CAD-4 diffractometer used. Unit-cell constants from least-squares refinement of 25 reflections with $5 < \theta < 14°$. Systematic absences $0kl$ ($k + l = 2n$) and $hk0$ ($h = 2n$). Space group *Pnma* (No. 62) or $Pn2_1a$ (No. 33). $\omega/2\theta$ scan, scan width

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Table 1. *Final atomic coordinates for* (CH$_3$)$_3$SOI *with e.s.d.'s in parentheses*

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

	x	y	z	B_{eq}(Å^2)
I	0·00372 (1)	0·250	0·20317 (5)	3·18 (1)
S	0·19664 (4)	0·250	0·6626 (1)	2·25 (2)
O	0·2656 (2)	0·250	0·8081 (3)	3·30 (5)
C(1)	0·0443 (2)	0·250	0·7008 (4)	2·92 (7)
C(2)	0·2236 (2)	0·0679 (2)	0·5427 (3)	3·29 (5)

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *for* (CH$_3$)$_3$SOI

Trimethyloxosulfonium ion

S—O	1·436 (3)	O—S—C(1)	112·4 (1)
S—C(1)	1·749 (3)	O—S—C(2)	112·6 (1)
S—C(2)	1·747 (3)	C(1)—S—C(2)	105·9 (1)
		C(2)—S—C(2)	106·8 (2)

Iodide coordination

I—S	4·608 (1)	4·603 (1)	4·391 (1)	
I—O	4·908 (1)	4·866 (3)	4·729 (3)	4·414 (2)
I—C(1)	4·194 (3)	4·155 (3)	3·969 (1)	
I—C(2)	4·152 (2)	4·126 (2)	4·016 (2)	4·008 (2)

Table 3. *Final atomic coordinates for* (CH$_3$)$_3$SOBr *with e.s.d.'s in parentheses*

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

	x	y	z	B_{eq}(Å^2)
Br	−0·00372 (3)	0·250	0·21254 (4)	3·974 (6)
S	0·19484 (6)	0·250	0·65219 (8)	2·24 (1)
O	0·2667 (2)	0·250	0·8006 (3)	3·34 (4)
C(1)	0·0398 (3)	0·250	0·6919 (4)	3·63 (6)
C(2)	0·2225 (2)	0·0630 (3)	0·5282 (3)	3·61 (4)

Table 4. *Main interatomic distances* (Å) *and bond angles* (°) *for* (CH$_3$)$_3$SOBr

Trimethyloxosulfonium ion

S—O	1·433 (2)	O—S—C(1)	112·7 (1)
S—C(1)	1·732 (4)	O—S—C(2)	112·5 (1)
S—C(2)	1·743 (2)	C(1)—S—C(2)	106·1 (2)
		C(2)—S—C(2)	106.3 (2)

Bromide coordination

Br—S	4·427 (1)	4·417 (1)	4·161 (3)	
Br—O	4·719 (1)	4·665 (3)	4·604 (1)	4·455 (7)
Br—C(1)	4·224 (4)	3·895 (4)	3·830 (1)	
Br—C(2)	4·148 (2)	3·950 (2)	3·840 (2)	3·819 (2)

1·2°. $1 < \theta < 30°$, $-5 < h < 15$, $-10 < k < 10$, $-11 < l < 11$. Four orientation reference reflections ($\bar{4}\bar{1}\bar{1}$, 011, 20$\bar{1}$, $\bar{3}$34) every 200 scans: no significant variations. Intensity reference reflections (011, 631, 2$\bar{2}$1, $\bar{3}$34) recorded every 2 h faded by −11·4% during 111·2 h; decay correction. 5832 measured reflections, 3496 reflections with $I > 3\sigma(I)$. Lorentz and polarization corrections. Absorption corrections from ψ scans: relative transmission factor between 0·779 and 0·999. 758 reflections after averaging: $R_{int} = 0·022$. Heavy-atom coordinates from assumed isostructural iodide used as initial model in *Pnma*. H atoms located by difference Fourier synthesis. Anisotropic full-matrix least-squares refinements (on F) for non-H atoms; isotropic for H atoms. Extinction coefficient refined $g = 8·412 \times 10^{-8}$ (Stout & Jensen, 1968). Unit weights. 54 variables. Final refinement with 758 reflections gave $R = 0·018$, $wR = 0·019$ and $S = 0·531$. Maximum and minimum peak heights in final Fourier synthesis 0·536 and −0·320 e Å^{-3}. $\Delta/\sigma_{max} = 0$.

Scattering factors for neutral atoms and f', f'' were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Enraf–Nonius (1977) *SDP* used for all calculations. Computer used: VAX 730.

Discussion. The final atomic coordinates are reported in Table 1 for the iodide and Table 3 for the bromide. The main interatomic distances and bond angles are listed in Table 2 for the iodide and Table 4 for the bromide.* The structure consists of a stacking of halogenide anions and trimethyloxosulfonium cations, each ion being surrounded by four of the opposite charge. The cell packing is shown in Figs. 1

* 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 53828 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

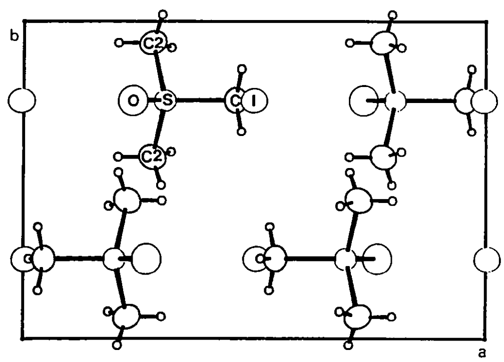

Fig. 1. Projection along the c axis of the atomic arrangement of (CH$_3$)$_3$SOI.

