

- (20) M. F. Hawthorne and R. L. Pilling, *J. Am. Chem. Soc.*, **88**, 3873 (1966).
 (21) H. R. Bachmann, H. Nöth, R. Rinek, and K. C. Kompa, *Chem. Phys. Lett.*, **29**, 627 (1974).
 (22) J. Plešek, S. Hermanek, B. Stibrand, and F. Hanousek, *Collect. Czech. Chem. Commun.*, **32**, 1095 (1967); **33**, 699 (1968).
 (23) J. Rathke and R. Schaeffer, *Inorg. Chem.*, to be published.
 (24) J. H. Hall, D. A. Dixon, D. A. Kleier, T. A. Halgren, L. D. Brown, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **97**, 4202 (1975).
 (25) D. A. Kleier, T. A. Halgren, J. H. Hall, and W. N. Lipscomb, *J. Chem. Phys.*, **61**, 3905 (1974).
 (26) (a) S. F. Boys, *Rev. Mod. Phys.*, **32**, 296 (1960); (b) J. M. Foster and S. F. Boys, *ibid.*, **32**, 300 (1960); (c) S. F. Boys, "Quantum Theory of Atoms, Molecules and the Solid State", P.-O. Löwdin, Ed., Academic Press, New York, N.Y., 1966, p 253.
 (27) C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 457 (1963).
 (28) D. A. Dixon, D. A. Kleier, T. A. Halgren, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **96**, 2293 (1974).
 (29) D. A. Dixon, J. H. Hall, D. A. Kleier, T. A. Halgren, and W. N. Lipscomb, to be submitted.
 (30) E. Switkes, R. M. Stevens, W. N. Lipscomb, and M. D. Newton, *J. Chem. Phys.*, **51**, 2085 (1969).
 (31) T. A. Halgren, R. J. Anderson, D. S. Jones, and W. N. Lipscomb, *Chem. Phys. Lett.*, **8**, 547 (1971).
 (32) T. A. Halgren, to be published.
 (33) R. L. Sneath and L. J. Todd, U.S. National Technical Information Service, AD Rep. No. 745355 (1972); *Chem. Abstr.*, **77**, 172107w (1972).

Vibrational Spectra and Structure of Methylberyllium Borohydride

Louis J. Allamandola and Joseph W. Nibler*

Contribution from the Department of Chemistry, Oregon State University, Corvallis, Oregon 97331. Received August 8, 1975

Abstract: Vapor density measurements of unsaturated methylberyllium borohydride at 1.2 Torr show that this species is predominantly dimeric in the gas phase. It was found that the major features of the infrared spectrum of the annealed solid agree with those of the vapor, implying that the solid is made up of dimeric units also. Infrared and Raman spectra further show the borohydride moiety is attached to beryllium by a double hydrogen bridge. From comparison with Raman spectra of solid dimethylberyllium, known to contain only methyl bridges, it is concluded that methylberyllium borohydride contains two bridging methyl groups. The spectra are consistent with C_{2h} molecular symmetry and vibrational assignments of $(CH_3BeBH_4)_2$ and $(CH_3Be^{10}BD_4)_2$ are presented on this basis. Vibrations characteristic of BeH_2BH_2 and bridging methyl groups are identified and compared with analogous compounds. With the exception of the deformation modes, the methyl vibrations are generally quite close to those of terminal methyl groups. The deformation frequencies are significantly higher for bridged methyls and thus serve as a basis for identification of this type of bonding.

