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BERYLLIUM

ANNUAL SURVEY COVERING THE YEARS 1977 AND 1978

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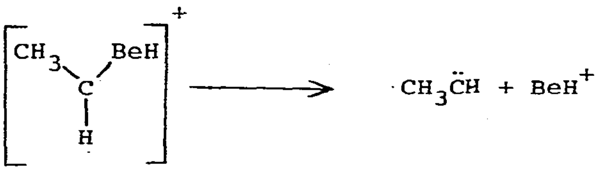
I. CALCULATIONS

During 1977 and 1978 the papers which report calculations on organoberyllium molecules and species, both real and fanciful, have outnumbered the papers in which experimental studies are described.

Dewar and Rzepa (1) have reported results of MNDO calculations (heats of formation, molecular geometries, ionization potentials, dipole moments) for more than 50 compounds containing beryllium. The list includes beryllium hydrides, borohydrides, alkyls, alkynyls and cyclopentadienyls. Partial results are shown in Tables 1 and 2. Others have reported MO calculations on CH_3BeH and $(CH_3)_2Be$ (2), CNDO/2 MO calculations on $(CH_3)_2Be\cdot$amine complexes (3), *ab initio* single determinant MO calculations (STO-3G, 6-31G*) on CH_3BeH, CH_2Be, BeH_2, $HBeBH_2$ (4,5), *ab initio* unrestricted Hartree-Fock calculations (4-31G and STO-3G) on $CH_2{=}C(BeH)_2$ (6), *ab initio* SCF MO Gaussian 70 (STO-3G, 4-31G) calculations on carbonium ions stabilized by BeH substitution, e.g., $[CH_2BeH]^+$ (7). The following dissociation energies were calculated:

$$[CH_2BeH]^+ \longrightarrow :CH_2 + BeH^+$$



$$[CH_3CH(BeH)]^+ \longrightarrow CH_3\ddot{C}H + BeH^+$$

$$[CH_2{=}C{-}BeH]^+ \longrightarrow CH_2{=}C: + BeH^+$$

(Continued on p. 6)

Previous survey see J. Organometal. Chem., Vol. 143 (1977) p. 129-139.

TABLE 1. Results of MNDO Calculations on Organoberyllium Compounds: Physical Properties (1)

Calculated(Observed) Properties of Beryllium Compounds

Compound	Point Group	ΔH_f calcd, kcal mol^{-1}	IP_1,[a] eV	μ, D
BeH_2	$D_{\infty h}$	5.6 (-8[c])	12.26	
Be_2H_4	D_{2h}	-45.8	12.10	
Be_3H_8	D_{2d}	-107.4	12.17	
HBH_3BeH	C_{3v}	-31.0	12.88	0.03
H_2BH_2BeH	C_{2v}	-26.7	12.90	0.78
HBH_3BeH_3BH	D_{3d}	-54.6	12.86	
$H_2BH_2BeH_2BH_2$	D_{2d}	-56.0	13.17	
$H_2BeH_2BH_2BH_2$	C_{2v}	-6.5	11.40	4.04
Me_2Be	D_{3d}	-47.2	10.77(10.67)[d]	
Me_4Be_2	C_{2h}	-119.5	10.67	
Et_2Be	C_{2h}	-58.7	10.42(9.46)[d]	
$C(BeH)_4$	T_d	-125.9	11.69	
$C(BeH)_4$	D_{4h}	-100.4	10.26	
η^5-CpBeH	C_{5v}	12.77	9.88(9.64)[e]	2.02(2.08)[f]
η^5-CpBeH	C_s	21.9	8.82	0.43
η^5-CpBeC≡CH	C_{5v}	33.9	9.45	1.27
η^1-CpBeC≡CH	C_s	41.5	8.66	1.52
$(\eta^5\text{-Cp})_2Be$	D_{5d}	47.6	8.42	
$(\eta^5\text{-Cp})_2Be$	D_{5h}	47.8	8.42	

