

bond, 1.469 (2) Å, is in the range found for the peroxides mentioned above. The isopropyl and the naphthylamino groups are bonded to the trioxane ring in equatorial positions. The naphthyl group is slightly twisted about the C(16)–C(21) bond. The bond lengths in the naphthyl ring are similar to those in 1,8-bis(dimethylamino)naphthalene (Einspahr, Robert, Marsh & Roberts, 1973). The two C–N distances and the C–N–C angle show that the N atom is in sp^2 hybridization. The dihedral angle between the plane C(5)–N–C(12) and the mean plane of the naphthylamino group is 12.0 (2)° by rotation about the C(12)–N bond. The torsion angles C(12)–N–C(5)–C(6) and C(12)–N–C(5)–O(4) are –165.1 (2) and 72.7 (3)°, respectively. Such a relative orientation of the bulky naphthylamino group and the trioxane ring could minimize the repulsions from H(5), O(4), and the two methyl groups at C(6). The C(sp^3)–C(sp^3) bond distances, 1.509–1.523 Å, are all shortened. The small expansion of the N–C(12)–C(13) angle and the resulting contraction of N–C(12)–C(21) are attributable to a repulsion between C(5) and C(13), their distance apart being 2.908 Å. The O(1)–O(2) bond is exposed relative to the molecule. This suggests that in solution the peroxide bond is susceptible to attack by

alkali and its bond cleavage is a trigger for chemiluminescence.

As shown in Fig. 2, the molecules are packed by van der Waals interactions. No hydrogen bonds are formed; the shortest intermolecular N···O distance is 3.555 (3) Å.

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Mercury Ethylxanthate

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Abstract. Hg(SSCOC₂H₅)₂, monoclinic, $P2_1$, $a = 9.904$ (2), $b = 6.903$ (7), $c = 9.104$ (8) Å, $\beta = 100.21$ (3)°, $Z = 2$, $D_m = 2.49$, $D_x = 2.40$ g cm⁻³, absorption coefficient $\mu(\text{Mo } K\alpha) = 136.49$ cm⁻¹, final $R = 0.058$. Each Hg atom is surrounded tetrahedrally by four S atoms at distances of 2.313 (8), 2.505 (9), 2.749 (8) and 2.943 (10) Å. A distorted two-dimensional network of 16-membered rings, $[-\text{Hg}-\text{S}-\text{C}-\text{S}-]_n$, is formed parallel to the (100) plane.

Introduction. The crystals were grown as thin plates or rectangular tablets from carbon tetrachloride. Intensities were collected on an equi-inclination type diffractometer READ-1 (Sakurai, Ito & Iimura, 1970) with

graphite-monochromated Mo $K\alpha$ radiation. The measurement was carried out in the ω -scan mode with a scan speed of 1° min⁻¹. 1180 independent reflexions with intensities larger than 2.5 times the standard deviations were obtained. A crystal elongated along **b** with a cross-section of 0.11 × 0.11 mm was used. Absorption correction by approximation to a cylinder ($\mu_r = 0.735$) was applied. No extinction correction was applied. The structure was analysed by heavy-atom Fourier synthesis. The atomic scattering factors and dispersion effects were taken from *International Tables for X-ray Crystallography* (1974). After three cycles of block-diagonal anisotropic least-squares refinement, in which the weighting scheme 1 for $0 < |F_o| < 90$ and $(90/|F_o|)^2$ for $|F_o| \geq 90$ was chosen, the R value reduced

to 0.058 with H atoms omitted. The final atomic coordinates and thermal parameters are given in Table 1,* interatomic distances and angles in Table 2.

