

Dimethyl 9-Thioxanthenyliidenemalonate, C₁₈H₁₄O₄S

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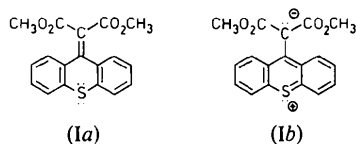
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(Received 9 December 1983; accepted 5 March 1984)

Abstract. $M_r = 326.4$, monoclinic, $I2/c$, $a = 21.613$ (5), $b = 7.536$ (1), $c = 19.576$ (4) Å, $\beta = 94.99$ (2)°, $V = 3176$ (1) Å³, $Z = 8$, $D_x = 1.365$ Mg m⁻³, $Cu K\alpha$, $\lambda = 1.5418$ Å, $\mu = 1.92$ mm⁻¹, $F(000) = 1360$, room temperature, $R = 0.044$ for 1897 independent reflections. The thioxanthene ring is folded along the S...C(9) line with an angle of 137.6 (6)° between the phenyl ring planes. The heterocyclic ring adopts a boat conformation with equal S—C distances of 1.765 (2), 1.757 (2) Å. An exocyclic double bond of length 1.347 (4) Å links the thioxanthene and malonyl fragments. Planarity of the π system is distorted by steric interactions between the ester groups and atoms of the tricyclic system.

Introduction. Some thioxanthenylienes (*e.g.* thiothixene) exhibit neuroleptic activity. In order to examine the propensity for such compounds to exist as vinyl analogs of sulfonium ylides, the title compound was prepared and studied by single-crystal techniques (in the solid state) and by NMR (in solution). The title compound was selected since it should offer an excellent opportunity for electron-pair density to be distributed from the sulfur to the methoxycarbonyl groups. Such distribution (Ib) would yield a highly delocalized (stabilized) carbanionic fragment as well as a highly stabilized (aromatic) heterocyclic ring.



Experimental. Preparation by desulfurization of corresponding episulfide with large excess of triethyl phosphite. (Desulfurization accomplished by stirring at 293 K for 7 d.) After removal of volatiles, residue recrystallized from 95% ethanol to afford the title

compound, m.p. 384–385 K, 83% yield. The ¹³C spectrum (50.3 MHz; CDCl₃; 293 K) exhibited a C=O resonance at 165.2 p.p.m. and an OCH₃ at 52.5 p.p.m. No other resonances were observed between 40 and 70 p.p.m., the region normally associated with the methylene carbon of related thioxanthenylienes (Abbad, Craig, Ternay, Martin, Galloy & Watson, 1981). The ¹H spectrum (200 MHz; CDCl₃; 293 K) consisted of three multiplets (7.61δ, 1H; 7.52δ, 1H; 7.26δ, 2H), assigned to aryl protons, and a sharp singlet (3.63δ, 3H) assigned to the methoxy group.

Crystals: pale-yellow monoclinic prisms with unique b axis parallel to direction of elongation. To minimize absorption effects, intensity data collected from a ground specimen (ellipsoidal, size range 0.27–0.33 mm) mounted on a Syntex P2₁ four-circle diffractometer. Lattice parameters obtained by least-squares refinement of angular data for 15 reflections in 2θ range 11.7–30.6°. Preliminary intensity scans indicated a centered monoclinic unit cell. Unconventional I -centered cell was chosen with $a = 21.613$ (5) Å, $\beta = 94.99$ (2)° in preference to corresponding C cell which has $a = 30.396$ (7) Å, $\beta = 134.90$ (1)°. Space group $I2/c$ or Ic deduced from systematic absences $h + k + l = 2n + 1$ for hkl , $h = 2n + 1$, $l = 2n + 1$ for $h0l$. 2350 independent intensities measured $[(\sin\theta/\lambda)_{\max} = 0.546$ Å⁻¹; hkl range: 22, 8, ± 20], $\theta:2\theta$ scan (scan speed range 3.91–29.30° min⁻¹). 1 check reflection (011) showed no systematic intensity variation. 190 systematically absent reflections removed, 1897 reflections with $I > 3\sigma(I)$ used in final refinement. Lorentz–polarization corrections applied, absorption ignored. Centrosymmetric space group $I2/c$ confirmed by intensity statistics and E map phased by MULTAN78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) revealed all non-hydrogen atoms. In final cycles of least-squares refinement with XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) all non-hydrogen atoms anisotropic. H atoms included at constrained positions [$C-H$ 1.08 (1) Å] based on those found in difference syntheses, with fixed isotropic U equal to those of parent atoms (0.040–0.063 Å²). Function minimized $\sum w(|F_o| -$

