

On the Molecular Structure of Dimethylberyllium Monomer

A. ALMENNINGEN, A. HAALAND and
C. L. MORGAN*

Department of Chemistry, University of Oslo,
Blindern, Oslo 3, Norway

Recently Kovar and Morgan¹ have recorded the infrared absorption spectra of dimethylberyllium vapors at temperatures ranging from 125° to 180°C. The spectra indicate that unsaturated vapor consists of monomeric species only, the effective molecular symmetry of the monomer being D_{3h}' . The asymmetric C—Be—C stretching frequency was found at $\nu_7=1081$ cm^{-1} . In di-*t*-butylberyllium the corresponding vibration has been assigned at much lower frequency; $\nu_6=458$ cm^{-1} .² Kovar and Morgan¹ pointed out that the Be—C bonds in dimethylberyllium might be significantly strengthened through hyperconjugation *i.e.* that the bonds have some π -character. In that case the Be—C bonds might be several hundredths of an Ångström unit shorter in dimethylberyllium than in di-*t*-butylberyllium. In order to test this hypothesis we have determined the molecular structure of monomeric dimethylberyllium by means of gas phase electron diffraction.

Dimethylberyllium was prepared by the reaction of beryllium metal with dimethylmercury and purified by sublimation at 100°C. The sample still contained some mercury as an impurity. The presence of atomic mercury in the molecular jet will not introduce any errors in the molecular intensity, but will increase the "background" of atomic intensity. Hence the accuracy with which the molecular parameters were determined (see Table 1) is not as high as one might expect.

The electron diffraction pattern was recorded on the Oslo electron diffraction unit³ with the sample reservoir at $150 \pm 10^\circ\text{C}$ and the nozzle heated to $160 \pm 10^\circ\text{C}$. Dimethylberyllium is thermally stable below 180°C.⁴ Exposures were made with a nozzle to photographic plate distance of about 48 cm. The plates thus obtained

* Present address: Department of Chemistry, The University of Wyoming, Laramie, Wyoming 82070, USA.

Table 1. Molecular parameters and estimated standard deviations of dimethylberyllium, D_{3h} . The bond distances are given as r_a .¹²

	r_a (Å)	u (Å)	Shrinkage (Å)
Be—C	1.698(5)	0.055(10)	
C—H	1.127(4)	0.063(9)	
Be···H	2.386(19)	0.123(18)	
C···C	3.357(10)	0.067(14)	0.035(13)
C···H	3.978(27)	0.184(22)	-0.028(36)
H···H	1.785(23)	0.120 ^a	0.000 ^a
H···H	4.304(53)	0.200 ^a	0.000 ^a
H···H	4.660(41)	0.200 ^a	0.000 ^a
\angle BeCH ^b	113.9°(1.5°)		

^a Not refined.

^b Calculated from Be—C, C—H and Be···H. Not corrected for shrinkage.

covered the diffraction range $s=2.0$ Å⁻¹ to 17.0 Å⁻¹. Beyond this point the molecular intensity was swamped by the unusually heavy background. Three plates were photometered and processed in the usual way.⁵

Fourier inversion of the modified molecular intensity yields the radial distribution curve shown in Fig. 1. The curve contains peaks at 1.1 Å (the C—H bond distance) 1.7 Å (the Be—C bond distance), 2.4 Å (the Be···H nonbonded distance), 3.4 Å (C···C) and 4.0 Å (C···H). In crystalline polymeric dimethylberyllium Be—C_p=1.93 (2) Å and, Be—Be=2.10 (3) Å.⁶ The absence of peaks in the region 1.90 to 2.15 Å in the radial distribution curve must be considered strong evidence against the presence of significant amounts of oligomers in the vapor under our experimental conditions.

The molecular structure was refined by least-squares calculations on the intensity data using a nondiagonal weight matrix.⁷ The C—H and Be—C bond distances, the Be···H nonbonded distance, and the shrinkages of the C···C and C···H distances were refined as independent parameters. The H···H interatomic distances were calculated from C—H, Be—C, and Be···H under the zero-shrinkage approximation. All vibrational amplitudes except those of H···H distances were refined.

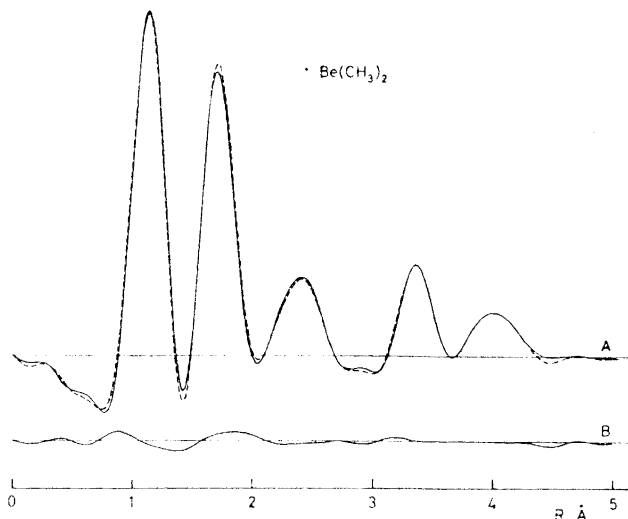


Fig. 1. A: Full line; experimental radial distribution curve. Stippled line; theoretical radial distribution curve. The artificial damping constant, $k=0.005 \text{ \AA}^2$. B: Difference curve.

Refinements were carried out on models with the methyl groups eclipsed (D_{3h}) and staggered (D_{3d}). The two models gave equally good agreement and yielded nearly identical estimates for the molecular parameters. The molecular parameters obtained by refinement on a D_{3h} model and their estimated standard deviations are listed in Table 1. A theoretical radial distribution curve calculated from these parameters is shown in Fig. 1.

The Be—C distance is seen to be nearly identical to the bond distance in di-*t*-butylberyllium, $1.699(3) \text{ \AA}$,⁸ though a difference of the order of 0.015 \AA cannot be ruled out. Hence the bond distance offers no indication of hyperconjugation. Similar negative conclusions were reached in recent electron diffraction studies of $B(\text{CH}_3)_3$,⁹ and monomeric $\text{Al}(\text{CH}_3)_3$.¹⁰ Indeed charge-iterated extended Hückel molecular orbital calculations¹¹ yield π -bond overlap populations of the M—C bonds that amount to less than 10% of the σ -bond overlap population in all three molecules.

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