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On the Molecular Structure of Methyl(cyclopentadienyl)-beryllium, $CH_3Be(C_5H_5)$

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The molecular structure of $CH_3Be(C_5H_5)$ has been determined by gas phase electron diffraction. The molecular symmetry (methyl hydrogen atoms excluded) is C_{5v}. The main band distances are Be–C(Me) = 1.706(3) Å, Be–C(Cp) = 1.923(3) Å, and C–C = 1.420(1) Å.

Methyl(cyclopentadienyl)beryllium, MeBeCp, has been synthesized by Drew and Morgan.[1] The compound is monomeric in hydrocarbon solution and in the gas phase. Infrared spectra demonstrated that the molecule is of the "half-sandwich" type with C_{5v} symmetry (methyl hydrogen atoms excluded).

Since the molecular structure would give clues about the bonding in this compound as well as in dicyclopentadienylberyllium, Cp_2Be, we have undertaken a structure determination through gas phase electron diffraction.

EXPERIMENTAL AND CALCULATION PROCEDURE

Methyl(cyclopentadienyl)beryllium had been prepared by Drew and Morgan. The electron scattering pattern was recorded on Balzers Eldiograph KD-G2 with the sample reservoir at 15°C and a nozzle temperature of about 25°C. Exposures were made with nozzle to photographic plate distances of 50 and 25 cm. The optical densities of the five plates from the first set were recorded at $\Delta s = 0.125$ Å^{-1} intervals; the optical densities of four plates from the last set were recorded at $\Delta s = 0.250$ Å^{-1} intervals. (The scattering parameter $s = (4\pi/\lambda) \sin(\theta/2)$ where λ is the electron wavelength (determined by diffraction from solid ZnO) and θ the diffraction angle.) The optical densities were converted into intensities and the data processed in the usual way.[2]

The modified molecular intensity points obtained from the 50 cm plates are shown in Fig. 1A and the modified molecular intensity points obtained from the 25 cm plates are shown in Fig. 2A.

Theoretical intensity curves were calculated from

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

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 C, Be, and H by

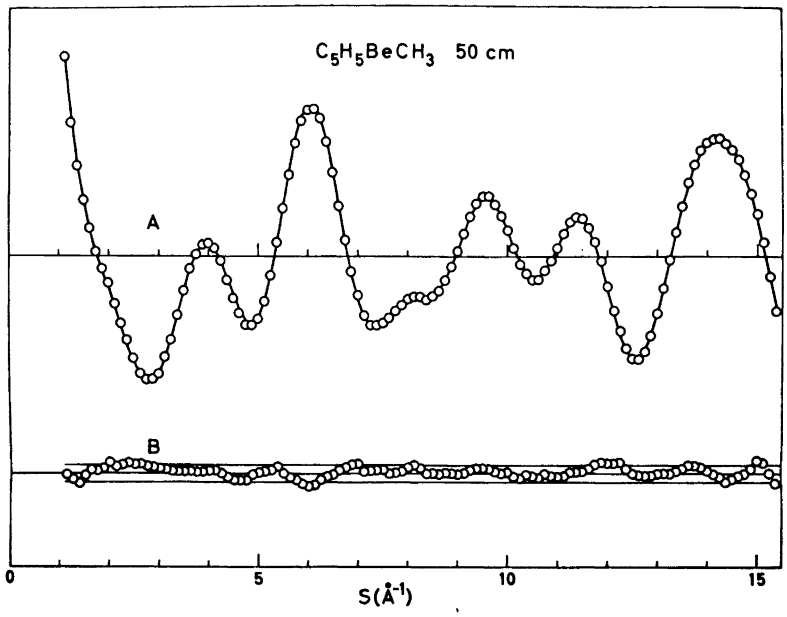

Fig. 1. A. O; Experimental modified molecular intensity points from $s = 1.125$ Å^{-1} to $s = 15.375$ Å^{-1}. The point density is eight points per Å^{-1}. Full line; theoretical modified molecular intensity curve calculated from the parameters in Table 1. *B.* O; difference curve. The two full lines indicate the estimated uncertainty (two standard deviations) of the experimental intensity points. Note: The scale of B is twice that of A.

