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Ab initio Calculations for Ground States of CH_2Li^- and CH_2Be*

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The ground state of CH_2Li^- and CH_2Be molecules has been investigated by an SCF calculation using a contracted Gaussian basis set. Only for the second system a bound state with respect to the ground states of the molecular fragments has been found.

Key words: CH_2Li^-, ground states of – CH_2Be, ground states of ~

Introduction

It has been suggested [1] on the basis of experience made in the field of geminal organometallic compounds, that a carbanion may be stabilized by an adjacent metal atom through formation of a π-bond. As an initial stage of an investigation in this direction, we have performed SCF calculations on the simplest systems of this kind *i.e.* CH_2Li^- and CH_2Be. The main aim was to verify if these compounds can present a ground state which results to be bound with respect to the most likely decomposition products.

Since no experimental result on the possible geometry of these systems was known, an energy minimization procedure has been performed on all involved geometrical parameters. In order to limit the range of the trials, a CNDO calculation on the same molecules has been previously carried out. As possible decomposition products, CH_2 and CH_2^-, Li^-, and Be^+ ions, besides Li and Be have been considered. For these systems only the ground state has been calculated, except for CH_2 and CH_2Be, for which two states ($^1A_1$ and $^3B_1$) have been considered. The geometrical minimization has been carried out also for CH_2 and CH_2^- states. In order to check the goodness of the chosen basis, a calculation for the CH_3^- molecule ground state has also been performed.

Basis Set and Preliminarly Calculations

Since the atoms involved have already been extensively studied [2, 3] the choice of the basis does not present any problem. A contracted basis of Gaussian orbitals has been chosen; in particular for Li, Be, and C atoms the four *s*-type atomic orbitals employed, are constructed by a linear combination of 3, 3, 2, and 3 primitive GTO's respectively [2] [short notation (3, 3, 2, 3)]. For the C atom the basis is completed with two contracted *p*-type atomic orbitals (3, 3). For the

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Table 1. Atomic basis set[a]

	Li		Be		C		H	
	Exp.	Coeff.	Exp.	Coeff.	Exp.	Coeff.	Exp.	Coeff.
(s.1)	3184.4671	0.02156739	6261.0585	0.02146629	16371.074	0.02120912	19.24060	0.032808
	480.51266	0.16658948	932.25914	0.16536998	2439.1239	0.16414017	2.89915	0.231208
	108.86325	0.87236365	209.70133	0.87375771	545.16766	0.87510685	0.65341	0.817238
(s.2)	30.289479	0.10008940	58.159285	0.09445342	151.00382	0.08646063	0.17758	1.00000
	9.6415137	0.30904943	18.468874	0.29979507	47.80399	0.28645409		
	3.3915559	0.66666616	6.4351438	0.68022669	16.43566	0.69939809		
(s.3)	1.2494133	0.7176500	2.3964825	0.70275612	5.9491182	0.72521862		
	0.46733513	0.31831711	0.95005883	0.33002620	2.2158781	0.31046045		
(s.4)	0.07980199	−0.05476751	0.18366835	−0.43979949	0.56937124	0.40210571		
	0.06613627	0.69883916	0.07393677	−0.48923130	0.21811018	0.51738733		
	0.02495205	0.39372345	0.03324251	−0.1281360	0.0884325	0.14631886		
(p.1)	4.802	0.04049609	8.356	0.04049609	24.178811	0.04081133	1.00000	1.00000
	1.076	0.24279555	1.883	0.24279555	5.7634925	0.23370981		
	0.311	0.81105297	0.576	0.81105297	1.7994821	0.81589670		
(p.2)	0.0877	0.42352267	0.208	0.42352267	0.62738153	0.44674694		
	0.0696	0.49704234	0.0779	0.49704234	0.22321395	0.50433069		
	0.0230	0.20556999	0.0296	0.20556999	0.07961811	0.18234560		

[a] For the references from which the most part of these data have been taken, see text.

H atom, we have chosen a (3, 1) *s* basis used by Neumann and Moskowitz [4] which seems to be comparable in extension to the above one.

