ELECTRONIC STRUCTURE OF FERROCENE DERIVATIVES STUDIED BY He(I) PHOTOELECTRON SPECTROSCOPY AND CNDO/2 METHOD

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Summary

The effect of substituents in the Cp ligands on the electronic structure has been studied for the 1,1'-disubstituted ferrocenes $Fe(CpX)_2$, with $X = C_2H_5$, OCH_3, CN, $COCH_3$, $COOCH_3$, $OOCCH_3$, $CH_2C_6H_5$, or C_6H_5, by UV photoelectron spectroscopy and by CNDO/2 calculations. The energy gap between the $^2E_{2g}$ and $^2A_{1g}$ ion states, 0.36 eV in the parent ferrocene, is affected only by the $COCH_3$ and $COOCH_3$ substituents, which lower it to 0.22 and 0.28 eV, respectively. Splitting of $e_{1u}(\pi)$ level due to the lowering of the symmetry is the only effect observed in the photoelectron spectra. There is a strong conjugation between the phenyl and cyclopentadienyl π-orbitals in 1,1'-diphenylferrocene. The changes in the $a_{1g}(d)$ ionization energy calculated by the ΔSCF method using CNDO/2 total energies are in a good agreement with the experimental data.

Introduction

Many transition metal sandwich compounds have been studied by ultraviolet photoelectron (PE) spectroscopy [1,2]. The dependence of the electronic structure of dicyclopentadienylmetal complexes upon the central atom was revealed by the pioneering studies of Orchard and coworkers [3,4], and the influence of the size of the ligand ring has been established [5]. In contrast, PE spectroscopic data for metallocene species in which the ligands bear substituents are scarce. To our knowledge the only ferrocene derivatives previously studied by PE spectroscopy are methylferrocenes [3,6,7], halogenoferrocenes [3,8], 1,1'-diacetylferrocene [9], [3]-ferrocenophane species [10], and biferrocenylene species [11]. PE spectroscopic investigations reveal the interesting fact that the substituents bring about a shift of ionization energies (IE's) of d-levels comparable in magnitude with that for the ligand π-levels. The XPS spectra of totally methylated ferrocene reveal that there is an increase in the electron density on the central atom, equivalent to a one-electron reduction [12]. On the other hand, the change of the charge on Fe atom calculated by the iterative EHT method is only slight [13].

The purpose of this study was to examine the effect of substituents having differing electron donor–acceptor properties on the electronic structure of ferrocene. We thus carried out He(I) PE spectroscopic investigations and CNDO/2 calculations on a set of 1,1'-disubstituted ferrocenes $Fe(Cp-X)_2$, namely those with $X = C_2H_5$, OCH_3, CN, $COCH_3$, $COOCH_3$, $OOCCH_3$, $CH_2C_6H_5$, or C_6H_5.

Experimental and computational details

Ferrocene derivatives were prepared by published methods: $Fe(CpOCH_3)_2$, $Fe(CpOOCCH_3)_2$ [14], $Fe(CpCH_2C_6H_5)_2$ [15], $Fe(CpC_6H_5)_2$ [16], $Fe(CpCOCH_3)_2$ [17], $Fe(CpC_2H_5)_2$ [18], $Fe(CpCOOCH_3)_2$ [19], and $Fe(CpCN)_2$ [20]. The purities and stability of the samples on heating were checked by mass spectrometry.

He(I) photoelectron spectra were recorded on a VG Scientific UVG 3 spectrometer with FWHM 30–40 meV on the Ar $^2P_{3/2}$ peak. Spectra were calibrated by simultaneously adding an Ar/Xe mixture. The temperature of evaporation of the samples varied between 100 and 200°C.

