

Crystal Structure of Triphenyl-7-cyclohepta-1,3,5-trienyltin, a Fluxional Organometallic Molecule

J. E. Weidenborner,* R. B. Larrabee, and A. L. Bednowitz

Contribution from the IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598. Received July 3, 1971

Abstract: The crystal structure of triphenyl-7-cyclohepta-1,3,5-trienyltin has been determined from single-crystal X-ray diffraction data. The atoms were located by the use of a three-dimensional Patterson map followed by successive Fourier syntheses of the electron density. Refinement of the structure by the least-squares method resulted in an $R = 0.061$. The compound crystallizes in space group $P\bar{1}$ with $a = 10.928 \text{ \AA}$, $b = 12.081 \text{ \AA}$, $c = 11.733 \text{ \AA}$, $\alpha = 120.96^\circ$, $\beta = 119.35^\circ$, and $\gamma = 94.83^\circ$. The molecule consists of an approximately tetrahedral triphenyltin ligand σ -bonded to a monocyclic seven-membered ring with alternating C-C distances indicative of considerable double bond character and with a nonplanar boat conformation. This structure is unlike that previously assigned to other fluxional cycloheptatrienes.

When grouped with other fluxional organometallic compounds,^{1a} triphenyl-7-cyclohepta-1,3,5-trienyltin (**1a**) is unique in that some principle other than least motion is required to rationalize the very rapid migration of the triphenyltin group to the most distant carbon of the seven-membered ring.^{1b} Such a principle might be found by consideration of the symmetries of molecular orbitals proposed for the transition state of this system.² The importance of this finding as a step toward a good test of predictions in sigmatropic rearrangements² from such symmetry considerations and the necessity of securing the proposed instantaneous structure of **1a** in view of the threshold uncertainty (qV) in this system prompted the determination of the crystal structure reported here.

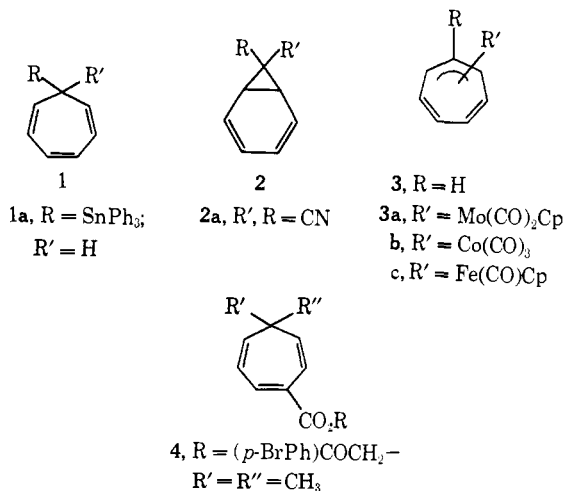
Three aspects of the structural problem may be defined: (a) the question of monocyclic or cycloheptatriene structures **1** vs. bicyclo[4.1.0]hepta-2,4-diene or

tures, the conformation, particularly the planarity of all or part of the ring;^{3b} (c) in organometallic structures, the character of bonding of the seven-membered ring to the metal substituent R: σ or monohapto (**1**)⁴ vs. π or trihapto bonding as in **3**. Accurate prediction of the relative stabilities of the potentially intraconvertible isomers **1**, **2**, and **3** is quite difficult for any new substituent, as the energy differences can be small and vary, in a manner not well understood, upon the nature of the substituent.^{3,5,6} While tin is most usually tetra-valent in compounds containing solely carbon and hydrogen,⁷ it may possibly be di- to hexavalent. Three previous fluxional cycloheptatrienyl organometallic compounds were assigned the monocyclic trihapto structure **3a-c** on the basis of spectral data; these assignments were not considered rigorous.⁸

Experimental Section

The preparation of triphenyl-7-cyclohepta-1,3,5-trienyltin has been described elsewhere.¹ Yellow single crystals of the material were obtained by recrystallization from hexane. Most of these were extremely small, but a careful search produced a specimen large enough for X-ray intensity measurements. The crystal selected for X-ray measurements had the form of an approximately hexagonal plate with an average diameter of 0.27 mm and a thickness of 0.10 mm. Preliminary work, using a precession camera with Cu K α radiation, showed no systematic absences among the reflections and indicated that the crystal system was triclinic. The lattice constants, obtained from a subsequent least-squares analysis of diffractometer data are: $a = 10.928 \pm 0.002 \text{ \AA}$, $b = 12.081 \pm 0.002 \text{ \AA}$, $c = 11.733 \pm 0.003 \text{ \AA}$, $\alpha = 120.96 \pm 0.02^\circ$, $\beta = 119.35 \pm 0.03^\circ$, $\gamma = 94.83 \pm 0.02^\circ$. The calculated density assuming two molecules per unit cell, is 1.415 g cm^{-3} , compared to a measured density, determined by flotation in aqueous potassium iodide, of 1.41 g cm^{-3} .

