Journal of Organometallic Chemistry, 364 (1989) 207–215
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09470

Orbital interactions in 1,*n*-dithia[*n*]ferrocenophanes; a He(I) photoelectron spectroscopic study

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(Received August 26th, 1988)

Abstract

The He(I) photoelectron spectra of 1,*n*-dithia[*n*]ferrocenophanes ($n = 3$–8, 10) and 1,1′-bis(methylthio)ferrocene are reported. The energy gap between the ${}^2A_1(a_1{}^1e_2{}^4)$ and ${}^2E_2(a_1'^2e_2'^3)$ ion states is decreased by the perturbation of the coplanarity of ligand planes and by a conjugative interaction of sulphur lone pairs with ferrocene orbitals. The inverse dependence of the two effects of the length of the interligand bridge leads to the observed minimal gap for $n = 5$. The splitting of sulphur lone pairs in the spectra reveals a strong interaction, the nature of which depends on the length of the interligand bridge. The "angle-determining" sulphur *p*-orbitals are split by a through-bond interaction if $n = 3$–5. The highest occupied π-orbitals of ferrocene relay the through-bond interaction of the orbitals localized on sulphur.

Introduction

Ultraviolet photoelectron (PE) spectroscopy has proved to be a powerful tool for the investigation of non-bonding exchange interactions [1]. An interaction between the sulphur and the iron *d*-orbitals in 1,*n*-dithia[*n*]ferrocenophanes was indicated by the electronic and ${}^{13}C$ NMR spectra and redox behaviour [2,3]. The changes of metal *d*-level energies brought about by bending of the metallocene unit were found in the PE spectra of [3]-ferrocenophane species [4]. The ligand substitution has no observable effect upon the energy difference between the ${}^2E_2'(a_1'^2e_2'^3)$ and ${}^2A_1'(a_1'^1e_2'^4)$ ion states except in the case of carbonyl substituents [5,6]. It follows from the substituent chemical shifts that the methylthio group is electron-attracting in the ferrocene system [2]. The overlap of the sulphur lone pair (n_S) with the cyclopenta-

0022-328X/89/$03.50

dienyl π-orbitals is a function of the dihedral angle θ between the alkylthio group and the cyclopentadienyl plane. The dihedral angle θ in 1,n-dithia[n]ferrocenophanes depends on the length of the interligand bridge, which forces the alkylthio group out of the planar conformation ($\theta = 0$) in which the interaction is maximal.

We have determined the He(I) PE spectra of 1,1′-bis(methylthio)ferrocene (**1**) and 1,n-dithia[n]ferrocenophanes where $n = 3$–8, 10 (**2**–**8**) with the aim of examining the effect of the alkylthio substituent and the influence of the interligand chain on the electronic structure of ferrocene.

Experimental

The samples were prepared by the published procedure [2]. The He(I) PE spectra were recorded on a VG Scientific UVG 3 instrument. The working resolution (full width at half maximum) was 30–40 meV. The spectrometer was operated in the constant passing energy mode. Spectra were calibrated by simultaneous addition of an Ar/Xe mixture.

A satisfactory signal/noise ratio was achieved in the temperature range 120–180 °C.

Results and discussion

The vertical ionization energies (IE's) are summarized in Table 1. The methythio substituent introduces no steric strain. The changes in the PE spectrum (Fig. 1 and 2) compared with that for the parent ferrocene are caused by electronic rather than steric effects. The IE's of the d-levels in **1** are comparable with those in ferrocene. This seems to indicate a small substituent parameter ($\sigma_p = 0.00$) for the methylthio group, because the d-levels IE's of substituted ferrocenes roughly correlate with the Hammett σ_p substituent constants [5]. The bands **a** and **b** coming from the ionization of the metal-based d-levels are less resolved owing to the perturbation of the five-fold symmetry. The energy difference between the $^2E_2'$ and $^2A_1'$ ion states decreased to 0.31 eV (0.36 eV for the parent ferrocene). The region of the ionization of the highest ligand π-levels is more complex owing to ionization of the sulphur lone pairs. The sulphur lone pair (n_S) can extensively conjugate with the cyclopentadienyl e_1'' and e_1' π-orbitals. The extent of this interaction is proportional to $\cos(\theta)$. In thioanisole a 10% population of the non-planar conformation was estimated from PE spectra [7]. A more realistic picture of a continuum of conformers with the dihedral angles between 0 and 90 °, each giving rise to its own PE spectrum, was suggested by Heilbronner et al. [8]. In thioanisole dihedral angles near zero are preferentially populated. An analogous situation can be assumed for **1**. The sulphur lone pairs interact according to the symmetry of their combinations with the ferrocene $e_1'(\pi)$ and $e_1''(\pi)$ level (Fig. 3).