The Clack version of the CNDO/2 method [21] was used with the standard parametrization for main groups elements [22,23]. Gouterman's orbital exponents [24] ($\zeta_{4s,4p} = 1.37$, $\beta^\circ_{4s,4p} = 26$ eV, $\zeta_{3d} = 2.722$, $\beta^\circ_{3d} = 27$ eV) and the electron affinities derived by Clack and coworkers [21] were used for Fe. The corresponding $(I + A)/2$ values were equal to 4.12, 5.504, and 1.062 eV for $4s$, $4p$, and $3d$ orbital of Fe atom, respectively. The $^2A_{1g}(a^1_{1g}e^4_{2g})$ ion states were calculated by the "half-electron" formalism [25].

The interatomic distances found by electron diffraction for vapour phase ferrocene were used for all calculations. The bond lengths are: Fe–C 2.057 Å, C–C 1.429 Å, and C–H 1.116 Å. The ligands were assumed to be planar and the planes of the rings parallel. The bond lengths and bond angles of substituents were taken from the analogous benzene derivatives [27–32], including the bond length X–C(Cp), for which the values X–C(benzene) were adopted.

Results and discussion

Photoelectron spectra

The vertical *IE*'s found are summarized in Table 1. The first two bands in PE spectra (*a*, *b*) unambiguously come from ionizations of metal *d* levels, since no ionizations of the substituents fall into this range. Only two bands are observed. We adopt the classification of the *d* levels in the D_{5d} point group although the highest symmetry attainable for the $Fe(CpX)_2$ molecule is C_{2h} (antiperiplanar conformation) or C_{2v} (synperiplanar conformation). The *a/b* intensity ratio is obviously conserved, and thus band *a* is assigned to the $e_{2g}(d)$ level and band *b* to the $a_{1g}(d)$ level, by analogy with the parent molecule (Fig. 1, 2). The CN and OCH_3 groups exert the strongest effect upon the *IE*'s of *d* levels; CN substituents bring about an increase of these *IE*'s by 1 eV, and the OCH_3 groups a decrease by 0.3 eV.

In comparison to the PE spectrum of ferrocene bands *a* and *b* are less resolved due to the lowering of the symmetry of the molecule. This effect is least apparent in PE spectra of the 1,1'-dicyano and 1,1'-diethyl derivative (Fig. 1). The alkyl group has only a weak positive inductive effect. The predominant effect of the CN group is also inductive; of all the electron accepting substituents studied it has the weakest

TABLE 1

VERTICAL IONIZATION ENERGIES (IE's) OF FERROCENE DERIVATIVES Fe(CpX)$_2$

Fe(CpX)$_2$		IE (eV) for X =								
Band	assignment	C$_2$H$_5$	OCH$_3$	CN	COCH$_3$	COOCH$_3$	OOCCH$_3$	CH$_2$C$_6$H$_5$	C$_6$H$_5$	H
a	$e_{2g}(d)$	6.60	6.55	7.85	7.36	7.17	6.81	6.57	6.63	6.85
b	$a_{1g}(d)$	6.94	6.91	8.18	7.58	7.45	7.11	6.87	6.97	7.21
c	$e_{1u}(\pi),b_u(\pi)$	8.33	7.98	9.51	9.17 [f]	8.95	8.63	8.32	7.88	8.72
c'	$a_u(\pi)$	8.60	8.48	9.80					8.15 [j]	
d	$e_{1g}(\pi)$	9.05	9.04	10.27	9.78	9.68	9.27	8.94 [i]	9.05 [k]	9.17 9.38
e			10.77 [a]	11.70 [c]		9.97 [g]	10.32 [g]		9.74 [l]	
f			11.54 [b]	11.95 [d]		10.68 [h]	11.21 [h]			
g				12.11 [d]						
h				12.66 [e]						

[a] n(O). [b] σ(CH$_3$O). [c] In-plane π(CN). [d] Out-of-plane π(CN). [e] σ(CN). [f] Overlapping with n(O). [g] n(O). [h] π(COO). [i] Overlapping with phenyl $e_{1g}(\pi)$. [j] Overlapping with phenyl $a_g(\pi)$. [k] Overlapping with phenyl $a_u(\pi)$, $b_g(\pi)$. [l] Phenyl $b_u(\pi)$.

mesomeric effect [33]. It can be concluded that the D_{5d} symmetry of the molecule is not much perturbed by the inductive effect of substituents.

