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2-Chloro-9-oxothioxanthenium-10-bis(methoxycarbonyl)methylide, $C_{18}H_{13}ClO_5S$

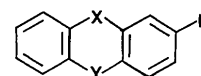
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Abstract. $M_r = 376.79$, triclinic, $P\bar{1}$, $a = 5.562$ (2), $b = 12.176$ (2), $c = 12.763$ (2) Å, $\alpha = 99.01$ (2), $\beta = 99.80$ (2), $\gamma = 78.35$ (2)°, $V = 827.8$ (3) Å³, $Z = 2$, $D_x = 1.511$, $D_m = 1.52$ Mg m⁻³ (by flotation), graphite-monochromatized Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.328$ mm⁻¹, $F(000) = 388$, $T = 298$ K, $R = 0.043$ and $wR = 0.042$ for 1720 observed reflections. The thioxanthone ring is nearly planar with a folding angle of 173.7 (2)°. The bis(methoxycarbonyl)methylide group is in a pseudoequatorial conformation with respect to the central ring of the thioxanthone ring system. Both of the ester groups have the *endo* conformation with one carbonyl O *anti* and the other *syn* to the nonbonding electron pair on S.

Introduction. The determination of the crystal structure of the title compound (I) is one of a series of thioxanthenium and 9-oxothioxanthenium ylides under study in this laboratory. It has been deduced from the NMR studies in solution that the sulfonium ylides derived from thioxanthene and thioxanthone have the same conformation as those of the corresponding sulfoxides (Tamura, Mukai & Ikeda, 1979; Ternay, Craig & O'Neal, 1980). The purpose of the present study is to determine the conformation of the sulfonium ylide in the solid state and to compare the conformation of the sulfonium ylide with that of the corresponding sulfoxides. Single crystals of the title compound were obtained through the courtesy of Dr A. L. Ternay Jr of the Department of Chemistry, University of Texas at Arlington.



X	Y	R
(I) C=O	S ⁺ C ⁻ (CO ₂ CH ₃) ₂	Cl
(II) C=O	S(O)	H
(III) C=O	S	Cl
(IV) C=O	S ⁺ C ⁻ (CO ₂ CH ₃) ₂	H
(V) S	S ⁺ C ⁻ (CO ₂ C ₂ H ₅) ₂	H

Experimental. Single crystals are in the form of transparent colorless elongated prisms; unit-cell parameters by least-squares analysis of 15 reflections with 2θ values from 20 to 30° measured on the diffractometer; two molecules in a unit cell; $P\bar{1}$ confirmed from the structure analysis; Syntex $P2_1$ automatic diffractometer; crystal $0.39 \times 0.15 \times 0.06$ mm; $\theta/2\theta$ scanning mode; 2968 independent reflections; $2\theta < 50^\circ$; range of hkl : $0 \rightarrow 6$, $-13 \rightarrow 14$, $-15 \rightarrow 15$; 1720 observed, $I > 3\sigma(I)$; three standard reflections measured after every 50 reflections showed no significant variation in intensities; Lorentz-polarization corrections; no absorption or extinction corrections; structure solved by direct methods (*MULTAN78*; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); refinement by full-matrix least squares using *SHELX76* (Sheldrick, 1976), anisotropic; H positions located in a difference Fourier synthesis, isotropic temperature factors for H atoms; 277 variables; $w = k/[\sigma(F)]^2$, with $\sigma(F)$ from counting statistics, $k = 1.508$ from least squares; $\sum w(|F_o| -$

$|F_c|$)² minimized; $R = 0.043$, $wR = 0.042$, $(\Delta/\sigma)_{\max} = 0.034$, max. and min. heights in final ΔF map 0.29 and -0.25 e Å⁻³; atomic scattering factors for Cl, S, O, C and H from *International Tables for X-ray Crystallography* (1974); structural data calculated using structural interpretation programs (Shiono, 1984).

Table 1. Fractional atomic coordinates ($\times 10^4$, for H $\times 10^3$) and isotropic thermal parameters ($\times 10^4$, for H $\times 10^3$)

