

## Crystal and Molecular Structure of *O*-Methylbenzoin Methylmercurio-(*p*-tolylsulphonyl)hydrazone

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The structure of the title compound was obtained by the heavy-atom method and refined to  $R$  0.08 for 2 386 observed reflections. Crystals are monoclinic, space group  $P2_1/a$ , with unit-cell dimensions  $a = 10.695(1)$ ,  $b = 14.166(2)$ ,  $c = 15.032(3)$  Å,  $\beta = 104.06(3)^\circ$ , and  $Z = 4$ . The co-ordination around mercury is linear, with a nitrogen atom from the azo-group on the side opposite to a methyl group, with Hg–N 2.05(2), Hg–C 2.04(2) Å, and N–Hg–C 175(5)°. Some chemical features of the hydrazones are discussed in terms of molecular geometry.

In the last few years it has been observed<sup>1</sup> that treatment of aldehyde and ketone *p*-tolylsulphonylhydrazones with mercury(II) acetate, phenylmercury(II) hydroxide or phenylmercury(II) acetate gave respectively *NN'*-mercuriobis-*p*-tolylsulphonylhydrazones and phenylmercurio-(*p*-tolylsulphonyl)hydrazones in nearly quantitative yields. These reactions are the first examples in which metal-hydrazone intermediates have been isolated from reactions of hydrazones with metal-containing oxidizing agents. On the other hand alarm has been expressed in recent reviews<sup>2</sup> on the chemistry of methylmercury(II), because of its toxic nature. In order to throw some light on the bonding properties of this group, Wong and co-workers<sup>3,4</sup> have published some exhaustive *X*-ray work, and the desirability of this from a purely structural point of view has been stressed.<sup>5-7</sup>

Recently we have synthesized several *N*-methylmercurio-*N*-*p*-tolylsulphonylhydrazones of ketones bearing an asymmetric centre in the  $\alpha$  position with respect to the iminium carbon. We describe here the detailed structure of *O*-methylbenzoin methylmercurio-(*p*-tolylsulphonyl)hydrazone (1).

### EXPERIMENTAL

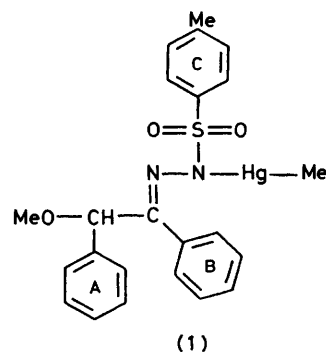
*Preparation of O-Methylbenzoin Methylmercurio-(p-tolylsulphonyl)hydrazone*, (1).—Benzoin methyl ether *p*-tolyl-

<sup>1</sup> R. N. Butler and W. B. King, *Chem. and Ind.*, 1975, 647; *J.C.S. Perkin I*, 1976, 986; G. Rosini and A. Medici, *Synthesis*, 1976, 530.

<sup>2</sup> L. Dunlop, *Chem. Eng. News*, 1971, 22; J. M. Wood, *Adv. Environmental Sci. Technol.*, 1971, 1, 39; F. M. D'Itri, 'The Environmental Mercury Problem,' CRC Press, Cleveland, 1972.

<sup>3</sup> Y. C. Wong, P. C. Chieh, and A. J. Canty, *J.C.S. Chem. Comm.*, 1973, 741; *Canad. J. Chem.*, 1973, 51, 2597.

sulphonylhydrazone (1.97 g, 5 mmol) was dissolved in boiling methanol (100 ml) and the solution cooled to 30 °C. Methylmercury(II) acetate (1.97 g, 5 mmol) was then added and after a few minutes the mercurio-derivative (I) crystallized as thin needles, which were dried *in vacuo* (2.8 g, 93%), m.p. 182–183 °C (Found: C, 45.1; H, 3.8;