In 1,1'-diacetylferrocene and dimethylferrocene-1,1'-dicarboxylate the IE difference $e_{2g}(d) - a_{1g}(d)$ is lowered to 0.22 and 0.28 eV, respectively. In the PE
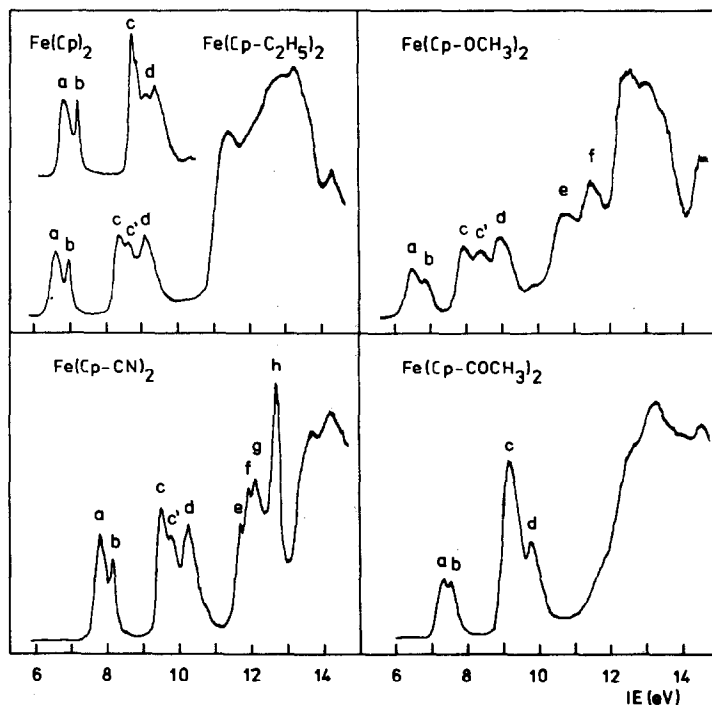

Fig. 1. He(I) photoelectron spectra of ferrocene, 1,1'-diethylferrocene, 1,1'-dimethoxyferrocene, 1,1'-dicyanoferrocene and 1,1'-diacetylferrocene.

spectra of the remaining ferrocene derivatives the energy gap between $^2E_{2g}(a_{1g}^2 e_{2g}^3)$ and $^2A_{1g}(a_{1g}^1 e_{2g}^4)$ is, within the experimental error (0.06 eV, estimated as twice the standard deviation), the same as in the parent molecule (0.36 eV).

The assignment of the highest ligand ionizations is a more complex task. The two-fold degeneracy of both the $e_{1u}(\pi)$ and $e_{1g}(\pi)$ level is lifted and the levels can be split into their components. The $b_u(\pi)$ and $a_g(\pi)$ orbitals (C_{2h} point group) have a non-zero p_z atomic orbital coefficient at the point of substitution, and can be destabilized by the conjugative or hyperconjugative interaction with the lower lying orbitals of substituents. The $a_u(\pi)$ and $b_g(\pi)$ components, which have a node at the point of substitution, are not influenced by this interaction. Moreover ionizations of the outermost orbitals of substituents can overlap with that of the highest cyclopentadienyl π levels.

