Journal of Organometallic Chemistry, 191 (1980) 339—345

THE CRYSTAL STRUCTURE OF DI-*ortho*-TOLYLMERCURY

DAVID LIPTAK, WILLIAM H. ILSLEY, MILTON D. GLICK and JOHN P. OLIVER *
Department of Chemistry, Wayne State University, Detroit, Michigan 48202 (U.S.A.)

(Received November 6th, 1979)

Summary

The structure of di-*ortho*-tolylmercury has been determined by single crystal X-ray methods from counter data. The compound crystallizes in the monoclinic space group $C2/c$ with unit cell dimensions a 10.970(2), b 10.448(3), c 11.409(3) Å; β 115.48(2)°, V 1180.5(5) Å^3, ρ_{calc} 2.158 g/cm^3 and $Z = 4$. The structure was solved with conventional heavy atom techniques. The crystal consists of individual molecular units with the mercury atom located on the crystallographic 2-fold axis of symmetry. The C—Hg—C fragment is nearly linear with an angle of 178.0(4)°. The methyl groups lie on the same side of the molecule and the rings are twisted with respect to one another by 58.9°. The Hg—C bond distance is 2.09(1) Å.

Introduction

In the past few years we have been interested in the structure of mercury compounds. In searching the literature for structures of simple organomercury derivatives we found that the structures of only four symmetrically substituted compounds have been reported: $(CH_3)_2Hg$ [1], $(C_6H_5)_2Hg$ [2], $[p\text{-}CH_3C_6H_4]_2$-Hg [3], and $(C_6F_5)_2Hg$ [4]. The structure of $(CH_3)_2Hg$ was obtained from electron diffraction data in the gas phase and the other three were determined by X-ray diffraction in the solid state. In both $(C_6H_5)_2Hg$ and $[p\text{-}CH_3C_6H_4]_2Hg$ the rings are coplanar and contain a linear C—Hg—C moiety. In $(C_6F_5)_2Hg$ the phenyl rings are twisted relative to each other by an angle of 59.4(1.2)° and the C—Hg—C moiety remains nearly linear with an angle of 176.2(1.2). These data, therefore, indicate that substitution of a fluorine in the *ortho* position of a phenyl ring results in steric repulsions large enough to force the two phenyl rings to be non-coplanar. In order to examine further the effects of steric repulsions on the relative orientation of the rings, we have determined the structure of $[o\text{-}CH_3(C_6H_4)]_2Hg$. In this derivative the phenyl rings may occupy the same plane if the methyl groups are *trans* to one another; however, if they are *cis* to one another, steric effects should prevent the rings from occupying the same plane with the dihedral angle between the rings serving as a rough measure of the repulsive interactions between the *ortho* substituents.

Experimental

Preparation of (o-tolyl)$_2$Hg

(o-tolyl)$_2$Hg was prepared by the addition of a THF slurry of Hg_2Cl_2 * (69.74 g 0.30 mol) to a solution of (o-tolyl)MgBr prepared from 7.87 g (0.324 mol) of Mg and 50.0 g (0.292 mol) of o-tolylbromide in 250 ml of THF. The resulting material was isolated and sublimed. A ^{13}C NMR spectrum of this material indicated that it was a mixture of (o-tolyl)$_2$Hg and (o-tolyl)HgCl. This mixture was then treated with sodium stannite using the procedure developed by Nesmeyanov [5]. The resulting product was purified by vacuum sublimation (10^{-5} Torr, 80°C, 2 days) to give 48.4 g of (o-tolyl)$_2$Hg.

X-Ray data collection

The crystal used for data collection was grown by slow sublimation at 80°C and 10^{-5} torr. The faces were not well defined but the approximate shape was that of a trigonal prism with triangular edges about 0.15 mm and height about 0.25 mm. The crystal was secured to a glass fiber with epoxy and mounted on a Syntex P2$_1$ four-circle X-ray diffractometer. Oscillation photographs followed by careful centering of fifteen reflections indicated a monoclinic crystal system having lattice constants a 10.970(2), b 10.448(3), c 11.409(3) Å and β 115.48(2)°. A preliminary data set indicated systematic absences of $h + k = 2n + 1$ for hkl and $l = 2n + 1$ for $h0l$, consistent with the space groups Cc and $C2/c$.