Recent studies of metal borohydrides have shown a variety of structures for these electron deficient compounds, with both double $[Al(BH_4)_3, C_5H_5BeBH_4]^2$ and triple $[Be(BH_4)_2, Zr(BH_4)_4]^5$ hydrogen bridges being observed. Perhaps the most unusual metal borohydride yet reported is $Be(BH_4)_2$, which is believed to exist in two vapor forms, one with double hydrogen bridges and a more stable linear C_{3v} form containing triple hydrogen bridges, HBH_3BeH_3BH . For the solid, however, x-ray⁶ and spectroscopic⁷ studies reveal a helical polymeric structure of linked ions: $\dots (BH_4^-) \dots (H_2BH_2Be^+) \dots (BH_4^-) \dots$. This borderline tendency of $Be(BH_4)_2$ toward an ionic structure is consistent with the fact that all the other group 2 (and group 1) borohydrides are ionic salts. Such unusual bonding and structural changes might well be expected for other metal borohydrides, and a number of those which are expected to lie between the ionic and covalent extremes have recently been investigated. One such compound is methylzinc borohydride which has been shown to convert from a double hydrogen bridged structure in the vapor phase to an ionic form $CH_3Zn^+ \dots BH_4^-$ in the solid.⁸ Similarly, $U(BH_4)_4$ is believed to change from a tetrahedral, triple-bridged vapor form to a polymeric ionic form involving both BH_4^- ions and double bridged (H_2BH_2U) units in the solid phase.⁹

At present a clear picture has not emerged as to which metal atom properties dominate in determining the structures (ionic or covalent) or the type of hydrogen bridging (double or triple) present in metal borohydrides. As part of a continuing effort in this direction, we report here the spectral investigation of a $Be(BH_4)_2$ derivative: methylberyllium borohydride, CH_3BeBH_4 . The gas-phase infrared spectrum of this molecule has been reported previously by

Cook and Morgan¹⁰ and they concluded that the vapor consists of a mixture of monomer and methyl-bridged dimer. A freezing point depression experiment showed the molecule to be dimeric in benzene. In our study we have examined this equilibrium by vapor density measurements and by trapping the vapor at low pressure using matrix isolation techniques. Our intention was to obtain infrared and Raman spectra of both monomer and dimer but, as described below, it was not possible to obtain significant amounts of the monomer. Thus this report deals primarily with the spectrum and structure of dimeric CH_3BeBH_4 in the solid phase.

Experimental Section

The samples of CH_3BeBH_4 , $CH_3Be^{10}BD_4$, and $(CH_3)_2Be$ were prepared by Dr. Thomas Cook and the syntheses have been described previously.¹⁰ Since these compounds are pyrophoric and poisonous, all sample handling was done in a greaseless vacuum system in a hood. The vapor density at 24 °C was measured at two pressures using a Granville Phillips capacitance manometer and an inert oil (Halocarbon Products Corp., series 10-25) manometer. At saturation, 129.4 ± 0.5 mg of CH_3BeBH_4 gave a pressure of 5.6 ± 0.2 Torr in 5.7 ± 0.1 l., yielding a molecular weight of 75 ± 5 g/mol (mol wt $CH_3BeBH_4 = 39$ g/mol). At lower pressures, 25.2 ± 0.5 mg of $CH_3Be^{10}BD_4$ in a volume of 5.89 ± 0.06 l. gave a pressure of 1.2 ± 0.1 Torr, from which the molecular weight is 69 ± 8 g/mol (mol wt $CH_3Be^{10}BD_4 = 42$ g/mol). Thus the material is largely dimeric in the vapor phase even under nonsaturated conditions.

Infrared and Raman spectra of films sublimed onto a polished aluminum block cooled by a Displex closed cycle cooler were obtained as follows. The samples were annealed to about 200 K at least three times until the infrared spectra no longer changed. In-

