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Short Communication

Carbon-Beryllium Binding in CH_2Be

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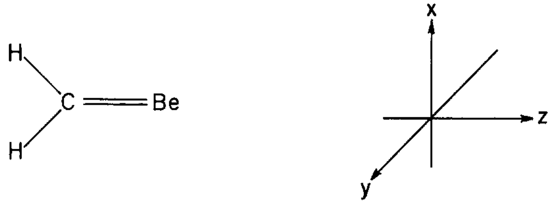
Ab initio molecular orbital theory is used to study carbon-beryllium binding in the lowest singlet and triplet states of CH_2Be. When electron correlation is included, both singlet and triplet states are significantly bound relative to the ground states of CH_2 and Be fragments.

Key words: CH_2Be, ground state of ~ – CH_2Be, singlet-triplet splitting of ~

1. Introduction

The molecule CH_2Be, in the planar C_{2v} form **1**, is important as a prototype of a possible carbon-beryllium double bond and of metal-carbene complexes which have been studied extensively in the transition metal series [1]. Its structure and stability have been studied theoretically by Lamanna and Maestro [2], using Hartree-Fock molecular orbital theory. They concluded that **1** is stable in a triplet ground state but that the stability of the lowest singlet state (which more correctly represents a C=Be double bond) is very small.



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In this short paper, we present the results of a study of the carbon-beryllium bond energies in **1** (singlet and triplet states), using theoretical methods which make allowance for the effects of correlation between electrons of antiparallel spin. This leads to conclusions somewhat different than those of Lamanna and Maestro. We concur that **1** has a bound triplet ground state, but also find that the singlet state is quite strongly bound relative to the ground states of separated CH_2 and Be fragments.

2. Methods

Singlet states were studied with closed-shell spin-restricted Hartree-Fock theory (RHF) [3] and triplet states with the spin-unrestricted version (UHF) [4]. Correlation corrections were introduced by Møller-Plesset (MP) perturbation theory to second and third order [5,6]. These techniques are denoted by RMP2 and RMP3 for singlets and UMP2 and UMP3 for triplets, respectively. The bases used were the minimal STO-3G set [7] and the split valence+polarization set 6-31G* [8].

The full procedure adopted was initial determination of geometry at the RHF/STO-3G or UHF/STO-3G level followed by single calculations at these geometries using the larger 6-31G* basis. These final runs were carried out at the RMP3/6-31G* and UMP3/6-31G* levels. CH_2Be and CH_2 were considered both as singlets ($^1A_1$) and triplets ($^3B_1$) but beryllium only as a singlet (^1S).

3. Results and Discussion

The STO-3G geometries of methylene have been reported previously [9]. For CH_2Be, the corresponding data are [10]

$^3B_1$: $R(\text{C–H}) = 1.086$ Å, $R(\text{C=Be}) = 1.652$ Å, $\widehat{\text{HCH}} = 111.2°$

$^1A_1$: $R(\text{C–H}) = 1.083$ Å, $R(\text{C=Be}) = 1.472$ Å, $\widehat{\text{HCH}} = 111.2°$

These are close to the structures reported previously [2]. Both structures were found to represent local minima on the potential surfaces. Total energies with the 6-31G* basis are given in Table 1. Table 2 lists significant energy differences.

The Hartree-Fock binding energies given in Table 2 are in reasonable agreement with the results of Lamanna and Maestro [2]. They obtained 50.3 and 3.2 kcal/mole

Table 1. Total energies (hartrees)[a]

Molecule	State	HF/6-31G*	MP2/6-31G*	MP3/6-31G*
Be	^1S	−14.56694	−14.59645	−14.60701
CH_2	$^1A_1$	−38.87150	−38.97376	−38.99185
CH_2	$^3B_1$	−38.92091	−39.00683	−39.02079
CH_2Be	$^1A_1$	−53.49046	−53.66723	−53.68053
CH_2Be	$^3B_1$	−53.57789	−53.71013	−53.72702

[a] Spin-restricted results (RHF, RMP2, RMP3) for singlets; spin-unrestricted results (UHF, UMP2, UMP3) for triplets.

Table 2. Energy differences (kcal/mole)

Process	HF/6-31G*	MP2/6-31G*	MP3/6-31G*
$CH_2(^3B_1) \rightarrow CH_2(^1A_1)$	31.0	20.8	18.2
$CH_2Be(^3B_1) \rightarrow CH_2Be(^1A_1)$	54.9	26.9	29.2
$CH_2Be(^3B_1) \rightarrow CH_2(^3B_1)+Be$	56.5	67.1	62.3
$CH_2Be(^1A_1) \rightarrow CH_2(^3B_1)+Be$	1.6	40.1	33.1

for the C=Be dissociation energies (D_e) of the triplet and singlet, respectively. However, it is clear that inclusion of correlation corrections greatly increases the binding in the singlet state, the best value (at third order MP) being 33.1 kcal/mole. The dissociation energy relative to the lowest singlet states of CH_2 and Be is even higher (51.3 kcal/mole). Correlation corrections also increase the predicted dissociation energy in the triplet ground state to 62.3 kcal/mole. These binding energies may be slightly decreased by zero-point vibrational corrections (estimated to be $\sim$4 kcal/mole [2]).

The $^1A_1$ state of CH_2Be has the electron configuration $(1a_1)^2$ $(2a_1)^2$ $(3a_1)^2$ $(4a_1)^2$ $(1b_2)^2$ $(1b_1)^2$. The $1b_1$ orbital is of π-type (with a node in the molecular plane). As indicated by the Mulliken populations [11], the two π-electrons are almost equally shared between the carbon (1.067) and beryllium (0.933) atoms. Furthermore, the total $p\pi$-population at beryllium (p_x and p_y in **1**) is 0.989, indicating acquisition of significant $p\pi$-character relative to a ground state beryllium atom. However, the overall electropositive nature of beryllium is clearly indicated, the *total* Mulliken population being only 3.844. It should also be noted that the lowest $^1A_1$ state of CH_2 and the ground state of Be have no π-electrons. Thus, if the C=Be bond is formed by direct approach along the twofold axis of singlet methylene, an orbital crossing must occur in which two electrons are transferred to the π-orbital from the σ-system.

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