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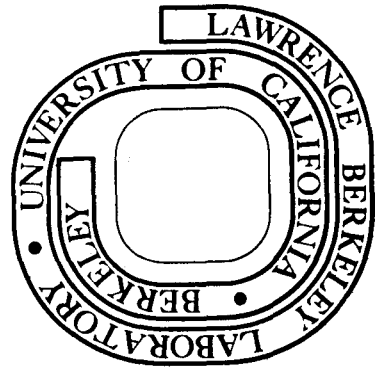
MOLECULAR STRUCTURE AND PROPERTIES OF
CH₃BeF AND CH₃MgF

Craig P. Baskin, Charles F. Bender, Robert R. Lucchese,
Charles W. Bauschlicher, Jr., and Henry F. Schaefer III

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Molecular Structure and Properties of CH_3BeF and CH_3MgF

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Abstract

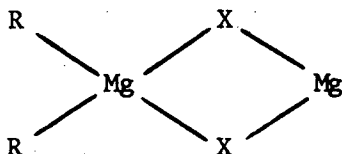
The molecules methylberyllium fluoride and methylmagnesium fluoride have been studied using a priori electronic structure theory. Self-consistent-field wave functions have been computed over a double zeta basis set of contracted gaussian functions. The geometrical structure of each molecule has been predicted assuming the three heavy atoms are collinear. For CH_3BeF , the predicted C-Be and Be-F distances are 1.70 and 1.40 Å. For CH_3MgF , the analogous bond distances are 2.08 Å and 1.78 Å. A number of molecular properties have been predicted including dipole moments, which are 1.75 and 2.38 debye for CH_3BeF and CH_3MgF .

Introduction

Primarily due to their unusual value as reagents for general laboratory synthetic purposes, Grignard compounds RMgX are frequently considered the most important of all organometallic compounds.¹ The simplest Grignard would be CH_3MgF , methylmagnesium fluoride. Actually fluorine-containing ($\text{X} = \text{F}$ in RMgX) Grignards are rarely mentioned since they are relatively difficult to prepare² and work with and have no particular advantages with respect to the Cl , Br , and I -containing compounds. Nevertheless, from a theoretical perspective CH_3MgF is the prototype Grignard and hence the subject of the present paper. For comparative purposes we have also studied the corresponding beryllium compound, CH_3BeF . In this regard it should be noted that the beryllium containing compound CH_3BeBr has been prepared in solution.³

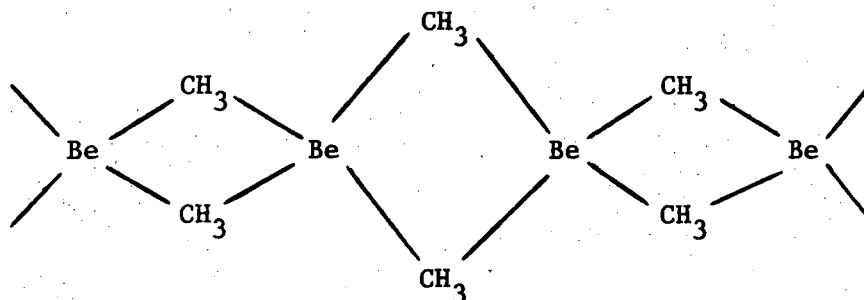
Our a priori theoretical results for CH_3BeF and CH_3MgF may be, strictly speaking, compared only to gas phase experimental findings, which sample the molecule as an isolated species. This might at first appear a hindrance, since Grignards are of primary value in solution, often diethyl ether. In fact, to our knowledge, Grignard reagents have not been prepared in the gas phase.

However, a reliable determination of the structure of isolated RMgX would be of considerable value in sorting out the complex nature of Grignard reagents in solution.^{1,4,5} Among the important species in Grignard solutions are RMgX , R_2Mg , MgX_2 , and the various dimers that can result, e.g.,



The structure of the isolated molecule may also be compared with that of several crystalline Grignards.⁶⁻⁸ For example, Guggenberger and Rundle⁷ found $C_2H_5MgBr \cdot 2(C_2H_5)_2O$ to have C-Mg and Mg-Br bond distances of 2.15 \AA and 2.48 \AA .

Also noteworthy is the fact that the structures of $(CH_3)_2Be$ and $(CH_3)_2Mg$ are known. The solid state C-Be and C-Mg distances^{9,10} are $1.93 \pm 0.02 \text{ \AA}$ and $2.24 \pm 0.03 \text{ \AA}$, and both substances are polymeric, e.g.,



However, and more directly relevant to the present research, the dimethylberyllium monomer has a significantly different gas phase structure, as determined by electron diffraction experiments.¹¹ The monomer has a linear C-Be-C skeleton, with $r(C-Be) = 1.698 \pm 0.005 \text{ \AA}$.

