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BERYLLOCENE, $(C_5H_5)_2Be$. THE He(I) PHOTOELECTRON SPECTRUM AND AB INITIO MOLECULAR ORBITAL CALCULATIONS

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Summary

Ab initio molecular orbital calculations with a double-ζ basis have been carried out on five models of beryllocene, Cp_2Be, with fixed geometries. The lowest energies are obtained for the π-Cp, σ-Cp and D_{5d} models.

The He(I) photoelectron spectrum of Cp_2Be was recorded and the ionization potentials of the first bands were compared with the orbital energies obtained from the molecular orbital calculations. A satisfactory fit between experiment and calculations was obtained for a slip sandwich model of C_s symmetry. A model of C_{5v} symmetry is only compatible with the PE spectrum if the Jahn—Teller splitting of the lowest $^2E_1$ state of the molecular ion is exceptionally large, 1.0 eV.

Introduction

The structure of dicyclopentadienylberyllium, Cp_2Be, has been the subject of debate since an early electron diffraction study [1] was questioned on the basis of X-ray investigations at —120°C and at room temperature [2,3]. The electron diffraction data were found to be compatible with a model of C_{5v} symmetry (model II in Fig. 1) [1]. The X-ray data, however, could best be interpreted by a slip sandwich structure (model III in Fig. 1) [2,3].

Molecular orbital calculations have been carried out on various models of

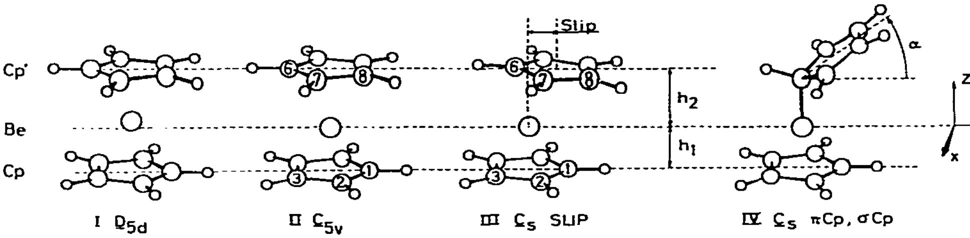

Fig. 1. Structural models of Cp_2Be.

Cp_2Be using semiempirical and ab initio procedures [4—8]. The calculations suggest that the most stable form of Cp_2Be can be described either by model I (D_{5d} symmetry) or model IV (one-ring π-bonded, the other ring σ-bonded to Be) in Fig. 1. A reinvestigation of Cp_2Be by gas phase electron diffraction [9] showed that neither of the two models I or IV was compatible with the experimental data, while satisfactory agreement was obtained with model II (symmetry C_{5v}) and III (in which both Cp rings have approximate D_{5h} symmetry but one ring has slipped sideways relative to the C_{5v} model).

To contribute to this discussion we have investigated the He(I) photoelectron (PE) spectrum of Cp_2Be and carried out ab initio molecular orbital calculations on various models of Cp_2Be with a larger basis than those in any calculations previously published.

Results and discussion

Total energies. The total energies obtained by ab initio molecular orbital calculations on the various models of Cp_2Be are listed in Table 1. It is seen that the disagreement with experimental results remains: the lowest energies are obtained with the two models (D_{5d} and π-Cp, σ-Cp), which are incompatible with the gas phase electron diffraction data.

The highest energy is obtained for the C_{5v} model, but the energy decreases somewhat on sideways displacement of the Cp' ring: A sideways displacement of 0.79 Å leads to an energy decrease of 3.3 kcal mol^{-1}, and when the displacement is increased to 1.21 Å the energy is decreased by another 0.6 kcal mol^{-1}. The relative insensitivity of the energy to the magnitude of the slip indicates that the potential energy minimum is very broad.