Intensity data were collected on the CCXD (computer controlled X-ray diffractometer), operated from a time-shared IBM 1800 computer.^{9,10} Integrated intensities were obtained by a continuous



norcaradiene structures **2**;^{3a} (b) in monocyclic struc-

(1) (a) For a general review of fluxional organometallic compounds, see F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968); (b) R. B. Larrabee, *J. Amer. Chem. Soc.*, **93**, 1510 (1971).

(2) R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry," Verlag Chemie-Academic Press, Weinheim/Bergstr., Germany, 1970.

(3) Review: G. Maier, *Angew. Chem., Int. Ed. Engl.*, **6**, 402 (1967). (b) See, however, R. Hoffmann, "Theory of the Structure and Reactivity of Small Rings," 23rd International Congress of Pure and Applied Chemistry, Boston, Mass., July 1971. We wish to thank Professor Hoffmann for a preprint.

(4) Hapto nomenclature: F. A. Cotton, *J. Amer. Chem. Soc.*, **90**, 6230 (1968).

(5) G. E. Hall and J. D. Roberts, *ibid.*, **93**, 2203 (1971).

(6) E. Ciganek, *ibid.*, **93**, 2207 (1971).

(7) E. A. V. Ebsworth, "Organometallic Compounds of Group IV Elements," A. G. MacDiarmid, Ed., Marcel Dekker, New York, N. Y., 1968, p 1.

(8) (a) J. W. Faller, *Inorg. Chem.*, **8**, 767 (1969); (b) M. A. Bennett, R. Bramley, and R. Watt, *J. Amer. Chem. Soc.*, **91**, 3089 (1969); (c) D. Ciappinelli and M. Rosenblum, *ibid.*, **91**, 6876 (1969); (d) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 785 (1964); (e) F. A. Cotton and C. R. Reich, *J. Amer. Chem. Soc.*, **91**, 847 (1969).

(9) H. Cole, Y. Okaya, and F. W. Chambers, *Rev. Sci. Instrum.*, **34**, 872 (1969).

(10) A. L. Bednowitz, R. Ryniker, and H. Cole, Description and Manual for AXDA III. IBM Research Report No. RC2313.

θ - 2θ scanning method,¹¹ using Cu K α radiation and a scintillation counter with pulse height discrimination. The stability of the equipment and possible deterioration of the crystal were monitored by periodic reference to two convenient reflections, the (200) and (022), throughout the period of data acquisition. Both standard reflections exhibited a gradual decrease in intensity which totaled 14% from the beginning to the end of the intensity measurements, and this decrease was taken into account during the processing. An on-line Tektronix Type 611 storage display unit was employed to display a profile of each reflection, as a further aid in judging the validity of the data. A total of 3015 reflections was investigated out to a limit of $\sin \theta/\lambda = 0.56 \text{ \AA}^{-1}$, of which 2380 were observable.¹²

The raw data in disk storage were converted to net integrated intensities and Lorentz-polarization corrections applied, using a program written for the IBM 1800. A calculation of the standard deviation for each reflection was also made in the course of the data processing according to the formula

$$\sigma^2 = \sigma_c^2 + (C_1 N)^2 + (C_2 N(1/A^* - 1))^2$$

where σ_c is the estimated standard deviation based on counting statistics, C_1 is an estimate of nonsystematic errors, C_2 is an estimate of the error due to uncertainty in the absorption correction A^* , and N is the total peak less background count recorded during the scan.

Structure Determination. A three-dimensional Patterson map showed one outstandingly high peak, evidently produced by the interatomic vector between tin atoms. Assuming $P\bar{1}$ as the space group, starting coordinates of $x = 0.083$, $y = -0.174$, $z = 0.231$ were derived for the tin atom. Phases calculated on the basis of the tin coordinates were assigned to the observed structure factors and used to calculate a three-dimensional Fourier synthesis of the electron density. Twelve carbon atoms, comprising portions of all four ring systems (see Figure 1) closest to the tin atom were clearly distinguished from the peaks in this synthesis, and their positions were added to that of the tin atom for the next set of structure factor and electron density calculations. Two further iterations of this procedure finally located all 25 carbon atoms. The reliability index at this point had a value of $R = 0.290$ (where $R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$), which was deemed sufficiently good to begin a least-squares refinement of the structure.