The symmetric combination (n_S^+) can interact with the $e_1'(\pi)$ level, namely its a_1 component (the C_{2v} symmetry of the substutited ferrocene is assumed). The antisymmetric combination n_S^- can conjugate with the a_2 component of the $e_1''(\pi)$ level. The exchange interaction is inversely proportional to the difference of the energy of overlapping orbitals, thus the overlap with the lower lying $e_1''(\pi)$ level brings about a weaker destabilization than the interaction with the $e_1'(\pi)$ level. The

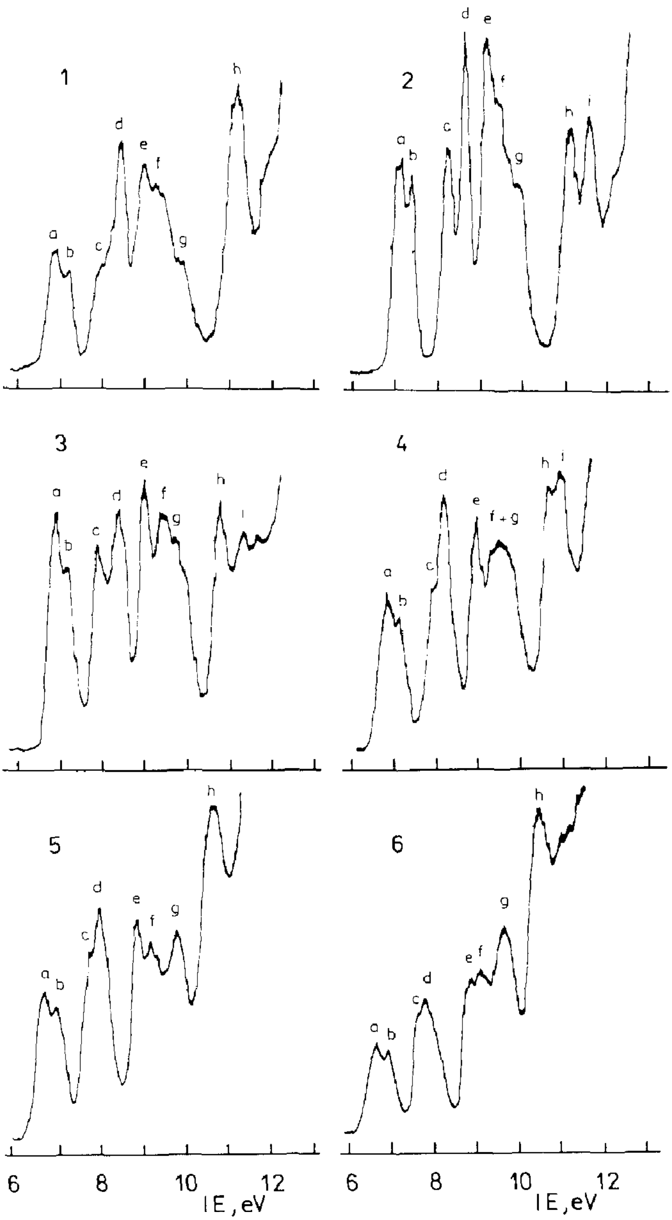

Fig. 1. He(I) photoelectron spectra of 1,1′-bis(methylthio)ferrocene (**1**), 1,3-dithia[3]ferrocenophane (**2**), 1,4-dithia[4]ferrocenophane (**3**), 1,5-dithia[5]ferrocenophane (**4**), 1,6-dithia[6]ferrocenophane (**5**) and 1,7-dithia[7]ferrocenophane (**6**).