Since the possibility of bound ground states in CH_2Li^- and CH_2Be, seems to be related to the existence of some degree of sharing of *p* electrons to bond orbitals, an extension of the basis with *p* AO's is appropriate also for H, Li, and Be atoms.

For the H atom, we have made the same basis choice as Neumann and Moskowitz [4], *i.e.* $\zeta_p = 1.0$; for Li and Be *p* exponents, we have applied an extrapolation procedure based on the variation of *s* and *p* exponents along the first row of the periodic system, as it is exhibited by Huzinaga results. A similar procedure has been used by Kaufman and Sachs [5, 6] in their work on HeLiH and $HeBeH_2$; the basis set reported in Table 1 has been used.

The minimization of the energy with respect to all geometrical parameters is required, as already said, by the lack of experimental information. Moreover, particularly in the case of CH_2Li^-, the optimal geometry can indicate the existence of a "π-stabilization" in comparison, for instance, with the very similar molecule CH_3^- which is known [7] to be non planar in the ground state.

Since the chosen basis is rather limited, one can have some doubt about the possibility of a correct prediction of the molecular geometries; therefore we have tested the basis by searching for the optimum geometry of CH_3^-. The results are the following:

$$E = -39.45363 \text{ a.u., C–H} = 2.14 \text{ a.u., } \varphi \text{ (out of plane angle)} = 26°;$$

it can be seen that they compare rather favourably with those of Kari and Csizmadia [7], obtained by using different extended basis sets; the best results by these authors are in fact:

$$E = -39.50810;\ \text{C–H} = 2.14;\ \varphi = 22.5°.$$

Since we have not found reliable data for C–Be and C–Li equilibrium distances in the literature, we decided to carry out a preliminary calculation by the CNDO method. The results for these quantities were 3.25 and 2.66 a.u. for C–Li and C–Be respectively. In both cases we obtained a planar configuration.

Results and Discussion

In Table 2 the main results of the calculations are reported. The most striking aspect is that for CH_2Be a triplet ground state has been found in analogy with CH_2.

Our results for CH_2 are comparable with those of the literature [8–10]. Some comparisons are reported in Table 3. For the $^1A_1$ states of CH_2Be and CH_2Li^-, from the CNDO calculations the following optimum geometries have been obtained:

$$\text{H}\hat{\text{C}}\text{H} = 112°,\ \text{C–H} = 2.12 \text{ a.u., C–Be} = 2.66 \text{ a.u.}$$

$$\text{H}\hat{\text{C}}\text{H} = 105°,\ \text{C–H} = 2.17 \text{ a.u., C–Li} = 3.25 \text{ a.u.}$$

The geometry is planar in both cases.

In Table 4 the orbital energies and coefficients for the relevant orbitals for CH_2Be $^3B_1$ and $^1A_1$ states are reported. The most interesting aspect is the structure of the π-type orbital that appears to have, in both states, a negative energy. This fact, and the sign of the coefficients seems to suggest some stabilization effect

Table 2. Relevant results of the calculations

Molecule	State		Equilibrium parameters (a.u.)		Energy (a.u.)
Li	$(1s)^2(2s)$	^2S			-7.4322474[a]
Li$^-$	$(1s)^2(2s)^2$	^1S			-7.394014
Be	$(1s)^2(2s)^2$	^1S			-14.572461[a]
Be$^+$	$(1s)^2(2s)$	^2S			-14.26356
CH_2	$(1a_1)^2(2a_1)^2(3a_1)^2(1b_2)^2$	$^1A_1$	C–H $=2.07$	$\alpha=105°$	-38.86954
CH_2	$(1a_1)^2(2a_1)^2(3a_1)(1b_2)^2(1b_1)$	$^3B_1$	C–H $=2.02$	$\alpha=130°$	-38.92300
CH_2^-	$(1a_1)^2(2a_1)^2(3a_1)^2(1b_2)^2(1b_1)$	$^2B_1$	C–H $=2.06$	$\alpha=100°$	-38.82455
CH_2Li^-	$(1a_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(1b_2)^2(1b_1)^2$	$^1A_1$	C–H $=2.06$ C–Li $=3.40$	 $\alpha=105°$	-46.29361
CH_2Be	$(1a_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(1b_2)^2(1b_1)^2$	$^1A_1$	C–H $=2.04$ C–Be $=2.83$	 $\alpha=113°$	-53.50059
CH_2Be	$(1a_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(5a_1)(1b_2)^2(1b_1)$	$^3B_1$	C–H $=2.04$ C–Be $=3.12$	 $\alpha=111°$	-53.57559