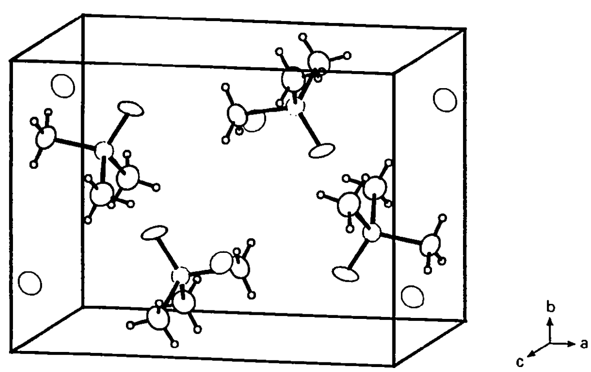

Fig. 2. Atomic packing in the unit cell of (CH$_3$)$_3$SOI.

and 2. The well individualized thiocation is pyramidal, suggesting an sp^3 hybridation state for the S atom; it possesses only one symmetry plane (for $y = 0{\cdot}25$ or $0{\cdot}75$), in which the S, O and C(1) atoms are located; but it approximates very much to the $3m$ symmetry assigned to the free ion. The bond distances S—C(1) and S—C(2) are equal and the bond angles C(1)—S—C(2) and C(2)—S—C(2) are slightly different.

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Non-Natural 14-Hydroxy Steroids. II. 13α,14α and 13β,14β Isomers of Methyl 14-Hydroxy-1,7,17-trioxo-5β-androst-8-ene-19-oate

BY MARC DROUIN

Laboratoire de chimie structurale, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1

RÉJEAN RUEL

Laboratoire de synthèse organique, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1

AND ANDRÉ G. MICHEL*

Laboratoire de chimie structurale, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1

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Abstract. $C_{20}H_{24}O_6$, $M_r = 360{\cdot}41$, $\lambda(\text{Cu } K\alpha) = 1{\cdot}54056$ Å, room temperature. (I) (5β,10β,13α,14α)-Methyl 14-hydroxy-1,7,17-trioxoandrost-8-ene-19-oate, triclinic, $P\bar{1}$, $a = 7{\cdot}9514\,(5)$, $b = 9{\cdot}2892\,(5)$, $c = 12{\cdot}8534\,(12)$ Å, $\alpha = 81{\cdot}256\,(6)$, $\beta = 75{\cdot}796\,(6)$, $\gamma = 77{\cdot}908\,(5)°$, $V = 894{\cdot}85\,(11)$ Å^3, $Z = 2$, $D_x = 1{\cdot}338$ Mg m^{-3}, $\mu = 0{\cdot}77$ mm^{-1}, $F(000) = 383{\cdot}96$, final $R = 0{\cdot}043$ for 2912 observed reflections. (II) (5β,10β,13β,14β)-Methyl 14-hydroxy-1,7,17-trioxoandrost-8-ene-19-oate, monoclinic, $P2_1/n$, $a = 12{\cdot}8704\,(9)$, $b = 10{\cdot}4481\,(9)$, $c = 13{\cdot}1482\,(5)$ Å, $\beta = 104{\cdot}103\,(5)°$, $V = 1714{\cdot}77\,(20)$ Å^3, $Z = 4$, $D_x = 1{\cdot}396$ Mg m^{-3}, $\mu = 0{\cdot}81$ mm^{-1}, $F(000) = 767{\cdot}92$, final $R = 0{\cdot}055$ for 2516 observed reflections. These two non-natural steroids bear a methoxycarbonyl group at C(10). In both molecules the relative stereochemistry is *cis* for the *A*/*B* ring junction and *cis* for the *C*/*D* ring junction. The relative orientations of MeO_2C—C(10) and HO—C(14) are *anti* for (I) and *syn* for (II). The methoxycarbonyl group lies at the axial position for (I) and equatorial for (II), relative to ring *A*. The energies of possible conformations for (I) and (II) are evaluated, wherein the *A* rings adopt a chair conformation.

Introduction. Cardioactive steroids used in the treatment of heart disease have the ability to slow the heart rate and, at the same time, increase the contractility of the muscle. However, the natural steroids used exhibit a dangerously high toxicity, while most patients receive 60% of the toxic dose in order to obtain the desired therapeutic response (Weisner & Tsai, 1986). The synthesis of new cardioactive steroids having a wider margin of safety has thus become a major goal shared by many research groups. Furthermore, the synthesis of such non-natural 14-hydroxy steroids, and subsequent analyses of their activity will hopefully allow a better understanding of the structure–activity relationships.

As part of a study aimed at the synthesis of various natural and non-natural 14-hydroxy steroids, (I) and (II) (Fig. 1) were obtained upon alkaline treatment (Cs_2CO_3, CH_3CN, reflux) of tetraketone (III) as a 3:2 mixture (Ruel & Deslongchamps, 1990).

* To whom correspondence should be addressed.

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