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MICROWAVE SPECTRUM, STRUCTURE AND DIPOLE MOMENT OF CYCLOPENTADIENYLBERYLLIUM HYDRIDE

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Summary

Microwave spectra of C_5H_5BeH, C_5H_5BeD, $^{13}CC_4H_5BeH$, and $^{13}CC_4H_5BeD$ are reported. The molecule is a C_{5v} symmetrical top. The Be—H bond length was found to be 1.32 Å with an error limit of 0.01 Å and the C—C bond length was determined as 1.423 Å with one standard deviation of 0.001 Å. The distance from the beryllium atom to the centre of the cyclopentadienyl ring, *h*, and the C—H bond length were assumed to be 1.49 Å and 1.09 Å, respectively. The dipole moment was determined through the Stark effect to be 2.08 D with one standard deviation of 0.01 D. Four different vibrationally excited normal modes were identified and their frequencies determined by relative intensity measurements.

Introduction

G.L. Morgan and his coworkers at the University of Wyoming have synthesized a series of compounds of formulae CpBeX (Cp = cyclopentadienyl), and a number of these have been the subject of structure investigations at the University of Oslo. $CpBeCH_3$ [1], CpBeCCH [2], CpBeBr [2] and $CpBeBH_4$ [3] have been studied by means of gas phase electron diffraction and CpBeCl by both electron diffraction [4] and microwave spectroscopy [5].

Recently Bartke and Morgan have succeeded in synthesizing the simplest member of the series CpBeH [6], and we decided to determine the length of a terminal Be—H bond in this compound, no such bond distance having been published hitherto, in order to obtain structure parameters for ab initio molecular orbital calculations.

Experimental

CpBeH and CpBeD were synthesized as described elsewhere [6]. The microwave spectrum was measured with the brass absorption cells cooled to

TABLE 1

MICROWAVE SPECTRUM OF C_5H_5BeH AND C_5H_5BeD

$v = 0$ denotes ground vibrational state, while $v_1 = 1$, $v_2 = 1$, $v_3 = 1$ and $v_4 = 1$ denote first excited vibrational states of four different normal modes.

Transition	C_5H_5BeH										C_5H_5BeD	
	$v = 0$		$v_1 = 1$		$v_2 = 1$		$v_3 = 1$		$v_4 = 1$		$v = 0$	
	Obs. [a]	Calc.	Obs. [b]	Calc.	Obs. [b]	Calc.	Obs. [b]	Calc.	Obs. [b]	Calc.	Obs. [a]	Calc.
$J = 0 \rightarrow 1$	12425.31	12425.24	12376.93	12376.98	12399.68	12399.64	12414.14	12414.10	—	—	11480.89	11480.53
$J = 1 \rightarrow 2$	24850.50	24850.47	24753.83	24753.96	24798.98	24799.01	24828.41	24828.21	24879.87	24879.81	22960.98	22961.06
$J = 2 \rightarrow 3$	37275.67	37275.71	37131.06	37130.95	37198.51	37198.52	37242.18	37242.32	37319.67	37319.71	34441.51	34441.58

[a] ± 0.10 MHz. [b] ± 0.15 MHz.

about −10°. The compound was quite unstable under these conditions having a half life of a few minutes. Decomposition was accompanied by a rapidly increasing pressure and a "flow-through" arrangement was necessary to minimize the undesirable reaction products. One of these was identified by its microwave spectrum as cyclopentadiene. The spectrometer was of the conventional Stark modulation type and has been described briefly before [7]. Measurements were made in the 10-38 GHz spectral region with apparent pressures in the 2-40 micron range.

Attempts were also made to record the electron diffraction pattern of CpBeH, but analysis of diffraction data recorded on Balzers Eldiograph KD-G2 with a nozzle temperature of 65° revealed that the compound had partially decomposed. A quantitative structure determination by this method was therefore impossible.

