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JAHN-TELLER EFFECTS IN THE MNDO APPROXIMATION: STRUCTURES OF THE MOLECULAR CATIONS OF SOME SIMPLE ORGANOBERYLLIUM COMPOUNDS

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Summary

The MNDO method gives geometries for the molecular cations of organoberyllium compounds of types BeR_2 and HBeR (R = CH_3, $CHCH_2$, CCH, CN, C_5H_5), of C_4H_4Be and CH_3BeBeH_3, and of the series $CH_{4-n}(BeH)_n$ (n = 0—4) which have symmetries in precise accord with the predictions of the Jahn-Teller theorem. In the series $CH_{4-n}(BeH)_n$ and $CH_{4-n}(BeH)_n^+$, the barriers to inversion via a planar intermediate decrease with increasing n, are significantly smaller for the cations than for the neutral molecules, and are zero for $CH(BeH)_3^+$ and $C(BeH)_4^+$, both of which have their minimum energy when strictly planar at carbon.

Introduction

In previous papers [1,2] we have demonstrated the reliability of the MNDO semi-empirical SCF-MO technique [3] in predicting Jahn-Teller distortions, consequent upon ionisation, in a wide range of silicon compounds. The molecules previously studied have included only a limited selection of molecular point groups (T_d, D_{3d}, C_{3v}, C_3, D_{2d}, D_2, C_{2v}, C_2 and C_s): the characteristic linear two coordination commonly adopted by beryllium, together with its ready formation of organometallic compounds, opens up the possibility of investigating the structure of molecular cations derived from the organic derivatives of another metallic element, in another selection of point groups. Additional point groups studied in this paper include $D_{\infty h}$, $C_{\infty v}$, D_{5d}, C_{5v}, C_{4v}, and C_{2h}.

Method

Computations were undertaken using MNDO [4] implemented on a VAX 11/780 computer: energies were minimised with respect to all internal coordi-

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TABLE 1

SYMMETRIES AND ENERGIES OF NEUTRAL MOLECULES

Molecule	Optimised point-group	ΔH_f^0 (kJ mol^{-1})	HOMO
$Be(CN)_2$	$D_{\infty h}$	−24.8	$E_{1u}(\Pi_u)$
$Be(CCH)_2$	$D_{\infty h}$	+86.6	$E_{1u}(\Pi_u)$
HBeCN	$C_{\infty v}$	−0.6	$A_1(\Sigma^+)$
HBeCCH	$C_{\infty v}$	+106.1	$E_1(\Pi)$
$(\eta^5\text{-}C_5H_5)_2Be$	D_{5d}	+199.6	E_{1g}
$(\eta^5\text{-}C_5H_5)BeH$	C_{5v}	+53.7	E_1
$(\eta^4\text{-}C_4H_4)Be(^1A_1)$	C_{4v}	+453.8	E
$(\eta^2\text{-}C_4h_4)Be(^3B_2)$	C_{2v}	+480.1	A_1
$Be(CH_3)_2$	D_{3d}	−197.4	A_{2u}
$HBeCH_3$	C_{3v}	−86.9	A_1
$(HBe)_2CH_2$	C_{2v}	−170.2	B_1
$(HBe)_3CH$	C_{3v}	−318.3	E
$(HBe)_4C$	T_d	−525.8	T_2
CH_3BeBeH_3	C_{3v}	−233.5	A_1
$Be(CHCH_2)_2$	C_{2h}	−23.4	B_g
$Be(CHCH_2)_2$	C_{2v}	−23.5	A_2
$HBeCHCH_2$	C_s	+0.4	A''

nates and no geometrical assumptions were made, of any kind. Table 1 contains the optimised point groups, ΔH_f^0 values and the symmetry classes of the HOMO for the neutral molecules, and Table 2 contains optimised point groups, ΔH_f^0 and molecular states for the cations. Optimised geometries are listed in Tables 3 and 4.

