

On the Molecular Structure of Cyclopentadienyl-beryllium Chloride

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The molecular structure of C_5H_5BeCl has been determined by gas phase electron diffraction. The molecular symmetry is C_{5v} . The main bond distances are: $Be-Cl=1.837(6)$ Å, $Be-C=1.916(6)$ Å, $C-C=1.424(1)$ Å, and $C-H=1.097(4)$ Å.

A series of cyclopentadienylberyllium compounds, C_5H_5BeX (where $X=CH_3, Cl, Br, \text{ or } BH_4$), has recently been synthesized and investigated by Drew and Morgan.¹ The compounds are monomeric in the vapor and also in benzene solutions. Analysis of the infrared spectra show the cyclopentadienyl rings to have D_{5h} symmetry, *i.e.* to be of the penta-hapto type. In each case the beryllium atom lies on the five-fold symmetry axis of the ring.

Haaland and Drew have determined the vapor phase electron diffraction structure of methyl (cyclopentadienyl)beryllium, $C_5H_5BeCH_3$.² They suggest that the absence of oligomers in solution is due to multiple bonding between beryllium and the cyclopentadienyl ring which satisfies the electronic requirement of the metal. Their bonding scheme is shown to be consistent with the unusual asymmetric structure of dicyclopentadienylberyllium, $(C_5H_5)_2Be$, in the gas phase.³

In order to further explore and compare the metal-ring interaction in these unusual compounds and also to examine the $Be-Cl$ bond, the electron diffraction study of cyclopentadienylberyllium chloride was undertaken.

EXPERIMENTAL AND CALCULATION PROCEDURE

Cyclopentadienylberyllium chloride was provided by Drew and Morgan. The electron scattering pattern was recorded on Balzers Eldiograph KD-G2. The sample reservoir was maintained at 58°C and the nozzle heated to about 65°C. Exposures were made with nozzle to photographic plate distances of 50 and 25 cm. The optical densities of six plates from the 50 cm distance were recorded at s intervals of 0.125 \AA^{-1} ; the five plates from the 25 cm distance were recorded at intervals of 0.250 \AA^{-1} . Together the plates covered the s range $2.625-29.250 \text{ \AA}^{-1}$. The scattering parameter s is defined: $s = (4\pi/\lambda \sin(\phi/2))$, where λ is the electron wavelength and ϕ the diffraction angle. The electronic wavelength

was determined by diffraction from solid ZnO. The optical densities were converted into intensities and the data processed in the usual way.⁴

The modified molecular intensity points for the average curves from the 50 and 25 cm distances are shown in Figs. 1A and 2A, respectively.

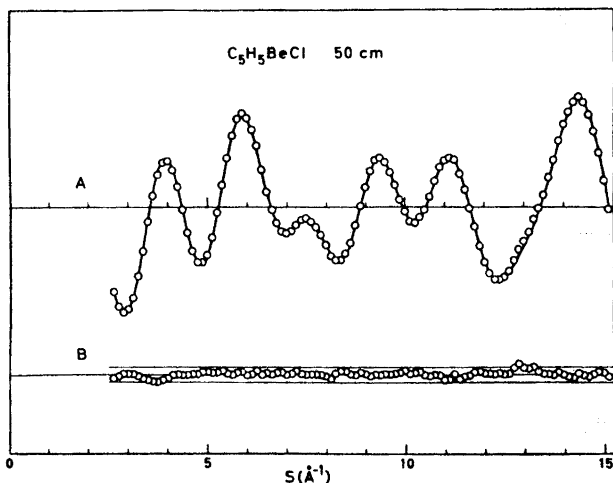


Fig. 1. A. Experimental modified molecular intensity points (O) from $s = 2.625$ to 15.125 \AA^{-1} . The full line is the theoretical modified molecular intensity curve calculated from the parameters in Table 1. B. Difference curve. The two full parallel lines indicate the estimated uncertainty (two standard deviations) of the experimental intensity points. Note: The scale of B is twice that of A.

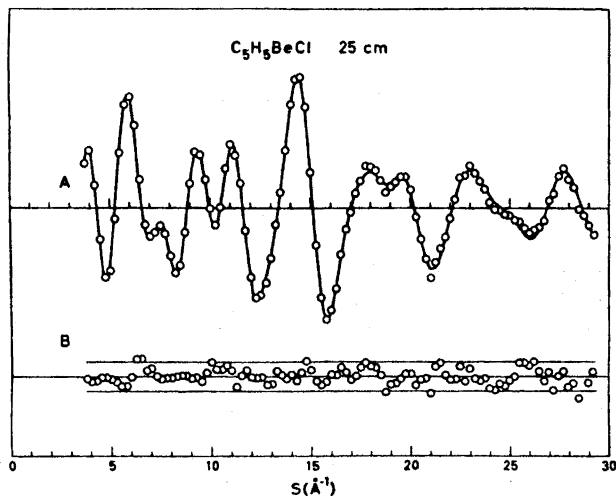


Fig. 2. A. Experimental modified molecular intensity points (O) from $s = 3.750$ to 29.250 \AA^{-1} . The full line is the theoretical modified molecular intensity curve calculated from the parameters in Table 1. B. Difference curve. The two full parallel lines indicate the estimated uncertainty (two standard deviations) of the experimental intensity points. Note: The scale of B is twice that of A.