1,1'-Diethylferrocene (Fig. 1). Only three bands c, c' and d coming from the highest ligand π levels are observed before the onset of σ ionizations. In ferrocene itself the $e_{1g}(\pi)$ level is located below the $e_{1u}(\pi)$ level. Thus we assign band c to the $b_u(\pi)$ orbital, which is destabilized by the interaction with ethyl groups. The intensity ratio c'/c is < 1, and thus band c' cannot come from overlapping ionizations of components of both the $e_{1u}(\pi)$ level and $e_{1g}(\pi)$ level. We assign band c' to the $a_u(\pi)$ orbital and the remaining band d to the $e_{1g}(\pi)$ level. A similar absence of the splitting of the $e_{1g}(\pi)$ level was found in PE spectra of halogenoferrocenes [8]; the earlier onset of the σ ionizations, (with the first band peaks at 11.32 eV, whereas for the parent molecule the first σ ionization is at 12.32 eV) can be assigned to the highest orbitals of the ethyl groups.

1,1'-Dimethoxyferrocene (Fig. 1). The assignments of the bands c, c' and d to the $b_u(\pi)$, $a_u(\pi)$ and $e_{1g}(\pi)$ levels, respectively, are based on the same arguments as those applied to 1,1'-diethylferrocene. The splitting of $e_{1u}(\pi)$ level is 0.5 eV. This is the largest value observed, and shows that there is a strong conjugative interaction between the oxygen non-bonding orbital and the cyclopentadienyl π system. Despite the strong interaction with the oxygen non-bonding orbitals no splitting of the $e_{1g}(\pi)$ level is observed, and band d is only broadened.

The subsequent bands e and f lie at 10.77 and 11.54 eV, respectively. In the PE spectrum of methoxybenzene the IE for the oxygen non-bonding orbital is 11.06 eV [34]. A destabilization of chlorine non-bonding orbitals by 0.3 eV was found on going from chlorobenzene to 1,1'-dichloroferrocene [8]. Thus we assign the band e to the oxygen non-bonding orbitals. The band f at 11.54 eV also has its counterpart in the PE spectrum of methoxybenzene, where the band coming from the highest bonding orbitals of the CH_3O group lies at 11.52 eV.

1,1'-Dicyanoferrocene (Fig. 1). The assignment of the bands c, c' and d to the $a_u(\pi)$, $b_u(\pi)$ and $e_{1g}(\pi)$ levels follows from the assignment of the highest ligand ionizations in PE spectra of 1,1'-diethylferrocene and 1,1'-dimethoxyferrocene. Sharp bands in the range from 11 to 13 eV are absent from the spectrum of the parent molecule; these bands come from ionizations involving orbitals of the CN groups. The most intense band, h, comes from ionization of the non-bonding orbitals localized predominantly on the nitrogen atoms ($\sigma(CN)$). The assignment of the band h to $\pi(CN)$ orbitals would imply, unreasonably, that these orbitals are stabilized compared with those of benzonitrile [35]. The $\sigma(CN)$ orbitals cannot be split into symmetric and antisymmetric combinations by through-space or through-bond interactions since they overlap to a negligible extent, and are orthogonal to the
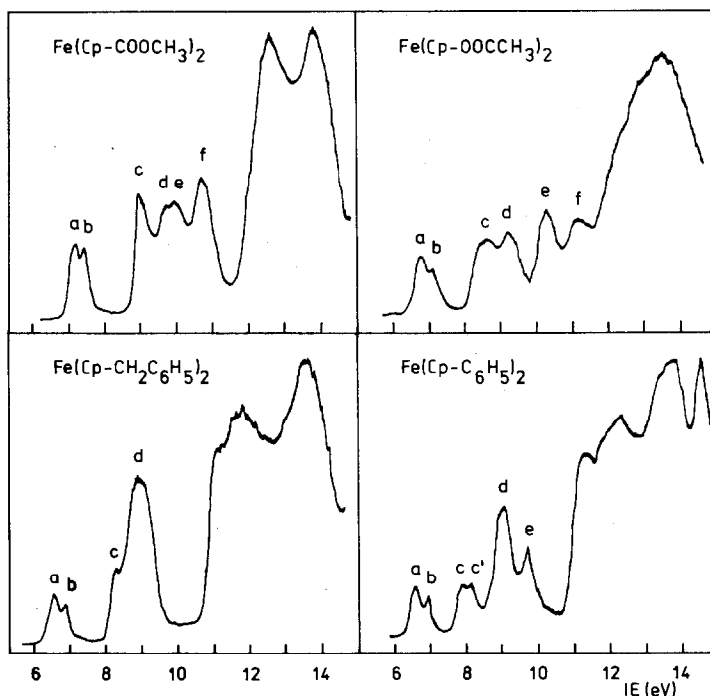
Fig. 2. He(I) photoelectron spectra of dimethylferrocene-1,1'-dicarboxylate, 1,1'-diacetoxyferrocene, 1,1'-dibenzylferrocene and 1,1'-diphenylferrocene.