Least-squares refinement was begun, using a modified version of a full-matrix least-squares program of Gantzel, Sparks, and Trueblood¹³ for the calculations on an IBM System/360, Model 91 computer. The starting coordinates were those from the last Fourier synthesis. In general, the least-squares weight was computed as $w = 1/\sigma^2$, where σ^2 is the value of the variance; unobserved reflections were given zero weight and included in the structure factor calculations but not included in the calculation of R . Scattering factors for tin and carbon and dispersion corrections for the tin atom were taken from International Tables for X-Ray Crystallography.¹⁴ Four cycles of refinement with individual isotropic temperature factors and an additional four cycles with anisotropic thermal parameters assigned to the tin atom reduced R only to a value of 0.193. It became clear, at this point, that the high linear absorption coefficient of the material ($\mu_{\text{Cu K}\alpha} = 101.92 \text{ cm}^{-1}$) necessitated an absorption correction before any further significant progress could be made in the refinement. This was accomplished by carefully measuring the bounding faces of the crystal and performing a numerical integration of the absorption integral with the aid of a program, DATAB, which implements a method described by Coppens, Leiserowitz, and Rabinovich.¹⁵ The output of this program also provided information used as input for an extinction correction in the next stage of the structure refinement.

(11) Scan lengths were computed by the control program, using the formula $\alpha + \alpha K \tan \theta$ where α and K are empirically determined constants for a given crystal and θ has the usual meaning.

(12) A complete listing of the observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-4140. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

(13) P. Gantzel, R. A. Sparks, and K. N. Trueblood, unpublished work.

(14) "International Tables for X-Ray Crystallography," Vol. II, Kynoch Press, Birmingham, England, 1962.

(15) P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Crystallogr.*, **18**, 1035 (1965).

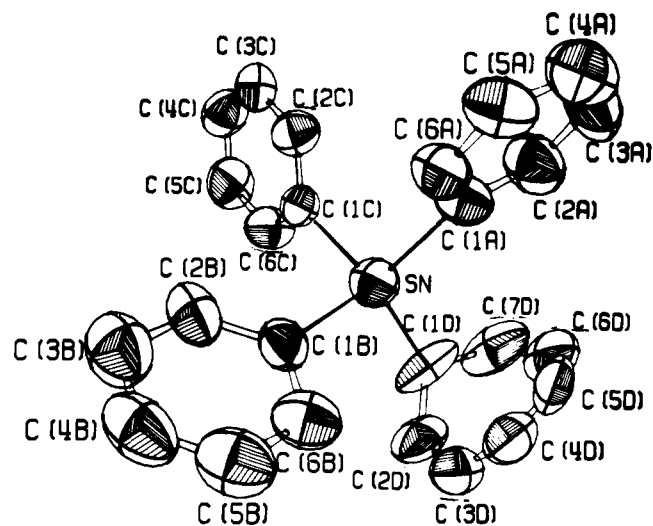


Figure 1. A molecule of triphenyl-7-cyclohepta-1,3,5-trienyltin showing 50% probability thermal ellipsoids.

Least-squares refinement of the absorption-corrected data was resumed using a version of the Busing, Martin, and Levy¹⁶ least-squares program, modified by Coppens and Hamilton¹⁷ to include a correction for extinction by the method suggested by Zachariasen.^{18,19} An isotropic extinction parameter and anisotropic thermal parameters for the carbon atoms were introduced at this point, and after four iterations, a value of $R = 0.080$ was obtained. As a final step, the positions of the hydrogen atoms were calculated and isotropic temperature factors assigned to them.²⁰ The contributions of the hydrogens were added to the structure factor calculations, but neither the positional nor thermal parameters were allowed to vary in the refinement. After three additional cycles, the parameter shifts were reduced to less than one-tenth of their calculated standard deviations, and the structure refinement was terminated at this point with $R = 0.061$.

Results

The standard deviation of an observation of unit weight = $[\Sigma(|F_o| - |F_c|)]^{1/2}/(n - \nu) = 0.970$, for the data used in this structure analysis. Table I shows the atomic coordinates and thermal parameters along with their standard deviations (obtained in the usual way from the inverse least-squares matrix). The latter are quite large for the carbon atom parameters, as expected, because of the presence of the heavy tin atom. A value of $g = 0.08 \times 10^{-6}$ was obtained for the extinction parameter, indicating the effect to be essentially negligible in this crystal. (However, the behavior of this parameter during refinement was rather interesting. Before the contribution of the hydrogen atoms was added to the structure factor calculations, this parameter showed a tendency to converge to a small negative value, although this was avoided by constraints in the program. The addition of the hydrogens, however, reversed the direction of the shifts, and the small positive value given above was obtained for g . Although it is difficult to draw any firm conclusions from the small effects noted in this investigation, this may serve as a warning that erroneous results could be

(16) W. R. Busing, K. O. Martin, and H. A. Levy, ORFLS, A Fortran crystallographic least-squares program, Technical Memorandum 305, Oak Ridge National Laboratory, Tenn.

