

and 3.81 Å, the latter distance being greater than the 3.63 Å distance in the octahedra about Co(2). The angle Cl-Co(2)-

Table 3. Selected interatomic distances with standard deviations

Mo(1)-O(2)	1.75 Å	(0.008)
-O(3)	1.81	(0.012)
-O(6)	1.77	(0.012)
Mo(2)-O(1)	1.77	(0.007)
-O(4)	1.82	(0.012)
-O(5)	1.72	(0.012)
Co(1)-O(1)	2.06, 2.21	(0.007)
-O(2)	2.02	(0.008)
-O(3)	2.08	(0.008)
-O(4)	2.09	(0.008)
-Cl	2.43	(0.003)
Co(2)-O(6)	2.01	(0.012)
Cl	2.51	(0.003)
Na-O(5)	2.36, 2.80	(0.016)
-O(6)	2.37	(0.016)
-Cl	2.97, 3.10	(0.005)
Cl-Cl	3.48, 3.63, 3.81	(0.004)

Cl is 87.6 and has not changed significantly from the previously published result. Also the refinement has not significantly altered the octahedron about Co(1).

All the nearest O-O distances are now confined to a narrower range of values 2.71-3.02 Å with the bulk of these lying between 2.83 and 2.98 Å. The average standard deviation of these distances is 0.01 Å.

The calculations were performed on an ICL-1907 computer using programs written by F. R. Ahmed for the IBM 360 and modified by Dr J. D. Lee (Loughborough Univ.) and by one of us (BGAM).

Permission to publish this paper has been given by The British Petroleum Company Limited.

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**On the structure of  $\beta$ -thianthrene dioxide.** By HERMAN L. AMMON,\* *Division of Natural Sciences, University of California, Santa Cruz, California, U.S.A.* and PLATO H. WATTS, JR and JAMES M. STEWART, *Department of Chemistry, University of Maryland, College Park, Maryland, U.S.A.*

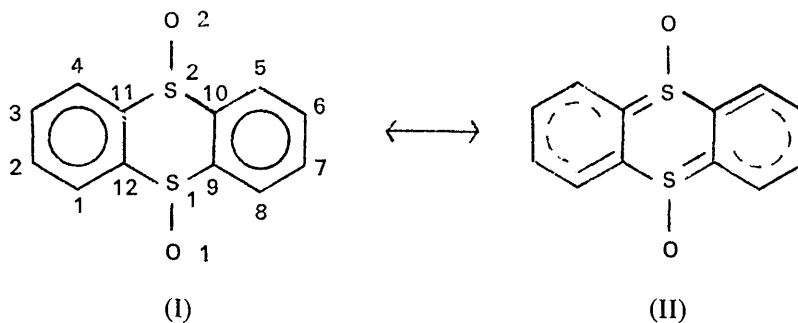
(Received 14 April 1969 and in revised form 24 June 1969)

The published X-ray diffraction data for  $\beta$ -thianthrene dioxide have been re-examined. Bond lengths and angles were obtained which are in agreement with the expected symmetry of the central, heterocyclic ring.

In connection with some recent work on the crystal structure of a sulfone (Ammon, Watts, Stewart & Mock, 1968), we have made an extensive literature search for information on carbon-sulfur bond lengths in sulfides, sulfoxides, and sulfones. The four  $C_{sp^2}$ -S distances reported (Hosoya, 1966) for  $\beta$ -thianthrene dioxide (I) showed a symmetrical pattern of short and long bonds and, in conjunction with bond distances in the two benzene nuclei, suggested that structure (II) might make a significant contribution to the resonance hybrid. This represented an intriguing possibility, and we have further studied the data published for

$\beta$ -thianthrene dioxide to check the C-S bond length asymmetry.

Our work started with a recalculation of bond lengths, angles, and their estimated standard deviations using the cell constants and carbon, oxygen, and sulfur coordinates reported by Hosoya (1966). The lengths and angles obtained from this calculation differed markedly from many of those in the original work (Tables 1 and 2).\* Several characteristics of the new values relative to the old data were: (a) the C-S bond length differences were considerably smaller; (b) bond length e.s.d.'s were smaller; (c) differences



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\* Jacobs & Sundaralingam (1969) have reported a partial list of bond length and angle data which was derived from a similar recalculation.

