Diphenylmercury: a Refinement

By D. Grdenić, B. Kamenar and A. Nagl

Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, PO Box 153, 41001 Zagreb, Yugoslavia

Abstract. $C_{12}H_{10}Hg$, monoclinic, $P2_1/c$, $a = 5.519(2)$, $b = 8.341(3)$, $c = 11.663(5)$ Å, $\beta = 112.78(4)°$, $V = 495.0$ Å^3, $Z = 2$, $D_m = 2.35$, $D_x = 2.380$ g cm^{-3}, μ(Mo $K\alpha$) $= 158.1$ cm^{-1}. Refinement with diffractometer data yielded a final R value of 0.023. The Hg—C bond length is 2.085(7) Å.

Introduction. Crystals of diphenylmercury were grown by slow evaporation of an ethanol solution at room temperature. The single crystal used was ground to an oval shape with dimensions 0.21 × 0.21 × 0.27 mm. The unit-cell dimensions were determined by a least-squares refinement of the angular settings of 20 reflexions at room temperature with Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). The intensities of 789 independent reflexions within the range $4° < 2\theta < 60°$ were measured on a Philips PW 1100 four-circle automatic computer-controlled diffractometer (graphite-monochromatized Mo $K\alpha$ radiation) with the $\omega-2\theta$ scanning technique, scan range of 1.80° and scan speed of 0.03° s^{-1}. The intensities and ω angles of three reference reflexions, measured periodically every two hours, showed no appreciable variation during the course of data collection. The usual corrections were made for Lorentz–polarization and absorption effects. There was no evidence of secondary extinction. The 725 reflexions with $I \geq 3\sigma(I)$ were used for the structure determina-

tion. Unit weights were allotted to all reflexions. Among them only 57 reflexions of the general type had no Hg atom contribution, *i.e.* those with $k + l$ odd (and only 24 had negative phases, as shown subsequently). Starting with the C atom coordinates given by Ziólkowska, Myasnikova & Kitaigorodsky (1964), structure refinement by the full-matrix least-squares method with isotropic thermal parameters gave an R value of 0.049. A difference Fourier synthesis revealed all the H atom positions. With anisotropic thermal parameters for the Hg and C atoms, the H atoms were also included in the structure factor calculations with the isotropic thermal parameters of the bonded C atoms, but the parameters were not refined. The final R value was 0.023.*

The atomic scattering factors were those of Cromer & Mann (1968) with corrections for anomalous scattering for the non-hydrogen atoms according to Cromer & Liberman (1970).

Discussion. In spite of its simplicity the crystal structure of diphenylmercury has not yet been satisfactorily

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32190 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final positional and thermal parameters* (×10^4)

The anisotropic temperature factor is exp$[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$. Standard deviations in units of the last significant digits are given in parentheses.

	x	y	z	B_{11} (or B)	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Hg	0.0000	0.0000	0.0000	236 (1)	101 (1)	59 (0)	−48 (4)	90 (1)	−72 (2)
C(1)	0.3560 (15)	0.1207 (10)	0.0848 (7)	247 (27)	85 (11)	44 (6)	5 (29)	77 (22)	−34 (14)
C(2)	0.4404 (17)	0.2374 (11)	0.0237 (7)	324 (35)	118 (13)	39 (7)	108 (35)	44 (22)	−4 (15)
C(3)	0.6789 (18)	0.3129 (10)	0.0794 (7)	411 (38)	95 (12)	35 (6)	−78 (36)	125 (25)	6 (14)
C(4)	0.8485 (16)	0.2680 (11)	0.1978 (8)	266 (29)	103 (13)	58 (7)	−25 (33)	58 (24)	−58 (16)
C(5)	0.7688 (17)	0.1525 (11)	0.2596 (7)	324 (33)	115 (13)	38 (6)	−41 (35)	35 (23)	12 (15)
C(6)	0.5249 (18)	0.0794 (11)	0.2046 (8)	377 (37)	125 (15)	55 (7)	−118 (39)	146 (27)	−18 (17)
H(2)	0.320	0.271	−0.063	2.1					
H(3)	0.731	0.387	0.029	1.7					
H(4)	1.004	0.328	0.241	2.2					
H(5)	0.889	0.103	0.337	2.1					
H(6)	0.472	0.017	0.257	2.4					