(17) P. Coppens and W. C. Hamilton, *Acta Crystallogr., Sect. A*, **26**, 71 (1970).

(18) W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139 (1963).

(19) W. H. Zachariasen, *ibid.*, **23**, 558 (1967).

(20) Each hydrogen atom was assigned an isotropic temperature factor equal to that of the corresponding carbon atom.

Table I

(a) Final Coordinates, Thermal Parameters, and Standard Deviations for Triphenyl-7-cyclohepta-1,3,5-trienyltin ^a									
Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sn	0.0876 (1)	-0.1705 (1)	0.2390 (1)	159 (1)	147 (1)	199 (2)	62 (1)	112 (1)	103 (1)
C(1A)	0.1752 (14)	0.0611 (12)	0.3885 (13)	199 (16)	151 (16)	188 (20)	63 (14)	126 (17)	94 (15)
C(2A)	0.1237 (17)	0.1404 (16)	0.4686 (17)	244 (21)	202 (22)	272 (27)	102 (19)	186 (22)	122 (20)
C(3A)	0.1925 (25)	0.2899 (20)	0.5652 (22)	392 (40)	232 (29)	360 (39)	204 (31)	280 (37)	174 (29)
C(4A)	0.3143 (22)	0.3604 (16)	0.5846 (19)	316 (30)	190 (23)	263 (30)	90 (22)	164 (26)	130 (23)
C(5A)	0.3727 (17)	0.2797 (14)	0.5094 (16)	227 (19)	159 (19)	224 (24)	39 (15)	118 (19)	90 (18)
C(6A)	0.3064 (14)	0.1335 (12)	0.4144 (14)	196 (16)	148 (16)	201 (21)	67 (14)	123 (17)	92 (16)
C(1B)	0.1842 (12)	-0.2361 (11)	0.1066 (13)	162 (13)	112 (13)	203 (20)	61 (11)	109 (14)	78 (14)
C(2B)	0.3021 (16)	-0.2736 (13)	0.1601 (16)	239 (20)	171 (18)	286 (27)	114 (17)	195 (22)	129 (19)
C(3B)	0.3776 (20)	-0.3095 (17)	0.0901 (21)	276 (26)	250 (26)	369 (37)	137 (23)	236 (29)	184 (27)
C(4B)	0.3221 (20)	-0.3155 (16)	-0.0487 (20)	292 (27)	216 (24)	333 (34)	100 (21)	252 (29)	128 (23)
C(5B)	0.2065 (20)	-0.2791 (17)	-0.1052 (19)	290 (28)	235 (25)	299 (32)	91 (23)	209 (27)	156 (25)
C(6B)	0.1310 (18)	-0.2432 (15)	-0.0330 (17)	268 (23)	210 (21)	232 (25)	95 (19)	170 (22)	135 (20)
C(1C)	0.1973 (12)	-0.2116 (12)	0.4148 (13)	154 (13)	159 (16)	214 (21)	73 (13)	118 (15)	113 (15)
C(2C)	0.3360 (14)	-0.1027 (14)	0.5772 (15)	180 (16)	189 (19)	245 (25)	68 (15)	120 (18)	132 (19)
C(3C)	0.4140 (16)	-0.1272 (16)	0.6919 (17)	224 (20)	214 (23)	263 (27)	130 (19)	149 (21)	136 (21)
C(4C)	0.3552 (18)	-0.2568 (18)	0.6494 (18)	246 (22)	268 (28)	269 (29)	138 (22)	156 (23)	201 (25)
C(5C)	0.2123 (23)	-0.3686 (18)	0.4836 (21)	349 (33)	221 (25)	352 (37)	155 (26)	221 (32)	216 (28)
C(6C)	0.1291 (18)	-0.3445 (14)	0.3684 (16)	267 (23)	164 (19)	242 (26)	70 (17)	129 (21)	132 (19)
C(1D)	-0.1687 (14)	-0.3013 (20)	0.0722 (20)	146 (16)	383 (34)	387 (38)	54 (21)	65 (22)	325 (33)
C(2D)	-0.2424 (17)	-0.3835 (17)	-0.1096 (20)	193 (20)	215 (24)	284 (33)	25 (18)	26 (22)	136 (25)
C(3D)	-0.2587 (20)	-0.3229 (20)	-0.1771 (19)	259 (25)	258 (31)	257 (31)	107 (24)	139 (25)	141 (27)
C(4D)	-0.2095 (19)	-0.1747 (21)	-0.0911 (22)	246 (24)	255 (31)	311 (36)	105 (24)	123 (26)	193 (30)
C(5D)	-0.2073 (21)	-0.0796 (19)	0.0361 (26)	269 (28)	244 (29)	413 (48)	167 (26)	131 (32)	213 (34)
C(6D)	-0.2609 (24)	-0.1141 (31)	0.1076 (25)	318 (39)	568 (62)	363 (44)	325 (47)	234 (37)	284 (46)
C(7D)	-0.2445 (18)	-0.2148 (31)	0.1262 (24)	184 (22)	645 (66)	431 (47)	191 (35)	200 (30)	394 (51)