Table 1. Bond lengths and estimated standard deviations

	Original*	Recalculation†	Refinement‡
S(1)—O(1)	1.479 (16) Å	1.482 (9) Å	1.483 (7) Å
S(2)—O(2)	1.474 (16)	1.470 (9)	1.471 (7)
S(1)—C(9)	1.753 (21)	1.778 (12)	1.781 (10)
S(1)—C(12)	1.828 (22)	1.796 (12)	1.786 (9)
S(2)—C(10)	1.866 (21)	1.806 (11)	1.793 (9)
S(2)—C(11)	1.720 (21)	1.778 (12)	1.782 (9)
C(1)—C(2)	1.397 (35)	1.373 (20)	1.369 (15)
C(1)—C(12)	1.324 (31)	1.369 (18)	1.368 (13)
C(2)—C(3)	1.450 (37)	1.449 (21)	1.401 (16)
C(3)—C(4)	1.379 (36)	1.426 (21)	1.389 (15)
C(4)—C(11)	1.400 (32)	1.373 (18)	1.379 (13)
C(5)—C(6)	1.465 (33)	1.417 (18)	1.411 (15)
C(5)—C(10)	1.329 (30)	1.350 (17)	1.348 (14)
C(6)—C(7)	1.358 (34)	1.354 (19)	1.361 (16)
C(7)—C(8)	1.404 (32)	1.426 (18)	1.399 (15)
C(8)—C(9)	1.433 (29)	1.386 (16)	1.386 (13)
C(9)—C(10)	1.431 (28)	1.429 (16)	1.416 (12)
C(11)—C(12)	1.429 (30)	1.429 (17)	1.427 (12)
C(1)—H(1)			1.22 (8)
C(2)—H(2)			1.26 (11)
C(3)—H(3)			1.06 (7)

Table 1 (cont.)

C(4)—H(4)	1.12 (6)
C(5)—H(5)	0.96 (9)
C(6)—H(6)	0.99 (17)
C(7)—H(7)	1.07 (7)
C(8)—H(8)	1.07 (9)

\* Hosoya (1966).

† Recalculation using the original atomic coordinates.

‡ After further least-squares refinement including hydrogen atoms.

in structurally similar bond angles were smaller; (*d*) angle e.s.d.'s were more realistic.

We have also refined the structure using the published structure factor data and including hydrogen atoms. Positions for the eight hydrogen atoms were calculated assuming an idealized  $sp^2$  geometry for the necessary carbon atoms. Least-squares refinement used the full matrix of the normal equations and a Hughes (1941) weighting scheme ( $4F_{\min} = 24.0$ ). Anisotropic temperature factors were used for the carbon, oxygen and sulfur atoms, and individual isotropic temperature factors were applied to the hydrogen