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Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3$) for non-hydrogen atoms with e.s.d.'s in parentheses

	x	y	z	$U_{eq}(\text{\AA}^2)\ddagger$
S	2468.6 (3)	5249 (1)	1586.5 (4)	52 (<1)
C(1)	3972 (1)	6364 (4)	571 (1)	46 (2)
C(2)	3769 (2)	7826 (4)	184 (2)	51 (2)
C(3)	3167 (2)	8451 (5)	214 (2)	54 (2)
C(4)	2774 (1)	7630 (4)	631 (2)	48 (2)
C(5)	2828 (1)	4494 (4)	2920 (2)	49 (2)
C(6)	3246 (2)	3947 (5)	3454 (2)	54 (2)
C(7)	3843 (2)	3453 (5)	3329 (1)	51 (2)
C(8)	4016 (1)	3468 (4)	2668 (1)	44 (2)
C(9)	3773 (1)	3895 (4)	1397 (1)	37 (1)
C(11)	3575 (1)	5486 (4)	985 (1)	37 (1)
C(12)	2982 (1)	6176 (4)	1029 (1)	40 (2)
C(13)	3007 (1)	4525 (4)	2252 (1)	39 (2)
C(14)	3601 (1)	3935 (4)	2115 (1)	37 (1)
C(15)	4100 (1)	2554 (4)	1150 (1)	40 (1)
C(16)	4353 (1)	2571 (4)	466 (2)	46 (2)
O(16)	4893 (1)	2781 (5)	387 (1)	81 (2)
C(17)	4150 (2)	2257 (6)	-724 (2)	68 (2)
O(17)	3922 (1)	2312 (3)	-46 (1)	50 (1)
C(18)	4297 (1)	917 (4)	1552 (1)	41 (2)
O(18)	4813 (1)	344 (4)	1581 (1)	70 (2)
C(19)	4000 (2)	-1288 (4)	2310 (2)	56 (2)
O(19)	3835 (1)	174 (3)	1850 (1)	47 (1)

$$\ddagger U_{eq} = \frac{1}{3} [U_{11}(aa)^2 + U_{22}(bb)^2 + U_{33}(cc)^2 + 2U_{13}aca^*c^*\cos\beta + 2U_{23}cb^*c^*\cos\alpha + 2U_{12}aba^*b^*\cos\gamma].$$

Table 2. Selected bond distances (\AA), valence angles ($^\circ$) and torsion angles ($^\circ$) with e.s.d.'s in parentheses

S-C(12)	1.765 (2)	C(16)-O(16)	1.201 (3)
S-C(13)	1.757 (2)	C(18)-O(18)	1.193 (3)
C(9)-C(11)	1.487 (4)	C(16)-O(17)	1.322 (4)
C(9)-C(14)	1.485 (3)	C(18)-O(19)	1.324 (3)
C(9)-C(15)	1.347 (4)		
C(12)-S-C(13)	99.8 (1)	C(9)-C(15)-C(16)	124.1 (2)
C(11)-C(9)-C(14)	114.4 (2)	C(9)-C(15)-C(18)	124.1 (2)
C(11)-C(9)-C(15)	123.1 (2)	C(16)-C(15)-C(18)	111.6 (2)
C(14)-C(9)-C(15)	122.5 (2)		
S-C(12)-C(11)-C(9)	2.2 (3)	C(9)-C(15)-C(16)-O(17)	-75.3 (3)
C(9)-C(14)-C(13)-S	-1.0 (4)	C(9)-C(15)-C(18)-O(18)	-132.3 (3)
C(14)-C(13)-S-C(12)	-32.5 (3)	C(9)-C(15)-C(18)-O(19)	49.3 (3)
C(13)-S-C(12)-C(11)	32.1 (2)	C(15)-C(16)-O(17)-C(17)	-178.0 (3)
C(12)-C(11)-C(9)-C(14)	-43.5 (3)	C(15)-C(18)-O(19)-C(19)	-173.2 (2)
C(11)-C(9)-C(14)-C(13)	42.8 (3)	O(16)-C(16)-O(17)-C(17)	1.3 (5)
C(11)-C(9)-C(15)-C(16)	6.0 (4)	O(18)-C(18)-O(19)-C(19)	8.5 (4)
C(14)-C(9)-C(15)-C(18)	3.4 (4)	O(18)-C(18)-C(15)-C(16)	43.3 (3)
C(9)-C(15)-C(16)-O(16)	105.4 (4)	O(19)-C(18)-C(15)-C(16)	-135.1 (2)