solved. The first X-ray crystallographic data (Kitaigorodsky & Grdenić, 1948) promised a straightforward structure analysis, but the significant absorption factor (Howells, 1950) as well as the inadequacy of the projection method (Ziólkowska, 1962), prevented a successful solution of the structure. Neither was the first three-dimensional analysis (Ziólkowska, Myasnikova & Kitaigorodsky, 1964) satisfactory; the photographic intensity data without absorption correction gave a solution of the structure with an R value of 0·213. In addition, the twinning of the crystals prevented to a great extent accurate intensity measurements, as has been reported (Ziólkowska, 1962; Ziólkowska *et*
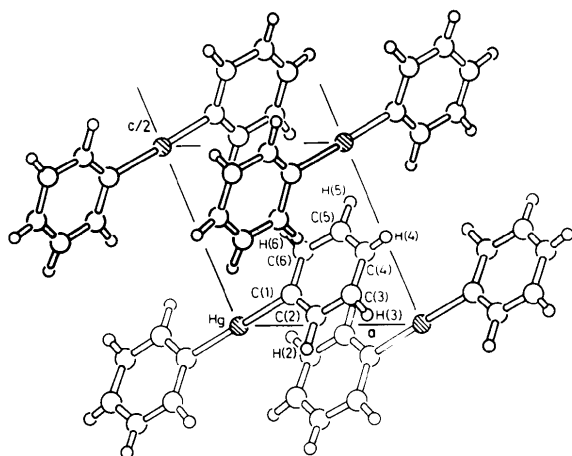

Fig. 1. The crystal structure of diphenylmercury viewed along **b**.

Table 2. *Interatomic distances* (Å) *and angles* (°)

The estimated standard deviations are in parentheses.

Hg—C(1)	2·085 (7)	Hg—C(1)—C(4)	176·9 (4)
C(1)—C(2)	1·389 (13)	Hg—C(1)—C(2)	122·4 (5)
C(2)—C(3)	1·374 (12)	Hg—C(1)—C(6)	120·0 (7)
C(3)—C(4)	1·387 (10)	C(6)—C(1)—C(2)	117·5 (7)
C(4)—C(5)	1·373 (14)	C(1)—C(2)—C(3)	121·9 (7)
C(5)—C(6)	1·388 (12)	C(2)—C(3)—C(4)	120·0 (8)
C(6)—C(1)	1·389 (10)	C(3)—C(4)—C(5)	118·8 (8)
C(2)—H(2)	1·02	C(4)—C(5)—C(6)	121·0 (7)
C(3)—H(3)	0·97	C(5)—C(6)—C(1)	120·6 (9)
C(4)—H(4)	0·96		
C(5)—H(5)	0·98		
C(6)—H(6)	0·93		
C(1)···C(1ⁱ)	3·596 (12)	C(5)···H(2ⁱⁱⁱ)	3·01
C(1)···C(2ⁱ)	3·590 (12)	C(5)···H(4ⁱᵛ)	2·98
C(3)···H(6ⁱⁱ)	2·91	H(2)···H(4ᵛ)	2·42
C(4)···H(2ⁱⁱⁱ)	3·00	H(2)···H(5ᵛ)	2·45
C(4)···H(6ⁱⁱ)	2·91		

Symmetry code

(i)	$1-x$,	$-y$,	$-z$	(iv)	$2-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$
(ii)	$1-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$	(v)	$-1+x$,	$\frac{1}{2}-y$,	$-\frac{1}{2}+z$
(iii)	$1+x$,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$				

al., 1964). The present authors also observed twinned crystals of diphenylmercury but the conditions in which twinning occurs are not yet understood.