Molecular structures

Alkynyls and cyanides

The molecular structures of $Be(CN)_2$, $Be(CCH)_2$, HBeCN, and HBeCCH are

TABLE 2

SYMMETRIES AND ENERGIES OF MOLECULAR CATIONS

Cation	Optimised point-group	ΔH_f^0 kJ mol^{-1}	Molecular state
$Be(CN)_2^+$	$D_{\infty h}$	+1219.9	$^2E_{1u}(^2\Pi_u)$
$Be(CCH)_2^+$	$D_{\infty h}$	+1172.6	$^2E_{1u}(^2\Pi_u)$
$HBeCN^+$	Dissociates to $BeCN^+ + H\cdot$		
$HBeCCH^+$	$C_{\infty v}$	+1108.0	$^2E_1(^2\Pi)$
$(\eta^5\text{-}C_5H_5)_2Be^+$	C_{2h}	+978.8	^2A_g
$(\eta^5\text{-}C_5H_5)BeH^+$	C_s	+948.1	$^2A'$
$(\eta^2\text{-}C_4H_4)Be^+$	C_{2v}	+1160.0	$^2A_1$
$Be(CH_3)_2^+$	D_{3d}	+795.6	$^2A_{2u}$
$HBeCH_3^+$	C_{3v}	+913.2	$^2A_1$
$(HBe)_2CH_2^+$	C_{2v}	+747.5	$^2B_1$
$(HBe)_3CH^+$	C_{2v}	+617.1	$^2B_1$
$(HBe)_4C^+$	D_{4h}	+468.7	$^2A_{2u}$
$CH_3BeBeH_3^+$	C_{3v}	+656.4	$^2A_1$
$Be(CHCH_2)_2^+$	C_{2h}	+876.5	^2B_g
$Be(CHCH_2)_2^+$	C_{2v}	+877.2	$^2A_2$
$HBeCHCH_2^+$	C_s	+903.4	$^2A''$

TABLE 3

GEOMETRIES OF NEUTRAL MOLECULES [a]

$Be(CN)_2$	BeC, 1.614; CN, 1.170
$Be(CCH)_2$	BeC, 1.598; CC, 1.210; CH, 1.053
BHeCN	HBe, 1.271; BeC, 1.627; CN, 1.170
HBeCCH	HBe, 1.275; BeC, 1.604; CC, 1.290; CH, 1.053
$(\eta^5\text{-}C_5H_5)_2Be$	BeC, 2.071 (1.907, 2.256); CC, 1.449 (1.425); CH, 1.084 (1.103); HCC, 125.6; HCCC, 170.4
$(\eta^5\text{-}C_5H_5)BeH$	BeC, 1.990; CC, 1.458 (1.423); CH, 1.084; BeH, 1.284 (1.32); HCC, 125.6; HCCC, 174.9
$(\eta^4\text{-}C_4H_4)Be({}^1A_1)$	BeC, 1.785; CC, 1.514; CH, 1.076; HCC, 131.6; HCCC, 161.2
$(\eta^2\text{-}C_4H_4)Be({}^3B_2)$	BeC(1), 1.809 (X2), BeC(2), 2.014(X2); CC, 1.504 (X4), 2.033 (X1), 2.044 (X1); C(1)H, 1.081 (X2); C(2)H, 1.074 (X2); HC(1)C(2), 128.7; HC(2)C(1), 134.4; HC(1)C(2)C(1′), 158.7; HC(2)C(1)C(2′), 152.1; ring dihedral, 150.5
$Be(CH_3)_2$	BeC, 1.659 (1.698); CH, 1.115 (1.127); BeCH, 111.9 (113.9)
$HBeCH_3$	HBe, 1.279; BeC, 1.661; CH, 1.116; BeCH, 111.6
$(HBe)_2CH_2$	HBe, 1.279; BeC, 1.646; CH, 1.126; HCH, 106.6; BeCBe, 114.0
$(HBe)_3CH$	HBe, 1.280; BeC, 1.637; CH, 1.140; BeCH, 107.9
$(HBe)_4C$	HBe, 1.280; BeC, 1.636
CH_3BeBeH_3	HC, 1.115; CBe(1), 1.683; Be(1)Be(2), 1.708; HBe(1), 1.701; HBe(2), 1.415; HCBe(1), 112.1
$Be(CHCH_2)_2$	BeC(1), 1.637; C(1)C(2), 1.343; C(2)H, 1.106; C(2)H(*trans*), 1.092; C(2)H(*cis*), 1.092; BeC(1)C(2), 128.7; BeC(1)H, 114.5; C(1)C(2)H (*trans*), 123.5; C(1)C(2)H(*cis*), 124.0
$HBeCHCH_2$	HBe, 1.277; BeC(1), 1.640; C(1)C(2), 1.342; C(1)H, 1.106; C(2)H(*trans*), 1.092; C(2)H(*cis*), 1.092; BeC(1)C(2), 128.6; BeC(1)H, 114.4; C(1)C(2)H(*trans*), 123.5; C(1)C(2)H(*cis*), 124.1