the partial wave approximation with a program written by Peacher.[3] The scattering potentials of C and Be have been found by non-relativistic Hartree-Fock calculations.[4]

Radial distribution (RD) functions were calculated by Fourier inversion of experimental or theoretical intensity curves after multiplication with the artificial damping function $\exp(-ks^2)$, $k = 0.002$ Å^2. The experimental intensity functions were then first spliced to each other and then to the theoretical curve obtained for the best model below $s = 1.125$ Å^{-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 for each nozzle to plate distance.[5]

STRUCTURE REFINEMENT

An experimental radial distribution curve for methyl(cyclopentadienyl)-beryllium is shown in Fig. 3. This curve confirms that the cyclopentadienyl ring is of the *penta-hapto* type. The area under the peak at 1.95 Å corresponds to *five* Be – C distances, and the narrowness of the C – C bond distance peak at 1.42 Å shows that all C – C bond distances must be equal or very nearly equal. Refinements based on a model with five equal C – C bond distances give a root mean square vibrational amplitude of $l_{CC} = 0.051(1)$ Å; the corresponding amplitude in six other *penta-hapto*-cyclopentadienyl compounds investigated in this laboratory range from 0.046 to 0.052 Å.[6]

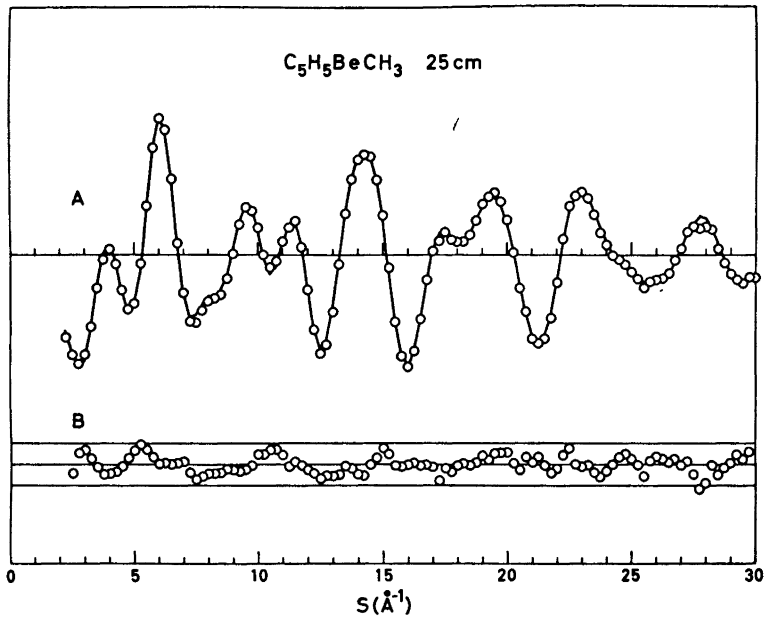

Fig. 2. A. O; Experimental modified molecular intensity points from $s = 2.250$ Å^{-1} to 30.000 Å^{-1}. The point density is eight points per Å^{-1}. Full line; theoretical modified molecular intensity curve calculated from the parameters in Table 1. *B.* O; difference curve. The two full lines indicate the estimated uncertainty (two standard deviations) of the experimental intensity points. Note: The scale of B is twice that of A.