N, 4.45.  $C_{23}H_{24}HgN_2O_3S$  requires C, 45.35; H, 3.97; N, 4.59%,  $\nu_{\max}$  (KBr) 1 610 (C=N), 1 135, and 1 280  $cm^{-1}$  (both  $SO_2$ ) (no N–H bands);  $\tau$  2.05 (2 H, part of  $A_2B_2$ ,  $J = 8.0$  Hz), 2.4–3.35 (12 H, overlapping m, other aromatic protons), 4.8 (1 H, s, benzylic proton), 6.55 (3 H, s, OMe), 7.45 (3 H, s, *p*-Me), and 9.75 [3 H, s, HgMe,  $J(^{199}HgMe)$  210 Hz].

*Crystal Data*.— $C_{23}H_{24}N_2HgO_3S$ ,  $M = 609.1$ . Monoclinic,

<sup>4</sup> Y. C. Wong, N. J. Taylor, P. C. Chieh, and A. J. Canty, *J.C.S. Chem. Comm.*, 1974, 625.

<sup>5</sup> D. Grdenic, *Quart. Rev.*, 1965, 19, 303.

<sup>6</sup> L. D. Kosturko, C. Folzer, and R. F. Stewart, *Biochemistry*, 1974, 13, 3949.

<sup>7</sup> M. B. Hursthouse, 'Molecular Structure by Diffraction Methods,' *Chem. Soc. Specialist Periodical Report*, 1973, vol. I, p. 724.

$a = 10.695(1)$ ,  $b = 14.166(2)$ ,  $c = 15.032(3)$  Å,  $\beta = 104.06(3)^\circ$ ,  $U = 2209.2$  Å<sup>3</sup>,  $D_c = 1.84$ ,  $Z = 4$ ,  $F(000) = 1088$ . Mo- $K_\alpha$  radiation,  $\lambda = 0.7107$  Å. Space group  $P2_1/a$  from systematic absences.

**Intensity Data Collection.**—Unit cell parameters were determined from the least squares fit to the  $(\theta, \phi, \chi)_{hkl}$  values of 20 reflections measured on a diffractometer. A crystal fragment of dimensions  $0.015 \times 0.02 \times 0.01$  mm was sealed in a capillary owing to its low stability. Intensities were collected on a Philips PW 1100 single-crystal diffractometer by the  $\omega$ — $2\theta$  scan technique. As the intensities of three standard reflections showed evidence of crystal decay, the final data were obtained after a rescaling procedure based on the observed variations. Of 4153 independent reflections, 2386 having  $I > 3\sigma(I)$  were considered observed and used in the analysis. No corrections for absorption was made ( $\mu R$  0.9). After corrections for Lorentz and polarization factors, structure amplitudes were put on absolute scale, first by Wilson's method and then by correlation between calculated and observed values.

**Structure Determination and Refinement.**—The structure was solved by the heavy-atom method. Two subsequent Fourier maps gave the co-ordinates of all non-hydrogen atoms. Least-squares refinement converged to an agreement factor  $R$  of 0.08 anisotropic temperature factors being assigned only to Hg, S(21), O(22), O(23), C(2), and C(8). By use of unit weights, a flat variance resulted in terms of

TABLE 1

Fractional atomic co-ordinates ( $\times 10^4$ ) with estimated standard deviations in parentheses