(b) Calculated Positions and Isotropic Temperature Factors for the Hydrogen Atoms									
Atom	x	y	z	B, Å ²	Atom	x	y	z	B, Å ²
H(2A)	0.040	0.088	0.460	6.9	H(3C)	0.513	-0.055	0.805	6.6
H(3A)	0.145	0.345	0.616	8.0	H(4C)	0.414	-0.262	0.739	6.8
H(4A)	0.363	0.467	0.656	7.7	H(5C)	0.172	-0.464	0.454	7.5
H(5A)	0.461	0.328	0.521	6.8	H(6C)	0.025	-0.422	0.253	6.7
H(6A)	0.350	0.079	0.364	5.7	H(1D)	-0.166	-0.365	0.099	8.3
H(2B)	0.339	-0.265	0.260	6.1	H(2D)	-0.288	-0.492	-0.198	9.0
H(3B)	0.456	-0.344	0.123	7.8	H(3D)	-0.306	-0.388	-0.301	8.2
H(4B)	0.368	-0.342	-0.109	7.7	H(4D)	-0.175	-0.132	-0.128	8.1
H(5B)	0.173	-0.283	-0.202	7.5	H(5D)	-0.173	0.022	0.083	9.3
H(6B)	0.046	-0.216	-0.074	6.7	H(6D)	-0.307	-0.063	0.161	10.6
H(2C)	0.382	-0.004	0.617	6.1	H(7D)	-0.297	-0.230	0.171	10.0

^a The β_{ij} have been multiplied by 10^4 and are defined by $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

obtained for the extinction parameter if the light atoms (*i.e.*, hydrogens) are omitted from a structure refinement of this type.) Table II lists bond distances and

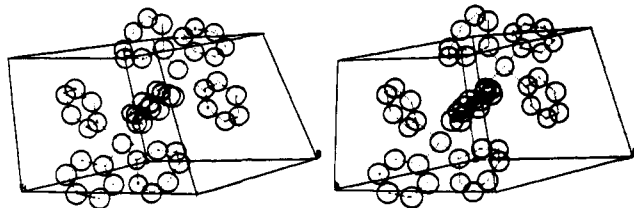


Figure 2. Stereoscopic view of the unit cell.

interbond angles along with their standard deviations.²¹ Figure 1 is a drawing of the molecule of triphenyl-7-cyclohepta-1,3,5-trienyltin, showing thermal ellipsoids, prepared with the ORTEP²² computer program. A stereoscopic picture of the contents of the unit cell²³

(21) Calculations were carried out with an IBM 360 version of the DISTANG program: Y. Okaya, ACA Computing Conference, Yorktown Heights, N. Y., 1963.

(22) C. K. Johnson, ORTEP, A Fortran thermal-Ellipsoid plot program for crystal structure illustrations, Report ORNL-3794, Oak Ridge National Laboratory, Tenn., 1965.

(23) The origin of the unit cell has been translated $-1/2t$ along both *a* and *b* for the purposes of this illustration.

is shown in Figure 2, as viewed following a 40° clockwise rotation about a vector normal to the *ab* plane and a 10° counterclockwise rotation about the abscissa.

Discussion

A choice between alternative structures follows clearly from the crystallographic data. In triphenylcycloheptatrienyltin (**1a**) an approximately tetrahedral Ph_3Sn ligand is σ bonded to a monocyclic seven-membered ring (Figures 1 and 2). This ring exists in the boat conformation now commonly assigned to simpler cycloheptatrienes.³ The structure differs, however, from the trihapto structure proposed for other fluxional organometallic cycloheptatrienes (**3a-c**).

Three phenyl rings σ bonded to tin are evident, with average carbon-carbon bond distances of 1.38, 1.38, and 1.39 Å in the A, B, and C rings, respectively; deviation from planarity (Table III) is not significant relative to the average errors (in parentheses) in calculation of the shifts. Their skewed orientation probably reflects the requirements of minimized inter- and intramolecular nonbonded interactions.