Spectra

The spectra of CpBeH and CpBeD are typical of symmetric tops, consisting of groups of lines separated by constant intervals, and the C_{5v} symmetry of the molecule was thus confirmed. The individual group encompasses the very strong ground state line surrounded by some few moderate intensity vibrationally excited satellite lines. The $J = 0 \rightarrow 1$, $1 \rightarrow 2$, and $2 \rightarrow 3$ transitions were measured and are reported in Table 1. No effect of centrifugal distortion was noted and the lines could be least squares fitted satisfactorily to the simple formula (eqn. 1)

$$\nu = 2B_v J(J + 1) \tag{1}$$

with the results shown in Tables 1 and 3.

The moderately strong ground state spectra of $^{13}CC_4H_5BeH$ and $^{13}CC_4H_5BeD$ are characteristic of slightly oblate asymmetric rotors. The measured transitions are shown in Table 2 and the results of a rigid-rotor least squares analysis are found in Tables 2 and 3.

Beryllium is known to have a spin of 3/2. This should lead to quadrupole splittings of the observed transitions. The $J = 0 \rightarrow 1$ is predicted to have the largest splittings and a thorough examination at very low pressures of this line was undertaken. However, no splitting was observed indicating that it must be less

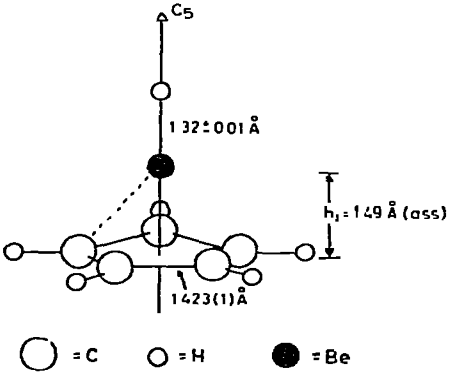

Fig. 1. Molecular model of C_5H_5BeH.

TABLE 2

MICROWAVE SPECTRA OF $^{13}CC_4H_5BeH$ AND $^{13}CC_4H_5BeD$

Transition	$^{13}CC_4H_5BeH$		$^{13}CC_4H_5BeD$	
	Obs. [a]	Obs. — Calc.	Obs. [a]	Obs. — Calc.
$0_{0,0}\rightarrow 1_{1,0}$	12310.95	−0.03	—	—
$1_{0,1}\rightarrow 2_{1,1}$	24511.28	0.08	22667.10	0.02
$1_{1,0}\rightarrow 2_{2,0}$	24625.02	−0.11	22765.15	0.11
$1_{1,1}\rightarrow 2_{2,1}$	24728.94	−0.17	22853.18	0.00
$2_{1,1}\rightarrow 3_{2,1}$	36770.02	0.04	34003.65	−0.13
$2_{0,2}\rightarrow 3_{1,2}$	36910.38	0.01	34120.80	0.14
$2_{1,2}\rightarrow 3_{2,2}$	36930.12	−0.11	34140.08	−0.12
$2_{2,0}\rightarrow 3_{3,0}$	36050.09	0.00	34159.89	−0.12
$2_{2,1}\rightarrow 3_{3,1}$	37096.92	0.20	34282.65	−0.12
σ (MHz) [b]	0.11		0.11	

[a] ± 10 MHz. [b] σ is the standard deviation of the fit.

than about 0.5 MHz. This indicates that the absolute value of the beryllium atom quadrupole coupling constant is less than about 2 MHz.

Vibrationally excited states

Four vibrationally excited states presumably belonging to four different normal modes were assigned as shown in Table 1. Relative intensity measurements were performed observing most but not all of the precautions of ref. 8. As indicated in Table 4, all excited state lines are weak in comparison with the ground state line. This behaviour is expected for a very rigid molecule. Owing to the relative feebleness of the excited state lines they were compared to the ground state $0_{0,0}\rightarrow 1_{1,0}$ transition of $^{13}CC_4H_5BeH$ rather than to the parent species ground state line as improved accuracy was obtained this way. Table 4 yields the vibrational frequencies derived assuming Boltzmann distribution and statistical weights of 1 and 2, respectively. The results are expected to be accurate to within ± 75 cm^{-1}.