Intensity data were collected by the $\theta - 2\theta$ scan technique using Mo-K_α radiation (λ 0.71069 Å), which had been diffracted from a highly oriented graphite crystal, at a scan rate of 2°/min and a scan range of 2θ (Mo-$K_{\alpha 1}$) $- 1.0$ to 2θ (Mo-$K_{\alpha 2}$) $+ 1.0$. Background counts were collected for a time equal to one-half the scan time and the standard deviations on the intensities were assigned as follows:

$$(I) = [\sigma(I)^2_{\text{counter}} + (0.04 \times I)^2]^{1/2}$$

where $\sigma(I)^2_{\text{counter}} = (I + K^2B)^{1/2}$, I = net intensity, B = total background counts and K is the ratio of scan time to background time.

Independent data ($\bar{h}$, $\bar{k}$, $\pm l$, $h + k = 2n$) totalling 1438 reflections were collected to a maximum 2θ of 55°. Of these reflections, 207 data had $I < 2.5\sigma$ and were therefore considered unobserved. In addition, 16 weak reflections were symmetry forbidden in the space group $C2/c$ and were deleted from the data set yielding a total of 1215 data which were used in the refinement. The intensities of three standard reflections were measured every 97 reflections and

---

* Mercurous chloride was accidently used rather than mercuric chloride for this preparation. This, however, has been shown to yield the corresponding organomercuric halide, but in approximately half the yield for the reaction with the mercuric halide. The resulting reaction yielded the (p-tolyl) mercuric halide in moderate yield with elimination of metallic mercury.

showed no significant decrease in intensity throughout data collection.

Due to the inability to obtain a crystal with well defined morphology we were unable to make the standard analytical absorption correction and therefore used an empirical method. The method chosen was that involving the psi-scan technique as reported by North, et al. [6]. A total of 12 curves were used covering the 2θ range 7.5 to 39 degrees. The high angle data were not corrected for absorption since curves were not available at that time, but were scaled appropriately. Each reference curve was collected at 10° intervals in psi from 0 to 350° at 2°/min. Empirical correction factors varied from 1.0 to 2.3.

Solution

The structure was solved in the monoclinic space group $C2/c$ by conventional heavy atom techniques [7]. Solution of a three dimensional Patterson function gave the position of the mercury atom. Subsequent Fourier and difference syntheses established the remaining non-hydrogen positions. Hydrogen atom positions were then calculated and assigned positions 1.08 Å from the carbon atoms in expected geometry, with the methyl hydrogens in the staggered configuration.

Subsequent full matrix least squares refinement of the non-hydrogen atomic

TABLE 1

ATOMIC COORDINATES AND THERMAL PARAMETERS FOR $(o\text{-tol})_2Hg$ [a, b]

Atom	x	y	z	B_{iso}
Hg(1)	0.2500(—)	0.2986(1)	−0.2500(—)	
C(2)	0.1165(10)	0.2950(8)	−0.0532(9)	
C(3)	0.0277(12)	0.1920(8)	−0.0040(11)	
C(4)	−0.0607(12)	0.1844(9)	−0.1264(12)	
C(5)	−0.0614(13)	0.2803(9)	−0.2117(10)	
C(6)	0.0243(10)	0.3831(10)	−0.1629(9)	
C(7)	0.1143(8)	0.3922(8)	−0.0309(8)	
C(8)	0.2047(11)	0.5082(11)	−0.0161	
H(9)	0.0281	0.1166	−0.0690	3.68
H(10)	0.1290	0.1042	−0.1619	4.10
H(11)	0.1279	0.2742	−0.3141	3.99
H(12)	0.0223	0.4589	−0.2281	3.74
H(13)	0.1831	0.5583	−0.0879	4.58
H(14)	0.3091	0.4781	−0.0590	4.58
H(15)	0.1867	0.5711	−0.0648	4.58