The tin-carbon distances fall within the expected range for such bonds (Table II). Although few reliable data exist for comparison, values of 2.14–2.18 Å

Table II. Interatomic Distances (Å) and Bond Angles (deg)

Sn-C(1A) = 2.16 (1)	C(1A)-Sn-C(1B) = 106.8 (1.0)
Sn-C(1B) = 2.16 (1)	C(1A)-Sn-C(1C) = 107.2 (1.0)
Sn-C(1C) = 2.16 (1)	C(1A)-Sn-C(1D) = 117.1 (1.5)
Sn-C(1D) = 2.21 (2)	C(1B)-Sn-C(1C) = 104.2 (0.9)
Sn-C(2D) = 3.09 (2)	C(1B)-Sn-C(1D) = 113.4 (1.4)
Sn-C(7D) = 3.07 (3)	C(1C)-Sn-C(1D) = 107.2 (1.3)
Sn-C(3D) = 3.61 (2)	Sn-C(1D)-C(2D) = 112.1 (1.8)
Sn-C(4D) = 3.61 (2)	Sn-C(1D)-C(7D) = 111.8 (2.4)
Sn-C(5D) = 3.61 (2)	
Sn-C(6D) = 3.62 (2)	
C(1A)-C(2A) = 1.34 (2)	C(6A)-C(1A)-C(2A) = 118.6 (2.7)
C(2A)-C(3A) = 1.39 (3)	C(1A)-C(2A)-C(3A) = 119.9 (3.4)
C(3A)-C(4A) = 1.37 (3)	C(2A)-C(3A)-C(4A) = 121.9 (3.9)
C(4A)-C(5A) = 1.38 (3)	C(3A)-C(4A)-C(5A) = 118.1 (3.6)
C(5A)-C(6A) = 1.36 (2)	C(4A)-C(5A)-C(6A) = 120.5 (3.1)
C(6A)-C(1A) = 1.42 (2)	C(5A)-C(6A)-C(1A) = 120.8 (2.7)
C(1B)-C(2B) = 1.36 (2)	C(6B)-C(1B)-C(2B) = 118.0 (2.7)
C(2B)-C(3B) = 1.38 (3)	C(1B)-C(2B)-C(3B) = 123.3 (3.1)
C(3B)-C(4B) = 1.39 (3)	C(2B)-C(3B)-C(4B) = 117.2 (3.2)
C(4B)-C(5B) = 1.34 (3)	C(3B)-C(4B)-C(5B) = 121.2 (3.7)
C(5B)-C(6B) = 1.40 (3)	C(4B)-C(5B)-C(6B) = 120.7 (3.5)
C(6B)-C(1B) = 1.40 (2)	C(5B)-C(6B)-C(1B) = 119.2 (2.9)
C(1C)-C(2C) = 1.38 (2)	C(6C)-C(1C)-C(2C) = 119.5 (2.7)
C(2C)-C(3C) = 1.40 (2)	C(1C)-C(2C)-C(3C) = 121.0 (2.7)
C(3C)-C(4C) = 1.35 (3)	C(2C)-C(3C)-C(4C) = 121.2 (3.2)
C(4C)-C(5C) = 1.42 (3)	C(3C)-C(4C)-C(5C) = 118.0 (3.4)
C(5C)-C(6C) = 1.41 (3)	C(4C)-C(5C)-C(6C) = 121.5 (3.5)
C(6C)-C(1C) = 1.39 (2)	C(5C)-C(6C)-C(1C) = 118.4 (3.0)
C(1D)-C(2D) = 1.48 (3)	C(1D)-C(2D)-C(3D) = 123.0 (3.8)
C(2D)-C(3D) = 1.29 (3)	C(2D)-C(3D)-C(4D) = 125.6 (4.1)
C(3D)-C(4D) = 1.40 (3)	C(3D)-C(4D)-C(5D) = 128.1 (4.6)
C(4D)-C(5D) = 1.32 (3)	C(4D)-C(5D)-C(6D) = 124.5 (4.9)
C(5D)-C(6D) = 1.42 (4)	C(5D)-C(6D)-C(7D) = 124.6 (5.3)
C(6D)-C(7D) = 1.35 (4)	C(6D)-C(7D)-C(1D) = 122.5 (4.9)
C(7D)-C(1D) = 1.47 (3)	C(7D)-C(1D)-C(2D) = 113.5 (3.4)

Table III. Least-Squares Plane Deviations (Å) for Phenyl Groups

	Phenyl ring		
	A	B	C
C(1)	-0.026 (0.027)	-0.014 (0.014)	0.021 (0.022)
C(2)	0.016 (0.017)	0.014 (0.015)	-0.008 (0.015)
C(3)	0.007 (0.023)	-0.013 (0.020)	-0.006 (0.017)
C(4)	-0.019 (0.020)	0.015 (0.019)	0.001 (0.019)
C(5)	0.008 (0.016)	-0.016 (0.019)	0.021 (0.021)
C(6)	0.014 (0.014)	0.014 (0.017)	-0.029 (0.028)

have been reported.²⁴⁻²⁶ The length for the tin-cycloheptatriene linkage (2.21 Å) relative to that of the tin-phenyl linkages (2.16 Å) is changed in the way expected from considerations of the orbital hybridization at the carbon atoms; carbon-carbon bond lengths, at least, can decrease with increasing s character.²⁷ As all other tin to D-ring distances exceed 3.0 Å, these are not taken as chemical bonds and the seven carbon ring is given the monohapto designation.