As no complete vibrational analysis of the molecules is as yet availabe,

TABLE 3

ROTATIONAL CONSTANTS FOR DIFFERENT SPECIES OF CYCLOPENTADIENYLBERYLLIUM HYDRIDE

Uncertainties represent one standard deviation

Species		A (MHz)	B (MHz)	C (MHz)
C_5H_5BeH	$(v = 0)$	6212.619 ± 0.008	6212.619 ± 0.008	—
	$v_1 = 1$	6188.492 ± 0.017	6188.492 ± 0.017	—
	$v_2 = 1$	6199.753 ± 0.008	6199.753 ± 0.008	—
	$v_3 = 1$	6207.054 ± 0.023	6207.054 ± 0.023	—
	$v_4 = 1$	6219.952 ± 0.010	6219.952 ± 0.010	—
C_5H_5BeD		5740.264 ± 0.036	5740.264 ± 0.036	—
$^{13}CC_4H_5BeH$		6209.52 ± 0.03	6100.56 ± 0.03	4369.1 ± 8.6
$^{13}CC_4H_5BeD$		5736.56 ± 0.03	5643.51 ± 0.03	4368.0 ± 6.8

TABLE 4

RELATIVE INTENSITIES AND VIBRATIONAL FREQUENCIES FOR C_5H_5BeH

Temperature 264 K.

Vibrational mode [a]	Relative intensity	Vibrational frequency [b] (cm^{-1})	Vibrational frequency [c] (cm^{-1})
$\nu_1 = 1/\nu = 0$	0.165	325	452
$\nu_2 = 1/\nu = 0$	0.061	516	643
$\nu_3 = 1/\nu = 0$	0.066	487	614
$\nu_4 = 1/\nu = 0$	0.020	717	843

[a] See text. [b] Assuming *A* symmetry (statistical weight = 1). [c] Assuming *E* symmetry (statistical weight = 2).

assignment of the various excited state lines to distinct normal modes is quite uncertain. However, the ν_4 frequency of Tables 1 and 4 is tentatively assigned to the ring—beryllium—hydrogen bending mode. This assignment is made because its rotational transitions appear at the high frequency side with respect to the ground state transitions and because a substantial increase in its intensity was seen for the deuterated species. The other three modes presumably involve the ring—beryllium stretching mode and two low-frequency ring-bending frequencies.

Dipole moment

The $M = 0$ component of the $J = 0 \rightarrow 1$ transition of CpBeH was used to determine the dipole moment. A d.c. voltage was applied between the Stark septum and the cell with the modulating square wave voltage superimposed. The d.c. voltage was measured with a digital voltmeter having an accuracy of 0.025%. The electric field was calibrated using the OCS $J = 0 \rightarrow 1$ transition with $\mu_{OCS} = 0.71521$ D (ref. 9).

A dipole moment of 2.08 ± 0.01 D for CpBeH was derived from the second order Stark effect of the above named transition. The error limit quoted represents one standard deviation with possible systematic errors taken into account.

Structure

The coordinates of the ring-carbon atoms and the hydrogen atom attached to beryllium can be calculated by the substitution method [10]. Both CpBeH and CpBeD can be employed as the parent molecule. The results in each case are shown in Table 5.

Two important structural parameters may be calculated from these coordinates. The first is the C—C distance which is found to be 1.4235 ± 0.0002 Å with CpBeH as the parent species, and 1.4222 ± 0.0003 Å with CpBeD as the basic molecule. The uncertainties were calculated from the standard deviations of the rotational constants. The best estimate is considered to be the average of the two, viz. 1.423 Å, which is presumably very close to the equilibrium C—C distance because of the rigid nature of the molecule and the large off-symmetry *y*-axis coordinate. The standard deviation is estimated to be 0.001 Å.