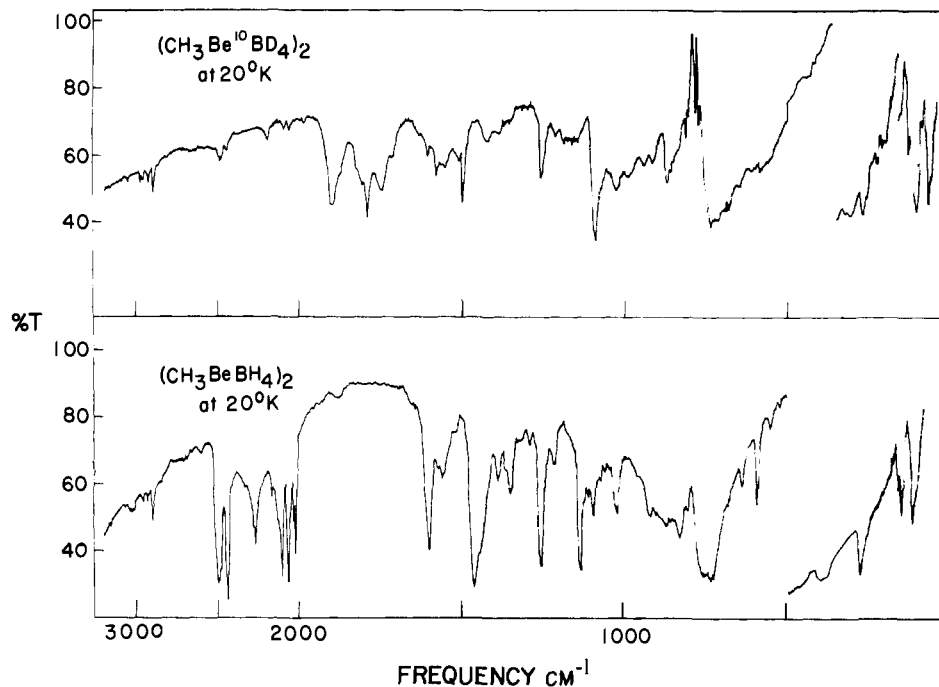


Figure 1. Infrared spectra of solid methylberyllium borohydride dimer.

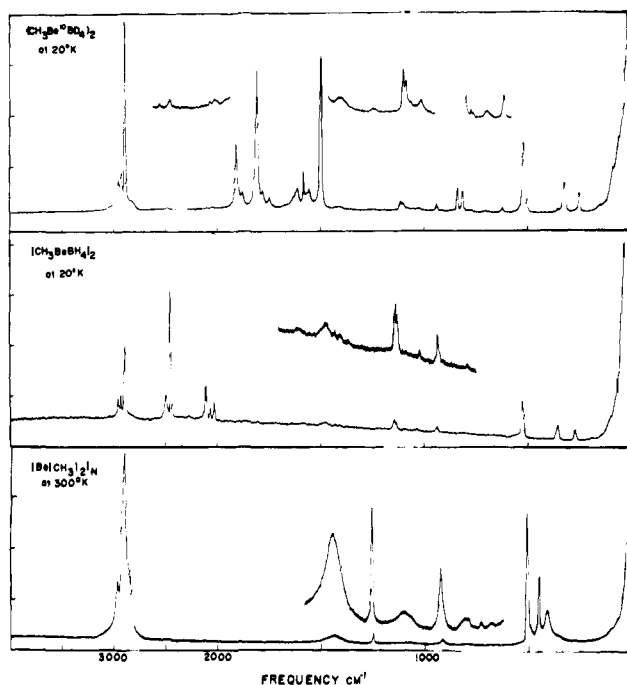


Figure 2. Raman spectra of solid methylberyllium borohydride dimer and dimethylberyllium polymer.

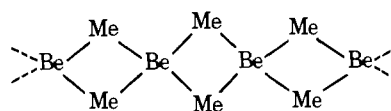
frared and far-infrared spectra were recorded at 20 K using a Perkin-Elmer 180 spectrophotometer with a reflection arrangement. The entire cell was then positioned in a Cary 82 Raman spectrometer and the Raman spectrum of the same sample was recorded. This spectrum was unchanged from that obtained at room temperature for the compound (in its original glass sample container), thus the low-temperature spectra properly represent the annealed crystalline state.

Some efforts were made to obtain matrix spectra of both monomeric $(\text{CH}_3)_2\text{Be}$ and CH_3BeBH_4 by co-depositing separate sample and Ar beams. The sample jet was heated to try to increase the amount of monomeric species but, in all cases, the spectra were characteristic of mostly dimer plus some decomposition products (CH_4 and B_2H_6). Further work on the monomer using much lower sample pressures and premixed samples is planned.

