

trans-Bis(3-dimethylsulfoniocyclopentadienylide)-di- μ -iodo-diiododimercury(II)

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Abstract. $[(\text{CH}_3)_2\text{SC}_5\text{H}_4\text{HgI}_2]_2$, triclinic, $P\bar{1}$, $a = 9.188$ (5), $b = 7.272$ (2), $c = 9.493$ (3) Å, $\alpha = 96.87$ (5), $\beta = 101.66$ (4), $\gamma = 77.38$ (4)°, $Z = 1$, $D_m = 3.19$, $D_x = 3.19$ Mg m⁻³, $M_r = 1160.9$, $R_1 = 0.053$, $R_2 = 0.044$ based on 1843 reflections collected by an automated diffractometer. The compound is an iodine-bridged dimer [Hg—I(bridge), 2.896 (1), 3.031 (1) Å; Hg—I(external), 2.706 (1) Å] with a Hg—C σ bond attached two C atoms away from the ylide C atom of the cyclopentadienylide. The ylide S—C distance [1.738 (13) Å] is slightly longer than that in the unsubstituted ylide [1.712 (8) Å].

Introduction. The crystal structure was investigated for comparison with the triphenylphosphonio ylide complex, $[(\text{C}_6\text{H}_5)_3\text{P}-\text{C}_5\text{H}_4\text{HgI}_2]_2$ (Baenziger, Flynn, Swenson & Holy, 1978) and, in particular, to determine whether the Hg would be attached at the C atom adjacent to, or two C atoms away from, the ylide C atom. The total number of reflections measured with an automated FACS I diffractometer (4430) yielded 2215 independent reflections of which 1843 were greater than 3σ above background ($\sin \theta/\lambda_{\text{max}} \leq 0.595$ Å⁻¹, graphite-crystal-monochromatized Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å). The density was determined by flotation in a dibromoethane/diiodomethane mixture. A stepped θ - 2θ scan data-collection method was used (Baenziger, Foster, Howells, Howells, Vander Valk & Burton, 1977) with the step size varying from 0.14 to 0.18° (2θ) and background measured at $\pm 1.5^\circ$ (2θ). The data were corrected for absorption (Templeton & Templeton, 1973), since $\mu = 18.33$ mm⁻¹. The crystal dimensions were: [(planes), distance in mm] $\pm(100)$, 0.0075; $\pm(001)$, 0.041; $\pm(010)$, 0.0129; $\pm(018)$, 0.0026. The maximum and minimum correction factors were 10.61 and 2.46. The structure was found from Patterson and electron density maps. Full-matrix least-squares refinement (using a locally written program) of a model with 100 parameters (Hg, I, S and C atoms with anisotropic thermal parameters; H atoms

were placed 0.95 Å from C atoms with thermal parameters the same as those of the C atoms to which they are attached) gave $R_1 = \sum |F_o| - |F_c| / \sum F_o = 0.053$; $R_2 = (\sum w|F_o| - |F_c|)^2 / \sum wF_o^2)^{1/2} = 0.044$. Atom scattering factors used for Hg, I, S and C were from *International Tables for X-ray Crystallography* (1962) and that for H was from Stewart, Davidson & Simpson (1965). Anomalous-dispersion terms were included for Hg, I and S. Atomic positions are given in Table 1. Bond lengths and angles are given in Table 2.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35160 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic parameters for the title compound ($\times 10^5$ for Hg, I; $\times 10^4$ for S, C; $\times 10^3$ for H)

Estimated standard deviations in the last decimal place are in parentheses.

	x	y	z
Hg	86601 (6)	-18082 (9)	-4025 (7)
I(1)	83528 (11)	-31798 (14)	-32021 (11)
I(2)	79334 (9)	22577 (12)	-5227 (10)
S	7605 (4)	1920 (6)	4176 (4)
C(11)	7384 (13)	-10 (17)	2941 (15)
C(12)	8544 (11)	-1360 (21)	2638 (17)
C(13)	8038 (14)	-2627 (19)	1515 (16)
C(14)	6415 (15)	-2077 (18)	1308 (16)
C(15)	6007 (13)	-484 (20)	2129 (16)
C(2)	6777 (25)	3861 (27)	3249 (21)
C(3)	6277 (14)	2029 (20)	5286 (16)
H(12)	960	855	309
H(13)	843	610	176
H(14)	572	724	66
H(15)	500	20	215
H(21)	656	446	402
H(22)	579	383	252
H(23)	733	446	281
H(31)	523	234	500
H(32)	656	82	565
H(33)	656	294	613

Weights in the least-squares refinement were $1/S_F^2$, where S_F is the estimate of the standard deviation of F_{ave} . The standard deviation of F_{ave} was estimated both from counting statistics and from the agreement among equivalent reflections. The largest estimate was taken as S_F . An ORTEP plot of the molecule is shown in Fig. 1.