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hg(1)	0.0076(1)	0.0080(1)	0.0057(1)	0.0(—)	0.0018(1)	0.0(—)
C(2)	0.0071(9)	0.0075(8)	0.0056(7)	0.0016(6)	0.0018(7)	0.0001(6)
C(3)	0.0098(12)	0.0073(9)	0.0074(9)	0.0003(7)	0.0037(9)	0.0007(6)
C(4)	0.0096(12)	0.0078(10)	0.0099(11)	0.0007(8)	0.0038(10)	−0.0017(7)
C(5)	0.0099(12)	0.0093(10)	0.0066(9)	0.0013(8)	0.0026(9)	0.0003(7)
C(6)	0.0084(9)	0.0096(10)	0.0067(8)	0.0012(8)	0.0029(7)	0.0019(7)
C(7)	0.0059(8)	0.0075(8)	0.0075(7)	0.0011(7)	0.0035(6)	0.0004(7)
C(8)	0.0104(12)	0.0089(10)	0.0122(12)	0.0011(9)	0.0069(10)	0.0007(9)

[a] Standard deviations from the variance-covariance matrix are given in parentheses for the least significant digit(s) in all tables. [b] The form of the anisotropic temperature factor reported here is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

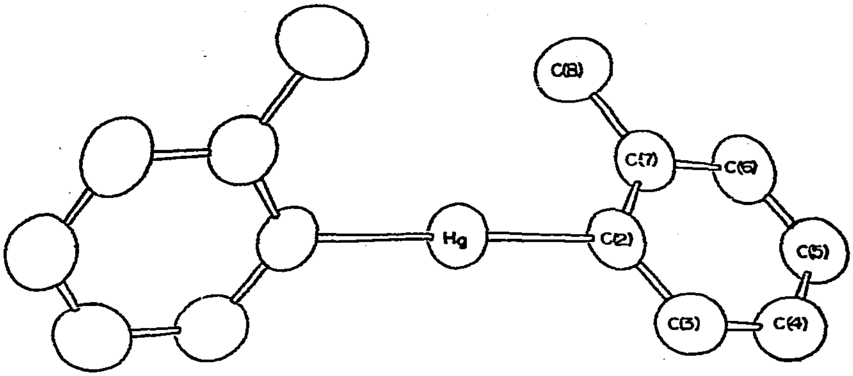


Fig. 1. A perspective view of the di(*o*-tolyl)mercury molecule. The pertinent distances and angles are given in Table 2.

positional parameters and anisotropic temperature factors, with fixed contributions from the hydrogen atoms having isotropic thermal parameters assigned values 10% higher than those of the heavy atoms to which they are attached, yielded final values for the discrepancy factors of

$$R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0| = 0.047 \text{ and}$$

$$R_2 = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2)]^{1/2} = 0.064.$$

The maximum residual electron density in the final difference synthesis was 1.2 $e/\text{Å}^3$ in the vicinity of the mercury atom. In view of the reasonable agree-

TABLE 2

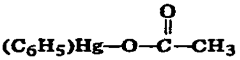
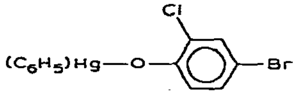
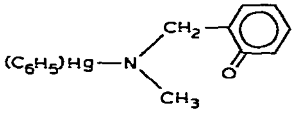
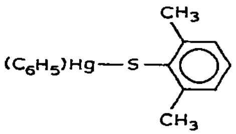
BOND DISTANCES AND ANGLES FOR $(o\text{-tol})_2\text{Hg}$ [a]

	Distance (Å)
Hg(1)—C(2)	2.09(1)
C(2)—C(3)	1.40(1)
C(2)—C(7)	1.39(1)
C(3)—C(4)	1.38(2)
C(4)—C(5)	1.40(2)
C(5)—C(6)	1.38(2)
C(6)—C(7)	1.40(1)
C(7)—C(8)	1.51(1)
	Angle (°)
C(2')—Hg(1)—C(2)	178.0(4)
Hg(1)—C(2)—C(3)	119.4(7)
Hg(1)—C(2)—C(7)	121.7(7)
C(7)—C(2)—C(3)	118.9(9)
C(2)—C(3)—C(4)	121.4(9)
C(3)—C(4)—C(5)	120.0(10)
C(4)—C(5)—C(6)	118.7(10)
C(5)—C(6)—C(7)	122.0(9)
C(6)—C(7)—C(2)	119.1(8)
C(2)—C(7)—C(8)	121.8(8)
C(6)—C(7)—C(8)	119.2(9)

[a] The primed atom corresponds to the atom generated by the 2 fold axis of symmetry.