$|F_c|$ with $w = 1/\sigma^2(F_o)$ (derived from counting statistics) for 208 variable parameters. Refinement terminated at $R = 0.044$, $R_w = 0.064$, $S = 3.252^*$ with max. and av. Δ/σ of 0.2 and 0.03, respectively. Largest peak in final difference map 0.28 e \AA^{-3} . Atomic scattering factors for non-hydrogen atoms those of Cromer & Mann (1968) with anomalous-dispersion corrections applied to those for S. For H atoms, those of Stewart, Davidson & Simpson (1965) were used.

* Lists of structure factors, thermal parameters, H-atom coordinates, bond lengths, valence angles, torsion angles and equations of least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 9370 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fractional atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1. Selected bond distances, valence angles and torsion angles are listed in Table 2.

Discussion. The molecular structure is shown in Fig. 1. The tricyclic ring is folded along the S...C(9) line with an angle of $137.6 (6)^\circ$ between the phenyl ring planes, a value similar to that observed in the closely related compound dimethyl 1,4-dimethyl-9-thioxanthenyl-malonate (134.9°) (Abbadly, Craig, Ternay, Martin, Galloy & Watson, 1981). In the latter compound, the two S-C distances differ significantly (by 0.015 \AA) but their mean is the same as the mean of the statistically equivalent S-C distances here. The heterocyclic ring adopts the boat conformation. Atoms S and C(9) deviate by $0.520 (4)$ and $0.480 (4) \text{ \AA}$ respectively from the plane of the four atoms C(11) to C(14).

The presence of the exocyclic double bond C(9)=C(15) restricts freedom of the ester groups to rotations about bonds C(15)-C(16) and C(15)-C(18). This arrangement differs from that in dimethyl 1,4-dimethyl-9-thioxanthenylmalonate, where a pseudo-axial single bond links the thioxanthenyl and malonyl residues. In related thioxanthenium ylides, the linkage is *via* S⁺-C⁻ bonds and the generally planar malonyl fragment is oriented perpendicular to the tricyclic ring, permitting ester and carbonyl O atoms to interact with the S atom (Abbadly *et al.*, 1981). The unit including the tricyclic system and its exocyclic double bond is common to several neuroleptic agents and the C(9)-C(15) distance lies within the range of equivalent distances in α and β isomers of clopenthixol and flupenthixol (Jones, Sheldrick & Horn, 1981). The six atoms associated with the C(9)-C(15) π system are coplanar to within $0.07 (5) \text{ \AA}$, but valence angles and torsion angles associated with C(9) and C(15) indicate distortions due

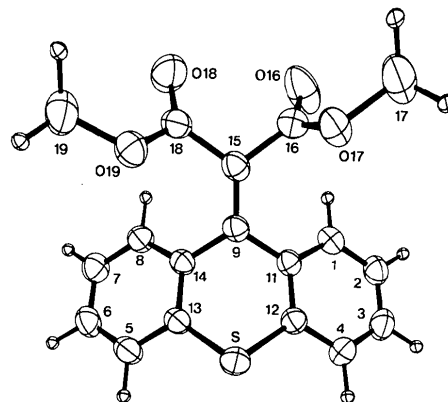


Fig. 1. ORTEP plot (Johnson, 1971) of the title molecule. Thermal ellipsoids are drawn at the 50% probability level. Atoms bearing numerals only are carbon. H atoms are drawn as spheres of arbitrary radius.