cyclopentadienyl π system. Thus we assign both the symmetric and antisymmetric combination to the single band h. The overlapping bands e, f, and g then come from ionizations involving $\pi(CN)$ orbitals. In benzonitrile the in-plane $\pi(CN)$ orbital lies higher than the out-of-plane one, which is stabilized by the conjugative interaction with the $e_{1g}(\pi)$ level of benzene. Therefore we assign band e to the in-plane $\pi(CN)$ orbitals, which, on the basis of the reasoning applied to the $\sigma(CN)$ orbitals, cannot be split. In benzonitrile the in-plane $\pi(CN)$ ionization is accompanied by a very weak vibrational structure. Thus we think that bands f and g come from the ionization of out-of-plane $\pi(CN)$ orbitals; their separation is 1300 cm^{-1}. The stretching vibrational frequency of the weakened C≡N bond observed in the benzonitrile PE spectrum amounts to 1800 cm^{-1}. We believe that bands f and g are to be assigned to the symmetric and antisymmetric combination of out-of-plane $\pi(CN)$ orbitals rather than to a vibrational progression. The symmetric combination can be stabilized by the through-bond interaction mediated by $e_{1g}(d)$ orbitals of the central atom. An analogous splitting of out-of-plane chlorine p orbitals was observed previously in the PE spectrum of 1,1'-dichloroferrocene [8].

1,1'-Diacetylferrocene (Fig. 2). The ionizations involving the oxygen non-bonding orbitals lie in the range 8–11 eV range. We assign the band c to the overlapping ionizations of the $e_{1u}(\pi)$ level and $n(O)$ orbitals. The $n(O)$ orbitals are not split, for the reasons discussed in the case of 1,1'-dicyanoferrocene. The remaining band d is assigned to the $e_{1g}(\pi)$ level. The assignment of the band d to the $n(O)$ orbitals is

ruled out by the intensity observations and implying that they are destabilized relative to those for acetophenone [34].

Dimethylferrocene-1,1'-dicarboxylate (Fig. 2). Before the onset of the σ ionizations four bands appear, in the range 8.5–11.5 eV. The $COOCH_3$ substituent does not introduce any observable splitting of the $e_{1g}(\pi)$ level of benzene [39]. The splitting of the $e_{1u}(\pi)$ level of ferrocene is lower than that of the analogous $e_{1g}(\pi)$ level in the PE spectra of benzene derivatives [8]. Thus we assign band c to the $e_{1u}(\pi)$ level. The two following bands d and e overlap to a large extent. If we assume that the shift of the $e_{1g}(\pi)$ level is the same as that of the $e_{1u}(\pi)$ level, band d can be assigned to the $e_{1g}(\pi)$ level and band e to the $n(O)$ orbitals of the carbonyl oxygen atoms. Owing to the close vicinity of these bands this assignment must remain tentative. The second band of the ester group is located 0.6 to 0.7 eV below the $n(O)$ ionization [36]. This band comes from ionization involving the highest $\pi(COO)$ orbital. Thus the band f at 10.68 eV can be unequivocally assigned to the $\pi(COO)$ ionization.