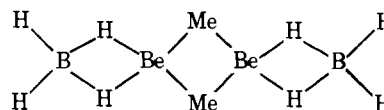
Results and Discussion

Structure of the Dimer. The vapor density measurements confirm that CH_3BeBH_4 is predominantly dimeric in the vapor phase and the close correspondence of the infrared spectra of the vapor and the solid implies that the latter is also composed of dimeric units. The infrared spectra of the solid are present in Figure 1 while Raman spectra of $(\text{CH}_3\text{BeBH}_4)_2$, $(\text{CH}_3\text{Be}^{10}\text{BD}_4)_2$, and $(\text{CH}_3\text{BeCH}_3)_n$ are displayed in Figure 2. The frequencies are tabulated in Table I along with our assignments where the choices seem reasonably clear.

There seems little doubt that $(\text{CH}_3\text{BeBH}_4)_2$ contains two methyl bridges; the spectra contain all of the major features of the $(\text{CH}_3\text{BeCH}_3)_n$ spectrum and the latter compound is known from x-ray studies¹¹ to be



The relative simplicity of the spectra suggests a symmetric configuration and, as discussed below, the terminal and bridge BH stretching regions clearly indicate double bridged BeH_2BH_2 units. Thus the structure can be represented as



This model has been proposed previously for the gaseous dimer by Cook and Morgan. The exact configuration of the methyl group relative to the framework is not known, as is also the case for the only other extensively studied methyl-bridged compounds, $(\text{CH}_3\text{BeCH}_3)_n$ ¹¹ and $(\text{CH}_3)_6\text{Al}_2$.¹² However, it seems likely that the three-center bridge bonds involve an sp^3 hybrid orbital from each Be and C atom. This would align the two methyl threefold axes in the bridging plane, but it is not clear what relative orientation of these groups would be preferred. For $(\text{CH}_3)_6\text{Al}_2$, it has been assumed that an inversion center would be retained

Table I. Vibrational Frequencies (cm⁻¹) of Methylberyllium Compounds

(CH ₃ BeBH ₄) ₂ (20 K)		(CH ₃ BeBD ₄) ₂ (20 K)		(CH ₃ BeCH ₃) _n (20 K)		Assignment		
Raman	Infrared	Raman	Infrared	Raman	Infrared ^a			
2959 m	2952 w	2960 m	2962 vw	2970 m	2912 vw } 2885 w }	νCH ₃ asym		
2933 m	2926 w	2934 m	2925 vw	2900 vs			νCH ₃ sym	
2896 s	2890 m	2896 s	2891 m		1897 s	νBH _{2t} asym		
2502 m	2493 s	1909 s	1897 s	1793 s			νBHD _t } νBH _{2t} sym	
2444 s	2437 s	2497 w }	1747 s		1498 s	νBH _{2b} sym		
		1880 m }		1607 m }			1580 m }	νBH _{2b} asym
		1810 s }						
1782 m }	1440 bd, m	δCH ₃ asym						
1748 m }			1250 m	1255 vs } 1243 vs }	δCH ₃ sym			
2103 s						2097 s	1503 s	1498 s
2063 m	2056 s	1614 m				1607 m }	νBH _{2b} asym	
2023 m	2017 s	1586 m	1580 m }	νBeH _{2b}				
1615 vw	1607 s	1117 w	1095 s }		1440 bd, m	δCH ₃ asym		
							1480 bd, w	1468 bd, vs
1430 vw	1397 m	1430 bd, w	1429 bd, w	1250 m	1255 vs } 1243 vs }	δCH ₃ sym		
1408 w	1353 m	1270 vvw	1388 w, sh					
1143 m	1143 w	819 m	873 s	918 m	835 vs	τBH _{2t} } δBH _{2t}		
		1134 m					843 m	800 w }
1026 w	1029 m	789 w	788 s	918 m	835 vs	νBeC asym		
		937 m	924 m				945 m	942 m
796 w	831 m	712 w	814 m	800 w }	835 vs	ρBH ₂ wag		
		627 vw	874 m				628 m	680 w }
526 s	594 s	524 s	588 m, sh	505 vs	567 m }	νBeB		
		357 m	332 m				310 w	455 s
273 m	277 s	261 m	268 m	410 s	427 s }	νBeBe		
		194 w	152 s				162 w	132 w
194 w	120 s	162 w	132 w	410 s	403 s }	δCBeC ₂ Be		
		120 s	105 s				105 s	105 s
						δBeC ₂ Be		