to steric hindrance between the ester O atoms and the phenyl ring atoms. Three of the O...H contact distances involving H(1), H(8) and the four O atoms are close to 3.0 Å, but the fourth [O(16)...H(1)] is 2.548 (4) Å. Torsion angles O—C—O—C and C—C—O—C (Table 2) and least-squares planes reflect a higher degree of planarity for the ester group containing C(16) than for that containing C(18). The least-squares plane fitted to C(15)C(16)O(16)O(17)C(17) shows a maximum deviation of 0.015 (12) Å while a plane fitted to C(15)C(18)O(18)O(19)C(19) shows deviations larger than 0.1 Å; however, omission of C(19) results in a maximum deviation of 0.008 (6) Å. The angle between the two ester planes is 62.5 (6)° while the angles between these planes and C(9)C(11)C(14)C(15)C(16)—C(18) are 72.2 (6) and 48.2 (6)°.

The shortest contact distances between molecules translated along the *b* axis are of the type C...H [2.836 (2) to 3.070 (5) Å] and H...H (2.356 Å).

Based upon these results, it seems quite unlikely that simple thioxanthenylienes bearing alkyl groups on the exocyclic double bond (e.g. thiothixene) will exist as sulfonium ylide vinyl analogs.

Acta Cryst. (1984). **C40**, 1712–1715

Structure of 3',5'-Di-*O*-acetylthymidine, C₁₄H₁₈N₂O₇

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(Received 5 April 1984; accepted 30 May 1984)

Abstract. $M_r = 326.3$, monoclinic, $P2_1$, $a = 9.796$ (6), $b = 18.758$ (8), $c = 8.829$ (5) Å, $\beta = 100.72$ (8)°, $U = 1594.04$ Å³, $Z = 4$, $D_x = 1.36$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.070$ mm⁻¹, $F(000) = 688.0$, $T = 293$ K, $R = 0.086$ for 2232 observed reflexions. The hydrogen-bonded base-paired dimer has both molecules in the *anti* conformation, both displaying sugar pucker ²*E* [C(2')-*endo*]. The conformation about C(4')—C(5') for both molecules is *gauche-gauche* (*g*⁺). A close contact of O(3')I with a neighbouring base ring occurs.

Introduction. This structure determination was undertaken as part of a series of studies of nucleoside analogues, including heavy-atom- and acetyl-substituted compounds. It is hoped that such determinations will aid conformational studies currently in progress.

We thank The Robert A. Welch Foundation [P-074 (WHW) and Y-484 (ALT)], the CSIR (Pretoria) and the University of Port Elizabeth for their financial support. This is FASTBIOS Contribution No. 123.

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Experimental. Crystals grown from aqueous ethanol solution. D_m not determined. Crystal approximately 0.25 × 0.35 × 0.3 mm. Cell dimensions obtained by diffractometry from crystals mounted along **a**, **b**, and **c**. Intensity data collected using the **a** and **c** crystals. Stoe STADI 2 diffractometer. Attempts to solve the structure using direct methods in *SHELX76* (Sheldrick, 1976) and *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) unsuccessful; structure finally solved using the direct-methods package *MITHRIL* (Gilmore, 1983), employing the modules *QUARTETS* and *YZARC*. *XANADU* (Roberts & Sheldrick, 1975) and *PLUTO* (Motherwell & Clegg, 1978) programs also used; all calculations performed on the Dundee University DEC-10 computer. Data collected from *a*-axis crystal in the range $h = 0$ to 8, $0 < 2\theta < 55^\circ$, and *c*-axis crystal in the range $l = 0$ to 6, $0 < 2\theta < 55^\circ$. Max. $\sin\theta/\lambda = 0.77$ Å⁻¹.