While the present work was in progress Demuynck and Rohmer published the results of ab initio molecular orbital calculations on various models of Cp_2Be with a minimal basis set for inner shells together with a double-ζ set for the valence shells [8]. Their calculations, which should be of similar accuracy to ours, yielded the lowest energy for the D_{5d} model (398.637 au) by the slip sandwich model: ΔE 5.5 kcal mol^{-1}, the C_{5v} model: ΔE 10.5 kcal mol^{-1}, and finally the π-Cp, σ-Cp model: ΔE 17.0 kcal mol^{-1}. The difference between the results of the two sets of calculations may be due to differences in the geometries assumed for the various models. As pointed out by Demuynck and Rohmer, the Cp_2Be molecule is so large and the energy differences so small that geometry optimization of the various models may well remove the disparity between experiment and calculations [8].

TABLE 1

TOTAL ENERGIES, DIPOLE MOMENTS AND ENERGIES OF THE HIGHEST OCCUPIED MOLECULAR ORBITALS CALCULATED FOR VARIOUS MODELS OF $(C_5H_5)_2Be$

Model	I, D_{5d}	II, C_{5v}	III, *Slip*(*Slip* 0.79 Å)	III, *Slip*(*Slip* 1.21 Å)	IV, π-Cp, σ-Cp
Total energy (au)	−398.6457	−398.6362	−398.6413	−398.6413	−398.6621
Relative energy (kcal mol^{-1})	9.2	16.3	13.0	12.4	0
Dipole moment (Debye)	0	2.39	3.12	3.75	2.87
Orbital energies (eV)	−7.64(e_{1g}, π-CC)	−7.45(e_1, Cp′)	−7.30(a'', Cp′) −7.72(a', Cp′)	−7.12(a'', Cp′) −7.97(a', Cp′)	−7.58(a'', Cp′) −9.22(a', Cp′)
	−10.11(e_{1u}, π-CC)	−10.33(e_1, Cp)	−10.21(a', Cp) −10.29(a'', Cp)	−10.07(a', Cp) −10.26(a'', Cp)	−9.82(a', Cp) −9.89(a'', Cp)
	−14.05(e_{2g}, C—H)	−13.53(e_2, CH)	−13.32(a', CH) −13.44(a'', CH)	−13.20(a', CH) −13.35(a'', CH)	−12.19(a', CH) −12.68(a'', CH)

The PE spectrum. The PE spectrum of Cp_2Be (Fig. 2) displayes three nearly equidistant peaks in the region below 10.5 eV, namely at 7.45, 8.42 and 9.5 eV, with relative intensities approximately 1/1/2, followed by a complex of unresolved peaks starting at 11.25 eV. The first two peaks have a Gaussian shape while the third peak is somewhat unsymmetrical and appears to consist of two strongly overlapping bands at 9.5 and 9.7 eV.

To assign the first four bands in the PE spectrum we invoke Koopmans' theorem ($-\epsilon_J = I_{V,J}$) [10], and correlate the measured vertical ionization potentials, $I_{V,J}$, with the molecular orbital energies, ϵ_J, obtained by calculations on the ground state of Cp_2Be.

The energies of the highest occupied molecular orbitals obtained by the ab initio calculations on the various models of Cp_2Be are listed in Table 1 and are displayed graphically in Fig. 3. It is seen that the orbital energies show a gradual change as the D_{5d} model is deformed, first to a C_{5v} model, then to a slip sandwich model and finally to a π-Cp, σ-Cp model.

For a D_{5d} model the highest occupied molecular orbitals are two pairs of degenerate levels belonging to the irreducible representations e_{1g} ($\epsilon_J = -7.64$ eV) and e_{1u} ($\epsilon_J = -10.11$ eV). Reduction of the molecular symmetry to C_{5v} by moving the Be atom closer to one ring does not destroy the degeneracy of the e_{1g} and e_{1u} orbitals which both correspond to e_1 in the C_{5v} point-group. Inspection of the corresponding wavefunctions (see Fig. 4) reveals, however, that the degenerate highest molecular orbitals are now localized predominantly on the loosely bonded ring, Cp′, while the molecular orbitals corresponding to the second highest niveaus ($\epsilon = -10.33$ eV) are localized primarily on the firmly bonded ring and the Be atom.