[a] Reference [2].

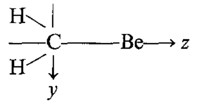

Table 3. Some results (in a.u.) for CH_2 states

	A		B		C		D		
	$^3B_1$	$^1A_1$	$^3B_1$	$^1A_1$	$^3B_1$	$^1A_1$	$^3B_1$	$^1A_1$	Exp $(^3B_1)$[a]
Total energy	-38.904	-38.865	-38.9136	-38.8620	-38.893	-38.843	-38.9230	-38.8695	
HCH angle	129°	90°	130.4°	106.5°	133°	111°	130°	105°	136°
CH distance	2.11	2.21	2.03	2.09			2.02	2.07	2.02

A Ref. [8]; B Ref. [10]; C Ref. [9]; D our results.
[a] See Refs. reported in [10].

related to the contribution of p-orbitals of Be to the molecular bond. In the same Table are reported, as a check, the results of a SCF calculation for both states on an atomic basis obtained from that reported in Table 1 by dropping out the p_x orbitals from Be and H. The total energies for these states obtained in such a way are respectively -53.56280 and -53.37329 a.u. An SCF calculation for $^3B_1$ state of CH_2 without the p_x orbitals on H gives -38.92174 a.u. From these results the π-stabilization effect seems to be confirmed.

In CH_2Li^- the $1b_1$ orbital has a very small positive orbital energy in $^1A_1$ and $^3B_1$ states; therefore we have not considered this molecule further.

In Table 5 the results for the energy differences between the ground states of CH_2Li^- and CH_2Be and some types of dissociation products are reported. As it can be seen, the first molecule is not stable with respect to the most probable type of dissociation. For CH_2Be the result shows a decidedly stable triplet ground state and a very small energy in the formation of the lowest singlet from the ground state of the fragments. However, if one considers the most probable dissociation products of this last state ($CH_2(^1A_1)+Be(^1S)$), one can see that this also appears to be stable with respect to them. Therefore, for these states, we have considered it to be worthwhile to obtain a rough estimate of the dissociation energy. For that,

Table 4. MO's and energies for relevant orbitals of $^3B_1$ and $^1A_1$ CH_2Be states

	$^3B_1{}^a$	$^3B_1{}^b$		$^3B_1{}^a$	$^3B_1{}^b$	$^1A_1{}^a$	$^1A_1{}^b$
	$5a_1$	$5a_1$		$1b_1$	$1b_1$	$1b_1$	$1b_1$
S_C^1	0.000309	0.000312	X_C^1	0.179646	0.195133	0.133520	0.177781
S_C^2	0.014646	0.014785	X_C^2	0.798514	0.897570	0.580589	0.907940
S_C^3	0.035444	0.035801	X_{Be}^1	0.068383		0.133149	
S_C^4	−0.166102	−0.164418	X_{Be}^2	0.192419		0.469425	
S_{Be}^1	−0.001614	−0.001574	X_{H1+H2}	0.019358		0.016916	
S_{Be}^2	−0.066262	−0.064697	ε	−0.376837	−0.379328	−0.261785	−0.208607
S_{Be}^3	−0.157383	−0.153405					
S_{Be}^4	−0.852606	−0.835491					
S_{H1+H2}^1	0.017327	0.020109					
S_{H1+H2}^2	0.099055	0.107842					
Y_{H1-H2}	−0.002028	−0.002497					
Z_C^1	−0.039022	−0.040287					
Z_C^2	−0.153718	−0.155190					
Z_{Be}^1	0.147593	0.152356					
Z_{Be}^2	0.519921	0.534597					
Z_{H1+H2}	−0.001067	−0.000450					
ε	−0.308656	−0.313215					

[a] With the p_x atomic orbitals on Be and H.