Table 2. Bond angles and estimated standard deviations

	Original*	Recalculation	Refinement
O(1)—S(1)—C(9)	108.2°	106.0 (5)°	105.5 (4)°
O(1)—S(1)—C(12)	103.2	105.4 (5)	105.9 (4)
C(9)—S(1)—C(12)	96.7	96.8 (6)	96.5 (4)
O(2)—S(2)—C(10)	109.7	108.1 (5)	108.4 (4)
O(2)—S(2)—C(11)	106.3	107.8 (5)	108.1 (4)
C(10)—S(2)—C(11)	95.7	95.6 (5)	95.2 (4)
C(2)—C(1)—C(12)	120.8	121.4 (1.3)	120.0 (9)
C(1)—C(2)—C(3)	120.4	117.5 (1.3)	119.7 (1.0)
C(2)—C(3)—C(4)	119.5	121.7 (1.3)	121.5 (1.0)
C(3)—C(4)—C(11)	117.2	117.7 (1.2)	118.5 (9)
C(6)—C(5)—C(10)	117.7	117.1 (1.2)	118.0 (9)
C(5)—C(6)—C(7)	124.6	122.6 (1.3)	122.4 (1.0)
C(6)—C(7)—C(8)	117.8	120.5 (1.2)	119.5 (1.0)
C(7)—C(8)—C(9)	118.3	117.7 (1.1)	118.8 (9)
C(8)—C(9)—C(10)	122.0	119.9 (1.1)	120.3 (9)
C(8)—C(9)—S(1)	118.4	117.9 (9)	118.3 (7)
C(10)—C(9)—S(1)	119.5	122.1 (9)	121.4 (7)
C(5)—C(10)—C(9)	119.6	122.2 (1.1)	120.9 (8)
C(5)—C(10)—S(2)	118.9	118.3 (9)	118.4 (7)
C(9)—C(10)—S(2)	121.3	119.4 (9)	120.5 (7)
C(4)—C(11)—C(12)	123.1	120.4 (1.1)	119.6 (8)
C(4)—C(11)—S(2)	116.6	117.2 (1.0)	118.1 (7)
C(12)—C(11)—S(2)	120.0	122.1 (9)	122.1 (7)
C(1)—C(12)—C(11)	118.9	121.2 (1.1)	120.6 (8)
C(1)—C(12)—S(1)	118.8	119.3 (1.0)	119.8 (7)
C(11)—C(12)—S(1)	122.2	119.5 (9)	119.6 (7)
C(2)—C(1)—H(1)			117.0 (4.0)
C(12)—C(1)—H(1)			123.0 (4.0)
C(1)—C(2)—H(2)			127.0 (5.0)
C(3)—C(2)—H(2)			112.0 (5.0)
C(2)—C(3)—H(3)			118.0 (4.0)
C(4)—C(3)—H(3)			119.0 (4.0)
C(3)—C(4)—H(4)			125.0 (3.0)
C(11)—C(4)—H(4)			116.0 (3.0)
C(6)—C(5)—H(5)			120.0 (5.0)
C(10)—C(5)—H(5)			121.0 (5.0)
C(5)—C(6)—H(6)			114.0 (9.0)
C(7)—C(6)—H(6)			123.0 (9.0)
C(6)—C(7)—H(7)			114.0 (4.0)
C(8)—C(7)—H(7)			125.0 (4.0)
C(7)—C(8)—H(8)			111.0 (5.0)
C(9)—C(8)—H(8)			129.0 (5.0)

\* Hosoya (1966). The original angles have been rounded to one decimal place and the reported e.s.d.'s (0.01–0.04°) have not been given.

Table 3. Atomic fractional coordinates, thermal parameters ( $\text{\AA}^2$ ) and estimated standard deviations

