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9-Methylthioxanthenium-10-bis(methoxycarbonyl)methylide 10-Oxide, C₁₉H₁₈O₅S

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Abstract. $M_r = 358 \cdot 42$, $P\bar{1}$, $a = 15 \cdot 159$ (3), $b = 8 \cdot 672$ (2), $c = 7 \cdot 178$ (1) Å, $\alpha = 93 \cdot 80$ (2), $\beta = 101 \cdot 12$ (2), $\gamma = 104 \cdot 91$ (2)°, $V = 888 \cdot 0$ (3) Å³, $Z = 2$, $D_x = 1 \cdot 340 \text{ g cm}^{-3}$, Cu $K\alpha$, $\lambda = 1 \cdot 54178$ Å, $\mu = 18 \cdot 08 \text{ cm}^{-1}$, $F(000) = 376$, room temperature, $R = 0 \cdot 051$ for 2016 unique reflections. The $^+$S–C$^-$ distance of 1·689 (3) Å in the title oxysulfonium ylide is shorter than the average $^+$S–C$^-$ distance of 1·718 (8) Å observed for a series of sulfonium ylides. The two $^+$S–C(sp^2) distances are 1·760 (4) and 1·768 (4) Å while the $^+$S–O distance is 1·445 (3) Å. The central ring in the tricyclic system is in a boat conformation with the methyl and carbanion moieties occupying axial sites. The C(17) carbanion carbon atom is 0·11 (1) Å out of the plane of the attached atoms and toward the C(15) methyl group. An intramolecular interaction between the π cloud of the carbanion and the methyl hydrogen, C(17)···H(15b) = 2·56 Å, may lead to a slight pyramidalization of C(17).

Introduction. Although the chemistry of organosulfur compounds has been of interest for many years, there still remains some controversy concerning the nature of the sulfur bonding (Bernardi, Csizmadia, Mangini, Schlegel, Whangbo & Wolfe, 1975; Minyav, Minkin, Sadikov & Naddaka, 1977; Tatsumi, Yoshioka, Yamaguchi & Fueno, 1976). Ylides derived from organosulfur compounds have added to the controversy (Block, 1981; Trost & Melvin, 1975; Borden, Davidson, Anderson, Denniston & Epiotis, 1978). In most

hypervalent compounds *d* orbitals need not be invoked to rationalize molecular geometry and bonding; however, many theoretical calculations include some *d*-orbital participation in order to correlate more accurately specific physical properties. When the sulfur atom possess a formal positive charge, the 3*d* orbitals are contracted and should provide a better opportunity for overlap with the *s* and *p* orbitals of second- and third-row elements. Sulfonium ylides and oxysulfonium ylides can be viewed as carbanions stabilized by an adjacent positively charged sulfur atom. These systems should provide the best opportunity for observing any effects of *d*-orbital participation. Recent structural studies of sulfonium ylides (Abbady, Craig, Ternay, Martin, Galloy & Watson, 1981; Abbady, Askari, Morgan, Ternay, Galloy & Watson, 1982; Galloy, Watson, Craig, Guidry, Ternay & Martin, 1983) did not require the inclusion of *d* orbitals although such interactions were not symmetry forbidden. We now present a structural investigation of an oxysulfonium ylide.
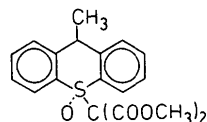
Experimental. Crystal 0·12 × 0·17 × 0·51 mm, Syntex $P2_1$ diffractometer, data collected using θ:2θ scan, $2\theta_{max} = 115 \cdot 0°$, graphite-monochromated radiation, lattice parameters from least-squares refinement of 15 medium-angle reflections, angles measured by centering

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Table 1. *Atomic positional parameters* $(\times 10^4)$ *and* U_{eq} *values* $(\text{Å}^2 \times 10^3)$