Atom	$x$	$y$	$z$
Hg	7 633(1)	7 771(1)	6 320(1)
C(2)	5 989(21)	7 654(18)	5 302(15)
N(3)	9 357(14)	7 804(13)	7 288(10)
N(4)	10 040(16)	8 531(12)	7 865(11)
C(5)	9 661(18)	9 389(14)	7 602(13)
C(6)	10 510(21)	10 116(16)	8 261(15)
O(7)	9 669(14)	10 588(11)	8 679(10)
C(8)	10 347(30)	11 097(17)	9 484(17)
C(9)	11 076(17)	10 808(13)	7 702(12)
C(10)	10 470(21)	11 661(17)	7 369(15)
C(11)	11 068(25)	12 282(21)	6 880(18)
C(12)	12 209(23)	11 991(18)	6 696(17)
C(13)	12 690(24)	11 125(19)	6 951(17)
C(14)	12 190(22)	10 567(17)	7 479(16)
C(15)	8 720(18)	9 715(13)	6 802(13)
C(16)	7 430(20)	9 996(16)	6 906(14)
C(17)	6 553(24)	10 294(18)	6 084(17)
C(18)	6 888(25)	10 328(19)	5 250(18)
C(19)	8 084(23)	10 010(18)	5 203(16)
C(20)	9 042(24)	9 689(18)	5 976(17)
S(21)	9 996(5)	6 810(4)	7 669(4)
O(22)	11 371(13)	6 785(10)	7 760(10)
O(23)	9 231(14)	6 140(10)	7 060(10)
C(24)	9 683(19)	6 624(15)	8 718(13)
C(25)	8 429(20)	6 693(16)	8 819(14)
C(26)	8 228(22)	6 484(16)	9 669(15)
C(27)	9 236(20)	6 272(15)	10 390(14)
C(28)	10 473(22)	6 232(17)	10 285(15)
C(29)	10 729(22)	6 431(17)	9 464(15)
C(30)	8 916(24)	6 019(18)	11 270(17)

$\sin \theta$  and the magnitude of  $|F_o|$ ; no attempt was made to locate hydrogen atoms.

After the last cycle of refinement the maximum shift-error was 0.16, 0.30, 0.18, and 0.5 for  $x$ ,  $y$ ,  $z$ , and  $B$  parameters.

\* See Notice to Authors No. 7, in *J.C.S. Perkin I*, 1977, Index issue.

<sup>8</sup> A. Immerzi, *Ricerca Sci.*, 1973, **37**, 743.

Final positional parameters with their estimated standard deviations are quoted in Table 1; observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22218 (20 pp.).\*

Calculations were performed on the CDC system installed at the Centro di Calcolo dell'Italia Nord-Orientale with locally modified versions of programs written by A. C. Larson and W. D. S. Motherwell. The least-squares program of Immerzi<sup>8</sup> was also used.

## RESULTS AND DISCUSSION

The molecular structure of the compound is shown in Figure 1 together with the arbitrary crystallographic

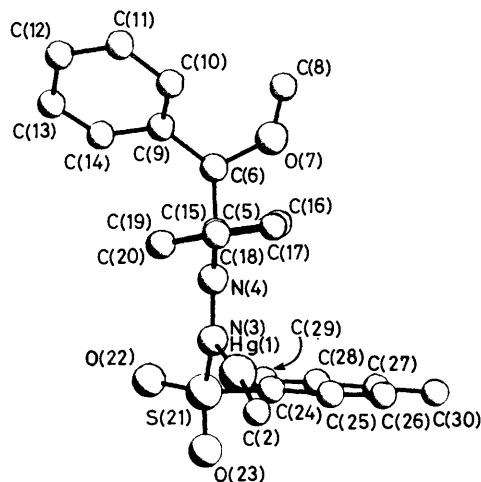


FIGURE 1 The molecule viewed along the line C(18) ··· C(15) atom system. The most significant distances and angles are listed in Table 2.

TABLE 2

Bond distances (Å) and angles ( $^\circ$ ), with standard deviations in parentheses