two bands **c** and **d** can be assigned to the antibonding combinations of a_1 and a_2 sulphur lone pairs with the $e_1'(\pi)$ and the $e_1''(\pi)$ level, respectively. The bands **c** and **d** are found at similar IE's in the PE spectra of ferrocenophanes (**2**, **3**), where owing to the steric constraint the conjugation is weaker. The assignment of the cyclopentadienyl π orbitals to bands **c** and **d** would imply an unreasonably high destabilization of ligand π levels compared with the d-based levels. Thus the antibonding combination of the $p(\pi)$ orbitals of substituents with $e_1(\pi)$ levels has a

Table 1

Vertical ionization energies (IE's) of 1,1′-bis(methylthio)ferrocene (**1**) and 1,*n*-dithia[*n*]ferrocenophanes (n = 3–8, 10) (**2**–**8**) (eV)

Assignment	Band **a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**	Δ IE		
	Fe d		n_S	n_S	Ligand π			$\bar{n}_S$	$\bar{n}_S$	$a_1' - e_2'$	Δn_S	$\Delta \bar{n}_S$
	e_2'	a_1'			b_1 [a]	e_1''	a_1 [a]					
1	6.84	7.15	7.97	8.36	8.89	9.23	9.82	11.10	11.10	0.31	0.39	0
2	7.07	7.36	8.20	8.60	9.12	9.37	9.83	11.06	11.54	0.29	0.40	0.48
3	6.88	7.15	7.87	8.38	8.96	9.48	9.80	10.76	11.29	0.27	0.51	0.53
4	6.85	7.09	7.89	8.15	8.90	9.48	9.48	10.66	10.88	0.24	0.26	0.22
5	6.72	7.01	7.78	8.00	8.89	9.26	9.83	10.72	10.72	0.29	0.22	0
6	6.64	6.92	7.67	7.82	8.88	9.12	9.74	10.60	10.60	0.28	0.15	0
7	6.67	6.97	7.67	8.00	8.87	9.04	9.68	10.55	10.55	0.30	0.33	0
8	6.70	7.01	7.73	8.10	8.87	9.10	9.70			0.31	0.36	

[a] Components of the $e_1'(\pi)$ level. [b] Overlapping $e_1''(\pi)$ and $a_1(\pi)$ ionizations.

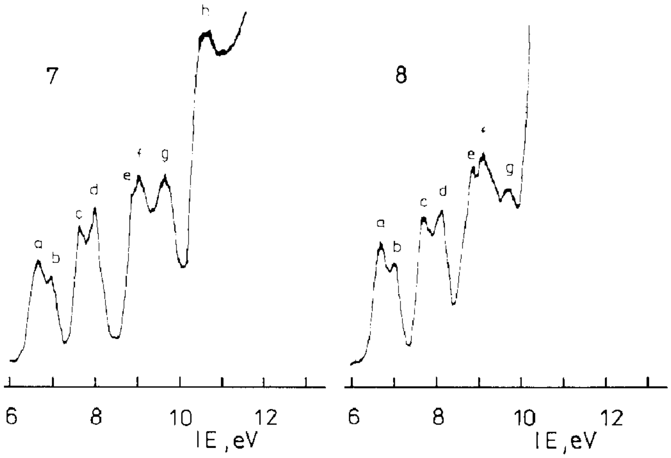

Fig. 2. He(I) photoelectron spectra of 1,8-dithia[8]ferrocenophane (**7**) and 1,10-dithia[10]ferrocenophane (**8**).