TABLE 5

SUBSTITUTION COORDINATES [a] FOR CYCLOPENTADIENYLBERYLLIUM HYDRIDE

Atom	Parent molecule	z (Å)	y (Å)
C	C_5H_5BeH	0.2070 ± 0.0011	1.2109 ± 0.0002
H	C_5H_5BeH	−2.5964 ± 0.0001	0.0
Be [b]	C_5H_5BeH	−1.204 ± 0.007	0.0
C	C_5H_5BeD	0.2461 ± 0.0028	1.2098 ± 0.0003
H	C_5H_5BeD	−2.5621 ± 0.0001	0.0
Be [b]	C_5H_5BeD	−1.36 ± 0.02	0.0

[a] The uncertainties represent one standard deviation calculated from the standard deviations of the rotational constants. They are thus only a mesure for the precision with which the operationally defined substitution coordinates are obtained. [b] Calculated from $\Sigma m_i z_i = 0$ assuming the hydrogens attached to the carbons to be coplanar with these.

The second structural parameter is the distance from the centre of the Cp-ring to the hydrogen atom bonded to beryllium. In the CpBeH system this is calculated to be 2.803 ± 0.001 Å, whereas with CpBeD this distance is calculated as 2.808 ± 0.003 Å. The best value is considered to be the average, i.e. 2.806 ± 0.003 Å as shown in Table 6.

The position of the beryllium atom cannot be determined by the substitution method because it has no stable isotopes. If the hydrogen atoms in the Cp-ring are assumed to be coplanar with the carbons the first moment equation $\Sigma m_i z_i = 0$ can be employed to locate beryllium. The results of such a procedure are seen in Table 5. Unfortunately, no accurate z-coordinate for beryllium could be obtained this way, largely because of the small and uncertain z-coordinate of the carbon atoms. Therefore, in order to determine the Be—H bond length, the distance from beryllium to the centre of the Cp-ring had to be assumed. A value of 1.49 Å was preferred, since in $CpBeCH_3$ [1], CpBeCl [4, 5], CpBeCCH [2] and $CpBeBH_4$ [3] the height was found to lie in the range $h = 1.49 \pm 0.01$ Å. (In CpBeBr [2] h could only be very inaccurately determined, but the value obtained was not significantly different from 1.49 Å.) This assumption leads to a Be—H bond distance of 1.32 ± 0.01 Å, where the uncertainty represents the error limit.

The microwave data contain little information on the C—H distance which has been assumed to be 1.09 Å as shown in Table 6.

TABLE 6

MOLECULAR STRUCTURE [a] OF C_5H_5BeH

	Distance (Å)
C—C	1.423 ± 0.001
C—H [b]	1.09
Be—ring (h) [b]	1.49
Be—H	1.32 ± 0.01
H···ring	2.806 ± 0.003

[a] See text. [b] Assumed.

Discussion

The Be—H bond distance in CpBeH is somewhat greater than the Be—H bond distance (1.28 Å) calculated from the Be—C bond distance in monomeric $(CH_3)_2Be$ [11] (1.70 Å) by first adding the C—H bond distance (1.11 Å) and then subtracting the C—C bond distance in ethane [12] (1.53 Å). It is, however, somewhat shorter than the Be—H distance in the shortlived species BeH [13], 1.343 Å. As is to be expected it is considerably shorter than the Be—H (bridge) distance in $(Et_4Be_2H_2)Na_2 \cdot 2Et_2O$, 1.48 (0.03) Å [14, 15].

The C—C bond distance obtained for CpBeH by microwave spectroscopy is in excellent agreement with the C—C distances obtained for the other compounds of type CpBeX previously investigated by electron diffraction [1-4]. These ranged from 1.420 to 1.428 Å, all with estimated standard deviations of 0.002 Å.

We wish to postpone discussion of the dipole moment until the results of ab initio molecular orbital calculations are available, and will only note that the dipole moment of CpBeH, as was to be expected, is considerably smaller than in CpBeCl [5], 4.26 ± 0.16 D.

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