(a) Distances			
Hg—C(2)	2.04(2)	C(6)—O(7)	1.39(3)
Hg—N(3)	2.05(2)	C(6)—C(9)	1.51(3)
N(3)—N(4)	1.43(2)	O(7)—C(8)	1.44(3)
N(3)—S(21)	1.61(2)	S(21)—O(22)	1.44(2)
N(4)—C(5)	1.31(3)	S(21)—O(23)	1.43(2)
C(5)—C(6)	1.56(3)	S(21)—C(24)	1.71(2)
C(5)—C(15)	1.44(3)		
(b) Angles			
C(2)—Hg—N(3)	175(5)	C(6)—O(7)—C(8)	111.9(9)
Hg—N(3)—N(4)	133(1)	C(6)—C(9)—C(10)	123(1)
Hg—N(3)—S(21)	117.5(4)	C(6)—C(9)—C(14)	118(1)
N(4)—N(3)—S(21)	107.8(4)	N(3)—S(21)—O(22)	112.9(5)
N(3)—N(4)—C(5)	114.2(8)	N(3)—S(21)—O(23)	103.1(5)
N(4)—C(5)—C(6)	109.4(7)	N(3)—S(21)—C(24)	107.6(5)
N(4)—C(5)—C(20)	117.2(4)	O(22)—S(21)—O(23)	117.1(6)
C(6)—C(5)—C(20)	120.1(5)	O(22)—S(21)—C(24)	109.4(5)
C(5)—C(6)—O(7)	105.4(8)	O(23)—S(21)—C(24)	106.2(5)
C(5)—C(6)—C(9)	109.0(8)	S(21)—C(24)—C(25)	119.9(9)
O(7)—C(6)—C(9)	109.3(7)	S(21)—C(24)—C(29)	118(1)

In this compound the diagonal linear co-ordination, considered normal<sup>5,9</sup> for mercury(II) derivatives, is maintained. Table 3 gives a comparison of available data<sup>10</sup> for methylmercury(II) bonded to nitrogen. It

<sup>9</sup> I. P. Beletskaya, K. P. Butin, A. N. Ryabtsev, O. A. Reutov, *J. Organometallic Chem.*, 1973, **59**, 1.

<sup>10</sup> Cambridge Crystallographic Data File, 1976.

shows that there is no difference in bond length between mercury and  $sp^2$  or  $sp^3$  hybridized carbon and nitrogen atoms.

A review of the existing literature on mercury(II) organometallic compounds reveals a surprising lack of

TABLE 3

Comparison of C-Hg-N linear co-ordination

Compound	C-Hg	Hg-N	C-Hg-N
Methylmercury azide <sup>a</sup>	2.27 Å	2.22 Å	173.4°
Methyl-(DL-methioninato)-mercury <sup>b</sup>	2.11	2.06	173.0
Penicillaminebis(methylmercury) <sup>c</sup>	2.16	2.21	168.0
Methyl-(2,2'-bipyridyl)-mercury nitrate <sup>d</sup>	2.06	2.23	164.0
Methylmercurio-( <i>p</i> -tolylsulphonyl)hydrazone <sup>e</sup>	2.04	2.05	174.9

<sup>a</sup> U. Müller, *Z. Naturforsch.*, 1973, **B28**, 426. <sup>b</sup> Ref. 4. <sup>c</sup> Ref. 3. <sup>d</sup> A. J. Canty, A. Marker, and B. M. Gatehouse, *J. Organometallic Chem.*, 1977, **88**, C31. <sup>e</sup> Present work.

accurate data: even the first decimal place is quite uncertain, if one allows for  $3\sigma$  of the bond length. This is due predominantly to the quality of the reflection data for organomercury(II) compounds. Another consideration is that the nature and number of the bonds also causes confusion in determining the existing pattern of experimental bond distances: a review of structural data on mercury(II) organometallic compounds is therefore being planned.

The mercury atom has an intermolecular contact of 2.93 Å with O(22) and an intramolecular contact of 2.89 Å with O(23): from a consideration of the van der Waals radius<sup>5</sup> of mercury and of the sphere of influence of benzene any interaction with the benzene ring has to be excluded, the mercury lying 3.09 Å above the edge [C(15)-C(20) bond] of the hexagon.

The overall geometry of the remainder of the molecule is as expected; the least-squares planes calculated for the phenyl rings show root-mean-square deviations of 0.017–0.033 Å.