^a Reference 14.Table II. BeH₂BH₂ Group Vibrations of (CH₃BeBH₄)₂ and Related Compounds

	C _{2h} species	(CH ₃ BeBH ₄) ₂		(CH ₃ Be ¹⁰ BD ₄) ₂		C ₅ H ₅ BeBH ₄ ^a		C ₅ H ₅ BeBD ₄ ^a		BeBH ₄ ^{+b}		BeBD ₄ ^{+b}	
		H/D	H/D	H/D	H/D	H/D	H/D	H/D	H/D	H/D	H/D		
νBH _{2t} asym	B _g R	2502	1.31	1909	2475	1.33	1864	2510	1.32	1892			
	B _u Ir	2493	1.31	1897									
sym	A _g R	2444	1.35	1810	2424	1.35	1789	2450	1.36	1802			
	A _u Ir	2437	1.36	1793									
νBH _{2b} sym	A _g R	2103	1.40	1503	2166	1.38	1574	2118	1.41	1502			
	A _u Ir	2097	1.40	1498									
asym	B _g R	2043 ^c	1.29	1586 ^c	2170	1.33	1627	2075	1.33	1557			
	B _u Ir	2037 ^c	1.29	1580 ^c									
νBeH _{2b} sym	A _g R	1615	1.45	1117	1477	1.36	1087	1540	1.43	1077			
	A _u Ir	1607	1.47	1095									
asym	B _g R	1480	1.43	1032	1470	1.35	1092	(1540)	1.43	(1077)			
	B _u Ir	1468	1.42	1032									
τBH _{2t}	A _g R	1143	1.40	819	1173	1.40	836						
	A _u Ir	1143											
δBH _{2t}	A _g R	1134	1.35	843	1131	1.21	(938)	1128	1.37	823			
	A _u Ir	1138	1.30	873									
ρBH _{2t} rock	B _g R	1026	1.30	789	990	1.32	752	1010	1.27	791			
	B _u Ir	1029	1.31	788									
ρBH _{2t} wag	B _g R	874	1.20	712	823	1.17	704	970	1.16	834			
	B _u Ir			~730									
νBeB	A _g R	~740	1.01	~730	888	1.05	847	722	1.04	700			
	A _u Ir												
δBeH ₂ B	B _g R	194	1.20	162	182	1.20	152	405	1.17	346			
	B _u Ir	152	1.15	132									

^a Reference 2. ^b Reference 7. ^c Average of several components.

and that a reflection plane would bisect that Al ... Al axis to give C_{2h} overall symmetry.¹³ We have made a similar assumption for (CH₃BeBH₄)₂ on the basis that the rule of mutual exclusion seems to generally apply when the spectra

are examined closely. For C_{2h} symmetry, half the 54 normal modes are Raman active (14 A_g + 13 B_g) and half are infrared active (12 A_u + 15 B_u); these have been broken down further by group vibrations in Tables II and III.