Thermal parameters are in the form:  $\exp[-0.25(B_{11}h^2a^*2 + \dots B_{23}2klb^*c^*)]$ .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>11</sub>	<i>B</i> <sub>22</sub>	<i>B</i> <sub>33</sub>	<i>B</i> <sub>12</sub>	<i>B</i> <sub>13</sub>	<i>B</i> <sub>23</sub>
S(1)	0.1260 (2)	0.2610 (2)	-0.1040 (3)	3.8 (1)	3.8 (1)	2.8 (1)	-0.2 (1)	0.1 (1)	0.5 (1)
S(2)	0.1341 (2)	0.1715 (2)	0.3579 (3)	3.7 (1)	4.5 (1)	2.6 (1)	-0.2 (1)	0.1 (1)	0.1 (1)
O(1)	0.1202 (6)	0.3428 (5)	0.0389 (10)	5.0 (3)	4.0 (4)	4.5 (3)	0.3 (3)	0.0 (3)	-0.1 (3)
O(2)	0.1409 (6)	0.0976 (6)	0.5176 (9)	3.6 (3)	6.6 (4)	3.4 (3)	-0.7 (3)	-0.2 (2)	1.6 (3)
C(1)	0.3408 (8)	0.1803 (8)	-0.1390 (15)	3.9 (4)	4.8 (5)	3.8 (4)	-0.7 (4)	0.4 (3)	0.2 (4)
C(2)	0.4376 (10)	0.1327 (8)	-0.0671 (18)	4.2 (5)	5.3 (6)	5.5 (5)	-0.5 (4)	0.8 (4)	-1.2 (5)
C(3)	0.4397 (10)	0.0937 (8)	0.1313 (18)	4.8 (5)	4.2 (6)	5.9 (6)	0.9 (4)	-0.5 (4)	-1.2 (5)
C(4)	0.3460 (9)	0.1030 (7)	0.2587 (15)	4.4 (5)	3.6 (5)	4.0 (4)	0.3 (4)	0.0 (3)	-0.7 (3)
C(5)	-0.0664 (9)	0.0839 (8)	0.2367 (16)	4.0 (4)	4.4 (5)	4.2 (4)	-0.3 (4)	0.9 (3)	0.2 (4)
C(6)	-0.1592 (10)	0.0644 (8)	0.0953 (18)	4.2 (5)	4.6 (6)	5.9 (6)	-0.4 (4)	0.1 (4)	0.7 (5)
C(7)	-0.1651 (9)	0.1023 (8)	-0.0974 (17)	4.1 (5)	4.5 (6)	5.7 (5)	0.1 (4)	-1.1 (4)	0.3 (4)
C(8)	-0.0746 (8)	0.1601 (7)	-0.1625 (15)	3.8 (4)	4.3 (5)	3.8 (4)	-0.1 (4)	-0.5 (3)	0.2 (4)
C(9)	0.0168 (8)	0.1806 (7)	-0.0250 (13)	3.4 (4)	3.7 (5)	3.5 (4)	0.7 (3)	-0.2 (3)	0.0 (3)
C(10)	0.0200 (8)	0.1407 (7)	0.1749 (13)	3.5 (4)	4.2 (5)	3.0 (3)	0.4 (3)	0.5 (3)	0.1 (3)
C(11)	0.2492 (8)	0.1522 (6)	0.1864 (13)	3.6 (4)	3.5 (4)	3.6 (4)	0.2 (3)	-0.1 (3)	0.3 (3)
C(12)	0.2479 (7)	0.1919 (7)	-0.0155 (13)	3.3 (4)	4.3 (5)	3.2 (3)	-0.6 (3)	0.1 (3)	0.1 (3)
H(1)	0.345 (7)	0.216 (6)	-0.310 (13)	3.0 (2.0)					
H(2)	0.535 (10)	0.127 (7)	-0.151 (16)	5.0 (3.0)					
H(3)	0.505 (6)	0.043 (5)	0.171 (10)	1.0 (1.0)					
H(4)	0.341 (5)	0.072 (4)	0.416 (10)	1.0 (1.0)					
H(5)	-0.073 (8)	0.068 (6)	0.379 (13)	3.0 (2.0)					
H(6)	-0.217 (15)	0.019 (12)	0.146 (24)	12.0 (5.0)					
H(7)	-0.248 (6)	0.094 (5)	-0.175 (11)	1.0 (1.0)					
H(8)	-0.097 (7)	0.193 (6)	-0.306 (14)	3.0 (2.0)					

atoms; all parameters were varied simultaneously. The *R* index was 0.093 and the maximum parameter shift was  $0.029\sigma$  from the last cycle of least-squares. The atomic scattering factors used were: carbon and oxygen, Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955); hydrogen, Stewart, Davidson & Simpson (1965); sulfur, *International Tables for X-ray Crystallography* (1962). The atomic coordinates and temperature factors, and bond length and angle data are given in Tables 3, 1, and 2 respectively. All computations were done on a UNIVAC 1108 computer with the *X-ray 67* (1967) system of programs.

There are no significant differences between the refined and recalculated bond lengths and angles. The six-membered sulfoxide ring now shows a symmetrical pattern of carbon-sulfur lengths (average value  $1.785 \text{ \AA}$ ) and pairs of equal C-S-O angles at the two sulfoxide groups. Although some of the carbon-carbon distances still differ appreciably from normal aromatic bond lengths, most have moved closer to the benzene distance. These new data rule out any major contribution from structure (II).

This work was supported by a grant from the Computer Center and Research Committee, University of California,

and by grant NSG-39 of the National Aeronautics and Space Administration to the Computer Science Center of the University of Maryland.

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