THE CRYSTAL AND MOLECULAR STRUCTURE OF DI-*trans*-β-STYRYLMERCURY

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(Received April 18th, 1983)

Summary

The structure of di-*trans*-β-styrylmercury has been determined by single crystal X-ray methods from counter data. The compound crystallizes in the orthorhombic space group *Pbcn* with unit cell dimensions *a* 15.413(6), *b* 11.161(9), *c* 7.668(5) Å, *V* 1319(1) Å^3, D_{calc} 2.049 g/cm^3, and $Z = 4$. The crystal was solved by conventional heavy atom techniques. The crystal consists of individual molecular units with the mercury atom located on a two fold axis of symmetry. The C–Hg–C fragment is nearly linear with an angle of 178°. The β-styryl groups are oriented so that a dihedral angle of 66.8° is formed between the planes defined by Hg–C(1)–C(2) and Hg–C(1)′–C(2)′ fragments. The Hg–C bond distance is 2.07(4) Å.

Introduction

We have a continuing interest in extending the structural data base for simple organometallic compounds for comparative purposes and for use in conjunction with other studies, especially in the development of relationships between structure and spectroscopic properties. As indicated previously, the number of simple symmetrical organomercury species is very limited and no structures of symmetrical vinyl derivatives have been reported [1]. For that reason, we now report the structure of di-*trans*-β-styrylmercury recently determined in our laboratory.

Experimental: Preparation of di-*trans*-β-styrylmercury

β-Styryl Grignard reagent was prepared by addition of β-bromostyrene (0.3 mol) to a stirred mixture of excess magnesium turnings covered by ether (400 ml) over a period of 90 minutes. The reaction was allowed to continue for an additional hour with stirring. Then approximately 0.3 mol HgCl$_2$ dissolved in 50 ml of THF was added dropwise. After complete addition of the HgCl$_2$ solution, the reaction was stirred at room temperature for an additional hours.

The crude β-styrylmercuric halide was separated and symmetrized by treatment

TABLE 1

EXPERIMENTAL DATA FROM THE X-RAY DIFFRACTION STUDY ON Hg(HC=CHPh)$_2$

mol. formula: $C_{16}H_{14}Hg$
mol. wt: 406.878
crystal system: orthorhombic
space group: *Pbcn*
cell dimensions
    a 15.413(6) Å, b 11.161(9) Å, c 7.668(5) Å
V 1319(1) Å^3, $Z = 4$, D_{calcd} 2.049 g/cm^3
radiation: Mo-$K_{\bar\alpha}$ (λ 0.71069 Å)
monochromator: graphite
reflections measured: $+ h, + k, + l$
2θ range: 0–45°
scan type: $\theta - 2\theta$; moving crystal-moving counter
scan speed: 2.0°/min(in 2θ)
scan width: $[2\theta(\text{Mo-}K_{\alpha_1}) - 1.2]° - [2\theta(\text{Mo-}K_{\alpha_2}) + 1.2]°$
background measurement: stationary crystal-stationary counter
at beginning and end of 2θ, each for one-fourth the
time taken for the 2θ scan
standard reflections: 4 ($40\bar2$; $\bar402$; $24\bar1$; $\bar241$) measured every 96
reflections; no significant deviation from the mean
was observed
unique data: 1086; unique data with $F_o^2 > 3.0\sigma(F_o^2)$: 508
absolute coeff: μ 116.39 cm^{-1}
F(000) = 760 electrons; $R_F = 0.056$; $R_{wF} = 0.097$

with sodium stannite using the procedures previously described [2]. The resulting
product was separated and recrystallized twice from hexane yielding 15 g of pure
di-*trans*-β-styrylmercury.

TABLE 2

ATOMIC COORDINATES FOR Hg(HC=CHPh)$_2$

Atom	x	y	z
Hg [a]	0.0	0.0766(1)	0.2500
C(1)	0.122(2)	0.074(3)	0.130(6)
C(2)	0.183(2)	0.150(3)	0.152(4)
C(3)	0.270(2)	0.146(3)	0.085(4)
C(4)	0.300(2)	0.059(3)	− 0.034(4)
C(5)	0.385(3)	0.060(3)	− 0.086(5)
C(6)	0.443(2)	0.146(3)	− 0.026(5)
C(7)	0.414(2)	0.232(3)	0.083(5)
C(8)	0.330(2)	0.233(3)	0.139(4)
H(11)	0.135	0.007	0.065
H(21)	0.170	0.218	0.224
H(41)	0.260	− 0.002	− 0.078
H(51)	0.405	− 0.005	− 0.161
H(61)	0.503	0.141	− 0.068
H(71)	0.453	0.295	0.123
H(81)	0.308	0.297	0.210

[a] The x and z-coordinates are fixed by crystallographic symmetry.