1,1'-Diacetoxyferrocene (Fig. 2). The band c is only broadened, and we assign it to the $e_{1u}(\pi)$ level and band d to the $e_{1g}(\pi)$ level. The ionization energy of the $n(O)$ and $\pi(COO)$ orbital of the ester group falls below that of the highest ligand π ionizations, the IE for the $n(O)$ orbital in acetates is round 10.4 eV [37]. Thus the band e at 10.32 eV can be assigned to the $n(O)$ orbitals. The next band, peaking at 11.21 eV, can be assigned to the $\pi(COO)$ orbitals (11 eV in acetates).

1,1'-Dibenzylferrocene (Fig. 2). The ionization of $e_{1g}(\pi)$ level of the benzene ring falls within the range of $e_{1g}(\pi)$ and $e_{1u}(\pi)$ ionization. Since the alkyl group brings about an observable splitting of the $e_{1u}(\pi)$ level, it is reasonable to assume that in the PE spectrum of 1,1'-dibenzylferrocene the $e_{1u}(\pi)$ level is split into its components. We assign band c to the $b_u(\pi)$ orbital. The broad intense band peaking at 8.94 eV comes from overlapping ionizations of the $a_u(\pi)$ orbital, $e_{1g}(\pi)$ level and the $e_{1g}(\pi)$ level of phenyl rings.

1,1'-Diphenylferrocene (Fig. 2). The PE spectrum differs substantially from that of 1,1'-dibenzylferrocene. π orbitals of a phenyl group can interact directly with π orbitals of cyclopentadienyl. The a_u and b_g orbitals (C_{2h} point group) remain unaffected since they have a nodal plane at the point of substitution. The b_u and a_g orbitals give rise to symmetric and antisymmetric combinations (Fig. 3). The benzene $e_{1g}(\pi)$ orbital is at a lower energy level than the $e_{1u}(\pi)$ orbital of ferrocene. Therefore we assign band c to the $b_u(\pi)$ orbital of ferrocene The $a_g(\pi)$ component of the phenyl $e_{1g}(\pi)$ level is destabilized by interaction with the lower lying ferrocene $e_{1g}(\pi)$ level. Thus band c' may come from overlapping ionizations of $a_g(\pi)$ orbital of phenyl rings and of the $a_u(\pi)$ orbital of ferrocene. The assignment of the band c' to the $a_g(\pi)$ orbital of phenyl rings alone would be less reasonable. $a_g(\pi)$ orbital of ferrocene must be slightly destabilized by the presence of hydrocarbon substituents and thus it cannot be assigned to the next band, d, peaking at 9.05 eV. Band d is the most intensive band in this region and undoubtedly comes from ionizations of the unperturbed $a_u(\pi)$ and $b_g(\pi)$ orbital of the phenyl rings and the $e_{1g}(\pi)$ level of ferrocene. In none of the PE spectra of ferrocene derivatives is splitting of the $e_{1g}(\pi)$ level observed. It is more resonable to assign the next band, e, to the $b_g(\pi)$ component of the phenyl $e_{1g}(\pi)$ level despite the fact that the interaction diagram predicts a large stabilization of the $b_g(\pi)$ orbital of ferrocene. The shape of band e supports its assignment to a single ionization.
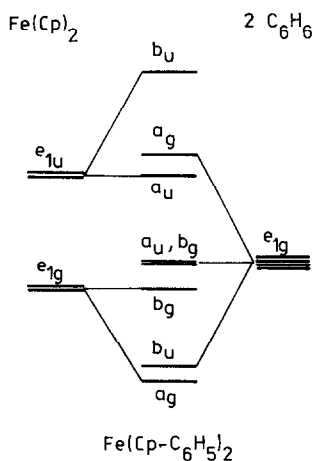
Fig. 3. Interaction diagram of the outermost occupied π orbitals of ferrocene, benzene and 1,1'-diphenyl-ferrocene.