Discussion. The heavy-metal-sulphur bond has been studied by recent crystal structure analyses of heavy-metal salts of dithioacid compounds (Iimura, Ito & Hagihara, 1972; Iwasaki, 1973). The crystal structure determination of $\text{Hg}(\text{SSCOC}_2\text{H}_5)_2$ was undertaken as part of this series. The atom Hg is connected to atoms Hg' and $\text{Hg}'(+c)$, related by the screw axis, through the $\text{S}(1')\text{-C}(1')\text{-S}(2')$ and $\text{S}(4)\text{-C}(2)\text{-S}(3)$ bridging groups respectively. By the screw operation of the $-\text{Hg}\text{-S}\text{-C}\text{-S}\text{-Hg}-$ chain a 16-membered ring $[-\text{Hg}\text{-S}\text{-C}\text{-S}]_4$ is formed parallel to the (100) plane (Fig. 1). The network of 16-membered rings stacks along *a* with sulphur-ethyl and ethyl-ethyl van der Waals contacts. The two-dimensional network is quite similar to those found in $\text{Cd}(\text{SSCOC}_2\text{H}_5)_2$ (Iimura, 1973), $\text{Zn}(\text{SSCOC}_2\text{H}_5)_2$ (Ikeda & Hagihara, 1966) and $\text{Cd}(\text{SSCOC}_2\text{H}_5)_2$ (Iimura, Ito & Hagihara, 1972). Each Hg atom is tetrahedrally surrounded by four S atoms. The four Hg-S bond lengths range from 2.313 (8) to 2.943 (10) Å. The shortest bond length Hg-S(1'), 2.313 Å, is almost equal to the linear covalent bond length of 2.36 Å in cinnabar (Aurivillius, 1950), and the collinear Hg-S bond length 2.36 Å in mercury methylmercaptide (Bradley & Kunchur, 1964). The bond length Hg-S(3''), 2.505 Å, is almost equal to the tetrahedral covalent bond length of 2.53 Å in meta-cinnabarite (Wells, 1962), and of 2.520 Å in dimeric mercury diethyldithiocarbamate (Iwasaki, 1973). According to Lawton's (1970) summary, the Hg-S bond

length of 2.50 ~ 2.60 Å is most frequently observed in the tetrahedral arrangement of S atoms around the Hg atom. The longest, 2.943 Å, is equal to the sum of the

Table 2. *Intramolecular distances (Å) and angles (°) with e.s.d.'s*

Notation: unprimed: x, y, z ; singly primed: $-x, y - \frac{1}{2}, -z$; doubly primed: $-x, y + \frac{1}{2}, 1 - z$.

Hg-S(1')	2.313 (8)	S(1')-Hg-S(2)	112.6 (3)
Hg-S(2)	2.943 (10)	S(1')-Hg-S(3'')	148.8 (3)
Hg-S(3'')	2.505 (9)	S(1')-Hg-S(4)	99.1 (3)
Hg-S(4)	2.749 (8)	S(2)-Hg-S(3'')	86.4 (3)
S(1)-C(1)	1.694 (28)	S(2)-Hg-S(4)	81.8 (3)
S(2)-C(1)	1.666 (29)	S(3'')-Hg-S(4)	108.3 (3)
C(1)-O(1)	1.35 (4)	Hg-S(1')-C(1')	102.1 (12)
O(1)-C(3)	1.41 (3)	Hg-S(2)-C(1)	103.7 (11)
C(3)-C(4)	1.52 (6)	S(1)-C(1)-S(2)	121.9 (21)
S(3)-C(2)	1.712 (29)	S(1)-C(1)-O(1)	115.0 (18)
S(4)-C(2)	1.629 (30)	S(2)-C(1)-O(1)	122.9 (19)
C(2)-O(2)	1.35 (3)	C(1)-O(1)-C(3)	118.5 (21)
O(2)-C(5)	1.45 (4)	O(1)-C(3)-C(4)	103.4 (26)
C(5)-C(6)	1.54 (6)	Hg-S(3'')-C(2'')	101.9 (10)
Hg-S(3)	3.382 (8)	Hg-S(4)-C(2)	98.4 (9)
		S(3)-C(2)-S(4)	124.4 (17)
		S(3)-C(2)-O(2)	114.3 (20)
		S(4)-C(2)-O(2)	121.4 (21)
		C(2)-O(2)-C(5)	119.9 (25)
		O(2)-C(5)-C(6)	104.6 (29)

Van der Waals contact distances

S(4)-C(6'', +a)	3.90 (4)
S(4)-C(5'', +a)	3.93 (3)
C(3)-C(4'', +a)	3.88 (6)
C(3)-C(6'', +a, +b)	3.66 (5)
S(1)-S(1', +b)	3.930 (13)
S(2)-S(4)	3.731 (13)
S(3)-S(3'')	3.854 (11)

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32826 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Atomic parameters with e.s.d.'s in parentheses ($\times 10^4$)*

The B_{eq} values are the equivalent isotropic temperature factors (Hamilton, 1959).