Table III. Be(CH₃)₂Be Group Vibrations of (CH₃BeBH₄)₂ and Related Compounds

		C _{2h} labels	(CH ₃ BeBH ₄) ₂	(CH ₃ BeBD ₄) ₂	(CH ₃ BeCH ₃) _n ^a	(CH ₃) ₆ Al ₂ ^b	CH ₃ ZnCH ₃ ^c
CH ₃ Modes							
νCH ₃	asym	$\left\{ \begin{array}{l} A_g \text{ R} \\ B_g \text{ R} \\ A_u \text{ Ir} \\ B_u \text{ Ir} \end{array} \right.$	2959	2960	2970	2932	2966
			2933	2934		2892	
			2926	2925	2912	2899	
			2952	2962		2941	
νCH ₃	sym	$\left\{ \begin{array}{l} A_g \text{ R} \\ B_u \text{ Ir} \end{array} \right.$	2896	2896	2900	2824	2900
			2890	2891	2885	2837	2915
δCH ₃	asym	$\left\{ \begin{array}{l} A_g \text{ R} \\ B_g \text{ R} \\ A_u \text{ Ir} \\ B_u \text{ Ir} \end{array} \right.$	1408	1430	1440	1436	1434
			1430	1430	1440	1436	
			1397	1429		1437	
			1353	1388		1437	
δCH ₃	sym	$\left\{ \begin{array}{l} A_g \text{ R} \\ B_u \text{ Ir} \end{array} \right.$		1270	1250	1255	1157
			1257	1258	1249 ^d	1255	1183
ρCH ₃		$\left\{ \begin{array}{l} A_g \text{ R} \\ B_g \text{ R} \\ A_u \text{ Ir} \\ B_u \text{ Ir} \end{array} \right.$	627	628	680	632	704
			796	789	800	725	
			831	819		768	
						608	
τCH ₃		$\left\{ \begin{array}{l} B_g \text{ R} \\ A_u \text{ Ir} \end{array} \right.$				(336)	620
						(328)	
Skeletal Modes							
νBeC		$\left\{ \begin{array}{l} A_g \text{ R} \\ B_g \text{ R} \\ A_u \text{ Ir} \\ B_u \text{ Ir} \end{array} \right.$	526	524	505	453	
			937	945	918	(390)	
			594	588	551 ^d	367	
			924	942	835	480	
νBeBe			357	332	455	313	
δBeC ₂ Be			120	105		(40)	
δBBE ₂ C ₂ Be or (δCBeC ₂ Be)		$\left\{ \begin{array}{l} B_g \text{ R} \\ B_u \text{ Ir} \\ B_u \text{ Ir} \end{array} \right.$	273	261	410		
				310	427		
			277	268	403		
τBH ₂ Be		$\left\{ \begin{array}{l} A_g \text{ R} \\ A_u \text{ Ir} \end{array} \right.$					

^aIr data from reference 14. ^bReference 13. ^cReference 15. ^dAverage of two components.

Vibrational Assignments

BeH₂BH₂ Group Vibrations. Table II presents assignments for the double-bridged BeH₂BH₂ fundamental vibrations and offers a comparison with previous results for C₅H₅BeBH₄² and for BeBH₄⁺ in solid Be(BH₄)₂.⁷ The appearance of *two* BH_t stretches in both the infrared and Raman spectra is strongly indicative of terminal BH₂ groups and the observations in the bridge stretch and bending regions further confirm the presence of double hydrogen bridges. The stretching assignments are straightforward since the symmetric and antisymmetric vibrations fall in different regions and one of each is expected in both the infrared and Raman spectra. Only the symmetric BeH_{2b} bridge stretches at 1615 and 1607 cm⁻¹ are perhaps questionable since these frequencies are high compared with those for C₅H₅BeBH₄ and BeBH₄⁺. However, the strong infrared intensity of the 1607-cm⁻¹ peak favors its assignment as a fundamental mode rather than as an overtone or combination band.

The BH_{2t} bending modes are assigned reasonable values but overlap with the CH₃ rocking bands makes it impossible to be certain of all the assignments (particularly for (CH₃BeBD₄)₂). The infrared active Be ... B stretching band is easily identified by its large intensity and breadth, features characteristic of a substantial ionic contribution (e.g., >Be⁺ ... BH₄⁻) to the bridge bonding. In line with this, the BeH_{2b} stretches display strong, broad infrared bands and the Raman intensities of such "interior" modes are low. The BeH_{2b}B out-of-plane bridge bending modes at 194 and 152 cm⁻¹ also fit this pattern and the low values observed for (CH₃BeBH₄)₂ and C₅H₅BeBH₄ cast doubt on the earlier BeBH₄⁺ assignment⁷ at 405 cm⁻¹.