sulphur lone pair character rather than a ligand π character. The appearance of the two lone pair ionizations is a result of a through-bond interaction mediated by the highest occupied ligand orbitals $e_1'(\pi)$ and $e_1''(\pi)$. The assignment of the bands **c** and **d** to the conformations differing in θ is less reasonable, since the relative intensity **c**/**d** seems much higher than the ratio of the conformers in the analogous methylthioanisole. If the ionizations **e**–**g** are compared with those of ferrocene, the bands **e** and **f** are seen to be close to the $e_1'(\pi)$ and $e_1''(\pi)$ ionizations of the parent compound. Thus the band e is assigned to the $e_1'(\pi)$ level, namely to the b_1 orbital having a zero overlap with the sulphur lone pair. The $e_1''(\pi)$ level is not split in the PE spectra of ferrocene derivatives, and the observed changes of IE's parallel those

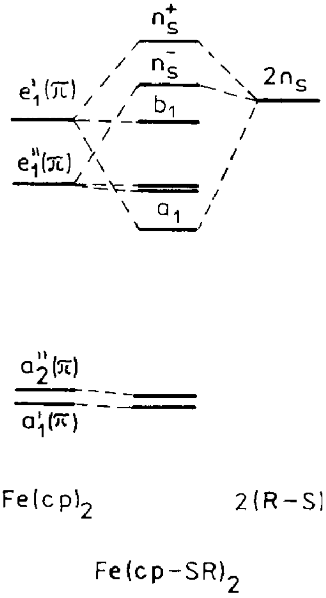

Fig. 3. Interaction diagram for the sulphur lone pairs and ferrocene occupied π-orbitals

of the d levels [5,6]. The band **f** is assigned to the $e_1''(\pi)$ level. Then the remaining band **g** comes from the ionization of the a_1 component of the $e_1'(\pi)$ level. The splitting of the $e_1'(\pi)$ level 0.93 eV is comparable to that observed in the PE spectrum of thioanisole. The band **h** superimposed on the onset of the envelope of σ ionizations has a counterpart in PE spectra of alkylthiocompounds [9,10]. It is assigned to the "angle-determining" orbital localized predominantly on sulphur ($\bar{n}_S$).

The methylene bridge brings about a tilting of ligand planes in **2**. To our knowledge no diffraction data are available for **2**, but in [3]ferrocenophane the angle between the planes of cyclopentadienyls is 10° [11]. The tilting of ring planes in [3]ferrocenophane brings about a decrease of $\Delta E(^2A_1' - {}^2E_2')$ to 0.28 eV (0.36 eV for ferrocene). The value 0.29 eV for **2**, compared with 0.31 eV for **1**, may somewhat reflect a distortion similar to the trimethylene analogue.

The shape of the ligand π-ionizations is the same as in **1** and the same assignment is adopted. The smaller splitting of the $e_1'(\pi)$ level (0.71 eV) compared with that (0.93 eV) for **1** is evidence of a decrease of the n_S–π conjugation due to the increase of θ. The splitting of sulphur lone pairs is essentially the same as in **1**, but the bands and narrower than those in the spectrum of **1**. It follows clearly from the molecular model that the distance between the sulphur atoms and the orientation of the lone pairs is similar to 1,3-dithiane where a through-space interaction brings about their splitting (0.41 eV) [12,13]. The mutual overlap of n_S orbitals destabilizes the antisymmetric combination and stabilizes the symmatric one, i.e. the through-space interaction acts in the direction opposite to the interaction relayed by the ligand π orbitals. Taking into account the weaker n_S–π conjugation, which implies a smaller n_S–π overlap, the observed splitting of n_S orbitals 0.40 eV can be seen to be brought about by a through-space rather than a through-bond interaction. Thus the antisymmetric combination n_S^- is assigned to the band **c** and the n_S^+ combination to the band **d**.

The shape of $\bar{n}_S$ ionizations differs dramatically from those for **1**. Instead of a single band two peaks split by 0.48 eV are observed. No splitting of $\bar{n}_S$ orbitals is found in the PE spectrum of 1,3-dithiane, where their mutual orientation and distance are similar. The splitting found in the PE spectrum of **2** seems to be brought about by a through-bond interaction relayed by the ferrocene orbitals. The $\bar{n}_S$ orbital lies in the C–S–C plane. No through-bond interaction is found in **1**, where the overlap with cyclopentadienyl σ-orbitals is maximal in the most populated planar conformation. Thus the cyclopentadienyl σ-orbitals cannot mediate the through-bond interaction of $\bar{n}_S$ orbitals. Since the splitting diminshes with the decreasing θ (Fig. 4) the cyclopentadienyl π orbitals seem to relay the interaction. The overlap with the $e_1(\pi)$ orbitals, $a_1'(\pi)$ and $a_2''(\pi)$ orbitals provide the antisymmetric combination of the $\bar{n}_S$ orbitals above the symmetric one (Fig. 5).