TABLE 2

SUMMARY OF STRUCTURAL DATA ON SELECTED ORGANO-MERCURY DERIVATIVES

Compound	Hg—C (Å)	Hg—X (Å)	X—Hg—Y (°)	Ref.
CH_3HgCN	2.05(1), 2.01(5) (cyanide) 2.08(2), 2.15(5) (methyl)		180(2), 180(6)	9, 10
$Cl—Hg—(CH_2)_2N(CH_2CH_3)_2$	2.13(3)	2.36(1)	167.1(8)	11
$(C_6F_5)_2Hg$	2.09		176.2(1.2)	3
$[p\text{-}CH_3(C_6H_4)]_2Hg$	2.08(2)		180.0	12
 $(C_6H_5)Hg—O—\overset{\overset{O}{\parallel}}{C}—CH_3$	1.92(6)	2.11(4)	170(2)	13
$(C_6H_5)CH_2Hg—S—C(Ph)_3$	2.10	2.363	179	14
trans—$ClCH{=}CHHgCl$	2.10(11)	2.30(2)	167(5)	2
$(C_6H_5)_2Hg$	2.10		180	15
$(C_6H_5)COCH{=}CHHg—Cl$	2.33	2.37	178	16
	2.07	2.01	174	17
	2.02(4)	2.12(3)	167(1)	18
	1.97(6)	2.33(1)	172(1)	19
$(C_6H_5)CH_2HgSC(C_6H_5)_3$	2.10	2.363	179	20
$(CH_3)_2Hg$	2.2(1), 2.23(4) 2.094(5), 2.083(5)		180	1a, 21 22, 23
CH_3HgCl	2.06(2), 2.06(3)	2.282(5)	180 (gas)	24, 25
CH_3HgBr	2.074(15)	2.406(5)	180,(gas)	24
$(CN)_2Hg$	1.99(9)		176.5(2.5)	26
CH_3HgI	2.087(10)	2.528(5)	180 (gas)	27

ment and parameter values for an organomercury structure, no attempt was made to refine the structure in the acentric space group. The atomic coordinates and anisotropic thermal parameters are presented in Table 1. A listing of the structure factors is available *.

---

* The Table of structure factors has been deposited as NAPS Document No. 03597 Order from ASIS/NAPS, c/o Microfiche Publications, 440 Park Avenue South, New York, New York 10016. A copy may be secured by citing the document number, remitting $ 5.00 for photocopies or $ 3.00 for microfiche. Advanced payment is required. Make checks payable to Microfiche Publications. Outside of the U.S.A. and Canada, postage is $ 2.00 for photocopies or $ 1.00 for a fiche.

Results and discussion

The compound di(*ortho*-tolyl)mercury consists of individual molecular units with the central mercury atom located on a crystallographic 2-fold axis of symmetry as shown in Fig. 1. The ring carbon distances vary from 1.38(1) to 1.40(1) Å as given in Table 2 with an average distance of 1.39(1) Å and with ring angles from 118.7(10) to 122.0(9)° in agreement with expected values. The methyl carbon—ring distance is 1.51(1) Å. The C—Hg—C fragment is nearly linear with an angle of 178.0(4)°. The mercury—carbon distance of 2.09(1) Å is in good agreement with the distances reported for other alkyl- and aryl-mercury compounds (see Table 3).

Each phenyl ring in $(o\text{-}CH_3C_6H_5)_2Hg$ is planar but, contrary to what has been observed in $(C_6H_5)_2Hg$ and $(o\text{-}CH_3C_6H_5)_2Hg$, the two phenyl rings are not coplanar. They are twisted relative to one another by an angle of 58.9° with the methyl groups on the same side of the molecule. This twisting is similar to that observed in $(C_6F_5)_2Hg$ where the dihedral angle is 59.4(1.2)° but significantly less than the 70.6° observed in *m*-tolidine hydrochloride [8]. These observations are in accord with the increasing steric interactions for this sequence of compounds. There should be essentially no interaction with $(C_6H_5)_2Hg$, increased interaction with two *ortho* fluorine atoms on $(C_6F_5)_2Hg$, roughly comparable interactions with $(o\text{-}CH_3C_6H_5)_2Hg$ and again significantly increased interactions with the *m*-tolidine derivative because of the reduction in distance separating the two rings.

Acknowledgements

This work was supported in part by NSF Grant No. CHE75-127217. W.H.I. was a Lubrizol Foundation Fellow (1977—1978).