TABLE 3

ISOTROPIC THERMAL FACTORS OF HYDROGENS AND ANISOTROPIC [a] THERMAL FACTORS OF NONHYDROGEN ATOMS IN $Hg(HC=CHPh)_2$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B (Å^2)
Hg [b]	3.6(1)	4.4(1)	5.1(1)	0.0(0)	0.0(2)	0.0(0)	4.3(1)
C(1)	2.8(15)	4.0(17)	8.9(27)	0.0(13)	2.2(17)	−0.6(17)	4.3(8)
C(2)	4.9(18)	3.8(17)	4.6(16)	0.8(14)	1.1(16)	−0.5(14)	4.2(5)
C(3)	3.7(15)	3.9(16)	2.9(13)	0.4(13)	−0.4(12)	−0.1(13)	3.5(6)
C(4)	4.7(18)	3.2(14)	3.8(15)	0.4(13)	−0.5(14)	−0.4(12)	3.8(7)
C(5)	5.7(20)	3.6(15)	4.6(17)	2.1(15)	−0.0(17)	−1.0(15)	4.1(5)
C(6)	5.2(19)	5.6(21)	3.8(17)	1.5(17)	1.0(16)	0.8(16)	4.5(7)
C(7)	5.0(19)	4.9(17)	4.3(17)	−1.0(16)	−0.8(16)	0.5(16)	4.6(4)
C(8)	5.8(19)	4.9(17)	2.3(14)	0.3(16)	0.2(14)	−1.1(13)	3.9(6)
H(11)							5.4
H(21)							4.4
H(41)							3.8
H(51)							4.7
H(61)							5.5
H(71)							5.3
H(81)							4.9

[a] The form of the anisotropic thermal ellipsoid is: $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] B_{12} and B_{23} are fixed by crystallographic symmetry.

X-Ray data collection

A portion of this product was subsequently dissolved in pentane and cooled yielding needle shaped crystals which were suitable for X-ray data collection. A small prismatic crystal was mounted in a thin walled capillary and then placed on the Syntex P2$_1$ four-circle X-ray diffractometer. Oscillation photographs followed by automatic centering of fifteen reflections indicated an orthorombic symmetry. The space group was subsequently determined to be *Pbcn*. All pertinent experimental data are collected in Table 1.

TABLE 4

INTERATOMIC DISTANCES (Å) AND ANGLES (Deg) FOR $Hg(HC=CHPh)_2$

Hg–C(1)	2.07(4)	C(1)–C(2)	1.28(5)
C(2)–C(3)	1.41(4)	C(3)–C(4)	1.38(5)
C(4)–C(5)	1.38(5)	C(5)–C(6)	1.39(5)
C(6)–C(7)	1.36(5)	C(7)–C(8)	1.37(5)
C(1)–Hg–C(1′)	178(2)	Hg–C(1)–C(2)	127(3)
C(1)–C(2)–C(3)	129(3)	C(2)–C(3)–C(4)	124(3)
C(2)–C(3)–C(8)	119(3)	C(3)–C(4)–C(5)	120(3)
C(4)–C(5)–C(6)	122(3)	C(5)–C(6)–C(7)	119(4)
C(6)–C(7)–C(8)	121(4)	C(7)–C(8)–C(3)	122(3)
C(8)–C(3)–C(4)	117(3)		

Solution

The structure was solved in the orthorhombic space group *Pbcn* by conventional heavy atom techniques [3]. 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 the expected geometry.

Subsequent full matrix least squares refinement of the non-hydrogen atomic 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 yield final values for the discrepancy factors of: $R_F = \Sigma ||F_o| - |F_c||/\Sigma |F_o| = 0.056$ and $R_{wF} = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.097$. The maximum residual electron density in the final difference synthesis was equal to 3.9 e/Å^3 and was in the vicinity of that of the mercury atom. All other residual electron densities were 0.5 e/Å^3 or less. The high residual electron density in the vicinity of mercury is a result of not correcting for absorption of mercury due to loss of the crystal prior to determination of the dimensions. The atomic coordinates and anisotropic thermal parameters are presented in Tables 2 and 3. Pertinent bond distance and bond angles are given in Table 4. A listing of the structure factors is available on request *.

Results and discussion

The compound, di-*trans*-β-styrylmercury consists of individual molecular units with the mercury atom located on a crystallographic 2-fold axis of symmetry as shown in Fig. 1. The styryl groups lie to the same side of the C–Hg–C axis and are twisted with a dihedral angle between the Hg–C(1)–C(2) and Hg–C(1)′–C(2)′ planes of 66.8°. The phenyl ring is twisted by 6.3° relative to the C(1)–C(2)–C(3) plane.

The most useful result provided is the Hg–C distance of 2.07 Å which should be compared with the value of 2.10(11) obtained in *trans*-ClCH=CHHgCl [4] and of 2.33 in PhCOCH=CHHgCl [5]. This result indicates that in the symmetrical
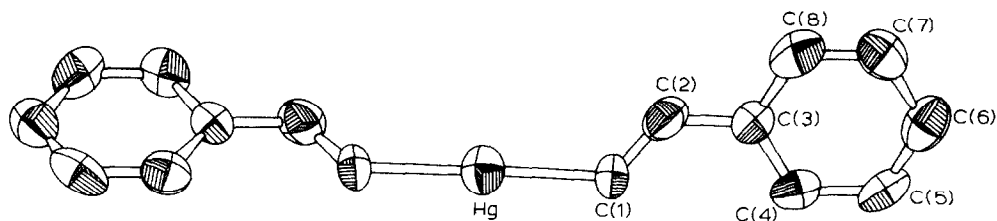

Fig. 1. A perspective view of the molecular structure of di-*trans*-β-styrylmercury with the atoms labeled.

vinylmercury compounds the Hg–C bond distances is similar to that observed in a wide variety of other organomercury species [1,6].

References

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