There are additional indications that the triphenyltin group is σ bonded to the seven-membered ring. Both tin-carbon-carbon bond angles about the methylene carbon are approximately tetrahedral, with values

(24) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

(25) "Tables of Interatomic Distances and Configurations in Molecules and Ions," *Chem. Soc., Spec. Publ.*, No. 11 (1958).

(26) D. R. Lide, *J. Chem. Phys.*, **19**, 1605 (1951); P. Cahill and S. Butcher, *ibid.*, **35**, 2255 (1961).

(27) R. A. Alden, J. Kraut, and T. G. Taylor, *J. Amer. Chem. Soc.*, **90**, 74 (1968).

about 4° greater than the ideal. In a trihapto structure, these angles are expected to be smaller.²⁸ Also the pattern of alternation of bond lengths is strongly suggestive of considerable double bond character between C(2)-C(3), C(4)-C(5), and C(6)-C(7) in the D ring. The trihapto alternative would require relatively shorter bonds between C(3)-C(4) and C(5)-C(6) as compared to C(4)-C(5). These expectations for a trihapto structure are confirmed in the crystallographic study by Cotton and Deboer which secures this assignment for **3a**.²⁹ Another distance of interest in this ring system is that from C(2D) to C(7D), calculated to be 2.47 (3) Å, thereby ruling out the possibility of the bicyclic structure **2**. The corresponding distance in a known norcaradiene derivative has been found to be 1.50 Å.³⁰ A least-squares plane with the equation

$$0.7902X + 0.1048Y + 0.6038Z = -2.458$$

can be drawn through the atoms C(2D), C(3D), C(6D), and C(7D), with none of these deviating from the plane by more than 0.003 Å, well within the limits of accuracy of the determination of the atomic positions in this ring. The other three atoms in this ring, however, are all displaced well above the plane: C(1D) by 0.58 Å; C(4D) by 0.53 Å, and C(5D) by 0.56 Å. The ring therefore is seen to possess a nonplanar boat conformation very similar to that reported in a thujic acid derivative **4** by Davis and Tulinsky.³¹ They also report that the cycloheptatriene ring possesses C_s symmetry. As our data are characterized by relatively larger errors for the C(2D)-C(3D) (1.29 \pm 0.03 Å) and C(6D)-C(7D) (1.35 \pm 0.04 Å) bond distances, they are not in disagreement with this symmetry assignment. In fact most of the angles and lengths in this ring are quite similar to those reported by these workers.

One last feature of the system requires brief comment. As seen in Figures 1 and 2, the triphenyltin group occupies the quasiaxial position at the methylene carbon, on the "top" side of the boat, rather than at the quasiaxial position, pointing away from the "bow." This is of particular interest, as the observed conformation is most favorable to the fluxional behavior observed in solution. With smaller groups, at any rate, the energy difference between conformers, as well as the barrier to inversion, is very small.^{3,32,33} Among possible explanations for the observed conformation are steric repulsion with hydrogens at C(2D) and C(7D) with the large Ph₃Sn group, as proposed for cycloheptatriene-7-d by Jensen,³³ or else secondary valence interactions between tin and the seven-membered ring. Possibly a small effect in this direction is the slightly larger out of plane angle for C(4D) and C(5D) (29.7°) compared to that in thujic acid (24.4°).³¹

Thus in this particular fluxional organometallic

(28) See, for instance, G. E. Coates, *et al.*, "Principles of Organometallic Chemistry," Methuen & Co., London, 1968, p 191.

(29) F. A. Cotton and B. G. Deboer, private communication. We wish to thank Professor Cotton for graciously communicating his results.

(30) C. J. Fritchie, *Acta Crystallogr.*, **20**, 27 (1966).

(31) R. E. Davis and A. Tulinsky, *J. Amer. Chem. Soc.*, **88**, 4583 (1966).

(32) C. H. Bushweller, M. Sharpe, and J. Weininger, *Tetrahedron Lett.*, 453, (1970), and earlier references therein; F. A. L. Anet, *J. Amer. Chem. Soc.*, **86**, 458 (1964).

(33) F. R. Jensen and L. A. Smith, *ibid.*, **86**, 956 (1964).

molecule, the migrating group is bonded to a normal cycloheptatrienyl ring. The fact that there are now examples of two kinds of bonding in fluxional cycloheptatrienes should be considered in any structural

decisions concerning new members of this interesting class of molecules.

