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ELECTRONIC STRUCTURE OF METALLOCENES

V *. PHOTOELECTRON SPECTRA OF CYCLOPENTADIENYLBERYLLIUM COMPOUNDS

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Summary

The He(I) photoelectron (PE) spectra of CpBeX (X = CH_3 (I), C_2H (II), C_3H_3 (III), Cl (IV) Br (V)) have been recorded. The first ionization energies were compared with the orbital energies obtained from a CNDO-type calculation. In case of II to V the bands 1, 2 and 3, 4 are due to two $^2E_1$ states with a Jahn-Teller splitting of 0.1—0.2 eV.

Introduction

In connection with our investigation of the electronic structure of beryllocene [2] it was of interest to study the photoelectron (PE) spectra of other compounds with a CpBe unit. Some questions of interest were as follows: Is Koopmans' theorem [3] approximately valid? Can a CNDO type calculation be

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* For Parts I—IV see refs. 1 and 2.

used to interpret the PE spectra? Is the Jahn-Teller splitting of the bands corresponding to ^2E states similar in size to those in Cp_2Be? To answer these questions we investigated compounds of the type CpBeX with X = CH_3 (I), C≡C—H (II), C≡C—CH_3 (III), Cl (IV) and Br (V).

Results and discussion

The He(I) photoelectron (PE) spectra of I to V are shown in Fig. 1. The PE spectra of II to V show two peaks (bands 1, 2 and 3, 4) well separated from others; a common feature of these peaks is the steep onset.

To interpret the PE spectra we first calculated the molecular orbital energies, ϵ_J, for the neutral species using a modified CNDO procedure [4]. The results are shown in Table 1. A comparison between the calculations and measurements shows a satisfactory agreement if we assume the sequence of bands indicated in Table 1. This means that Koopmans' theorem $(-\epsilon_J = I_{V,J})$ [3] is valid at least to a first approximation, a conclusion also reached in case of the PE spectrum of beryllocene [2] where we used ab initio calculations to derive the orbital energies. This theorem allows us to correlate calculated orbital energies $(-\epsilon_J)$ with measured vertical ionization potentials $(I_{V,J})$. The close agreement between calculation and experiment can be seen by comparing in Fig. 2a the experimentally determined ionization potentials with the results of a CNDO-type calculation (Fig. 2b). This comparison suggests that the first two peaks in

TABLE 1

COMPARISON BETWEEN MEASURED VERTICAL IONIZATION POTENTIALS, $I_{V,J}$, AND CALCULATED ORBITAL ENERGIES, ϵ_J (ALL VALUES IN eV)

Compound	Band	$I_{V,J}$	Assignment	$-\epsilon_J$
$CpBeCH_3$	1	9.43	$e_\pi(Cp)$	10.14
	2	~9.8		
	3	~10.3	σ(Be—C)	10.03
	4	12.40		
$CpBeC_2H$	1	9.40	e_π(C≡C)	9.69
	2	~9.6		
	3	10.30	$e_\pi(Cp)$	11.21
	4	~10.5		
	5	12.36	σ(Be—C)	12.12
$CpBeC_2CH_3$	1	8.82	e_π(C≡C)	9.33
	2	~9.1		
	3	9.85	$e_\pi(Cp)$	10.98
	4	~10.15		
	5	11.95	σ(Be—C)	12.11
CpBeCl	1	9.60	$e_n(Cl)$	9.88
	2	~9.9		
	3	11.15	$e_\pi(Cp)$	11.57
	4	11.5		
	5	12.45	σ(Be—Cl)	11.83
CpBeBr	1	9.52	$e_n(Br)$	9.23
	2	9.78		
	3	10.79		
	4	~11.0	$e_\pi(Cp)$	11.30
	5	12.00	σ(Be—Br)	11.77