[a] Distances XY in Å; bond angles XYZ and torsional angles WXYZ in degrees: experimental values in parentheses.

TABLE 4

GEOMETRIES OF MOLECULAR CATIONS [a]

$Be(CN)_2^+$	BeC, 1.628; CN, 1.212
$Be(CCH)_2^+$	BeC, 1.601; CC, 1.247; CH, 1.060
$HBeCCH^+$	HBe, 1.259; BeC, 1.687; CC, 1.284; CH, 1.065
$(\eta^5\text{-}C_5H_5)_2Be^+$	BeC(1), 2.062 (X4); BeC(2), 2.078 (X4); BeC(3), 2.076 (X2); C(1)C(1′), 1.489 (X2); C(1)C(2), 1.433 (X4); C(2)C(3), 1.466 (X4); C(1)H, 1.086 (X4); C(2)H, 1.087 (X4); C(3)H, 1.086 (X2)
$(\eta^5\text{-}C_5H_5)BeH^+$	BeC(1), 2.105 (X2); BeC(2), 2.054(X2); BeC(3), 2.123 (X1); C(1)C(1′), 1.514 (X1); C(1)C(2), 1.425 (X2); C(2)C(3), 1.479 (X2) C(1)H, 1.089 (X2); C(2)H, 1.090 (X2); C(3)H, 1.088 (X1)
$(\eta^2\text{-}C_4H_4)Be^+$	BeC(1), 1.772 (X2); BeC(2), 1.947 (X2); CC, 1.512 (X4), 2.068 (X1), 2.153 (X1); C(1)H, 1.085 (X2); C(2)H, 1.080 (X2); HC(1)C(2), 129.2; HC(1)C(2), 134.1; HC(1)C(2)C(1′), 158.4; HC(2)C(1)C(2″), 149.9; ring dihedral 154.7
$Be(CH_3)_2^+$	BeC, 1.687, CH, 1.115; BeCH, 105.0
$HBeCH_3^+$	HBe, 1.261; BeC, 1.786; CH, 1.116; BeCH, 98.8
$(HBe)_2CH_2^+$	HBe, 1.258; BeC, 1.756; CH, 1.126; HCH, 104.9; BeCBe, 89.0; CBeH, 172.7
$(HBe)_3CH^+$	HBe(1), 1.262 (X1); HBe(2), 1.260 (X2); Be(1)C, 1.723 (X1); Be(2)C, 1.750 (X2); CH, 1.149; Be(1)CBe(2), 91.2 (X2); CBe(2)H, 176.0 (X2)
$(HBe)_4C^+$	HBe, 1.266; BeC, 1.745
$CH_3BeBeH_3^+$	HC, 1.110; CBe(1), 1.858; Be(1)Be(2), 1.689; HBe(1), 1.566; HBe(2), 1.494; HCBe(1), 98.3
$Be(CHCH_2)_2^+$	BeC(1), 1.633; C(1)C(2), 1.388; C(1)H, 1.108; C(2)H(*trans*), 1.092; C(2)H(*cis*), 1.091; BeC(1)C(2), 130.5; BeC(1)H, 113.5; C(1)C(2)H(*trans*), 122.5; C(1)C(2)H-(*cis*), 123.0
$HBeCHCH_2^+$	HBe, 1.261; BeC(1), 1.719; C(1)C(2), 1.389; C(1)H, 1.111; C(2)H(*trans*), 1.099; C(2)H(*cis*), 1.097; BeC(1)C(2), 129.8; BeC(1)H, 111.1; C(1)C(2)H(*trans*), 122.2; C(1)C(2)H(*cis*0, 123.2

[a] Distances XY in Å; bond angles XYZ and torsional angles WXYZ in degrees.

all calculated to be linear. There are no experimental data for the structures of molecules of this type although the structure of C_5H_5BeCCH is known [5]: in this molecule the Be—C≡ distance is 1.634(8) suggesting that the values in Table 3 are slightly too low. It is interesting to note that in the corresponding pairs RBeCX (X = CH or N) the BeC distance is the larger when X = N: a similar difference is noted in species R_3SiCX for both R = H [6,7] and R = CH_3 [8,9].