The final atomic coordinates and thermal parameters with e.s.d.'s are given in Table 1. The stereochemical requirement for planarity of the phenyl group is fulfilled as indicated by the least-squares best plane through the six C atoms of the asymmetric unit given by the equation: $-0·40969X + 0·70323Y + 0·58105Z + 0·09928 = 0$ with respect to the orthogonal axes a, b and c^*, where X, Y, Z are in Å. The deviations (Å) of the C atoms from the mean plane are C(1) 0·001, C(2) 0·011, C(3) −0·016, C(4) 0·009, C(5) 0·002, C(6) −0·007. The molecule is not strictly planar, the Hg atom being 0·1 Å out of the C-atom mean plane; the Hg—C(1)—C(4) angle is 176·9 (4)°, so that the molecule is slightly bent at the C atoms linked to the Hg atom with the phenyl-group planes parallel to each other as required by the centre of symmetry at Hg. The packing of the molecules is shown in Fig. 1.

The interatomic distances and bond angles are given in Table 2. The Hg—C bond length, 2·085 (7) Å, is in agreement with the value previously obtained for diphenylmercury by X-ray analysis (Ziólkowska *et al.*, 1964) as well as with the value of 2·092 (5) Å obtained by electron diffraction in the gas phase (Vilkov, Anashkin & Mamaeva, 1968). Hg—C bond lengths of 2·09 and 2·10 Å were found in bis(pentafluorophenyl)mercury (Kunchur & Mathew, 1966) and 2·08 (2) Å in di-p-tolylmercury (Mathew & Kunchur, 1970). In the adducts of diphenylmercury with methylated phenanthroline (Canty & Gatehouse, 1972a) and bis(pentafluorophenyl)mercury with bis-(diphenylarsino)methane (Canty & Gatehouse, 1972b) Hg—C bond lengths of 2·10 and 2·15 (4) Å, respectively, were found; other organomercury structures (Kuz'mina, Bokij & Struchkov, 1975) have similar values. The C···C and C···H intermolecular contacts (Table 2) are consistent with Kitaigorodsky's (1973) scheme involving the van der Waals radii (1·80 and 1·17 Å for C and H respectively). The intermolecular distances involving the Hg atom are much greater than 3·30 Å, the sum of the van der Waals radii for C and Hg (1·50 Å for Hg, Grdenić, 1965).

References

CANTY, A. J. & GATEHOUSE, B. M. (1972a). *Acta Cryst.* B28, 1872–1888.
CANTY, A. J. & GATEHOUSE, B. M. (1972b). *J. Chem. Soc. Dalton*, pp. 511–514.
CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* 53, 1891–1898.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.

GRDENIĆ, D. (1965). *Quart. Rev.* **19**, 303–328.

HOWELLS, R. G. (1950). *Acta Cryst.* **3**, 366–369.

KITAIGORODSKY, A. I. (1973). *Molecular Crystals and Molecules*, pp. 11–13. New York, London: Academic Press.

KITAIGORODSKY, A. I. & GRDENIĆ, D. (1948). *Izv. Akad. Nauk SSSR Otd. Khim. Nauk*, p. 262.

KUNCHUR, N. R. & MATHEW, M. (1966). *Chem. Commun.* pp. 71–73.

KUZ'MINA, L. G., BOKIJ, N. G. & STRUCHKOV, YU. T. (1975). *Usp. Khim.* **44**, 134–155.

MATHEW, M. & KUNCHUR, N. R. (1970). *Canad. J. Chem.* **48**, 429–434.

VILKOV, L. V., ANASHKIN, M. G. & MAMAEVA, G. I. (1968). *Zh. Strukt. Khim.* **9**, 372–378.

ZIÓLKOWSKA, B. (1962). *Roczn. Chem.* **36**, 1341–1347.

ZIÓLKOWSKA, B., MYASNIKOVA, R. M. & KITAIGORODSKY, A. I. (1964). *Zh. Strukt. Khim.* **5**, 737–742.