References

1 a) L.O. Brockway and H.O. Jenkins, J. Amer. Chem. Soc., 58 (1936) 2036; b) T.A. Babushkina, E.V. Bryukhora, F.K. Velichko, V.I. Pakhomov and G.K. Semin, Zh. Strukt. Khim., 9 (1968) 207.
2 V.I. Pakhomov, A.I. Kitaizonskii, Zh. Strukt. Khim., 7 (1966) 860.
3 N.R. Kunchur and M. Mathew, Chem. Commun., 3 (1966) 71.
4 K. Thomas and G.G. Hess, J. Organometal. Chem., 49 (1973) 133.
5 A.N. Nesmeyanov, A.E. Borisov and N.V. Novikova, Izv. Akad. Nauk. SSSR, Otdel. Khim. Nauk., (1959) 1216.
6 A.C.T. North, D.C. Phillips and F.S. Mathews, Acta Cryst. A, 24 (1968) 351.
7 Local versions of the following programs were used: (a) SYNCOR, W. Schmonsees' program for data reduction; (2) FORDAP, A. Zalkin's Fourier Program; (3) ORFLS and ORFFE, W. Busing, K. Martin, and H. Levy's full-matrix least squares program and function and error program; (4) ORTEP, C.R. Johnson's program for drawing crystal models; scattering factors, including real and imaginary anomalous dispersion corrections for mercury, were taken from "The International Tables for X-Ray Crystallography", Vol. IV, J.A. Ibers and W.C. Hamilton, Eds., Kynoch Press, Birmingham, England, 1974.
8 F. Fowweather and A. Hargreaves, Acta. Cryst., 3 (1950) 81.
9 J.C. Mills, H.S. Preston and C.H.L. Kennard, J. Organometal. Chem., 14 (1968) 33.
10 J.C. Mills and C.H.L. Kennard, Chem. Commun., (1967) 834.
11 K. Toman and G.G. Hess, J. Organometal. Chem., 49 (1973) 133.
12 M. Mathew and N.R. Kunchur, Can. J. Chem., 43 (1970) 429.
13 B. Kamenar and M. Penavic, Inorg. Chim. Acta, 6 (1972) 191.
14 R.D. Bach, A.T. Weibel, W. Schmonsees and M.D. Glick, J. Chem. Soc. Chem. Commun., (1974) 961.
15 B. Ziolkovska, R.M. Myasnikova, A.I. Kitaigorodskii, Zh. Strukt. Khim., 5 (1964) 737.

16 L.G. Kuz'mina, N.G. Bokii, M.I. Rybinskaya, Yu.T. Struchkov and T.V. Popova, Zh. Strukt. Khim., 6 (1971) 1026.
17 L.G. Kuz'mina, N.G. Bokii, Yu.T. Struchkov, D.N. Kravtsov and L.S. Golovchenko, Zh. Strukt. Khim., 14 (1973) 508.
18 L.G. Kuz'mina, N.G. Bokii, Yu.T. Struchkov, V.I. Minkin, L.P. Olekhnovich and I.E. Mikhailov, Zh. Strukt. Khim., 15 (1974) 659.
19 L.G. Kuz'mina, N.G. Bokii, Yu.T. Struchkov, D.N. Kravtsov and E.M. Rokhlina, Zh. Strukt. Khim., 15 (1974) 491.
20 R.D. Bach, A.T. Weibel, W. Schmonsees and M.D. Glick, J. Chem. Soc. Chem. Commun., (1974) 961.
21 A.H. Gregg, B.C. Hamson, G.I. Jenkins, P.L.F. Jones and L.E. Sutton, Trans. Faraday Soc., 33 (1937) 852.
22 K.S. Rao, B.P. Stoicheff and R. Turner, Can. J. Phys., 38 (1960) 1516.
23 K. Kashiwabara, Sh. Konaka, T. Iijima and M. Kimura, Bull. Chem. Soc. Jpn., 46 (1973) 407.
24 W. Gordy and J. Sheridan, J. Chem. Phys., 22 (1954) 92.
25 D.R. Grdenic and A.I. Kitaigorodskii, Zh. Fiz. Khim., 23 (1949) 1161.
26 F.H. Kruse, Acta Cryst., 16 (1963) 105.
27 C. Feige and H. Hartman, Z. Naturforsch., A, 22 (1967) 1286.