

Acta Cryst. (1974). B30, 547**5-Methyl-2,2,4-triacetyl-1,3-oxathiole, C₁₀H₁₂O₄S***

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Abstract. (CH₃CO)₂COC(CH₃)C(COCH₃)₂S, a product of the reaction of thallos acetylacetonate with sulfur dioxide; monoclinic, $P2_1/c$, $a=9.817$ (4), $b=9.089$ (3), $c=13.776$ (2) Å, $\beta=114.35$ (6)°, $Z=4$, $d_x=1.354$ (2), $d_m=1.3$ (2) g cm⁻³, at ~23°C. Bond lengths in sequence in the ring are C–O=1.425 (6), O–C=1.377 (6), C–C=1.340 (8), C–S=1.775 (6), and S–C=1.821 (6) Å.

Experimental. A crystal, grown from hexane and 0.15 × 0.15 × 0.20 mm in size, was contained inside a 0.3 mm thin-walled capillary tube. Intensities of 1119 independent X-ray reflections, of which 193 were recorded as zero, were measured manually using the stationary-crystal stationary-counter technique with Mo $K\alpha$ radiation ($\lambda=0.70926$ Å for α_1). The apparatus and methods of measurement and data reduction have been described by Sime, Dodge, Zalkin & Templeton (1971). In the estimation of $\sigma(I)$ the parameters p for errors proportional to I , and q for uncertainty in background were 0.05 and 10, respectively. Systematic absences $h0l$, $l \neq 2n$ and $0k0$, $k \neq 2n$ were observed. All of the data in one quadrant of a sphere of reciprocal space in which $\lambda^{-1} \sin \theta$ was less than 0.48 were measured. The absorption parameter, μ , is 2.8 cm⁻¹. No absorption or extinction correction was made.

The positions of the sulfur atom and four carbon atoms were estimated from a Patterson function. A least-squares refinement was followed by an electron-density calculation which showed all of the atoms with the exception of hydrogen. Hydrogen atoms were included in the subsequent full-matrix least-squares refinement with isotropic thermal parameters. Since these thermal parameters refined poorly, the hydrogen thermal parameters of each methyl group were restrained to one value for the set. The resulting isotropic thermal parameters for H(1)–H(3), H(4)–H(6), H(7)–H(9) and H(10)–H(12) are 7.7 (1), 11.7 (2), 6.6 (1) and 8.9 (2) Å² respectively. With anisotropic temperature factors on all of the other atoms, the structure refined to $R = \sum |\Delta F| / \sum |F_o| = 0.060$ for 824 data with I greater than one standard deviation, and 0.105 for all of the data. The weighted R value, $R_2 = [\sum w(\Delta F)^2 / \sum wF_o^2]^{1/2}$, is

0.047. The goodness-of-fit is 0.99. Atomic scattering factors for neutral S, O and C (Cromer & Waber, 1965) and neutral spherical hydrogen (Stewart, Davidson & Simpson, 1965) were used. The anomalous dispersion for S (Cromer, 1965) was included.

A list of structure factors is available.‡ Positional and anisotropic thermal parameters are given in Tables 1 and 2.

Table 1. *Positional parameters* ($\times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>
S	2133 (2)	4534 (2)	4548 (1)
C(1)	2014 (7)	2717 (7)	3961 (5)
C(2)	1241 (8)	2750 (9)	2760 (5)
C(3)	1712 (14)	1609 (15)	2195 (8)
C(4)	1189 (8)	1722 (8)	4455 (5)
C(5)	9551 (11)	1979 (11)	4131 (7)
C(6)	3894 (7)	1003 (7)	543 (5)
C(7)	4513 (9)	35 (8)	1454 (6)
C(8)	5928 (10)	406 (10)	2387 (6)
C(9)	4425 (8)	2210 (7)	260 (5)
C(10)	5855 (10)	3056 (10)	750 (8)
O(1)	3506 (5)	2194 (5)	4291 (3)
O(2)	291 (6)	3634 (7)	2307 (4)
O(3)	1923 (6)	857 (5)	5127 (4)
O(4)	3850 (6)	6091 (5)	6450 (4)
H(1)	2746 (73)	1789 (75)	2232 (56)
H(2)	1230 (104)	1568 (107)	1672 (60)
H(3)	1681 (88)	723 (78)	2443 (58)
H(4)	822 (115)	6794 (114)	1458 (69)
H(5)	796 (103)	8049 (95)	973 (65)
H(6)	877 (93)	6588 (95)	355 (64)
H(7)	3207 (70)	5461 (77)	2843 (48)
H(8)	4123 (80)	6211 (74)	2304 (55)
H(9)	3843 (71)	4679 (68)	2061 (48)
H(10)	3516 (97)	7920 (101)	3709 (63)
H(11)	3438 (86)	7447 (88)	4454 (60)
H(12)	4274 (91)	8909 (81)	4044 (63)

Discussion. The material was prepared by G. H. Hawks, A. McKillop and E. C. Taylor at Princeton University by reaction of sulfur dioxide and the thallos salt of acetylacetonate (Taylor, 1968, private communication). The present investigation was undertaken to establish

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† Summer student, Lawrence Berkeley Laboratory, 1968.