No change in point group occurs upon ionisation for these molecules, but the ion $HBeCN^+$ is unstable and dissociates to $H^\cdot$ and $BeCN^+$. This ion is a 10-electron triatomic and is linear, as expected [10], with BeC = 1.551 Å and CN = 1.173 Å, and electronic configuration: $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^4$. On ionisation, the lengths of the bonds BeC, CN and CC all increase, while the bonds HBe and CH undergo little change, save in HBeCN where the hydrogen is lost entirely upon ionisation. This difference reflects the symmetry of the HOMO in these molecules, π spanning the heavy atoms in all except HBeCN where it is Σ^+, concentrated primarily in the HBe bond.

Polyhapto ligands

In common with most other metals, beryllium forms cyclopentadienyl derivatives, both $(C_5H_5)_2Be$ and those of type C_5H_5BeY where Y = H, Cl, Br, CH_3, and CCH. The species C_5H_5BeY (except for Y = CH_3) all have C_{5v} symmetry [5,11,12]: the structure of $(C_5H_5)_2Be$ is complex, having two pentahapto rings in the gas phase with C_{5v} symmetry [13], while in the solid the structure is temperature dependent, with at low temperature (—120° C) one pentahapto and one monohapto ring [14], and at room temperature two rings "slipped" with respect to one another [15], analogous to the "slipped" bis-dicarbollides.

The isomerism of $(C_5H_5)_2Be$ has been discussed in terms of MNDO calculations by Dewar and Rzepa [16]: the bis-pentahapto isomer optimises to a structure of D_{5d} symmetry, and in this we concur with Dewar. The calculated BeC distance is 2.071 Å compared with the observed [13] values for the isolated molecule of 1.907 Å and 2.256 Å. We have further investigated the structure of this molecule by calculating the potential function for the motion of the beryllium atom along the fivefold symmetry axis. For this calculation, some constraints were applied to the geometry, in order to economise on computation: since for free optimisation both rings are found to be of local C_{5v} symmetry (the hydrogens form a plane distinct from the plane of the carbon atoms), each ring was constrained to C_{5v} symmetry in the potential calculation, but with the dimensions of the two rings allowed to optimise separately; the two rings were further constrained to be parallel as the beryllium position was varied.

Only a single minimum was found: the energy variation ΔV was well fitted to a harmonic-quartic potential function in the displacement δr of the beryllium atom from the mid-point of the line joining the ring centres:

$$\Delta V/\text{kJ mol}^{-1} = 8.46 \times 10^{-4} (\delta r/\text{Å})^2 + 1.01 \times 10^{-6} (\delta r/\text{Å})^4$$

This contrasts with the electron-diffraction results [13] which show two minima corresponding to $\delta r = \pm 0.2$ Å. Significant changes are calculated to occur in the geometries of the two rings as the beryllium is displaced from its

TABLE 5

VARIATION OF $(C_5H_5)_2Be$ GEOMETRY AS Be IS DISPLACED FROM MID-POINT

δr (Å) [a]	$d(C_1Be)$ (Å)	$d(C_2Be)$ (Å)	h (Å) [b]	$d(C_1C_1')$ (Å)	$d(C_2C_2')$ (Å)	$d(C_1H)$ (Å)	$d(C_2H)$ (Å)
0.00	2.0708	2.0708	3.3274	1.4494	1.4494	1.0835	1.0835
0.01	2.0631	2.0785	3.3275	1.4500	1.4487	1.0836	1.0836
0.02	2.0556	2.0864	3.3280	1.4506	1.4481	1.0836	10.835
0.05	2.0341	2.1112	3.3314	1.4526	1.4462	1.0837	1.0835
0.10	2.0011	2.1556	3.3435	1.4560	1.4432	1.0837	1.0833
0.15	1.9722	2.2045	3.3649	1.4593	1.4406	1.0839	1.0833
0.20	1.9460	2.2566	3.3925	1.4626	1.4380	1.0838	1.0830
0.25	1.9238	2.3136	3.4300	1.4657	1.4357	1.0839	1.0829
0.30	1.9051	2.3753	3.4766	1.4686	1.4336	1.0840	1.0828
$C_5H_5^-$	—	—	—	—	1.4180	—	1.0827