The elongation of the interligand bridge by one carbon atom allows a larger n_S–π conjugation, as can be seen from the increase of the $e_1'(\pi)$ splitting for **3** compared with that for **2**. It seems from the molecular model that the dihedral angle θ is smaller, and the direction of the n_S orbitals more favourable for the through-space interaction. The observed splitting of n_S orbitals is 0.51 eV; this shows that there is a stronger interaction in **3** than in the three-membered bridge. This value is higher than that for **1**, where the maximal overlap with π orbitals can be attained. It follows from the higher value for **3** that the n_S splitting is brought about by the

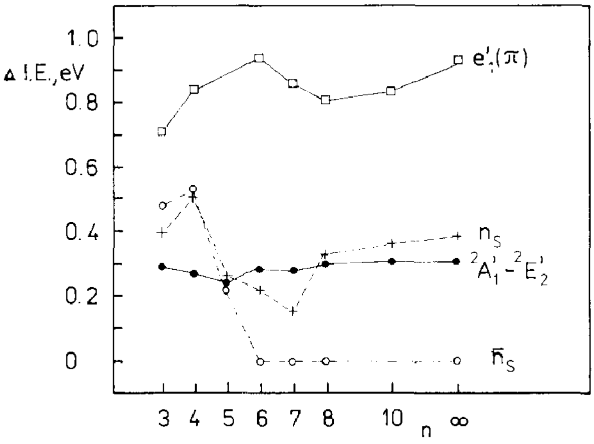

Fig. 4. Orbital splitting in PE spectra of 1,n-dithia[n]ferrocenophanes, ∞ denotes 1,1'-bis(methylthio)ferrocene.

through-space interaction. The same assignment of the bands **c** and **d** is adopted as for **2**. The splitting of $\bar{n}_S$ ionizations is 0.51 eV; that this is slightly larger than that for **2** indicates that another effect compensates for the smaller n_S–π overlap due to the decrease of θ. According the parity rule [14,15] the interaction through the dimethylene bridge tends to push the symmetric combination above the antisymmetric one, i.e. this effect is opposite to that of the overlap with the π orbitals. Thus it seems that the through-space interaction contributes to the observed splitting.

The five-atom bridged species **4** has the smallest energy gap between the $^2A_1'$ and $^2E_2'$ ion states for the whole series (0.24 eV). The combination of the electronic effect of the alkylthio group and of the distortion of the dicyclopentadienylmetal fragment seems to result in the observed minimum. The splitting of n_S orbitals is 0.26 eV, lower than that for **1** (0.39 eV). The observed splitting is clearly the result