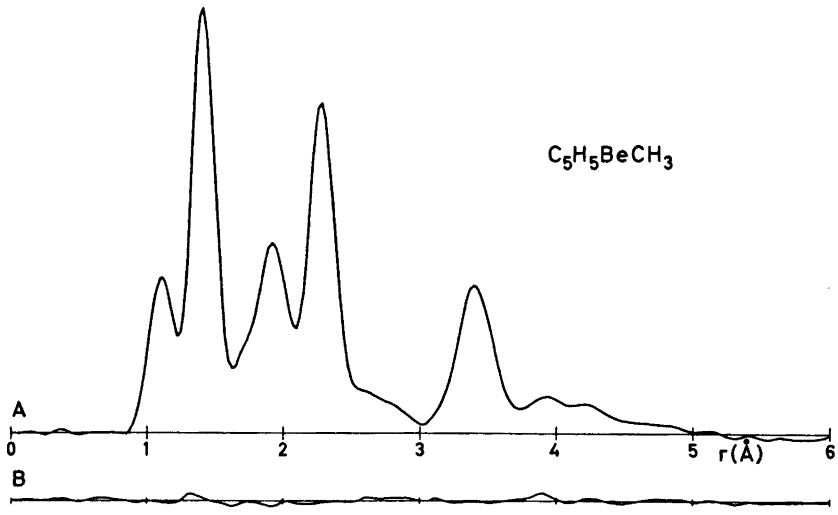

Fig. 3. A. Experimental radial distribution curve. *B.* Difference between the experimental radial distribution curve and a theoretical curve calculated from the parameters of Table 1.

The molecular structure was therefore refined under the assumption that the molecular symmetry (methyl hydrogen atoms excluded) is C_{5v}. As usual in electron diffraction it was not possible to locate the hydrogen atoms with great precision. The following additional assumptions were therefore made:

(i) The cyclopentadienyl ring has D_{5h} symmetry, *i.e.* the hydrogen atoms lie in the plane of the carbon atoms.

(ii) The methyl group have C_{3v} symmetry with the threefold axis coinciding with the fivefold axis of the rest of the molecule.

No attempt was made to determine the angle of rotation of the methyl group relative to the cyclopentadienyl ring. Most probably the barrier to internal rotation is very low. Refinements were carried out on a model of total symmetry C_s in which one methyl group hydrogen atom and one cyclopentadienyl hydrogen atom are eclipsed. This model is shown in Fig. 4.

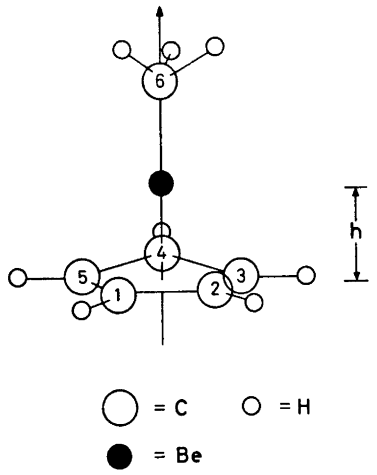

Fig. 4. Molecular model.

The molecular structure is then determined by six parameters, *e.g.* the bond distances C_1-H_1, C_1-C_2, $Be-C_1$, $Be-C_6$, C_6-H_6 and the valence angle $\angle Be-C_6-H_6$. (The hydrogen atoms are numbered as the carbon atoms to which they are bonded.) These parameters and nine vibrational amplitudes (the other amplitudes were fixed at estimated values) were refined by least-squares calculations on the intensity data with a nondiagonal weight matrix. The parameters obtained and their estimated standard deviations are given in Table 1.

Modified molecular intensity curves calculated from the parameters are shown in Figs. 1 and 2. Agreement with experimental data is seen to be satisfactory. The difference between the experimental radial distribution curve of Fig. 3A and a theoretical curve calculated from the parameters in Table 1 is shown in Fig. 3B. Again the agreement is satisfactory.

Table 1. Structure parameters of methyl(cyclopentadienyl)beryllium with estimated standard deviations in parentheses.