[a] Distance of Be atom from mid-point of ring centres. [b] Distance between ring centres.

minimum position (see Table 5). Naturally, one BeC distance decreases and the other increases, and it is perhaps noteworthy that the difference between the two distances equal to that, 0.349 Å, deduced from the electron-diffraction data, occurs at a value of δr somewhere between 0.20 and 0.25 Å, in good agreement with the experimental value 0.2 Å. As the beryllium is displaced the distance between the two rings becomes steadily larger, again passing the experimental value 3.37 Å at a tolerably good value of δr. Within the rings, that which is closer to the beryllium becomes steadily larger, both in CC and CH, while the more distant ring becomes steadily smaller, approaching in fact the dimensions calculated for the isolated $C_5H_5^-$ anion: this is indicative of increased ionicity of the bonding to the more distant ring, itself confirmed by the variation in the atomic charges as the beryllium is displaced. These data suggest that in the isolated molecule the two rings should not be considered to have the same dimensions, the difference in CC being ca. 0.027 Å, but in CH no more than 0.001 Å. The original gas-phase electron diffraction studies [12] assumed that the two rings have the same size.

For the carbocycle C_4H_4, all calculations agree that the singlet form is rectangular with D_{2h} symmetry while the triplet is square with D_{4h} symmetry. Because of the obvious relationship between this ligand and the cyclopentadienide ion, the molecule C_4H_4Be was investigated, in both singlet and triplet states. Of these the singlet optimised to a structure of full C_{4v} symmetry in

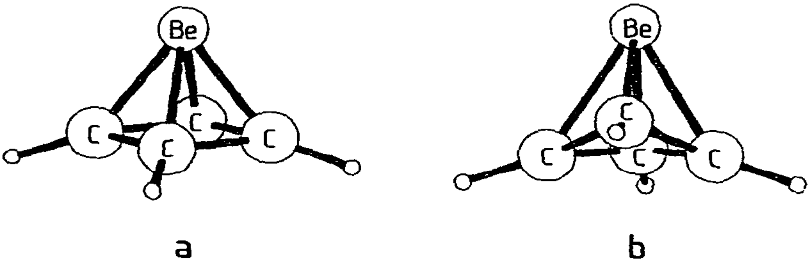

Fig. 1. (a) The structure of C_{4v} ($^1A_1$) C_4H_4Be; (b) The structure of C_{2v} ($^3B_2$) C_4H_4Be.

which the C_4 ring is entirely planar while the triplet optimised to a C_{2v} structure containing a puckered ring (dihedral angle 150.5) which may be described as a dihapto ligand in contrast to the tetrahapto ligand of the singlet. These two structures are shown in Figs. 1(1) and 1(b), respectively.

Vertical ionisation of both $(\eta^5\text{-}C_5H_5)BeH$ and $(\eta^5\text{-}C_5H_5)_2Be$ yields electronically degenerate molecular cations and both ions optimised to structures of lower symmetry, C_s for the hydride and C_{2h} for the bis compound. In each case the motion is along one component of an E_2 vibration to give a structure in which the beryllium is closer to one edge of the ring than to all the others: the local ring symmetry is reduced in each case from C_{5v} to C_s. The detailed geometries are given in Table 4, but are not illustrated as the differences from the neutral parents are not readily perceptible in a Figure.

Vertical ionisation of the singlet form of C_4H_4Be produces a degenerate cation which relaxes along a B_1 vibration of the C_4 ring to produce an ion containing a puckered ring, very similar to that of neutral triplet C_4H_4Be (cf. Fig. 1(a)). Ionisation of triplet C_4H_4Be produces a non-degenerate cation so that no change in symmetry is expected: the cations produced by ionisation of the singlet and triplet states of C_4H_4Be are identical which explains the similarity in structure between $(^3B_2)C_4H_4Be$ and $(^2A_1)C_4H_4Be^+$.