Consideration of Figure 1 and Table 4, which lists

TABLE 4

Relevant torsion angles (°)

O(23)-S(21)-N(3)-N(4)	-179
O(23)-S(21)-N(3)-Hg	-10
S(21)-N(3)-N(4)-C(5)	-176
Hg-N(3)-N(4)-C(5)	18
N(3)-N(4)-C(5)-C(6)	-178
N(3)-N(4)-C(5)-C(15)	-3
N(4)-C(5)-C(15)-C(16)	102
N(4)-C(5)-C(6)-H(6)	6
N(4)-C(5)-C(6)-O(7)	-115

relevant torsion angles, shows that: (i) phenyl ring B is normal to the supposedly conjugated planar system formed by N(3)-N(4)=C(5)-C(6), an effect often observed previously when steric hindrance occurs (calculations of

minimum potential energy have suggested that phenyl ring A, and not mercury, is responsible for the hindrance); (ii) O(23), S(21), N(3), N(4), C(5), C(6), and H(6) [this hydrogen attached to C(6) was located at the calculated position 1.1212, 0.9798, 0.8708] lie approximately in the same plane: the bonds C(6)-H(6) and N(3)-S(21) eclipse the double bond, and are respectively *cis* and *trans*; (iii) N(3) has an almost  $sp^2$  configuration, as is also shown by the bond angles, and is 0.1 Å from the plane formed by S(21), Hg, and N(4); and (iv) there is a remarkable approach between the Hg atom and the sulphonyl oxygen atoms, shown clearly in the i.r. spectra.

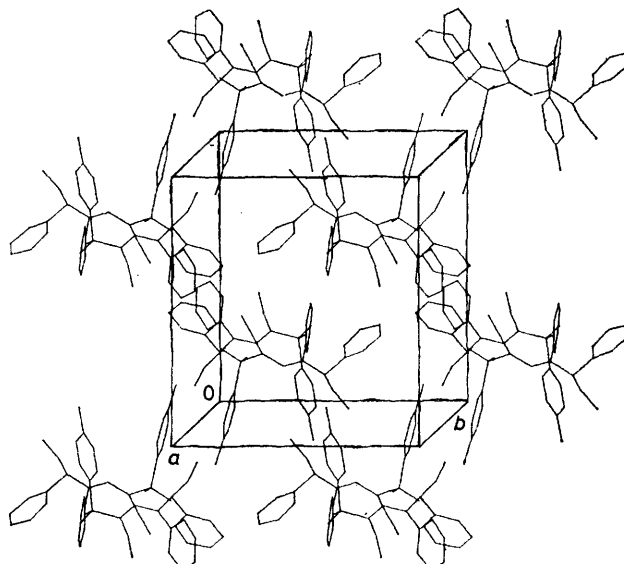


FIGURE 2 A perspective view of the molecular packing

Intermolecular contacts  $< 3.6$  Å are reported in Table 5, and the molecular packing is shown in Figure 2.

TABLE 5

Intermolecular distances  $< 3.6$  Å

Hg...O(22 <sup>II</sup> )	2.93	C(13)...C(19 <sup>I</sup> )	3.60
C(2)...C(11 <sup>III</sup> )	3.58	C(14)...O(23 <sup>II</sup> )	3.44
N(3)...O(22 <sup>II</sup> )	3.49	C(16)...O(22 <sup>II</sup> )	3.18
N(4)...C(25 <sup>II</sup> )	3.58	O(22)...C(25 <sup>II</sup> )	3.24

Roman numeral superscripts refer to the following atom positions relative to the reference molecule at  $x, y, z$ : II  $\frac{1}{2} + x, \frac{1}{2} - y, z$ ; III  $\frac{1}{2} - x, \frac{1}{2} + y, -z$ .

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[7/1133 Received, 29th June, 1977]

<sup>11</sup> W. D. S. Motherwell, in 'Crystallographic Data Centre Manual,' Cambridge, 1976.