Our major goal, then, is to determine the molecular structures of CH_3BeF and CH_3MgF . However, of nearly equal importance is the

understanding of their electronic structures. Finally a number of other molecular properties. e.g., dipole moments, have been predicted. There have been no previous ab initio studies of the electronic structure of Grignard reagents. However, Kato and Tsuruya¹² have carried out semi-empirical studies of the relative stabilities of several monomers and dimers using assumed molecular structures.

Theoretical Considerations

All wave functions reported here are of the single configuration self-consistent-field (SCF) variety. Although this type of wave function neglects electron correlation, it is well established¹³ that using suitable basis sets, SCF wave functions can provide realistic predictions of molecular geometries and one-electron properties.

Contracted gaussian basis sets of double zeta quality¹³ were used in the present work. This type of basis is twice as large as the better known minimum basis set, and yield significantly more reliable predictions of the properties of interest here. For carbon and fluorine, the standard Dunning (9s 5p/4s 2p) basis¹⁴ was adopted, as was his (4s/2s) basis for each hydrogen atom.

For the Be and Mg Atoms, we have been especially careful to include 2p and 3p basis functions, respectively, as these are not occupied in the atomic ground state configurations $1s^2 2s^2$ and $1s^2 2s^2 2p^6 3s^2$. For Be, we began with the standard (9s/4s) contraction¹⁴

of Huzinaga's primitive gaussian set.¹⁵ Then, following previous work¹⁶ on BeF₂, two primitive 2p gaussians with $\alpha = 0.509$ and 0.118 were added. For Mg we began with a (7s 2p) contraction of Huzinaga's (11s 5p) primitive set.¹⁷ The nature of the contraction was such as to maintain maximum flexibility in the valence shell, i.e., 5111111 for the s functions and 41 for the p's. Since Huzinaga's p functions describe only the Mg 2p orbital, two more diffuse primitives ($\alpha = 0.233, 0.075$) were added. The above orbital exponents continue the progression set by Huzinaga's last two exponents, i.e.,

$$\frac{2.25208}{0.72246} = 3.1172$$

Thus our four most diffuse 2p functions are "even-tempered" in the nomenclature introduced by Raffanetti and Ruedenberg.¹⁸ To summarize, the Mg basis adopted may be designated (11s 7p/7s 4p).

Both molecules were assumed to have structures belonging to the point group C_{3v}. In addition, all C-H bond distances were fixed at 2.06 bohrs = 1.09 Å, and the H-C-H bond angles assumed tetrahedral. The remaining two geometrical parameters are the carbon-metal and metal-fluorine distances. These two parameters were simultaneously varied to yield the minimum total energy, and hence the predicted equilibrium geometry.

Results and Discussion

The predicted molecular structures are seen in Table I, along

with a number of other molecular properties. The predicted C-Be separation in CH_3BeF is remarkably close to the electron diffraction result¹¹ $1.698 \pm 0.005 \text{ \AA}$ for gaseous dimethylberyllium. Since the experimental gaseous and crystalline bond distances in $(\text{CH}_3)_2\text{Be}$ differ by 0.23 \AA , it would appear unwise to compare our predicted C-Mg separation with that of $(\text{CH}_3)_2\text{Mg}$ in the solid state. However, the C-Mg distance in crystalline $(\text{CH}_3)_2\text{Mg}$ is 0.31 \AA longer than the analogous experimental separation in $(\text{CH}_3)_2\text{Be}$. This distance is in reasonable agreement with the ab initio difference 0.38 \AA between the carbon-metal bond distances in CH_3BeF and CH_3MgF . Thus the predicted Grignard C-M bond distances are consistent with the available experimental data for $(\text{CH}_3)_2\text{Be}$ and $(\text{CH}_3)_2\text{Mg}$. The C-Mg bond distance predicted for CH_3MgF may also be compared with the observed 2.15 \AA in $\text{C}_2\text{H}_5\text{MgBr} \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$.

Experimental values are not available for the Be-F and Mg-F bond distances in Grignard-like molecules. However for BeF_2 and MgF_2 these bond distances are known from electron diffraction studies¹⁴ to be 1.43 and 1.77 \AA . These experimental values are in quite reasonable agreement with our predicted values of 1.40 and 1.78 \AA for CH_3BeF and CH_3MgF . Thus we conclude that the structures of RMX ($\text{M} = \text{Be}, \text{Mg}, \text{Ca}$) molecules in the gas phase appear to be closely related to the analogous R_2M and MX_2 molecules.

Among the one-electron properties predicted in Table I, perhaps most important are the dipole moments. For both CH_3BeF (1.75 \AA) and CH_3MgF (2.38 \AA), sizeable dipole moments are predicted.

In keeping with the greater polarizability and lower ionization potential of Mg, the CH_3MgF value of μ is predicted to be the greater by 0.63 debye. This difference in dipole moments may also be correlated with the Mulliken population analyses, seen in Table II. There it is seen that Be in CH_3BeF loses 1.04 electrons relative to the neutral atom, while Mg loses 1.33 electrons by the same test. Interestingly this greater "loss" of electrons by Mg does not go exclusively to the electronegative fluorine, but is also shared by the carbon atom. Specifically the fluorine in CH_3MgF has 0.15 greater population than in CH_3BeF , but the C atom difference between the two compounds is also sizeable, 0.12 "electrons". The quadrupole moment tensor shows the same increased charge separation in CH_3MgF ; in fact the two components are more than twice as large for CH_3MgF than for CH_3BeF .