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Table 2. *Anisotropic thermal parameters* (\AA^2)

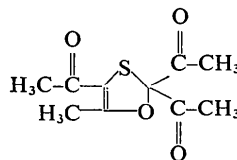
Values are $\times 10^2$. The temperature factor expression is $\exp[-(h^2a^{*2}B_{11}+2hka^*b^*B_{12}+\dots)/4]$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	424 (9)	368 (9)	436 (9)	12 (9)	136 (7)	6 (8)
C(1)	340 (36)	402 (37)	411 (38)	-16 (32)	182 (31)	-30 (28)
C(2)	475 (44)	606 (47)	348 (43)	-46 (38)	170 (39)	-42 (38)
C(3)	913 (81)	861 (68)	531 (54)	-96 (70)	325 (63)	-57 (61)
C(4)	397 (49)	456 (42)	365 (37)	-98 (33)	74 (35)	-84 (31)
C(5)	404 (55)	778 (56)	704 (56)	-87 (42)	149 (45)	83 (54)
C(6)	364 (36)	325 (36)	363 (34)	4 (29)	138 (30)	30 (29)
C(7)	544 (48)	387 (46)	436 (39)	75 (35)	263 (38)	61 (35)
C(8)	566 (50)	640 (53)	457 (47)	123 (54)	46 (45)	40 (39)
C(9)	404 (39)	365 (41)	327 (36)	113 (35)	159 (32)	13 (32)
C(10)	360 (49)	471 (48)	831 (58)	20 (44)	53 (42)	-141 (50)
O(1)	416 (26)	470 (26)	437 (24)	-21 (22)	158 (21)	-96 (20)
O(2)	726 (35)	937 (38)	419 (28)	211 (31)	75 (26)	117 (26)
O(3)	602 (30)	645 (32)	570 (28)	-81 (25)	118 (25)	223 (24)
O(4)	763 (35)	399 (29)	606 (28)	35 (25)	211 (26)	-147 (23)

Table 3. *Bond lengths* (\AA)

S—C(6)	1.775 (6)
S—C(1)	1.821 (6)
C(1)—O(1)	1.425 (6)
C(1)—C(2)	1.509 (8)
C(1)—C(4)	1.547 (8)
C(2)—O(2)	1.194 (7)
C(2)—C(3)	1.48 (1)
C(4)—O(3)	1.202 (7)
C(4)—C(5)	1.50 (1)
C(6)—C(9)	1.340 (8)
C(6)—C(7)	1.445 (8)
C(7)—O(4)	1.211 (7)
C(7)—C(8)	1.49 (1)
C(9)—O(1)	1.377 (6)
C(9)—C(10)	1.50 (1)
C(3)—H(2)	0.68 (7)
C(3)—H(3)	0.88 (7)
C(3)—H(1)	1.01 (6)
C(5)—H(4)	0.76 (8)
C(5)—H(5)	1.02 (9)
C(5)—H(6)	1.02 (8)
C(8)—H(8)	0.86 (6)
C(8)—H(9)	0.96 (6)
C(8)—H(7)	1.02 (6)
C(10)—H(10)	0.76 (8)
C(10)—H(12)	0.85 (7)
C(10)—H(11)	1.01 (8)

its identity, with the unexpected result that it is a substituted oxathiole with the following structure:



Other applications of thallium compounds in organic synthesis are reviewed by McKillop & Taylor (1973).

The bond geometry of the molecule (Fig. 1) is normal. Bond distances and angles are listed in Tables 3 and 4. The C(1)—O(1) and C(1)—S distances are typical of bond lengths found in paraffinic and saturated heterocyclic type compounds (Sutton, 1965). C(6)—C(9) is a typical double bond at 1.34 \AA . C(9)—O(1) and C(6)—S are shorter by 0.05 and 0.04 \AA respectively than the C(1)—O(1) and C(1)—S distances, probably because of their proximity to the double bond. The ring itself is puckerd, with the sum of the internal angles 533 $^\circ$,