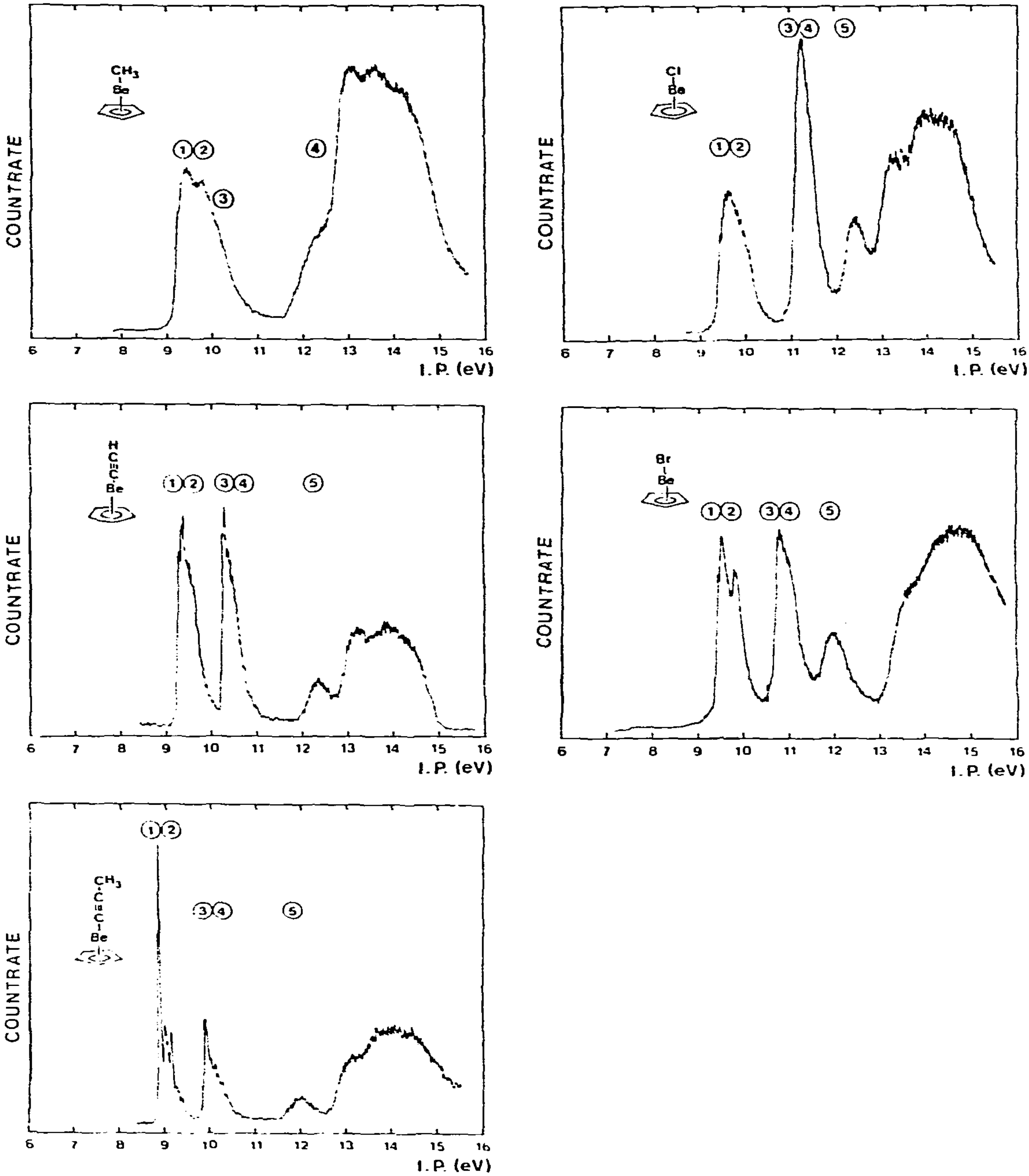

Fig. 1. PE spectra of $CpBeCH_3$, $CpBeC_2H$, $CpBeC_2CH_3$, CpBeCl, CpBeBr.

the PE spectra of II to V are to be assigned as to four ionization events from two *e* orbitals.

The calculations predict the π-orbitals localized on the acetylenic moiety in II and III and the 3*p* and 4*p* lone-pairs in IV and V on top of the $e(\pi)$ linear combination localized on the CpBe fragment. The following facts are in line