1-Cyclopentadienyl-2,3-dimethylcobalta-2,3-dicarbaheptaborane

BY R. WEISS AND R. F. BRYAN*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901, *USA*

Abstract. $C_9H_{15}B_4Co$, monoclinic, $P2_1/m$, $a = 8.284 (1)$, $b = 10.096 (2)$, $c = 6.836 (1)$ Å, $\beta = 104.95 (5)°$ ($\lambda = 0.7107$ Å), $U = 552$ Å^3, $Z = 2$, $D_x = 1.355$, $D_m = 1.33$ g cm^{-3}. The structure was solved by the heavy-atom method, and least-squares refinement gave $R = 0.050$ for 1498 unique significant reflections measured by counter diffractometry. The molecule has a crystallographic mirror plane of symmetry, and the basal plane of the polyhedron and the cyclopentadienyl plane are inclined at $7.5°$ to one another. The C—C bond in the polyhedron is $1.461 (2)$ Å and Co—C [$2.031 (1)$ Å] is close to the average Co—C bond length involving the cyclopentadiene residue, 2.036 Å. Co—B lengths are $2.086 (3)$ and $2.104 (4)$ Å.

Introduction. The title compound is a cobaltacenium analog with one of the cyclopentadienyl groups of that

compound replaced by the doubly charged dimethylcarborane anion to yield a neutral species. The synthesis, spectral characteristics, and other properties of the compound have been previously described (Grimes, Beer, Sneddon, Miller & Weiss, 1974) and we report here its crystal structure.

Crystallization of the compound from a heptane–dichloromethane mixture afforded a needle (0·75 × 0·25 × 0·12 mm) suited to X-ray study. Systematic absences are $0k0$ with k odd, indicating space groups $P2_1$ or $P2_1/m$. The latter was chosen, and with $Z = 2$ requires the molecule to have a mirror plane of symmetry. The correctness of the choice is confirmed by the results of the analysis. Intensity measurements were made by automatic single-crystal diffractometry for a quadrant of reciprocal space ($2\theta \leq 60°$). The θ–2θ scan method was used with monochromatic (HOG) Mo $K\alpha$ radiation, scintillation counting, and pulse-height analysis. Scattered intensity significantly above back-

* To whom correspondence should be addressed.

Table 1. *Heavy-atom parameters and their standard deviations*

Values have been multiplied by 10^4. The temperature factor has the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.
E.s.d.'s in parentheses are applicable to the least significant figures given.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	4080 (1)	2500 (–)	2280 (1)	47 (1)	49 (–)	92 (1)	0 (–)	26 (1)	0 (–)
C(2)	1762 (2)	1776 (2)	2120 (3)	67 (2)	57 (2)	121 (4)	−6 (2)	9 (2)	−1 (2)
B(4)	2454 (3)	1177 (3)	402 (4)	108 (3)	98 (3)	164 (5)	−2 (2)	29 (3)	−48 (3)
B(5)	2930 (6)	2500 (–)	−849 (6)	136 (6)	139 (6)	117 (7)	0 (–)	49 (5)	0 (–)
B(7)	980 (5)	2500 (–)	−305 (6)	97 (4)	119 (5)	116 (7)	0 (–)	1 (4)	0 (–)
C(21)	963 (3)	992 (3)	3501 (4)	93 (3)	88 (2)	206 (6)	−20 (2)	33 (3)	33 (3)
C(3a)	6436 (4)	2500 (–)	2019 (6)	80 (4)	99 (4)	189 (8)	0 (–)	57 (4)	0 (–)
C(4a)	6168 (3)	1365 (3)	3114 (4)	86 (3)	80 (2)	215 (5)	23 (2)	39 (3)	−4 (3)
C(5a)	5734 (3)	1800 (3)	4890 (4)	89 (3)	89 (2)	161 (5)	7 (2)	22 (3)	20 (3)