η^5-CpBe-η^1-Cp	C_s	31.8	8.38	2.53
$(\eta^1$-Cp$)_2$Be	C_{2h}	38.8	8.76	
$MeBeH_3BH$	C_{3v}	-55.6	11.46	0.49
$MeBeH_2BH_2$	C_{2v}	-52.0	11.57	1.35
$H_2BH_2BeMe_2BeH_2BH_2$	C_{2h}	-133.0	11.48	
$HBH_3BeMe_2BeH_3BH$	C_{2h}	-112.0	11.04	
η^5-CpBeH$_3$BH	C_s	-5.9	9.67	2.58
η^5-CpBeH$_2$BH$_2$	C_s	-6.4	9.70	3.46

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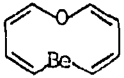
[a] Calculated using Koopman's theorem. [b] Calculated using the half-electron approximation. [c] M. Ducros, R.Levy, and G. Mehava, Bull. Soc. Chim.Fr., 2763 (1970). [d] D.B. Chambers, G.E. Coates, and F. Glockling, J. Chem. Soc. A. 741 (1970). [e] W. Goodman, personal communication. [f] T. Bartke, A. Bjørseth, A. Haaland, K.M. Marstokk, and H. Møllendal, J. Organometal. Chem., 85, 271 (1975).

TABLE 2. Results of MNDO Calculations on Organoberyllium Compounds: Molecular Geometries (1)

Molecule	Point Group	Calcd[a] (obsd) values for geometrical values	Ref
Be_4	Td	BeBe, 1,850	
Be_{13}	D_{3h}	a 2.090(2.287),c 3.704(3.584)	b
Be_{13}	D_{3d}	a 2.264, c 3.1364	
BeH^+	$C_{\infty v}$	BeH 1.247 (1.312)	c
$BeH\cdot$	$C_{\infty v}$	BeH 1.291 (1.343)	c
$BeH_3{}^+$	C_{2v}	BeH 1.253, BeH' 1.708, H'H 0.726	
BeH_4	C_{2v}	BeH 1.291, BeH' 1.862, H'H 0.690	
BeH_2	$D_{\infty h}$	BeH 1.278	
Be_2H_4	D_{2h}	BeH_t 1.285, BeH_b 1.504, BeBe 2.055	
Be_3H_6	D_{2d}	BeH_t 1.285, BeH_b 1.490, BeBe 2.018	
HBH_3BeH	C_{3v}	HB 1.156, BeH_t 1.277, BeH_b 1.711, BeB 1.752	
H_2BH_2BeH	C_{2v}	HB 1.164, BeH_t 1.276, BeH_b 1.543, BeB 1.903, HBBe 121.2	
HBH_3BeH_3BH	D_{3d}	BH_t 1.157(1.16)BH_b 1.242(1.303),BeB 1.779(1.790) H_bBH_t 111.4 (117.5)	d
$H_2BH_2BeH_2BH_2$	D_{2d}	BH_t 1.164, BH_b 1.309, BeB 1.911, H_tBH_t 118.6	
Me_2Be	D_{3d}	BeC 1.660 (1.698)BeCH 111.8 (113.9)	e
Me_4Be_2	C_{2h}	BeC_t 1.698,BeC_b 1.878,CH_t 1.114, 1.117, CH_b 1.125, 1.130	

Et_2Be	C_{2h}	BeC 1.669,CC 1.527,BeCC 115.9,CH 1.121, 1.111, CCH 108.4,111.9	
$C(BeH)_4$	T_d	CBe 1.636 (1.630)	f
$C(BeH)_4$	D_{4h}	CBe 1.656 (1.622)	f
η^5-CpBeH	C_{5v}	BeH 1.285 (1.320),BeC 1.991 (1.919),CC 1.458 (1.432),CH 1.084 (1.090)	g
η^5-CpBeC≡CH	C_{5v}	BeC 1.609(1.634),BeC 1.993 (1.919),C≡C 1.209 (1.231), CC 1.457 (1.428)	h
$(\eta^5\text{-Cp})_2Be$	D_{5d}	BeC 2.071(2.256,1.907)CC 1.449 (1.425)	i
η^5-$CpBeH_2BH_2$	C_s	BH_t 1.166(1.170),BH_b 1.271 (1.29)BeH_b 1.611(1.78),BeC 2.019^k (1.915), CC 1.456^k (1.422), CH 1.084 (1.116)	j
η^5-$CpBeH_3BH$	C_s	BH_t 1.159(1.16),BH_b 1.230 (1.28),BeH_b 1.818, BeC 2.021 (1.915) CC 1.455 (1.422),CH 1,084 (1.116)	j
	C_{2v}	BeO 1.833, OC^1 1.389, C^1C^2 1.363, C^2C^3 1.459, C^3C^4 1.360, C^4Be 1.680	