$U_{eq} = \frac{1}{3}[U_{11}(a^*a)^2 + U_{22}(b^*b)^2 + U_{33}(c^*c)^2 + 2(U_{12}a^*b^*ab\cos\gamma + U_{13}a^*c^*ac\cos\beta + U_{23}b^*c^*bc\cos\alpha)].$

	x	y	z	U_{eq}
C(1)	2584 (3)	12063 (4)	5379 (5)	51 (2)
C(2)	2670 (3)	13608 (5)	4841 (6)	59 (2)
C(3)	2861 (3)	13946 (4)	3061 (6)	58 (2)
C(4)	2963 (3)	12741 (4)	1838 (5)	49 (2)
C(5)	4395 (3)	8230 (5)	1996 (6)	60 (2)
C(6)	4899 (3)	7505 (5)	3285 (8)	75 (2)
C(7)	4678 (3)	7315 (5)	5038 (8)	77 (2)
C(8)	3953 (3)	7843 (4)	5553 (5)	61 (2)
C(9)	2681 (3)	9232 (4)	4859 (5)	48 (2)
S(10)	3074 (1)	9736 (1)	835 (1)	42 (0)
C(11)	2693 (2)	10838 (4)	4167 (5)	42 (1)
C(12)	2869 (2)	11208 (4)	2393 (5)	41 (1)
C(13)	3661 (2)	8722 (4)	2482 (5)	44 (1)
C(14)	3427 (2)	8570 (4)	4264 (5)	46 (2)
C(15)	1700 (3)	8012 (5)	4334 (5)	58 (2)
O(16)	3682 (2)	10502 (3)	−357 (3)	56 (1)
C(17)	2026 (2)	8456 (4)	−228 (5)	39 (1)
C(18)	1326 (2)	9235 (4)	−1008 (5)	42 (2)
O(19)	1491 (2)	10649 (3)	−1170 (4)	55 (1)
O(20)	467 (2)	8226 (3)	−1583 (4)	62 (1)
C(21)	1992 (2)	6765 (4)	−612 (5)	44 (1)
O(22)	2655 (2)	6284 (3)	−769 (4)	63 (1)
O(23)	1136 (2)	5804 (3)	−770 (5)	68 (1)
C(24)	−249 (3)	8906 (6)	−2568 (7)	76 (2)
C(25)	995 (4)	4110 (5)	−1350 (8)	86 (3)

routine associated with the diffractometer, no systematic absences observed, no change in intensity of monitored reflection greater than $3.8\sigma(I)$; 2416 independent reflections measured $(0 \leq h \leq 5, -9 \leq k \leq 9, -7 \leq l \leq 7)$ with 396 having intensities less than $3\sigma(I)$, Lorentz and polarization corrections applied, no absorption correction; direct methods (*MULTAN*78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) revealed all nonhydrogen atoms; hydrogen-atom positions obtained from difference Fourier synthesis but fixed at idealized positions (C—H = 1.08 Å); full-matrix least-squares refinement, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/\sigma^2(F_o)$, 244 parameters refined using 2016 reflections, 4 reflections omitted because of significant secondary extinction; final $R = 0.051$, $R_w = 0.067$, $S = 3.1$, $(\Delta/\sigma)_{av} = 0.08$, $(\Delta/\sigma)_{max} = 0.71$, highest peak in final difference map 0.72 e Å^{-3} (located at inversion center); all calculations performed with *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976); atomic scattering factors for C, S and O those of Cromer & Mann (1968), those of H from Stewart, Davidson & Simpson (1965); scattering factors were corrected for anomalous dispersion (*International Tables for X-ray Crystallography*, 1974).*

* Lists of structure factors, interatomic distances, valence angles, hydrogen-atom coordinates, thermal parameters and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39135 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. Table 1 gives a listing of atomic positional parameters. Fig. 1 is an *ORTEP* drawing (Johnson, 1971) of the title compound.