Table 2. Bond distances (Å) and angles (°)

Hg—Hg	3.892 (1)	I(1)—Hg—I(2)	104.3 (4)
Hg—I(1)	2.706 (1)	I(1)—Hg—I(2)'	102.83 (4)
Hg—I(2)	2.896 (1)	I(1)—Hg—C(13)	133.6 (4)
Hg—I(2)'	3.031 (1)	I(2)—Hg—I(2)'	97.93 (3)
Hg—C(13)	2.196 (14)	I(2)—Hg—C(13)	111.1 (4)
S—C(11)	1.738 (13)	I(2)′—Hg—C(13)	101.1 (3)
S—C(2)	1.704 (21)	C(11)—S—C(2)	105.5 (8)
S—C(3)	1.750 (15)	C(11)—S—C(3)	105.0 (6)
C(11)—C(12)	1.335 (19)	C(2)—S—C(3)	99.7 (8)
C(11)—C(15)	1.431 (19)	C(11)—C(12)—C(13)	110.3 (1.1)
C(12)—C(13)	1.398 (20)	C(12)—C(13)—C(14)	103.9 (1.1)
C(13)—C(14)	1.436 (20)	C(12)—C(13)—Hg	104.7 (1.0)
C(14)—C(15)	1.343 (20)	C(14)—C(13)—Hg	105.2 (1.0)
		C(13)—C(14)—C(15)	110.3 (1.2)
		C(14)—C(15)—C(11)	106.2 (1.1)
		C(15)—C(11)—C(12)	108.6 (1.2)
		C(12)—C(11)—S	123.2 (1.0)
		C(15)—C(11)—S	128.2 (1.0)
			360.0

Equation of the S, C(11), C(12), C(13), C(14), C(15) plane

$$0.32938x + 0.59620y - 0.73216z = -0.069$$

Deviations: -0.003, 0.011, 0.064, -0.063, 0.005, 0.016 Å, respectively [Cartesian coordinates are oriented with I parallel to a, k parallel to $\mathbf{a} \times \mathbf{b}$, and j parallel to $(\mathbf{a} \times \mathbf{b}) \times \mathbf{a}$].

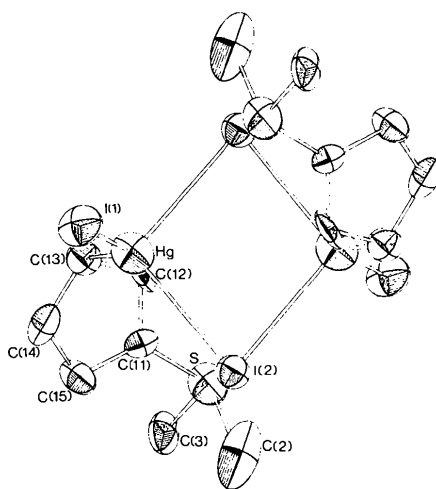


Fig. 1. ORTEP drawing (Johnson, 1965) of the title compound. The dimer has been rotated 10° about the Hg—Hg axis from the view normal to the Hg—I(2)—Hg bridge plane. [H atoms have been omitted.]

Discussion. In the solid state, the σ bond to Hg is localized at C(13), as in the related triphenylphosphonium ylide, even though NMR evidence indicates that in solution some molecules with the σ bond localized at C(12) also exist. C(13) has tetrahedral coordination with a Hg—C(13) distance of 2.196 (14) Å. [For comparison, the distance was 2.292 (8) Å in the P analog.] The ylide C atom, C(11), has planar coordination, with a S—C(11) bond distance of 1.738 (13) Å. This distance is not significantly longer than the corresponding bond in the uncomplexed ylide [1.712 (8) Å (Andrianov & Struchkov, 1977)]. The bond distances in the cyclopentadiene ring have also altered from the values in the uncomplexed ylide in a fashion similar to that also found in the P analog.