	R(Å)	l(Å)
C_1-H_1	1.084(9)	0.053(9)[a]
C_1-C_2	1.420(1)	0.051(1)
$Be-C_1$	1.923(3)	0.075(3)
C_6-H_6	1.145(21)	0.053(9)[a]
$Be-C_6$	1.706(3)	0.061(10)
$\angle Be-C_6-H_6$	120.2(2.8)° [b]	
$C_1\cdots C_3$	2.298(2)	0.056(2)
$C_1\cdots C_5$	3.423(7)	0.108(5)
$C_1\cdots H_2$	2.236(8)	0.101(11)
$C_1\cdots H_3$	3.345(9)	0.113(17)
$Be\cdots H_1$	2.737(8)	0.150[c]
$Be\cdots H_6$	2.487(31)	0.123[d]
h[e]	1.497(3)	

[a] These amplitudes were assumed to be equal. [b] The angle has not been corrected for shrinkage. [c] Assumed value. [d] Assumed equal to the corresponding amplitude in $(CH_3)_2Be$. [e] h is the perpendicular distance from the Be atom to the center of the cyclopentadienyl ring.

DISCUSSION

The Be – C(Cp) bond distance in MeBeCp is indistinguishable from the distance Be – C in the nearest ring in Cp_2Be, 1.907(5) Å, while the corresponding vibrational amplitude is significantly smaller than that observed in Cp_2Be, 0.098(4) Å. The reason for the difference may be the attraction to the other ligand ring felt by the Be atom in Cp_2Be.

The C – C bond distances and vibrational amplitudes in the two compounds are very similar; in Cp_2Be R(C – C) = 1.425(2) Å and l(C – C) = 0.052(1)Å.

The Be – C(Me) bond distance in MeBeCp is indistinguishable from the Be – C bond distance of gaseous monomeric dimethylberyllium, 1.698(5) Å,[8] or di-*tert*-butylberyllium, 1.699(2) Å.[9]

We would propose the following bonding scheme for MeBeCp: The Be atom is *sp*-hybridized and uses one such hybrid orbital for a two-center two-electron bond to the methyl C atom. One bonding molecular orbital is then formed by combination of the other *sp* hybrid with the a_1 π-orbital of the Cp ring. Two more, degenerate, bonding molecular orbitals of higher energy are formed by combination of the unhybridized Be ($2p$) orbitals with the two e_1 π-orbitals of the ring. The Be atom is therefore surrounded by an octet of electrons.

An entirely analogous scheme may be constructed for the bonding between Be and the nearest ring in Cp_2Be, leaving an *sp* hybrid atomic orbital to effect bonding to the other ring by combination with the ring a_1 π-orbital. While such a scheme is crude, it suggests that the asymmetric structure of Cp_2Be may not only be explained by repulsion between the two ligand rings, and that a similar asymmetry therefore might be expected in the isoelectronic compound dicyclopentadienylmagnesium. The dipole moment of the latter compound is found to be zero only if an unusually large (30 % of the electronic

polarizability) atomic polarizability is assumed.[10] If the atomic polarizability is fixed at 15 %, the dipole moment is calculated as 0.5 Debye.

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REFERENCES

1. Drew, D. A. and Morgan, G. L. *Unpublished results.*
2. Andersen, B., Seip, H. M., Strand, T. G. and Stølevik, R. *Acta Chem. Scand.* **23** (1969) 3224.
3. Peacher, J. L. and Wills, J. C. *J. Chem. Phys.* **46** (1967) 4807.
4. Strand, T. G. and Bonham, R. A. *J. Chem. Phys.* **40** (1964) 1686.
5. Seip, H. M., Strand, T. G. and Stølevik, R. *Chem. Phys. Letters* **3** (1969) 617.
6. Haaland, A. *Thesis*, University of Oslo, Oslo 1969.
7. Haaland, A. *Acta Chem. Scand.* **22** (1968) 3030.
8. Almenningen, A., Haaland, A. and Morgan, G. L. *Acta Chem. Scand.* **23** (1969) 2921.
9. Almenningen, A., Haaland, A. and Nilsson, J. E. *Acta Chem. Scand.* **22** (1968) 972.
10. Fischer, E. O. and Schreiner, S. *Chem. Ber.* **92** (1959) 938.

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