Theoretical intensity curves were calculated from:

$$I^{CC}(s) = \sum_{i \neq j} \frac{|f_i(s)||f_j(s)|}{|f_C(s)|^2} \cos(\eta_i(s) - \eta_j(s)) \frac{\sin(R_{ij}s)}{R_{ij}} \exp(-\frac{1}{2}l_{ij}^2s^2)$$

The sum extends over all atom pairs i, j in the molecule. R_{ij} is the internuclear distance, l_{ij} the root mean square amplitude of vibration. $f_j(s) = |f_j(s)| \exp(i\eta_j(s))$ is the complex atomic scattering factor of atom j . It has been calculated for Cl, C, Be, and H by the partial wave approximation with a program written by Peacher.⁵ The scattering potentials of Cl, C, and Be have been found by non-relativistic Hartree-Fock calculations.⁶

Radial distribution (RD) functions were calculated by Fourier inversion of experimental and theoretical intensity curves after multiplication with the artificial damping function $\exp(-ks^2)$, $k = 0.002 \text{ \AA}^2$. The experimental intensity functions were first spliced to each other and also to the theoretical curve for the best model below $s = 2.625 \text{ \AA}^{-1}$.

The molecular structure was refined by least-squares calculations on the intensity data with a non-diagonal weight matrix and a separately refined scale factor for the intensity values obtained from each nozzle to plate distance.⁷

STRUCTURAL REFINEMENT

The experimental radial distribution curve for C_5H_5BeCl is shown in Fig. 3. Inspection of this curve clearly confirms that the molecular symmetry of the molecule is C_{5v} .

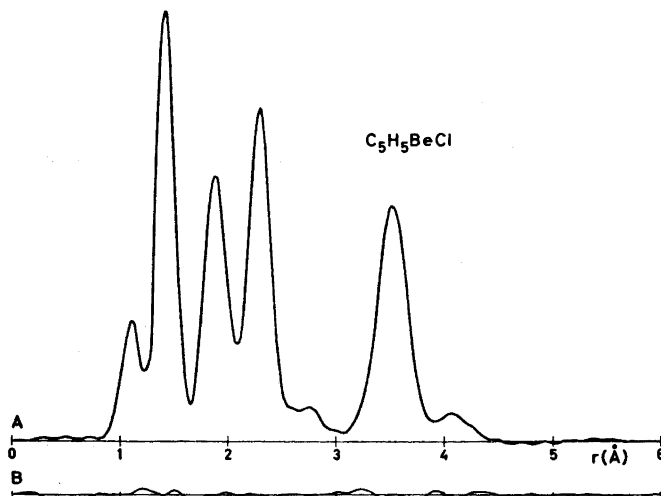


Fig. 3. A. Experimental radial distribution curve. B. Difference between the experimental and a theoretical radial distribution curve calculated from the parameters in Table 1.

The sharpness of the C–C bond distance peak at 1.42 \AA and also the non-bonded C–C peak at 2.30 \AA indicates that all carbon atoms occupy equivalent positions in the ring: Refinement based on a model with five equal C–C bond distances in a planar ring gives a root mean square vibrational amplitude for the bond distance of 0.53(2) \AA . The corresponding amplitudes in the penta-

hapto dicyclopentadienylberyllium and methyl (cyclopentadienyl)beryllium are 0.052(1) and 0.051(1) Å, respectively. Similarly, the amplitude for the non-bonded C...C distance at 2.30 Å is 0.059(3) Å compared with 0.051(1) in $(C_5H_5)_2Be$ and 0.056(2) Å in $C_5H_5BeCH_3$. The sharpness of the peak at 1.92 Å corresponding to five Be–C distances and of the peak at 3.36 Å corresponding to the five Cl–C distances indicate that the Be and Cl atoms lie on the five-fold axis of the ring.

The molecular structure was refined under the assumption that the symmetry is C_{5v} . Since it is not possible to locate hydrogen atoms with great precision, it was assumed that they lie in the plane of the carbon atoms. A model of the molecule is shown in Fig. 4.