The estimated standard deviations are given in parentheses. For non-hydrogen atoms $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	x	y	z	$U_{eq}/U(\text{Å}^2)$
S	-5684 (2)	-1856 (1)	2271 (1)	463 (2)*
Cl	1427 (2)	1634 (1)	3020 (1)	792 (4)
O(1)	-2389 (7)	-898 (3)	-292 (2)	1065 (12)
O(2)	-1185 (5)	-3575 (2)	2118 (2)	568 (7)
O(3)	-1504 (5)	-4451 (2)	3496 (2)	566 (7)
O(4)	-7455 (6)	-1918 (2)	4175 (2)	692 (8)
O(5)	-5220 (5)	-3559 (2)	4606 (2)	554 (7)
C(1)	-1082 (8)	135 (3)	1753 (3)	558 (11)
C(2)	-497 (8)	637 (3)	2773 (3)	507 (10)
C(3)	-1401 (9)	370 (3)	3623 (3)	563 (12)
C(4)	-2909 (9)	-416 (3)	3438 (3)	558 (12)
C(5)	-7109 (8)	-3360 (4)	632 (3)	642 (12)
C(6)	-7297 (9)	-3897 (4)	-412 (4)	780 (15)
C(7)	-6134 (9)	-3563 (4)	-1158 (3)	740 (14)
C(8)	-4831 (9)	-2702 (4)	-868 (3)	669 (13)
C(9)	-3154 (8)	-1209 (4)	434 (3)	621 (11)
C(11)	-2603 (7)	-672 (3)	1545 (3)	460 (9)
C(12)	-3516 (7)	-937 (3)	2410 (3)	445 (9)
C(13)	-5725 (7)	-2514 (3)	923 (3)	476 (10)
C(14)	-4591 (7)	-2149 (3)	180 (3)	509 (10)
C(15)	-4504 (7)	-2885 (3)	3092 (3)	418 (9)
C(16)	-2281 (7)	-3642 (3)	2847 (3)	423 (9)
C(17)	752 (8)	-5206 (3)	3314 (4)	619 (12)
C(18)	-5870 (7)	-2726 (3)	3981 (3)	436 (9)
C(19)	-6607 (8)	-3428 (3)	5488 (3)	623 (11)
H(1)	-42 (6)	32 (3)	124 (3)	58 (10)
H(3)	-91 (6)	73 (3)	432 (3)	59 (10)
H(4)	-352 (6)	-66 (3)	406 (3)	69 (11)
H(5)	-787 (6)	-361 (3)	124 (3)	69 (11)
H(6)	-832 (8)	-445 (4)	-65 (4)	119 (16)
H(7)	-625 (6)	-400 (3)	-192 (2)	57 (10)
H(8)	-399 (6)	-245 (3)	-137 (3)	64 (10)
H(17)1	132 (8)	-555 (3)	401 (3)	100 (14)
H(17)2	70 (8)	-569 (4)	276 (4)	102 (14)
H(17)3	197 (7)	-476 (3)	328 (3)	84 (12)
H(19)1	-620 (6)	-288 (3)	599 (2)	49 (9)
H(19)2	-854 (7)	-331 (3)	518 (3)	75 (12)
H(19)3	-603 (8)	-417 (3)	574 (3)	96 (13)

* The standard deviations of U_{eq} 's were calculated in accordance with the expressions derived by Schomaker & Marsh (1983).

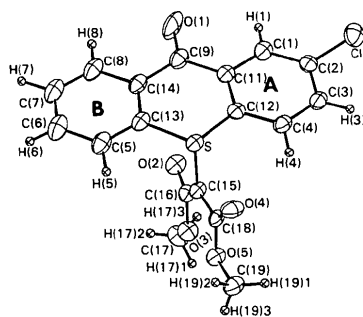


Fig. 1. ORTEP drawing of a molecule of (I).

Discussion. The final parameters are given in Table 1.* The identification of the atoms and the configuration of the molecule are shown in the ORTEP (Johnson, 1965) drawing in Fig. 1. The bond lengths and bond angles, with their standard deviations, are shown in Fig. 2. The bond lengths and bond angles of the thioxanthone ring system have values similar to those in thioxanthone 10-oxide (II) (Chu, 1976a) and 9-oxothioxanthene-10-bis(methoxycarbonyl)methylide (IV) (Abbadly, Craig, Ternay, Martin, Galloy & Watson, 1981). However, the mean value of the two C—S bond lengths within the central ring in the title compound [1.777 (4) Å] is significantly longer than that of 1.733 (3) Å in chlorothioxanthone (III) (Chu, 1976b). The short C—S bond length in (III) is due to the presence of electronic delocalization in the central ring. The thioxanthone ring system is slightly folded with the central ring in a flat boat conformation. The flatness of the boat can be shown by the small deviations of C(9) (-0.06 Å) and S (-0.18 Å) from the least-squares plane defined by C(11), C(12), C(13), and C(14) and can also be shown by the small magnitudes of the torsion angles and Cremer & Pople (1975) puckering parameters around the central ring. The torsion angles around the central ring are shown in Table 2 and the puckering parameters are $q_2 = 0.137$, $q_3 = -0.045$, $Q = 0.144$ Å, $q_2 = Q$, $q_3 = 0$, $\phi_2 = 360^\circ$, and $\theta = 90^\circ$. The equations of the least-squares planes of the two benzo rings have been deposited. The deviations of atoms from the planes range from 0.001 (5) to

* Lists of structure factors, anisotropic thermal parameters and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42095 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

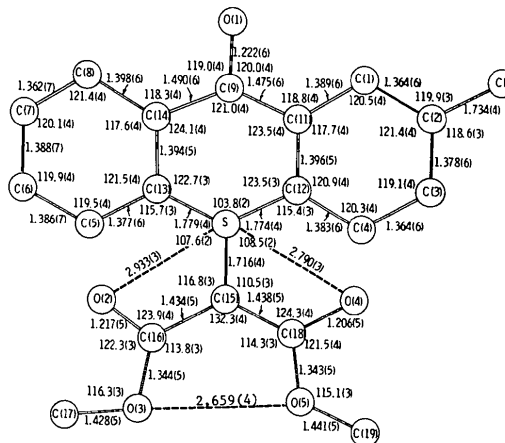


Fig. 2. The bond lengths (Å) and bond angles ($^\circ$) of (I) with e.s.d.'s in parentheses.