CNDO / 2 calculations

The orbital energies of the outermost occupied orbitals are summarized in Fig. 4. Though the relative orders of the d levels and of the ligand π levels do not agree with experiment, the variations of the energies of the d levels do match the experimental ones (Fig. 5). The changes for the $a_{1g}(d)$ level IE calculated by the Δ SCF method using CNDO/2 total energies are in a better agreement with the experimental values than those derived on the basis of Koopmans' theorem [38]
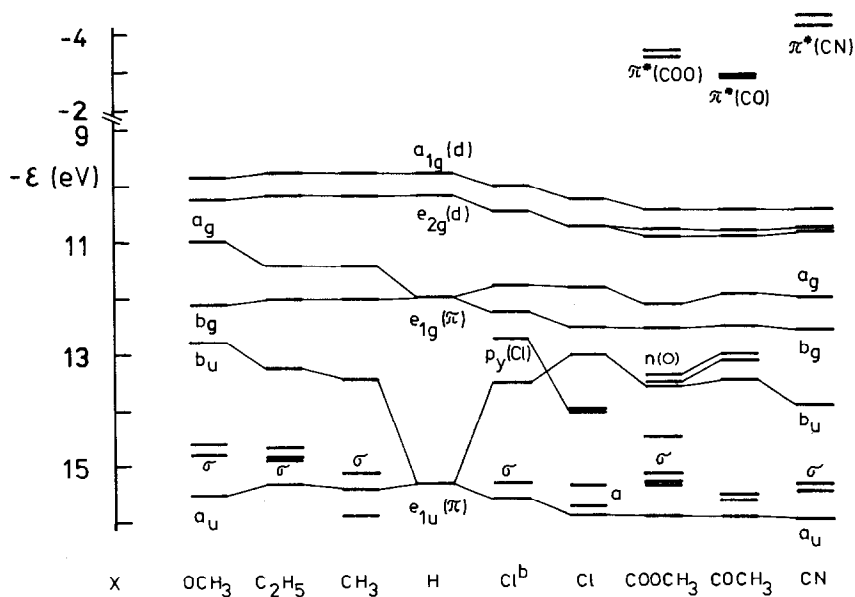

Fig. 4. Correlation diagram of CNDO/2 orbital energies of Fe(CpX)$_2$. p_y denotes in-plane p orbitals, (a) out-of-plane p(Cl) orbitals, (b) chloroferrocene.
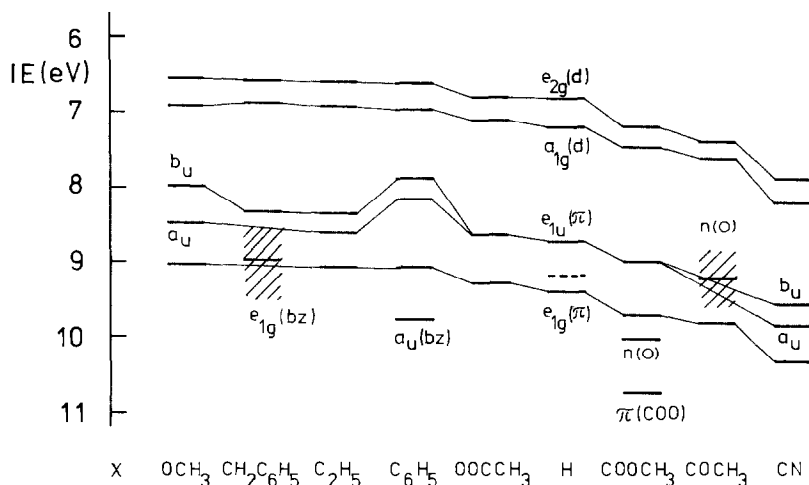
Fig. 5. Correlation diagram of experimental ionization energies of $Fe(CpX)_2$.