Alkyls and alkenyls

The calculated structures of $Be(CH_3)_2$ and $HBeCH_3$ have D_{3d} and C_{3v} symmetry, respectively: each on-vertical ionisation yields a non-degenerate cation, so that the optimised structures of the cations also have D_{3d} and C_{3v} symmetry, respectively. In each molecule the HOMO is concentrated in the BeC bonds, so that the BeC distances in the cations are larger than in the neutral parents. The CH distances are unchanged by ionisation, but the BeCH angles become smaller, indicative of more *s*-character in the CH bonds.

The molecule CH_3BeBeH_3, if it had the same geometry as $Be(CH_3)_2$, would be electron deficient of two electrons, and in this configuration the LUMO is concentrated in the BeBe vector: that is to say, on exchanging one carbon atom in $Be(CH_3)_2$ for a beryllium atom, the two electrons which are missing are the two from the BeBe bond. Consequently, when the optimisation of the structure of CH_3BeBeH_3 is started from a configuration like that in $Be(CH_3)_2$, the structure calculated contains no direct BeBe but three BeHBe bridges. The

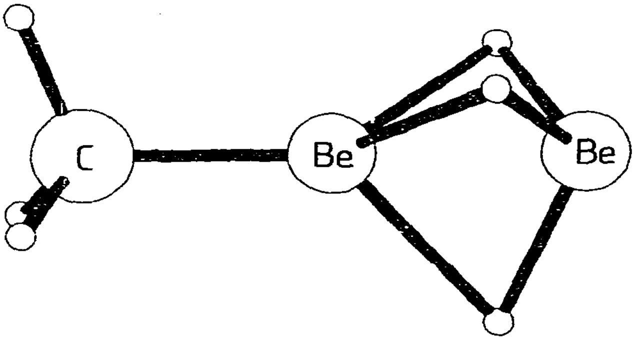

Fig. 2. The structure of CH_3BeH_3Be.

molecule, which is shown in Fig. 2, retains C_{3v} symmetry. The tendency of beryllium to form triple hydrogen bridges rather than double bridges has been noted previously [16,17]: boron, by contrast, generally although not always [18,19], forms double hydrogen bridges. The molecule CH_3BeH_3Be is remarkably stable, its formation as a vapour from CH_3BeH and monomeric BeH_2 being exothermic by 160.2 kJ mol^{-1}. The HOMO in CH_3BeH_3Be is of A_1 symmetry, concentrated in the CBe bond (cf. both $Be(CH_3)_2$ and $HBeCH_3$) so that ionisation effects no change in point group, but causes a large increase in the CBe bond length.

The neutral alkenyl molecules $Be(CHCH_2)_2$ and $HBeCHCH_2$ are both in planar so that $Be(CHCH_2)_2$ can exist in both *cis* (C_{2v}) and *trans* (C_{2h}) isomers: as expected no change in point group occurs on ionisation. In both isomers of $Be(CHCH_2)_2$ the HOMO is a π orbital, bonding within a ligand but antibonding between ligands and not involving the beryllium atom, so that the principal structural change on ionisation is an increase in the CC distance. In $HBeCHCH_2$ the HOMO is a π bonding orbital spanning BeCC so that ionisation causes increases in both the BeC and CC distances.

The series $CH_{4-n}(BeH)_n$

The neutral molecules having $n = 0$–4 optimise to structures having T_d, C_{3v}, C_{2v}, C_{3v}, and T_d symmetry, respectively, in which CBeH angles are always exactly 180°. As n increases the CBe distance steadily decreases and the CH distance increases. When $n = 0$, 3, or 4, vertical ionisation yields a degenerate cation whose structure on optimisation relaxes to a different point group: for $n = 1$ or 2 with non-degenerate HOMOs in the neutral molecule, no change in point group accompanies ionisation. As noted earlier for $Be(CH_3)_2$ and $HBeCH_3$ ($n = 1$), BeC distances throughout this series increase on ionisation.