The two phenyl rings of the tricyclic system are planar and form a dihedral angle of $130.3 (5)°$. The fold angle for a series of sulfonium ylides runs from $155.3 (6)$ to $177.3 (6)°$ (Galloy, Watson, Craig, Guidry, Ternay & Martin, 1983), that for thioxanthenium-10-bis(methoxycarbonyl)methylide 10-oxide (TBO) (Book & Chu, 1984) is $125.3°$ and that for thioxanthenium 10,10-dioxide (Chu & Chung, 1974) is $133.9°$. The central ring of the tricyclic system is in a boat conformation with C(15) and the carbanion moiety occupying axial sites. There is a pseudo plane of symmetry passing through C(9), C(15), S(10) and C(17). The angle between S(10)O(16)C(17) and the planar carbanion moiety is $83.5 (6)°$ while the two planes are coplanar in the sulfonium ylide series. In the sulfonium series the orientation of the carbanion moiety is determined by lone pair–π-electron repulsion, and there is a close approach between two oxygen atoms in the carbanion moiety and the sulfur atom. The orientation in the title compound is determined by steric repulsion between O(16) and two carbanion oxygen atoms which is minimized by the approximate 90° rotation. There is an attractive interaction between the methyl proton H(15b) and the carbanion carbon C(17), $\text{H}(15b)\cdots\text{C}(17) = 2.56$ Å. The C(17) carbon is pyramidalized and lies $0.11 (1)$ Å out of the S(10), C(18), C(21) plane and toward the methyl hydrogen. If the interaction were repulsive the carbon could adopt the normal planar conformation or pyramidalize in the opposite direction.
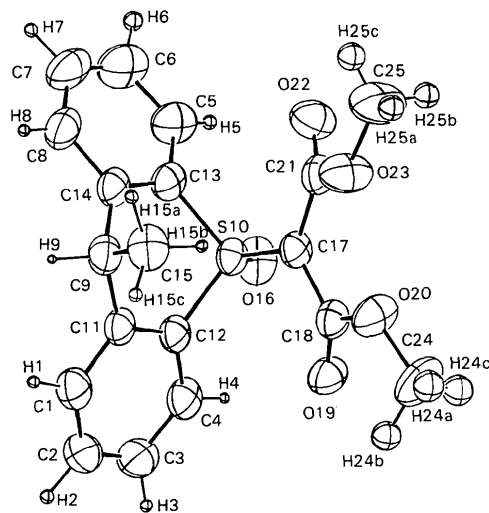

Fig. 1. *ORTEP* (Johnson, 1971) drawing of 9-methylthioxanthenium-10-bis(methoxycarbonyl)methylide 10-oxide. Thermal ellipsoids are drawn at the 50% probability level.

The $^+S-C^-$ distance of 1·689 (3) Å is statistically shorter than that observed in the sulfonium ylides series [1·715 (4) to 1·743 (4) Å], but it is equivalent to the 1·688 (3) Å value found in TBO. The two $^+S-C(sp^2)$ distances of 1·760 (4) and 1·768 (4) Å are equivalent to those reported in the sulfonium ylide series and to those in TBO. The ^+S-O distance of 1·445 (3) Å is statistically shorter than the 1·458 (3) Å value found in TBO but is equivalent to the mean value of 1·440 (2) Å found in thioxanthene 10,10 dioxide (Chu & Chung, 1974) and 9-isobutylthioxanthene 10,10-dioxide (Chu & Chung, 1973). The C—C distances around the phenyl rings average 1·389 (6) Å [1·373 (8) to 1·400 (6) Å] while the distances and angles associated with the carbanion moiety are internally consistent and equivalent to those in reference compounds cited above.

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N^1-Phenylsulphanilamide, $C_{12}H_{12}N_2O_2S$*

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Abstract. $M_r = 248\cdot3$, orthorhombic, *Pcab* [non-standard setting of *Pbca*, equivalent positions $\pm(x,y,z)$; $\frac{1}{2}-x,y, \frac{1}{2}+z$; $\frac{1}{2}+x, \frac{1}{2}-y,z$; $x, \frac{1}{2}+y, \frac{1}{2}-z)$], $a = 24\cdot230$ (8), $b = 15\cdot500$ (5), $c = 6\cdot034$ (2) Å, $V = 2266\cdot16$ Å³, $Z = 8$, $D_m = 1\cdot460$ (5), $D_x = 1\cdot455$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 0\cdot137$ mm⁻¹, $F(000) = 1040$, room temperature, $R = 0\cdot035$ for 814 reflexions $[I > 3\sigma(I)]$. The molecules are linked along **b** by a system of three hydrogen bonds N—H···O per molecule through the unsubstituted amino group. Apart from an appreciable quinonoid character in the aniline ring caused by proton transfer on nitrogen, bond lengths and inter-bond angles have standard values.

Introduction. This work was undertaken as part of a programme relating the crystal structures of various sulpha compounds (Cook & Turner, 1975, 1976) to their therapeutic activity in the treatment of infections in burns. The material was supplied by Messrs Smith & Nephew Limited, Harlow.

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* Sulphanilanilide.