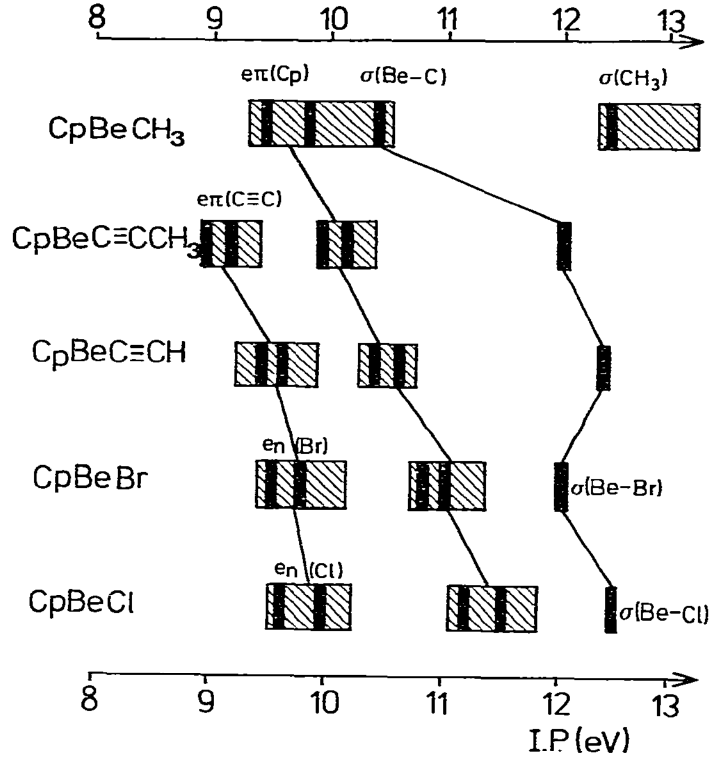

Fig. 2a. Correlation between the first bands in the PE spectra of $CpBeCH_3$, $CpBeC_2CH_3$, $CpBeC_2H$, CpBeBr and CpBeCl.

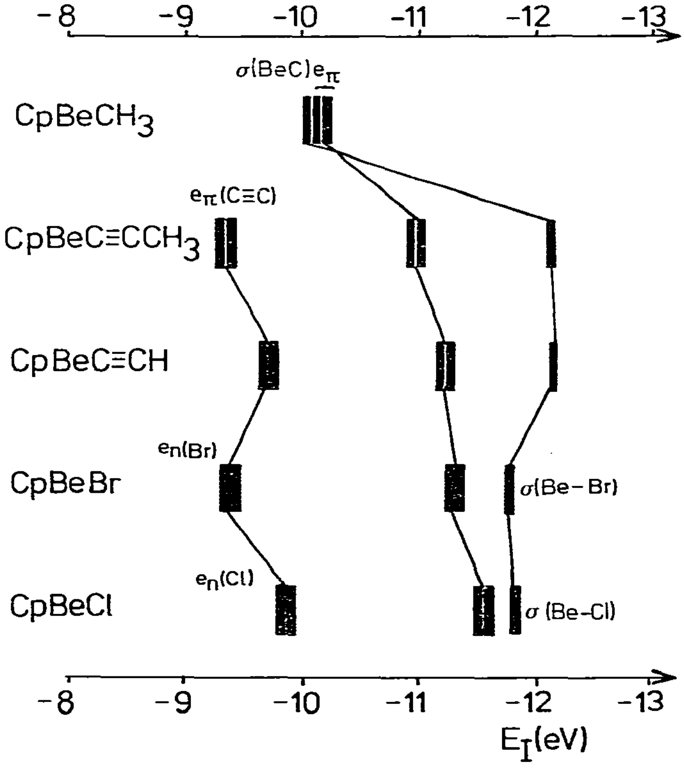

Fig. 2b. Correlation between the highest occupied MO's of the same compounds as in 2a.

with the prediction that both types of bands are due to ionization from *e* orbitals: the intensities of the corresponding bands and band 5 show a ratio of about 2 : 1, the shape of the bands corresponds to those found in acetylenes [5,6] or benzene [5], especially the encountered Jahn-Teller split is relatively small (0.1—0.2 eV) and typical for ionization from weakly bonding *e* orbitals. The assignment of the first band to the $e(\pi)$ level is consistent with the vibrational fine structure which is best interpreted as involving a progression with $\nu \approx 1900$ cm^{-1} which is typical for the C—C triple bond [6]. The splitting of 0.26 eV found in the first band of the PE spectrum of V is typical for the spin orbit coupling in bromides [6,7]. If we adopt the assignment given for II to V, that suggested for I seems logical. Substituting the CH_3 group in I by an acetylenic moiety should lower the $e(\pi)$ level localized at the CpBe fragment as indicated in Figs. 2a and 2b. The shift to higher ionization potentials of the Be—C σ bond is also in line with our interpretation. If we replace the sp^3 carbon by a *sp* one as in case of II or III we expect an increase of the corresponding energy.