When the loosely bonded ring is moved sideways the molecule is deformed to a "slip sandwich", and the degeneracy of the two highest occupied levels is removed, while the degeneracy of the next two levels remains essentially intact.

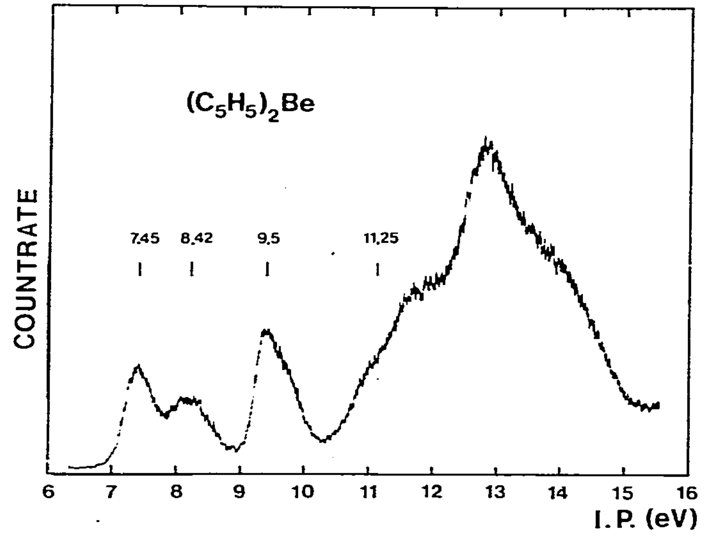

Fig. 2. PE spectrum of Cp_2Be.

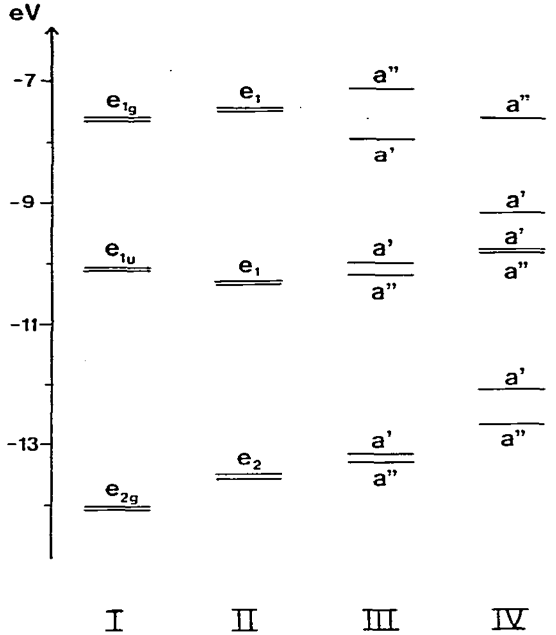

Fig. 3. Highest occupied MO's of Cp_2Be for the structural models I to IV. For III a slip of 1.21 Å has been chosen.

In model IV in which Cp′ is σ-bonded to the Be atom, the highest occupied molecular orbital can be considered as the $a_2(\pi)$ molecular orbital of the butadiene fragment of Cp′, while the next orbital can be described as a linear combination of the $b_1(\pi)$ orbital of the butadiene fragment and the Be—C σ bond. Close in energy to the latter our calculations predict two levels strongly localized on the Cp ring which is π-bonded to Be.

All models yield a large number of orbitals with closely placed energies below —12 eV. The highest of them are listed in Table 1. It is seen that the energy of these orbitals increases monotonically from —14.05 to —12.19 eV as the model is deformed from I to IV.