Table 2. *Torsion angles*

The central ring	
C(9)–C(11)–C(12)–S	–6.0 (6)°
C(11)–C(12)–S–C(13)	12.4 (4)
C(12)–S–C(13)–C(14)	–10.5 (4)
S–C(13)–C(14)–C(9)	2.4 (6)
C(13)–C(14)–C(9)–C(11)	6.8 (6)
C(14)–C(9)–C(11)–C(12)	–4.8 (6)
The ylide group	
C(12)–S–C(15)–C(16)	–64.4 (3)°
C(12)–S–C(15)–C(18)	109.4 (3)
C(13)–S–C(15)–C(16)	47.3 (3)
C(13)–S–C(15)–C(18)	–138.9 (3)
S–C(15)–C(16)–O(2)	1.8 (5)
S–C(15)–C(16)–O(3)	–177.8 (3)
S–C(15)–C(18)–O(4)	–6.9 (5)
S–C(15)–C(18)–O(5)	173.8 (3)
C(15)–C(16)–O(3)–C(17)	–177.9 (3)
C(15)–C(18)–O(5)–C(19)	–178.7 (3)
O(2)–C(16)–O(3)–C(17)	2.6 (5)
O(4)–C(18)–O(5)–C(19)	2.0 (5)

0.014 (6) Å and the deviation of the Cl atom from the plane is 0.010 (6) Å. The folding angle between the least-squares planes of the two benzo rings is 173.7 (2)°, which is similar to that of 169° in 9-oxothioxanthenium-10-bis(methoxycarbonyl)methylide (IV) (Abbady *et al.*, 1981). However, the folding angle in the 9-oxothioxanthenium ylides is considerably larger than that of 155.7° in the corresponding thioxanthenone 10-oxide (II) and this is due apparently to the nonbonded interaction between the S-ylide group and the thioxanthenone ring system. As in (IV), the methylide C in (I) is also in a pseudo-equatorial conformation. This has further demonstrated that the sulfonium ylides derived from thioxanthenone and thioxanthenone ring systems have the same conformation as those of the corresponding sulfoxides.

The bis(methoxycarbonyl)methylide group is close to a planar configuration. As in thianthrenium-5-bis(methoxycarbonyl)methylide (V) (Ternay, Baack, Chu, Napoleone, Martin & Alfaro, 1982) and 9-oxothioxanthenium-10-bis(methoxycarbonyl)methylide (IV) (Abbady *et al.*, 1981), the least-squares plane of the ylide group involving S, C(15), C(16), and C(18) in (I) is also approximately parallel to the plane bisecting the tricyclic ring system. The deviations of the ester fragments from the plane range from 0.030 (9) to 0.201 (6) Å. The torsion angles about the ylide group are shown in Table 2. Both of the ester groups in (I) have the *endo* conformation with one carbonyl oxygen, O(2), *anti* and the other, O(4), *syn* to the nonbonding electron pair on S. However, in (IV) and (V), one of the ester groups has the *endo* and the other the *exo* conformation. The separation between the S and the carbonyl oxygen, O(2), with the *anti* conformation in (I) is 2.933 (3) Å which is similar to that found in other sulfonium ylides (Ternay *et al.*, 1982; Abbady *et al.*, 1981). The carbonyl oxygen, O(4), with the *syn* conformation has a shorter intramolecular contact of 2.790 (3) Å with S. This distance is also similar to the

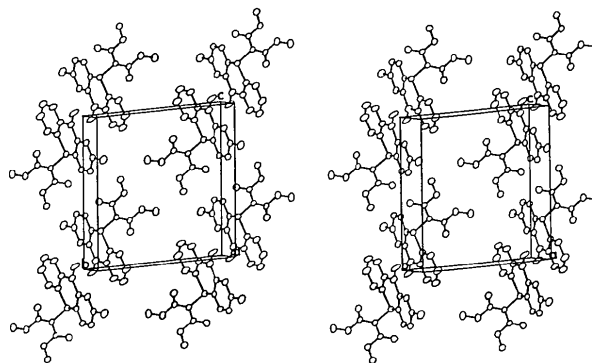


Fig. 3. Stereoscopic drawing of the molecular packing of (I), excluding H atoms, in the unit cell.

corresponding distance in (IV) and (V). The intramolecular separation between the two ether-like oxygens in (I), O(3) and O(5), is 2.659 (4) Å.

The packing of the molecules in the unit cell is shown in a stereoscopic drawing in Fig. 3. The closest intermolecular contacts are 3.191 (6) and 3.213 (5) Å for O(1)···C(9) and O(4)···C(3), respectively.

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