Most of the remaining properties are quite comparable for the two molecules. The most notable exceptions are the electric field gradients at the alkaline earth and fluorine nuclei. One is of course not surprised that $q(\text{Be})$ and $q(\text{Mg})$ should have rather different values, since two different atoms are being compared. However the field gradients at fluorine are also quite different, that for CH_3BeF being greater by 50%. This difference would be very difficult to observe since the naturally available isomer of fluorine, ^{19}F has nuclear spin 1/2, making the appropriate quadrupole coupling constants inaccessible. However, for the analogous chlorine compounds CH_3BeCl and CH_3MgCl , the 3/2 nuclear spins for both ^{35}Cl and ^{37}Cl could make the comparable effect observable.

Finally, Table III gives the orbital energies for the two molecules at their predicted equilibrium geometries. The ϵ values are displayed so as to show that the comparable orbital energies of CH_3MgF are always higher than those of CH_3BeF . The nature of the highest occupied orbital is of special interest. For CH_3BeF this orbital's population is predominantly carbon (1.38 electrons) and beryllium (0.46 electrons). While the carbon population is almost exclusively 2p (1.34), the beryllium population is split fairly evenly: Be s 0.27, Be p 0.19. For the magnesium compound an analogous result is found and one can conclude that the higher ϵ for CH_3MgF is primarily an atomic effect. This follows from a comparison²⁰ of the Be 2s orbital energy ($\epsilon = -0.3093$ hartree) with the Mg 3s orbital energy ($\epsilon = -0.2530$ hartree).

Acknowledgments

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TABLE I. Predicted properties of CH_3BeF and CH_3MgF . M refers to the alkaline earth atom, Be or Mg as the case may be. Unless indicated all quantities are given in atomic units.

	CH_3BeF	CH_3MgF
$r(\text{C-M}), \text{\AA}$	1.697	2.080
$r(\text{M-F}), \text{\AA}$	1.403	1.779
Total energy, hartrees	-153.7777	-338.7047
Dipole moment, debye	1.75 (Be^+F^-)	2.38 (Mg^+F^-)
Quadrupole moment		
θ_{xx}	-6.70	-13.95
$\theta_{yy} = \theta_{zz}$	3.35	6.97
Second moments of the electronic charge distribution		
$\langle xx \rangle$	-188.93	-287.01
$\langle yy \rangle = \langle zz \rangle$	-17.49	-19.79
Third moments		
$\langle xxx \rangle$	235.91	384.43
$\langle zzz \rangle = -\langle yyz \rangle$	-4.58	-4.61
$\langle xyy \rangle = \langle xzz \rangle$	31.59	39.07

Table I (continued)

Field gradient tensor

q_{xx} (C)	0.22	0.20
q_{yy} (C) = q_{zz} (C)	-0.11	-0.10
q_{xx} (H)	0.12	0.13
q_{yy} (H)	0.17	0.17
q_{zz} (H)	-0.29	-0.30
q_{xz} (H)	0.17	0.16
q_{xx} (M)	0.15	1.18
q_{yy} (M) = q_{zz} (M)	-0.08	-0.59
q_{xx} (F)	-0.50	-0.33
q_{yy} (F) = q_{zz} (F)	0.25	0.17

Potential at each nucleus

ϕ (C)	-14.76	-14.77
ϕ (H)	-1.10	-1.11
ϕ (M)	-8.40	-39.90
ϕ (F)	-26.63	-26.70

TABLE II. Mulliken atomic populations for CH_3BeF
and CH_3MgF .

		CH_3BeF	CH_3MgF
C	s	3.51	3.54
	p	3.55	3.64
	Total	7.06	7.18
H	s	0.79	0.79
	p		
	Total		
M	s	2.40	4.34
	p	0.55	6.33
	Total	2.96	10.67
F	s	3.95	3.97
	p	5.67	5.81
	Total	9.62	9.77

TABLE III. Orbital energies in hartrees (atomic units for CH_3BeF and CH_3MgF).

CH_3BeF		CH_3MgF	
		$1a_1$	-49.0453
		$2a_1$	-26.1732
		$3a_1$	-11.1963
$1a_1$	-26.2481	$4a_1$	- 3.7853
$2a_1$	-11.1973	$5a_1$	- 2.3059
$3a_1$	- 4.7105	$1e$	- 2.3058
$4a_1$	- 1.5395	$6a_1$	- 1.4429
$5a_1$	- 0.9291	$7a_1$	- 0.8996
$6a_1$	- 0.6644	$8a_1$	- 0.5597
$1e$	- 0.6163	$2e$	- 0.5370
$2e$	- 0.5503	$3e$	- 0.5243
$7a_1$	- 0.4461	$9a_1$	- 0.3863

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