Before proceeding to the assignment of the PE spectrum we make two points: (i) Koopmans' theorem is known to be invalid for transition metal metallocenes [11]. Because of strong localization of the molecular orbitals with large [11,12] metal 3*d* orbital contributions the approximate compensation of correlation effects and reorganization energies no longer occurs. However, in the case of molecules containing first and second row elements only, the molecular orbitals are in most cases delocalized over the entire molecule, as they are in the present case, and Koopmans' theory seems to hold [12].

(ii) ^2E states of Cp_2Be^+ resulting from the removal of an electron from an *e* orbital of Cp_2Be, are Jahn—Teller active. Consequently the corresponding bands in the PE spectrum may be split into a doublet: the magnitude of the split is usually large if the electron has been ejected from a strongly bonding orbital (e.g. 0.8 eV in cyclopropane [13]) and small if the ionization occurs from a weakly bonding orbital (e.g. 0.3 eV in 1,3,4-trioxane [14].

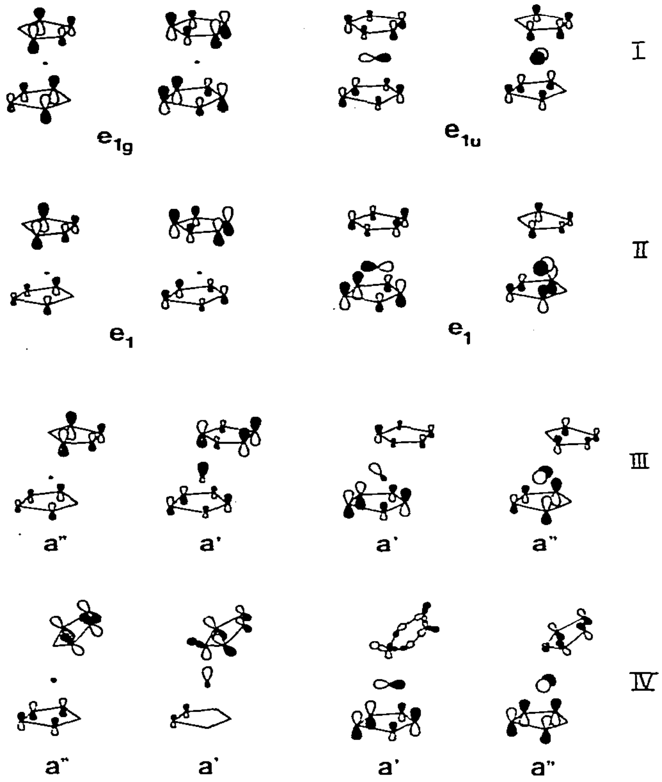

Fig. 4. Schematic drawing for the wave functions of the four highest occupied molecular orbitals corresponding to structures I to IV.

A good estimate of how the PE spectrum of Cp_2Be might look if the molecule had D_{5d} structure is provided by the PE spectrum of Cp_2Mg [15]. This consists of one peak at 8.11 eV with shoulders at 8.23 and 8.44 eV assigned to ionization from the e_{1g} π-CC orbital, and a second peak at 9.03 eV with a shoulder at 9.25 eV assigned to ionization from the e_{1u} π-CC orbital. The shoulders are attributed to Jahn—Teller effects. The first two peaks are followed by a complex of unresolved peaks starting at 12.2 eV. The large difference to the PE spectrum of Cp_2Be provides additional evidence against a D_{5d} structure for the latter.

The PE spectra of the compounds CpBeX when X = C≡CH, $C{\equiv}CCH_3$, Cl and Br show Jahn—Teller splittings of the bands assigned to ionization from the e_1 π-orbitals of 0.1 to 0.2 eV [16]. The PE spectrum of Cp_2Be can be assigned on the basis of a C_{5v} model only if one assumes that the band arising from ionization from the highest e_1 π-orbital exhibits a Jahn—Teller splitting of about 1.0 eV. This is larger than the splitting found to date in the PE spectrum of any metallocene. However, since the loosely bonded ring in Cp_2Be clearly is anomalous, we hesitate to rule out such a large Jahn—Teller splitting completely.