The molecular ion $CH(BeH)_3^+$ optimises to a structure which is exactly planar at the carbon atom with overall C_{2v} symmetry: two of the CBeH angles are now different from 180°, and the unique CBe distance is shorter than the other two: this ion is shown in Fig. 3. The ion $C(BeH)_4^+$ is also calculated to be planar at carbon, with full D_{4h} symmetry.

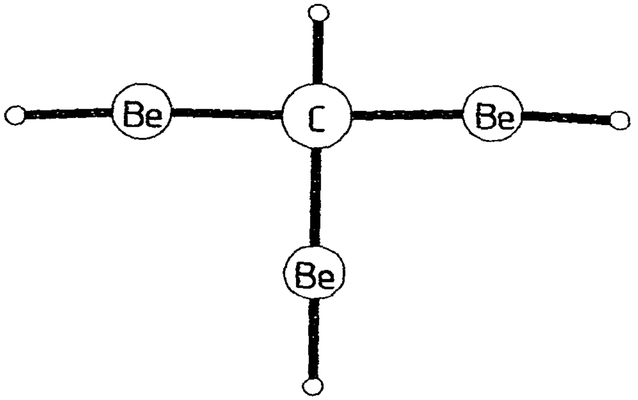

Fig. 3. The structure of $CH(BeH)_3^+$.

TABLE 6

ENERGIES FROM FREE AND CONSTRAINED OPTIMISATIONS IN THE SERIES $CH_{4-n}(BeH)_n$ AND $CH_{4-n}(BeH)_n^+$

n	$CH_{4-n}(BeH)_n$			$CH_{4-n}(BeH)_n^+$		
	ΔH_f^0 (kJ mol^{-1}) (free optimisation)	ΔH_f^0 (kJ mol^{-1}) (C planar)	$\delta(\Delta H_f^0)$	ΔH_f^0 (kJ mol^{-1}) (free optimisation)	ΔH_f^0 (kJ mol^{-1}) (C planar)	$\delta(\Delta H_f^0)$
0	−50.0	+539.1	+589.1	+1144.2	+1209.4	+65.2
1	−86.9	+190.1	+277.0	+913.2	+923.6	+10.4
2	−170.2	(*cis*) −49.3	+120.9	+747.5	(*cis*) +747.7	+0.2
		(*trans*) +95.3	+265.5		(*trans*) +846.5	+99.0
3	−318.3	−218.1	+100.2	+617.1	+617.1	0.0
4	−525.8	−419.0	+106.8	+468.7	+468.7	0.0

Extensive ab initio calculations on simple substituted methanes have indicated that the barrier to inversion via a planar tetracoordinated transition state should be decreased both by σ donation to carbon and π acceptance from carbon, by the ligands [20]. In view of the structures calculated for the cations $CH(BeH)_3^+$ and $C(BeH)_4^+$, we have compared the energies of all the neutral species $CH_{4-n}(BeH)_n$ and all the molecular cations $CH_{4-n}(BeH)_n^+$ for both free optimisation and for imposed planarity at carbon: in these species containing planar carbon atoms, no further geometric contraints were applied, but the remaining structural parameters were allowed to optimise freely. The energies resulting from these calculations are listed in Table 6.

For the neutral series, MNDO predicts a barrier to inversion in CH_4 of +589 kJ mol^{-1}: the most elaborate ab initio calculation yet undertaken, at the 6-31G** level (i.e. with *d*-type functions on carbon and *p*-type functions on hydrogen) including configuration interaction, gives [20] a value of ca. 625 kJ mol^{-1}, indicating that MNDO rapidly gives values of such parameters having reasonable agreement with the most sophisticated, and expensive, treatments. With increase in n the energy difference between planar and fully optimised geometries is markedly decreased although the barrier is much higher, when n = 2, for the *trans* planar form than for the *cis* (see Table 6). For comparison, the