CH₃ Group Vibrations. The fundamental assignments for the bridging methyl motions are given in Table III along with values for (CH₃BeCH₃)_n¹⁴ and (CH₃)₆Al₂.¹³ The observation of *three* CH stretches in both the infrared and Raman spectra is in accord with the assumed C_{2h} symmetry and indicates that "free" methyl rotation does not occur. The CH stretches and bends do not vary much among the four compounds, suggesting that there is little coupling between the CH₃ group and the framework. Frequencies are also listed in the last column of Table III for dimethylzinc¹⁵ to provide a comparison between bridge and terminal methyl groups. The values are rather similar but the low values of two of the terminal CH₃ deformations (~1300 asym, 1170 cm⁻¹ sym) compared to bridge CH₃ frequencies (~1400 asym, 1250 cm⁻¹ sym) establish a basis for distinction between the two bonding possibilities. The higher values for the bridging methyl deformations are reasonable in terms of increased repulsion by the delocalized electrons in the bridge bonds. The CH₃ torsional frequencies would be of particular interest in these compounds but, in the absence of CD₃ data, no basis for their identification is at hand. Ogawa has calculated values near 330 cm⁻¹ for these torsions in (CH₃)₆Al₂ but these results will depend strongly on the torsional force constants assumed. In dimethylzinc, the methyls are presumed to be freely rotating.

Skeletal Modes. Four BeC ring stretches are expected, two Raman active, two infrared active. The A_g Raman band near 500 cm⁻¹ stands out for all the compounds and its assignment is certain. There is also a medium infrared feature in this region for each molecule and we choose to label this the A_u mode by analogy with (CH₃)₆Al₂.¹³ For the remaining B_g and B_u stretches only a small frequency shift is expected on BH₄ deuteration, and we also anticipate

that these frequencies will change only slightly in going to $(\text{CH}_3\text{BeCH}_3)_n$. In the 200–1000- cm^{-1} Raman region in Figure 2, it can be seen that only a band near 930 cm^{-1} fits these expectations, and accordingly it is assigned as the B_g mode. This high value, compared to $(\text{CH}_3)_6\text{Al}_2$, is not unreasonable in view of the much lighter mass for the Be atom. Moreover, an infrared counterpart for the B_u mode occurs in the same frequency region. It should be noted however that these B_g and B_u assignments yield a slight *upward* shift in frequency on deuteration ($B_g = 937 \rightarrow 945$, $B_u = 924 \rightarrow 942 \text{ cm}^{-1}$). This behavior suggests that these frequencies may involve repulsive mixing with the BH_{21} twisting and deformation modes which drop *below* 900 cm^{-1} on BH_4 deuteration. A similar effect has been observed for the asymmetric BeC stretch in monomeric CH_3BeCH_3 in going to CD_3BeCD_3 (1081 \rightarrow 1150 cm^{-1}).¹⁶

The Be \cdots Be stretch would be of A_g symmetry and hence should have high Raman intensity but no nearby infrared counterpart. The $(\text{CH}_3\text{BeBH}_4)_2$ feature at 357 cm^{-1} satisfies this requirement and also gives an H/D ratio of 1.08, the same as that calculated for a $(\text{BH}_4\text{Be}) \cdots (\text{BeBH}_4)$ point mass model. For dimethylberyllium this frequency is significantly higher (455 cm^{-1}) whereas the BeC stretches are actually lower. This implies that the electron density has shifted somewhat from the bridge bonds into the middle of the Be \cdots Be region in $(\text{CH}_3\text{BeCH}_3)_n$. The lowest frequency skeletal mode should be the out-of-plane BeC_2Be bend and the far infrared band at 120 cm^{-1} seems a logical choice since no other feature was observed down to 33 cm^{-1} . The assignments of the remaining skeletal modes are uncertain but are not unreasonable.

Summary

From vapor density measurements, methylberyllium borohydride has been shown to be largely dimeric in the vapor phase even at low pressures. The infrared spectra of the

vapor and solid phases are quite similar, indicating that there is no significant structural change on condensation. The infrared and Raman spectra of the solid contain all of the major features of the spectra of $(\text{CH}_3\text{BeCH}_3)_n$, a polymer known to involve methyl bridges. The BH stretching and bending frequencies further establish the presence of double hydrogen bridges between the Be and B atoms, and thus a C_{2h} model with double hydrogen and methyl bridges is favored. The spectra are satisfactorily assigned in terms of this model and the BeH_2BH_2 and CH_3 group vibrations are compared with similar molecules.