Moving on to model III we find good qualitative agreement between calculated orbital energies and observed ionization potentials, especially for the model with *slip* = 1.2 Å (see Fig. 1). It is possible that the calculations on models derived from model III by relaxing the requirement that Cp′ should have exact D_{5h} symmetry (i.e. a model in between III and IV) would improve the fit further. Finally we note that model IV gives a less satisfactory fit between orbital energies and ionization potentials, since the distance between the first peak and second is calculated to be much larger than the distance between the second and the third. This model has already been shown to be incompatible with the electron diffraction data.

Calculations

The calculations were carried out with the program MOLECULE which solves the Roothaan—Hall equations for a Gaussian basis [17]. We used the following basis set: C: (7*s*, 3*p*) [18] contracted to ⟨4*s*, 2*p*⟩, H: (4*s*) [19] contracted to ⟨2*s*⟩, Be: (7*s*, 3*p*) contracted to ⟨4*s*, 2*p*⟩. The 7*s* type functions of Be were taken from Ref. 18, the 3 *p*-type functions have been obtained by Wisløff Nilssen by optimization on BeH_2 [20].

Calculations were first carried out on a model of D_{5d} symmetry (I). Both rings were assumed to have D_{5h} symmetry and the bond distances C—C 1.423 Å and C—H 1.100 Å selected after comparison of the structures of Cp_2Be [21] and $CpBeCH_3$ [22] as determined by gas phase electron diffraction and the structure of CpBeH as determined by microwave spectroscopy [23]. The perpendicular Cp...Cp distance was set equal to 3.375 Å, the distance obtained by refinement of a C_{5v} model in the *ED* investigation of Cp_2Be [9]. Calculations were then carried out on a model of C_{5v} symmetry by moving the Be atom out of the centre of symmetry to a position on the *z*-axis at a distance h_1 = 1.490 Å from the centre of one ring and h_2 = 1.885 Å from the centre of the other.

The next calculations were performed on two slip sandwich models. These were derived from the C_{5v} model by moving Cp′ sideways as indicated in Fig. 1 model III, and rotating it around the *x*-axis. The geometry of the CpBe fragment was held constant, and the D_{5h} symmetry of Cp′ retained even though the molecular symmetry was lowered to C_s. The first of the two slip sandwich models, where h_2 = 1.860 Å, *slip* = 0.790 Å and the angle between the planes of the two Cp rings is α = —4°, corresponds to the best electron diffraction model [9]. The second where h_2 = 1.821 Å. *slip* = 1.210 Å and α = —4°, corresponds roughly to the crystal structure at —120° C [23].

Finally we considered the π-Cp, σ-Cp model (IV). The geometry of the π-CpBe fragment was again held constant, while the bond distances and valence angles of the σ-Cp ring was taken from the recent microwave investigation of cyclopentadiene by Damiani et al. [24]. The molecular fragments were joined by removing one H atom from C_5H_6 and replacing it with the Be atom at a bond distance Be—C_α = 1.698 Å, equal to the Be—C(Me) bond distances in monomeric $Be(CH_3)_2$ [25] and π-$CpBeCH_3$ [22], and without changing the valence angles around the C_α atom. The Be—C bond was assumed to lie along the *z*-axis. The angle between the two Cp ring planes is then α = +36.9°.

Experimental

Cp_2Be was synthesized from NaCp and $BeCl_2$ in diethyl ether [26] and purified by vacuum sublimation. The crystalline, colorless samples were introduced into the PE spectrometer (PS 18, Perkin—Elmer Ltd., Beaconsfield, England) under nitrogen. The spectra were recorded at room temperature. The spectra were calibrated with argon; a resolution of about 20 meV was obtained.

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