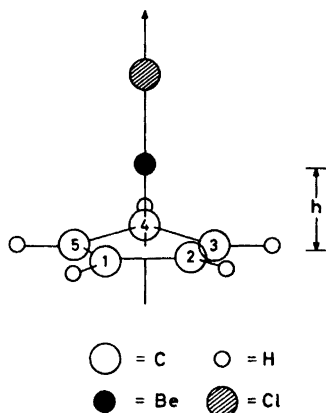


Fig. 4. Molecular model of C_5H_5BeCl .

Table 1. Bond distances and vibrational amplitudes for C_5H_5BeCl (estimated standard deviations in parentheses).

	R (Å)	(Å)
C_1-H_1	1.097(4)	0.049(6)
C_1-C_2	1.424(1)	0.053(2)
Be–Cl	1.837(6)	0.054(10)
Be–C	1.916(6)	0.075 ^a
Cl...C	3.535(5)	0.119(3)
Cl...H	4.044(5)	0.163(21)
$C_1...C_3$	2.304(2)	0.059(3)
$C_1...H_2$	2.251(4)	0.102(14)
$C_1...H_3$	3.364(4)	0.157(40)
Be...H	2.744(6)	0.110(33)
$H_1...H_2$	2.713(5)	0.100 ^b
$H_1...H_3$	4.390(8)	0.150 ^b
h^c	1.484(7)	

^a Assumed equal to the corresponding amplitude in $C_5H_5BeCH_3$. ^b Assumed value. ^c The distance from the Be atom to the center of the plane of the cyclopentadienyl ring.

The molecular structure is determined by four parameters, *e.g.* the bond distances C_1-H_1 , C_1-C_2 , $Be-C$, and $Be-Cl$. These independent distances and nine vibrational amplitudes were refined by least-squares calculation on the intensity data with a non-diagonal weight matrix. It was, however, not possible to refine the $Be-Cl$ and $Be-C$ bond distances and amplitudes simultaneously, the amplitude for the $Be-C$ distance was therefore fixed at 0.075 Å. The amplitude found in methyl (cyclopentadienyl)beryllium, $l(Be-C) = 0.075(3)$ Å. Additional refinements with this amplitude fixed at 0.078 and 0.072 Å caused no significant shifts in any of the other parameters. The parameters and the estimated standard deviations are presented in Table 1.

Theoretical intensity curves calculated from the parameters in Table 1 are shown in Figs. 1A and 2A. The differences between theoretical and experimental intensity points are shown in Figs. 1B and 2B. Good agreement is observed. The difference between the experimental radial distribution curve (Fig. 3A) and one calculated from the theoretical intensity is shown in Fig. 3B.

DISCUSSION

Structurally the interaction between the beryllium and the cyclopentadienyl ring in C_5H_5BeCl is indistinguishable from that in $C_5H_5BeCH_3$ or that of beryllium and the closer ring in $C_5H_5BeC_5H_5$. The $Be-C$ bond distances are 1.916(6) Å in C_5H_5BeCl ; 1.923(3) Å in $C_5H_5BeCH_3$; and 1.907(5) Å in $(C_5H_5)_2Be$.

The $C-C$ bond distances and vibrational amplitudes are indistinguishable for the three compounds: C_5H_5BeCl $R(C-C) = 1.424(1)$ Å, $l(C-C) = 0.053(2)$ Å; $C_5H_5BeCH_3$ $R(C-C) = 1.420(1)$ Å, $l(C-C) = 0.051(1)$ Å; and $(C_5H_5)_2Be$ $R(C-C) = 1.425(2)$ Å, $l(C-C) = 0.052(1)$ Å.

The $Be-Cl$ bond distance of 1.837(6) Å is significantly longer than that reported for monomeric $BeCl_2$, $R(Be-Cl) = 1.75(2)$ Å.⁸ In contrast the $Be-C$ (methyl) bond distance in $C_5H_5BeCH_3$ of 1.706(3) Å is not different from that reported for monomeric dimethylberyllium $R(Be-C) = 1.698(5)$ Å,⁹ or for ditertiarybutylberyllium $R(Be-C) = 1.699(2)$ Å.¹⁰

The bonding scheme proposed for $C_5H_5BeCH_3$ ² is easily fitted to C_5H_5BeCl . Briefly, the Be atom is (*sp*) hybridized, bonding with hybrid orbitals to the chlorine atom and to the $a_1 \pi$ molecular orbital of the ring. The two unhybridized $2p$ orbitals on the beryllium overlap with the filled $e_1 \pi$ orbitals on the ring forming two degenerate bonding molecular orbitals. The beryllium atom is therefore surrounded by an octet of electrons. Since the compound is not "electron deficient" there is relatively little tendency to form oligomers or to coordinate with solvents.¹

A lengthening of the $Be-Cl$ bond in C_5H_5BeCl with respect to $BeCl_2$ is not surprising. The additional dative bonding that exists between Cl and Be in $BeCl_2$ is not possible in C_5H_5BeCl if the p orbitals of beryllium are already involved in bonding to the ring.

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