Acknowledgment. The authors wish to thank Dr. Thomas Cook for providing the samples used in this work. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

References and Notes

- (1) A. Almenningen, G. Gundersen, and A. Haaland, *Acta Chem. Scand.*, **22**, 328 (1968).
- (2) D. A. Coe, J. W. Nibler, T. H. Cook, D. Drew, and G. L. Morgan, *J. Chem. Phys.*, in press.
- (3) G. Gundersen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.*, **59**, 3777 (1973).
- (4) J. W. Nibler, *J. Am. Chem. Soc.*, **94**, 3349 (1972).
- (5) V. Plato and K. Hedberg, *Inorg. Chem.*, **10**, 590 (1971).
- (6) D. S. Marynick and W. N. Lipscomb, *J. Am. Chem. Soc.*, **93**, 2322 (1971).
- (7) J. W. Nibler, D. F. Shriver, and T. H. Cook, *J. Chem. Phys.*, **54**, 5257 (1971).
- (8) J. W. Nibler and T. H. Cook, *J. Chem. Phys.*, **58**, 1596 (1973).
- (9) E. R. Bernstein, W. C. Hamilton, T. A. Keiderling, S. J. LaPlaca, S. J. Lippard, and J. J. Mayerlie, *Inorg. Chem.*, **11**, 3009 (1972).
- (10) T. H. Cook and G. L. Morgan, *J. Am. Chem. Soc.*, **92**, 6487 (1970).
- (11) A. Shaw and R. Rundle, *Acta Crystallogr.*, **4**, 348 (1951).
- (12) A. Almenningen, S. Halvorsen, and A. Haaland, *Acta Chem. Scand.*, **25**, 1937 (1971).
- (13) T. Ogawa, *Spectrochim. Acta*, **24**, 15 (1968).
- (14) G. Goubeau and K. Walter, *Z. Anorg. Allg. Chem.*, **322**, 58 (1963).
- (15) T. Shimanouchi, *J. Phys. Chem. Ref. Data*, **3**, 269 (1974).
- (16) R. A. Kovar and G. L. Morgan, *Inorg. Chem.*, **8**, 1099 (1969).

A Semiempirical Theory of Substituent-Induced ^{13}C Chemical Shifts in π Systems¹

D. J. Sardella

Contribution from the Department of Chemistry, Boston College, Chestnut Hill, Massachusetts 02167. Received March 19, 1975

Abstract: A general semiempirical theory of ^{13}C chemical shifts induced by substituents in hydrocarbon π systems is outlined. Beginning with the assumption that the shifts reflect substituent-induced electron density redistributions, it is shown that substituent chemical shifts in any π system can be calculated using a two-parameter equation, analogous to a linear free-energy equation, involving an atom-atom polarizability, obtained from Hückel molecular orbital calculations, and an empirically determined substituent parameter. Predictions of the theory are tested against available experimental data for four representative substituents: methyl, methoxyl, chloro, and cyano.

The earliest systematic studies of ^{13}C chemical shifts revealed cumulative effects of substituents to be remarkably additive.² Empirical additivity schemes abound in the literature and are frequently employed for shift assignments. Their major shortcomings are that each substituent requires one parameter for each unique carbon in the monosubstituted molecule, and that parameters are not transferable between different molecular systems. Thus, the wealth of tabulated data for benzene derivatives might be expected to

be applicable to systems such as styrenes, less useful for naphthalenes, and virtually useless for acyclic π systems or nonbenzenoid ring systems, such as azulenes. As Table I illustrates, even for closely related molecular systems, substituent-induced chemical shifts (SCS) can vary widely. The observed variability in the empirical parameters for any single type of carbon position (for instance, three bonds removed from the site of attachment of the substituent) suggests that SCS are governed by both the nature of the