[b] Without the p_x atomic orbitals on Be and H.

Table 5. SCF equilibrium energy differences

	ΔE kcal/mole
$CH_2(^3B_1) + Li + e^- \longrightarrow CH_2Li^-$	+38.96
$CH_2(^3B_1) + Li^- \longrightarrow CH_2Li^-$	+14.37
$CH_2(^3B_1) + Be \longrightarrow CH_2Be(^1A_1)$	− 3.22
$CH_2^-(^2B_1) + Li \longrightarrow CH_2Li^-$	−23.09
$CH_2(^1A_1) + Be \longrightarrow CH_2Be(^1A_1)$	−36.75
$CH_2(^3B_1) + Be \longrightarrow CH_2Be(^3B_1)$	−50.26

two main terms must be added to the energy difference that has been calculated: the zero point energy difference between the compound and the dissociation fragments, and the extra-correlation term.

The calculation of the normal frequencies leading to the evaluation of the zero point energy must be made on the basis of some assumption for the potential energy. For the $^1A_1$ of CH_2Be and for $^3B_1$ of CH_2, two different formulations have been made for this quantity. The first corresponding to the valence forces scheme and the second by coupling the C–H stretchings among themselves and, in CH_2Be, the planar bendings among themselves. For CH_2Be $^3B_1$ we have considered the valence forces scheme and the coupling between the planar bendings, because of the negligible coupling of the two C–H stretchings. The normal frequencies obtained in such a way are reported in Table 6 with the related results for zero point energy.

Since the extra-correlation energy is certainly negative, the sum of the two terms calculated in Table 5 and 6 furnishes a lower bound for the bond energy. In our case one obtains ~ -46.0 and $+0.5$ kcal/mole for $^3B_1$ and $^1A_1$ respectively.

Table 6. Normal frequencies and zero point energy for $^1A_1$ and $^3B_1$ states of CH_2Be and CH_2 ($^3B_1$)

	CH_2Be				CH_2	
	$^1A_1{}^a$	$^1A_1{}^b$	$^3B_1{}^a$	$^3B_1{}^c$	$^3B_1{}^a$	$^3B_1{}^b$
1. ν^d_{CH}	3217	3210	3212	3212	3236	3217
2. ν_{CH}	3360	3367	3355	3355	3419	3438
3. ν_{CBe}	1043	1043	1023	1023		
4. ν_{HCH}	1870	1651	1941	1969	1215	1215
5. ν_{HCBe}	463	444	460	461		
6. $\nu_{CBe\perp}$	735	735	945	945		
$\frac{1}{2}\Sigma h\nu^e$	15.30	14.93	15.62	15.67	11.24	11.24

[a] "Valence forces" potential.
[b] With added coupling terms 1–2 and 4–5.
[c] With added coupling terms 4–5.
[d] cm^{-1}.
[e] kcal/mole.

One can see that the triplet state results to be bound, while for $^1A_1$ a possible stability whith respect to the most stable dissociation products, should be merely attributed to the extra-correlation effect.

From the same calculations it is possible to evaluate the entropy contribution to the Free Energy of formation ΔF° for the same two states, related to the vibrational part of the partition function. The calculations show that these contributions are of the order of $+0.09$ kcal/mole for both states *i.e.* practically negligible in comparison with the rotational and translational ones. The total values for $T\Delta S^\circ$ are respectively -5.96 and -5.85 kcal/mole for $^1A_1$ and $^3B_1$ states.

As a conclusion, one may deduce that of the two molecules that have been considered, only CH_2Be is stable in a triplet ground state and it presents a singlet state whose stability, if it exists, is very small.

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