TABLE 7

JAHN-TELLER EFFECT

Initial point group	HOMO	Possible distortions	Observed distortion	Example
D_{5d}	E_{1g}	$A_{2g} \rightarrow S_{10}$ or C_5 $E_{2g} \rightarrow C_{2h}$	C_{2h}	$(C_5H_5)_2Be^+$
C_{5v}	E_1	$A_2 \rightarrow C_5$ $E_2 \rightarrow C_s$	C_s	$C_5H_5BeH^+$
C_{4v}	E	$A_2 \rightarrow C_4$ $B_1 \rightarrow C_{2v}$ $B_2 \rightarrow C_{2v}$	$C_{2v}(B_1)$	$C_4H_4Be^+$
C_{3v}	E	$A_2 \rightarrow C_3$ $E \rightarrow C_s \rightarrow C_{2v}$	C_{2v}	$(HBe)_3CH^+$
T_d	T_2	$E \rightarrow D_{2d}$ or $D_2 \rightarrow D_{4h}$ $T_1 \rightarrow S_4$ or C_3 $T_2 \rightarrow C_{2v}$	D_{4h}	$(HBe)_4C^+$

values obtained using minimal basis set ab initio calculations are for $n = 2$, 234 kJ mol^{-1} (*cis*) and 393 kJ mol^{-1} (*trans*), for $n = 3$, 171 kJ mol^{-1}, and for $n = 4$, 134 kJ mol^{-1}. That minimal basis set ab initio calculation yields a value in CH_4 itself as high as 1046 kJ mol^{-1} [21], (compared with 589 kJ mol^{-1} calculated by MNDO and 625 kJ mol^{-1} calculated by 6-31G**/CI) and suggests that minimal basis set barriers are much too high and that the MNDO values are more realistic. However MNDO and minimal basis ab initio calculations concur in finding for $n = 2$, a barrier significantly higher for the *trans* planar compared with the *cis* planar intermediate.

For the cations $CH_{4-n}(BeH)_n^+$, the energy differences are all much smaller than for the neutral molecules (Table 6): in particular for $n = 3$ and 4 the freely optimised geometry actually contains planar four-coordinate carbon. Most calculations agree in finding a very flattened D_{2d} structure for CH_4^+ as found experimentally [22]: the present work indicates that such an ion containing a few σ-donor, π-acceptor substituents will readily adopt a planar configuration.

Jahn-Teller effects

For linear molecules of $D_{\infty h}$ symmetry, the possible molecular vibrations fall into four symmetry classes, Σ_g^+, Σ_u^+, Π_g and Π_u: it is convenient in this context to employ the alternative notation for symmetry classes in linear molecules ($A_1 = \Sigma^+$, $A_2 = \Sigma^-$, $E_1 = \Pi$, $E_2 = \Delta$, $E_3 = \Phi$, etc.) so that the vibrations may span the symmetry classes A_{1g}, A_{1u}, E_{1g} and E_{1u}, but no others. For a molecule whose HOMO has A_1 or A_2 symmetry, vertical ionisation yields a non-degenerate cation. A molecule whose HOMO has symmetry E_{ng} or E_{nu} (n = any positive integer) yields an electronically degenerate cation; however, the direct product $[E_{ng}]^2 = [E_{nu}]^2 = A_{1g} + A_{2g} + E_{2ng}$, so that there is no non-totally symmetric vibration contained in this direct product for any value of n. For molecules in $C_{\infty v}$ the possible vibrations are of symmetry classes A_1 and E_1, and $[E_n]^2 = A_1 + A_2 + E_{2n}$, so that again no non-totally symmetric vibration is contained in the direct product. Consequently, no change of point group is expected for any linear molecule upon ionisation, regardless of the symmetry of its HOMO, in whatever basis set. For the linear molecules studied here no such change occurs, except in $HBeCN^+$ which dissociates along an allowed A_1 vibration.

For non-linear molecules, the data of Tables 1 and 2 indicate that all species having non-degenerate HOMOs yield molecular cations of the same point groups as their neutral parents, without exception. When the HOMO of the parent is degenerate, however, the molecular cation always has a different point group, and Table 7 records the possible modes of distortion in these cases.

The direct products $[\Gamma]^2$ all span more than one non-totally symmetric class, and molecular vibrations in all these classes always occur. For D_{5d} and C_{nv} (n = 3, 4, 5) the A_2 vibrations are such as to maintain the principal axis of the same order as in the undistorted molecule: these vibrations are in fact angular motions of hydrogen atoms which do not split the degeneracy of the HOMO, and in consequence motions along these vibrations are not observed.

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