Calculations

For our calculations a modified CNDO procedure had been used [4]. In the case of I, II, IV and V we used the experimental determined geometries [8]; in the case of III standard bond lengths were used for the C_3H_3 fragment [9]. The obtained orbital energies are listed in Table 1, the calculated net charges are given in Table 2. In Figure 3 a qualitative interaction diagram between the $e_1(\pi)$ MO's of the Cp fragment and the $e_1(\pi)$ orbitals of X is shown. Due to this interaction negative charge is transferred from the formal X^- fragment to the $CpBe^+$ unit.

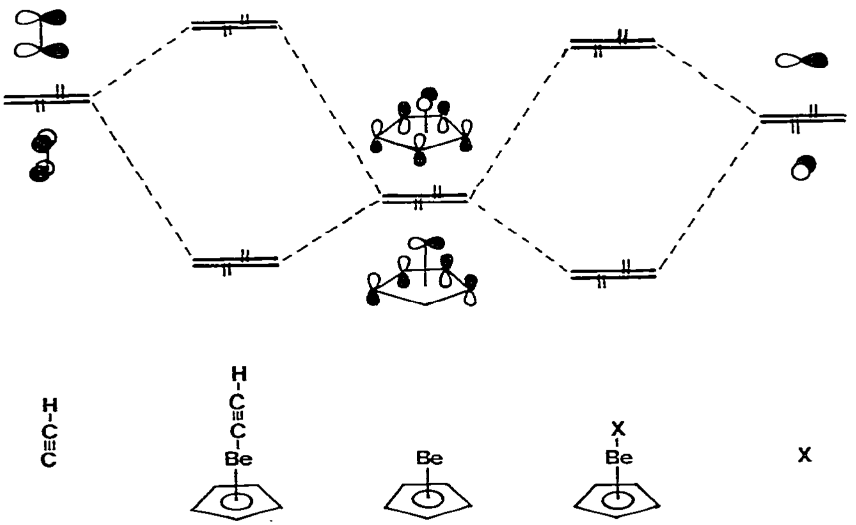

Fig. 3. Qualitative interaction diagram between the fragment orbitals of a CpBe unit and a halogen or acetylene unit.

TABLE 2

NET CHARGES OF Be, C AND HALOGENS (Hal) OF I TO V ACCORDING TO A CNDO CALCULATION

Compound	C(Cp)	Be	C$_1$	C$_2$	C(CH$_3$)	Hal
CpBeCH$_3$ [a]	—0.082	0.031	—	—	—0.282	—
CpBeC$_1$≡C$_2$—H	—0.072	0.068	—0.235	—0.170	—	—
CpBeC$_1$≡C$_2$CH$_3$	—0.073	0.075	—0.277	—0.107	—0.048	—
CpBeCl	—0.082	0.114	—	—	—	—0.276
CpBeBr	—0.086	0.077	—	—	—	—0.194

[a] Mean values.

Conclusion

Our investigations of a series of CpBeX compounds show that semiempirical methods can be used to interprete the PE spectra with the aid of the validity of Koopmans' theorem. In contrast to Cp$_2$Be where the split of the first band is found to be 1 eV, our examples show a small Jahn-Teller splitting in the order of 0.1—0.2 eV. This value is anticipated if the reported structures for I—V are present in the gas phase and the ionization occurs from weakly bonding MO's. On the other hand, our investigation supports the assumption that the Cp$_2$Be should have no C_3 or C_5 axis in the gas phase.

Experimental

The compounds IV and V were prepared according to the procedures described in ref. 10, compounds II and III as in ref. 11 and I as in ref. 12. The purities of the compounds were checked by ^{1}H NMR and Mass spectrometry. The colourless samples were introduced into the PE spectrometer (PS 18, Perkin Elmer Ltd., Beaconsfield, England) under nitrogen. The spectra were recorded at room temperature and calibrated with argon; a resolution of about 20 meV was obtained. Using the same conditions for CpBeH only the PE spectrum of Cp$_2$Be could be detected.

Acknowledgments

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