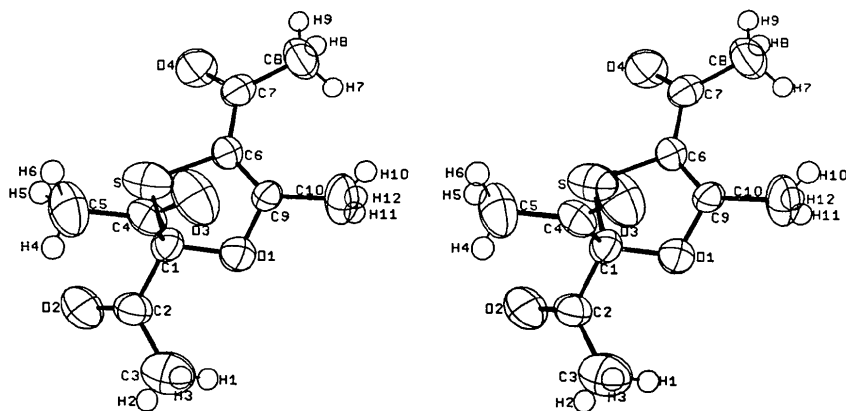


Fig. 1. Stereoscopic view of the molecular geometry.

Table 4. Bond angles (°)

C(1)—S—C(6)	87.6 (4)
S—C(1)—O(1)	107.0 (3)
C(1)—O(1)—C(9)	110.8 (6)
O(1)—C(9)—C(6)	115.3 (5)
S—C(6)—C(9)	111.9 (4)
S—C(1)—C(2)	112.4 (4)
S—C(1)—C(4)	106.5 (3)
S—C(6)—C(7)	115.5 (4)
C(2)—C(1)—O(1)	108.7 (6)
C(2)—C(1)—C(4)	112.1 (5)
C(1)—C(4)—O(3)	117.7 (6)
C(1)—C(4)—C(5)	118.1 (6)
C(1)—C(2)—O(2)	121.2 (6)
C(1)—C(2)—C(3)	116.0 (7)
C(4)—C(1)—O(1)	108.7 (6)
C(3)—C(2)—O(2)	122.9 (7)
C(5)—C(4)—O(3)	124.1 (6)
C(7)—C(6)—C(9)	132.5 (7)
O(4)—C(7)—C(8)	120.2 (6)
C(6)—C(7)—O(4)	118.5 (6)
C(6)—C(7)—C(8)	121.3 (7)
C(6)—C(9)—C(10)	134.0 (6)
C(10)—C(9)—O(1)	110.7 (7)

as opposed to a theoretical 540° for a planar model. The non-planarity consists mainly of a displacement of C(1) from the mean plane of the other four atoms.

We thank Professor Taylor for giving us this interesting compound.

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The crystal structure of Ba₂SiS₄. By J. T. LEMLEY, *Materials Science Laboratory, Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78712, U.S.A.*

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Crystals of Ba₂SiS₄ are orthorhombic, space group *Pnma*, with four formula equivalents in a unit cell of dimensions $a=8.93$, $b=6.78$ and $c=12.01$ Å. The structure was determined by standard Patterson and Fourier methods and is of the K₂SO₄ type. Intensity data were collected on a quarter-circle manual diffractometer. An *R* value of 0.061 was obtained for 695 observed reflections after least-squares refinement.

A crystallographic investigation of Ba₂SiS₄ was undertaken in an effort to confirm Susa & Steinfink's (1971) prediction on the basis of the ratio of atomic radii, $r_{\text{Si}}/r_{\text{Ba}}$, and a force constant, that its structure should correspond to that of K₂SO₄.

Experimental

Amber crystals of Ba₂SiS₄ were prepared in this laboratory by heating a stoichiometric mixture of barium sulfide, silicon, and sulfur at 1100° for 26h. Cooling was accomplished stepwise over approximately three days. The sample charges were placed in closed graphite crucibles and sealed in evacuated vycor tubes for firing.

A thin elongated hexagonal platelet (approximately 0.20 × 0.10 × 0.01 mm) was selected for X-ray examination. Diffraction symmetry and systematic extinctions ($0kl$, $k+l=2n+1$; $hk0$, $h=2n+1$) correspond to the orthorhombic space group *Pnma*. A least-squares refinement based upon

44 diffraction maxima measured on a General Electric XRD-5 manual diffractometer at 2θ values between 31 and 50° with Mo $K\alpha_1$ ($\lambda=0.7135$ Å) and Mo $K\alpha_2$ ($\lambda=0.7093$ Å) radiation, yielded the lattice parameters: $a=8.9304 \pm 0.0009$, $b=6.7821 \pm 0.0004$, $c=12.0106 \pm 0.0008$ Å. $V=727.4$ Å³; $Z=4$; $D_{\text{calc}}=3.936$ g cm⁻³.

Crystal structure determination

Diffraction intensities were measured on the XRD-5 diffractometer using Zr-filtered Mo $K\alpha$ ($\lambda=0.7107$) radiation and a stationary-crystal stationary-counter technique. Of the 905 non-systematically extinct reflections measured, 695 were regarded as observed on the basis that the peak count exceeded the background count by at least 6 counts in 20s; that is, approximately twice the standard deviation. Extinction corrections were found to be unnecessary, but Lorentz, polarization, and absorption corrections were