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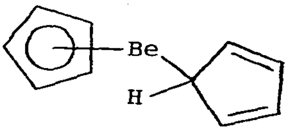
[a] Bond length A^iB^j (in angstroms) and bond angle $A^iB^jC^k$ (in degrees). [b] a and c are the unit cell dimensions; cf. K.J.H. Mackay and N.A. Hill, J. Nucl. Mater., 8, 263 (1963). [c] G. Herzberg, "Molecular Spectra and Molecular Structure. Infrared Spectra of Diatomic Molecules", 2nd ed, Van Nostrand, Princeton, N.J., 1960. [d] G. Gundersen, L. Hedberg, and K. Hedberg, J.Chem.Phys., 59, 3777 (1973). [e] A. Almenningen, A. Haaland, and G.L. Morgan, Acta Chem. Scand., 23, 2921 (1969). [f] Calculated using the Gaussian 70 program with a 3G basis set: J.B. Collins, J.D. Dill, E.D. Jemmis, Y. Apeloig, P.v.R. Schleyer, R. Seeger, and J.A. Pople, J.Am.Chem.Soc., 98, 5419 (1976). [g] Reference f, Table II. [h] A. Haaland and D.P. Novak, Acta Chem. Scand., 28, 153 (1974). [i] A. Almenningen, O. Bastiansen, and A. Haaland, J.Chem.Phys., 40, 3434 (1964); A. Haaland, Acta Chem. Scand., 22, 3031 (1968), [j] D.A. Drew, G. Gundersen, and A. Haaland, Acta Chem. Scand., 26, 2147 (1972). [k] Average values.

Similar calculations were made to determine the stabilizing effect of BeH and other substitution on D_{3h} pentacoordinate carbonium ions, $[H_3C(BeH)_2]^+$ in the case of BeH substitution (8). CH_3BeH was included in these calculations.

Also reported have been ab initio MO calculations on the reactions of $Be(2^3P)$ with CH_4 (9).

The most popular organoberyllium compound for calculations has been dicyclopentadienylberyllium, with calculational studies having been reported by Dewar and Rzepa (1), Chiu and Schäfer (10), Demuynck and Rohmer (11), Marynick (12), Jemmis, Alexandratos, Schleyer, Streitwieser and Schaefer (13) and Liu (14). MNDO, ab initio MO (STO-3G) and PRDDO calculations seem to agree that the π-σ structure, 1, is the most stable. It would appear, however, that most of the calculations made thus far, by their own admission, are not definitive. In view of this and in view of the conflicting experimental structural conclusions, beryllocene remains one of the more vexing molecules in organometallic chemistry. Calculations also have shown C_5H_5BeH to be a stable species. A C_{5v} structure with η^5 bonding and considerably greater covalent bonding than in C_5H_5Li was indicated (13).



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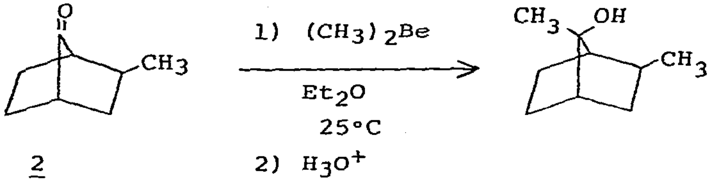
A theoretical (ab initio STO-3G,SCF) study of beryllium cyclooctatetraenide, BeC_8H_8, also has been carried out (15). A structure in which the divalent beryllium cation is outside, rather than inside, the C_8 plane was found to be more stable. Also considered was the possible structure of $C_8H_8(BeH)_2$.