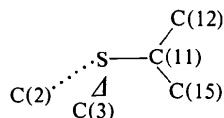
A comparison with the reported S ylides listed in Table 3 shows that the title compound has all the characteristic structural features: (1) the C(3)—S—C(2) angle is the smallest of the S angles; (2) the S—C(11)—C(15) angle is larger than S—C(11)—C(12); (3) the methyl groups are roughly symmetrically disposed above and below the S, C(11), C(12), C(15) plane. [The distances reported are all uncorrected for thermal motion. Thermal-motion corrections were calculated for all five compounds; the changes in bond lengths were small and in most cases less than the standard deviations in the bond lengths. Since the bond-length corrections did not vary widely, the comparisons among the uncorrected values are considered to be equally valid.] Again, because of the dominance of X-ray scattering by Hg and I, the errors in the light-atom positions are too large to make significant statements about particular bond lengths.

In comparing this structure to that of the P ylide, the conformation of the cyclopentadiene ring relative to the Hg—I—Hg bridge is strikingly different. In the P ylide, the cyclopentadiene ring was rotated about the Hg—C(13) bond so that the triphenylphosphorus group is extended away from the Hg—I—Hg bridge region of the dimer. In the S analog, the cyclopentadiene ring is rotated so that S and its two methyl groups are placed over the bridging I atoms. [In projection, the bridging I atom lies approximately in the middle of the S—C(2) bond.] It is clear that the bulky triphenylphosphorus group would not permit the compact arrangement shown by the S ylide. A conformation of the S ylide which parallels that of the P ylide [180° rotation about the Hg—C(13) bond] would also certainly reduce intramolecular interactions.

The Hg coordination distances are different in the P and the S ylide structures. The P ylide has more uniform bridging distances (2.937 and 2.982 Å vs 2.896 and 3.031 Å for the S compound), a shorter bond to the external I atom (2.681 vs 2.706 Å), and a longer bond to the cyclopentadienylylide ring (2.29 vs 2.20 Å). One might understand the differences by considering the S ylide as more strongly bound to an

Table 3. Bond distances (Å) and angles (°) in sulfur ylides

- (I) Dimethylsulfoniocyclopentadienide (Andrianov & Struchkov, 1977)
 (II) Tricarbonyl(dimethylsulfoniocyclopentadienylide)chromium(0) (Andrianov, Struchkov, Setkina, Zhakaeva & Zdanovitch, 1977)
 (III) The title compound
 (IV) 2-Dimethyl-λ⁴-sulfanylidene-1,3-indandione (Christensen & Thom, 1971)
 (V) 2-Dimethyl-λ⁴-sulfanylidene-malononitrile (Christensen & Witmore, 1969)



	(I)	(II)	(III)	(IV)	(V)
S—C(11)	1.712 (8)	1.743 (6)	1.738 (13)	1.707 (3)	1.719 (8)
S—C(3)	1.769 (9)	1.796 (10)	1.750 (15)	1.784 (3)	1.831 (10)
S—C(2)	1.791 (7)	1.795 (10)	1.704 (21)	1.787 (3)	1.800 (10)
C(11)—C(15)	1.394 (12)	1.438 (9)	1.431 (19)	1.420 (5)	1.388 (15)
C(11)—C(12)	1.394 (13)	1.430 (9)	1.335 (19)	1.437 (5)	1.403 (14)
Distance from S, C(11), C(15), C(12) plane					
C(3)	1.37	1.12	1.22	1.43	1.31
C(2)	-1.35	-1.60	-1.40	-1.28	-1.48
C(3)—S—C(11)	107.0 (4)	106.2 (4)	105.0 (6)	106.8 (1)	103.0 (5)
C(2)—S—C(11)	106.5 (4)	104.5 (4)	105.5 (8)	105.4 (1)	107.3 (7)
C(3)—S—C(2)	99.8 (4)	100.7 (4)	99.7 (8)	99.9 (1)	101.7 (7)
S—C(11)—C(15)	132.0 (7)	129.0 (5)	128.3 (1.0)	126.0 (3)	119.3 (1.2)
S—C(11)—C(12)	119.4 (7)	121.5 (5)	123.2 (1.0)	122.5 (3)	118.3 (1.0)

HgI₂ unit which is then more loosely dimerized than the P analog.

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