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Hg	346 (1)	10000 (7)	2618 (1)	3.4
S(1)	332 (8)	12559 (13)	-905 (8)	3.6
S(2)	2490 (8)	12491 (15)	1761 (9)	4.1
S(3)	287 (8)	7854 (11)	5946 (8)	3.5
S(4)	2588 (8)	8224 (14)	4292 (9)	3.9
O(1)	2192 (15)	15186 (49)	-343 (16)	3.0
O(2)	2321 (18)	5481 (30)	6174 (19)	3.2
C(1)	1709 (27)	13565 (51)	202 (30)	3.3
C(2)	1807 (26)	7112 (40)	5481 (30)	2.9
C(3)	3312 (31)	16148 (47)	535 (31)	3.7
C(4)	3489 (48)	17945 (78)	-368 (56)	7.4
C(5)	3599 (30)	4677 (74)	5863 (35)	6.6
C(6)	3751 (41)	2725 (61)	6691 (40)	5.9

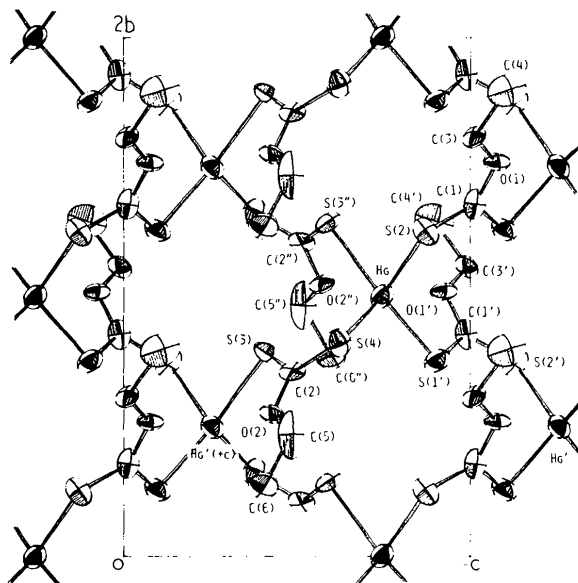


Fig. 1. The molecular aggregation of $\text{Hg}(\text{SSCOC}_2\text{H}_5)_2$ viewed along *a*.

ionic radii of Hg and S atoms, 2.95 Å (Pauling, 1960). The bond length 2.749 Å is intermediate between the tetrahedral covalent and ionic distances.

The S—Hg—S bond angles of the distorted tetrahedral configuration range from 81.8 to 148.8°; the widest takes the value intermediate between those of tetrahedral and linear bicovalent arrangements. It occurs between the two shortest bonds. The observed distortion of the metal—sulphur tetrahedral arrangement increases in the order: Zn(SSCOC₂H₅)₂, Cd(SSCOC₂H₅)₂ and Hg(SSCOC₂H₅)₂.

Calculations were carried out on a FACOM 230-75 computer with the program system UNICS2 (Sakurai, Iwasaki, Watanabe, Kobayashi, Bando & Nakamichi, 1974). Fig. 1 was drawn with ORTEP (Johnson, 1965). The author wishes to thank Professor H. Hagihara for his valuable advice.

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(RS)-1,4-Dibenzoyl-cis-2,5-dimethylpiperazine

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Abstract. C₂₀H₂₂N₂O₂, monoclinic, *P*2₁/*a*, *Z* = 4, *a* = 11.220 (6), *b* = 14.571 (6), *c* = 10.688 (7) Å, β = 99.38 (8)°, *U* = 1724 (2) Å³, *d_m* = 1.22, *d_c* = 1.24 g cm⁻³. The six-membered piperazine ring forms a twist-boat conformation.

Introduction. Ordinary N-containing six-membered rings have been known to form the chair conformation (Kellie & Riddell, 1974). During the NMR study of chiral piperazines, a twist-boat conformation of the piperazine ring was proposed for the title compound (Tsuboyama *et al.*, 1977). To verify this result an X-ray diffraction study was performed

Single crystals were grown by the slow evaporation of an ethyl acetate solution. Two different crystal forms were obtained from the same batch: one is prismatic, and the other is thick tabular. A careful examination of Weissenberg photographs revealed that these two forms have an identical unit cell. The prismatic form is

elongated in the *a* direction, and the tabular face is {001}. The tabular crystals were used for further X-ray investigations. Diffraction intensities were collected on a Rigaku automated four-circle diffractometer with graphite-monochromatized Cu K_α radiation and 2θ ≤ 140°. The size of the crystal used was 0.3 × 0.4 × 0.5 mm. The usual Lorentz and polarization corrections were applied. The number of observed reflections was 2190.

The structure was solved by a direct phasing method, and all H atoms were deduced from successive difference Fourier syntheses. The structure was refined by the block-diagonal least-squares method. Unit weight was given to all reflections, and anisotropic temperature factors were used for all non-hydrogen atoms. The final *R* index was 5.6%. Atomic parameters are given in Table 1.†

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32827 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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