2. EXPERIMENTAL STUDIES

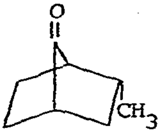
Details of the process for the preparation of beryllium hydride by the controlled pyrolysis of di-tert-butylberyllium diethyl etherate developed in the Ethyl Corporation laboratories in Baton Rouge, Louisiana, have been published (16). The product was obtained as a thermally stable, amorphous solid in purities of 90-98 weight percent. The residual impurities were found to be due to incomplete pyrolysis and ether cleavage. Also examined was the pyrolysis of $(n\text{-}C_4H_9)_2Be$, $(i\text{-}C_4H_9)_2Be$ and its diethyl etherate, $(t\text{-}C_4H_9)_2Be$, $(i\text{-}C_4H_9)(t\text{-}C_4H_9)Be$ and $(Me_3CCH_2)_2Be\cdot OEt_2$.

None gave BeH_2 of comparable purity. The decomposition of dineopentylberyllium diethyl etherate above 200°C resulted in formation of dimethylberyllium rather than beryllium hydride, which is not surprising since β-elimination of Be-H cannot take place. The conversion of amorphous to crystalline BeH_2 has been described (17).

The methylation of norbornanones by dimethylberyllium has been examined by Ashby and Noding (18):



In a competition of 2 and 3 for a deficiency of dimethylberyllium, the methylation of 3 was favored by a factor of two.



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The redistribution reaction was used to prepare cyclopentadienyl(methyl)beryllium and the cyclopentadienylberyllium halides (19):

$$(C_5H_5)_2Be + BeY_2 \xrightarrow{\text{no solvent}} 2\ C_5H_5BeY$$

$(Y = CH_3, Cl, Br, I)$

Cyclopentadienyl(methyl)beryllium, a volatile liquid, and the C_5H_5Be halides, all solids, are stable to redistribution and highly air- and moisture-sensitive. In benzene they are monomeric. The structure determination of those compounds where Y = CH_3, Cl and Br by gas phase electron diffraction has been detailed in previous Beryllium Annual Surveys. Their IR, proton NMR and mass spectra were studied. Another group has reported the vibrational spectra of C_5H_5BeCl and C_5D_5BeCl (20).

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Gaines and his coworkers have prepared $Be(B_3H_8)_2$, $C_5H_5Be-B_3H_8$ and $CH_3BeB_3H_8$ (21). The latter is a dimer. The reactions used in these syntheses are summarized below.

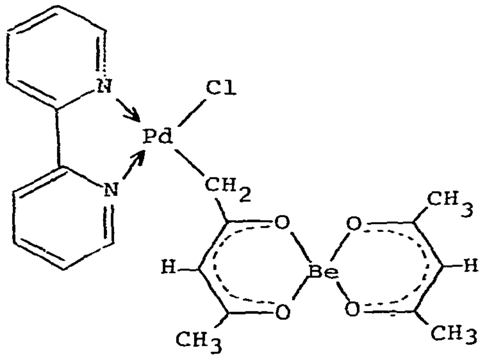
$$BeCl_2 + 2\ CsB_3H_8 \longrightarrow Be(B_3H_8)_2$$

$$Be(B_3H_8)_2 + NaC_5H_5 \longrightarrow C_5H_5BeB_3H_8$$

$$Be(B_3H_8)_2 + (CH_3)_2Zn \longrightarrow (CH_3BeB_3H_8)_2$$

The ^1H and ^{11}B NMR spectra of these compounds were studied. Also reported were the gas phase proton and ^{11}B NMR spectra of $Be(BH_4)_2$ (21,22).

Although organoberyllium compounds are not involved, worth noting is a study of the thermochemistry of some beryllium ß-diketonates and the determination of their Be-O bond energies (23) and the preparation of a novel beryllium chelate, 4 (24).



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