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Redetermination of the Structure of Porphine

Betty M. L. Chen and A. Tulinsky*

*Contribution from the Departments of Chemistry and Biochemistry,
Michigan State University, East Lansing, Michigan 48823.*

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Abstract: The structure of porphine has been redetermined with intensity measurements made in such a way as to optimize the reliability of the hydrogen atom structure, particularly that of the imino hydrogen atoms. The porphine molecule is composed of two like-opposite pairs of pyrroles rings, one pair of which carries imino hydrogen atoms. The different pairs of pyrroles show additional small but significant differences in bond distances and bond angles. The molecule is planar within about ± 0.02 Å and possesses C_{2h} symmetry (approximate D_{2h} symmetry with the mirror planes bisecting the pyrrole rings). The different pyrroles are very similar to the two different pyrroles described in tetraphenylporphine. The structure of the free base macrocycle corresponds approximately with the hybrid of the two classical resonance forms of the porphine molecule. The new observations reported here were probably obscured in the original determination by the presence of a metalloporphine impurity.

As the parent compound of the porphyrin series, porphine occupies a unique position by virtue of its relative structural simplicity. Therefore, any comprehensive understanding of the structural interrelationships among the various members of the porphyrin series must rest intimately upon the fundamental understanding of the structural relationships within the simplest member itself. For such reasons, we have been concerned about the structure of the porphine molecule.

An X-ray crystallographic structure determination has been reported for the free base of porphine by Webb and Fleischer (hereafter referred to as W & F)¹ and the structure can be summarized briefly as (1) the macrocyclic ring (Figure 1) of four pyrroles alternately linked with bridging methine carbon atoms is essentially planar; (2) the average symmetry of the molecule corresponds closely to D_{4h} ($4/mmm$); and (3) the imino hydrogen atoms are apparently equally distributed among the four pyrrole rings and they are half-weight. The latter observations suggest the four pyrrole rings are equivalent and this has been attributed to a rapid interconversion of N-H tautomers. Although this structure for porphine is certainly a plausible one, when it is compared with the free base of tetraphenylporphine (TPP)² and tetra-*n*-propylporphine (TPrP),³ certain aspects of the porphine structure are perplexing: TPP and TPrP have two localized imino hydrogen atoms on opposite pyrrole rings and these rings differ structurally from the other two pyrrole rings. Such very different structural features for the porphine molecule are thus difficult to reconcile simply in terms of the substitution of phenyl or propyl groups for methine hydrogen atoms at the bridge positions.

Upon a more thorough and critical examination of

the reported X-ray structure determination of porphine, it becomes clear that the work was unnecessarily complicated by the presence of an apparent metalloporphine impurity in the crystal which was used to collect the intensity data for the structure determination.¹ This fact was uncovered during the course of the structure analysis when a difference electron density map showed a residual peak of 2–3 electrons at the center of the molecule. The peak was ascribed to a metallo purity (5–10%) and it was included into least-squares refinement calculations as Cu^{2+} ion with partial occupancy. The atomic parameters of the impurity were then refined (multiplier, coordinates, anisotropic thermal parameters) and this resulted in considerable improvement in the agreement between the observed and calculated structure factors (decrease of about 0.09 in conventional R factor, $R = \sum ||F|_o - |F|_c| / \sum |F|_o$). A difference electron density map based on a structure factor calculation including the impurity revealed 12 peaks averaging about $0.45 e \text{ \AA}^{-3}$ in peak height at the expected positions of the four methine and eight outer pyrrolic hydrogen atoms. The map also contained four slightly smaller peaks (averaging about $0.35 e \text{ \AA}^{-3}$ in height) near the center of the molecule and since these peaks had fairly reasonable positions with respect to the four pyrrole nitrogen atoms (0.8–0.9 Å), they were interpreted to be four half-hydrogen atoms corresponding to the imino hydrogen atoms of the pyrrole rings. Since the half-hydrogen atom result is a rather subtle one and in this case would depend upon how well the metallo impurity can be and was removed from the observed data via calculation, it is clear that under the circumstances, some of the foregoing procedures and results are questionable. Finally, the peak heights of the half-hydrogen atoms are too large compared to the full occupancy hydrogen atoms. This is all the more important since the final difference elec-

(1) L. E. Webb and E. B. Fleischer, *J. Chem. Phys.*, **43**, 3100 (1965).

(2) S. J. Silvers and A. Tulinsky, *J. Amer. Chem. Soc.*, **89**, 3331 (1967).

(3) P. W. Coddling and A. Tulinsky, *ibid.*, **94**, 4151 (1972).