(Table 2). The electron densities on Fe are influenced to a negligible extent and the changes do not correlate with the electron donor–acceptor properties of substituents. The difference in behaviour between $e_{1u}(\pi)$ and $e_{1g}(\pi)$ on substitution is qualitatively reproduced. The $e_{1g}(\pi)$ is split to a smaller extent than the $e_{1u}(\pi)$ level; this is in agreement with the absence of the splitting of the $e_{1g}(\pi)$ level in PE spectra, though the absolute values calculated are far from the experimental ones.

The splitting of out-of-plane $p(Cl)$ orbitals previously observed in the PE spectrum of 1,1'-dichloroferrocene [8] also appears in the results of the CNDO/2 calculations. The calculated energy gap between a_g and b_u combination is 0.45 eV, whereas the two in-plane $p(Cl)$ orbitals nearly degenerate.

The antibonding π orbitals of $COCH_3$, $COOCH_3$ and CN substituent are located below the $e_{2g}(\pi)$ level. These orbitals are partly delocalized over the cyclopenta-

TABLE 2

RELATIVE CHANGES OF $a_{1g}(d)$ VERTICAL IONIZATION ENERGY (Δ IE), AND CENTRAL ATOM CHARGE (q_{Fe}) (Δ IE_{exp} denotes experimental values, Δ IE_{calc} denotes values calculated by the Δ SCF method and $\Delta\epsilon$ values calculated from Koopmans theorem [38])

compound	IE (eV)			q_{Fe}
	Δ IE_{exp}	Δ IE_{calc}	$\Delta\epsilon$	
$Fe(CpOCH_3)_2$	-0.30	-0.04	0.05	-0.54
$Fe(CpC_2H_5)_2$	-0.27	-0.22	-0.03	-0.52
$Fe(CpCH_3)_2$	-0.15 [a]	-0.14	0.00	-0.52
$Fe(Cp)_2$	0	0	0	-0.54
$Fe(Cp)(CpCl)$	0.17 [b]	0.23	0.28	-0.53
$Fe(CpCl)_2$	0.37 [b]	0.47	0.55	-0.53
$Fe(CpCOOCH_3)_2$	0.24	0.45	0.67	-0.51
$Fe(CpCOCH_3)_2$	0.37	0.4	0.63	-0.51
$Fe(CpCN)_2$	0.97	0.47	0.62	-0.52

[a] Ref. 3. [b] Ref. 8.

dienyl ring. The $e_{2g}(d)$ level can be additionally stabilized by the interaction with these orbitals. The result is the lowering of the energy gap between the $^2E_{2g}$ and $^2A_{1g}$ ion state observed in PE spectra. The $\pi^{\star}(CN)$ orbital lies at a higher energy than the $\pi^{\star}(COO)$ and $\pi^{\star}(CO)$ orbitals, and thus its effect is probably within the experimental uncertainty of the *IE* measurements.

Conclusions

The PE spectra of ferrocene derivatives have been interpreted by a comparative analysis. Only the carbonyl substituents affect the energy gap between $^2E_{2g}$ and $^2A_{1g}$ ion state. The $e_{1u}(\pi)$ level alone is split into its components due to the loss of fivefold symmetry. The $e_{1g}(\pi)$ level in which the central atom d orbitals participate remains unaffected. This effect of substituents can be used as an experimental probe for the participation of transition metal d orbitals in degenerate ligand π levels. A similar behaviour of the ligand π levels was recently observed in the PE spectra of uranocene derivatives [39].

The PE spectrum of 1,1'-diphenylferrocene shows that there is a strong interaction between π orbitals of the phenyl and cyclopentadienyl rings. The resulting orbitals differ significantly in energy from those of ferrocene and benzene.

The agreement between the variations in the observed $a_{1g}(d)$ *IE*'s and those calculated indicate that CNDO/2 total energies in the Δ SCF method can possibly be used for prediction of substituent effects.

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