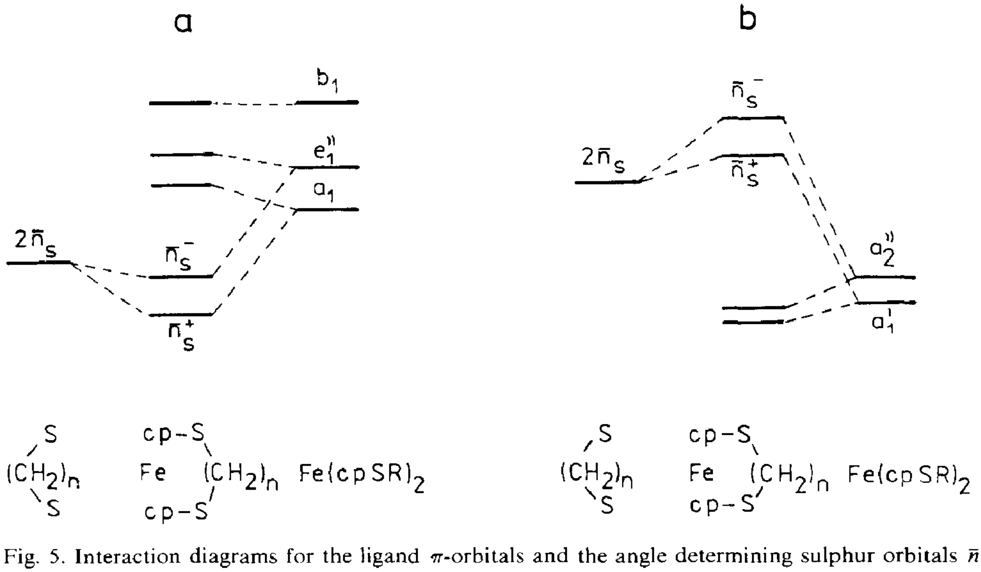

Fig. 5. Interaction diagrams for the ligand π-orbitals and the angle determining sulphur orbitals $\bar{n}_S$; (a) interaction with the higher lying π-orbitals; (b) interaction with the lower lying π-orbitals.

of the opposing effects of the through-space interaction and the overlap with ring π orbitals, but it is unclear which interaction predominates and what are the relative energies of the n_S combinations. The band **g** is not resolved in the PE spectrum, and thus the degree of the n_S–π interaction cannot be estimated. Nevertheless the splitting of $\bar{n}_S$ orbitals 0.22 eV can be rationalized in terms of the smaller dihedral angle θ compared, with that in **2**, or and **3**.

With a further increase of the length of the interligand bridge up to ten atoms (**5**–**8**), $\Delta\ E(^2A_1' - {}^2E_2')$ converges to the value found for the non-bridged **1**. The absence of any detectable splitting of $\bar{n}_S$ ionizations for $n \geqslant 6$ shows that conformations with small θ are populated when the bridge is sufficiently long. The splitting of the $e_1'(\pi)$ level is not a monotonous function of the bridge length. The tilting of the dicyclopentadienyl metal fragment influences the energy of the ligand levels [4]. Thus variations of the angle of the ligand planes can contribute to the observed dependence. The n_S splitting decreases on going from the four- to seven-atom bridge. The distance between the ring planes is 3.3 Å in unperturbed ferrocene [17]. The n_S–n_S overlap becomes negligible if the interatomic distance exceeds 3 Å [14]. The observed dependence on the bridge length reflects the decreasing n_S–n_S overlap and the increasing overlap with the ring π orbitals. The smallest value, 0.15 eV, was found in the spectrum of **6**, for which a fall in the redox potential was also observed [2]. The $e_2'(d)$ IE has also its lowest value in the case of **6**, but the differences between particular members of the series are close to the experimental uncertainty of the vertical IE determination. An X-ray diffraction study of **6** has shown that the dihedral angle θ is close to zero [18]. That the splitting of the n_S orbitals is smallest for **6** may indicate an interaction of occupied d orbitals with the sulphur lone pairs. It follows from the relative energies and the symmetries of the orbitals that the interaction tends to stabilize the n_S^+ combination, i.e. it acts in the direction opposite to the interaction with the ligand π levels. In the [8]- and [10]-ferrocenophane species (**7**, **8**) the n_S splitting converge to the value found for **1**. It seems that the long bridge does not bring about any tilting of the ring planes and conformations with small θ are energeticly feasible. The S–S distance is greater than 3 Å. The observed splitting of n_S ionizations is due to through-bond interaction, and the same assignment of bands **c** and **d** as for **1** can be made.

Conclusions

The PE spectral patterns of the sulphur-localized orbitals in 1,n-dithia[n]ferrocenophanes can be interpreted in terms of a balance between the through-space interaction and the through-bond interaction due to the overlap with the cyclopentadienyl occuped π orbitals. The through-space interaction of sulphur lone pairs predominates for $n = 3$ and 4, whereas the through-bond interaction is responsible for the splitting of the sulphur lone pairs for $n = 8$ and 10. The "angle-determining" sulphur localized orbitals are split if $n = 3$, 4 and 5. The same orbitals seem to relay this interaction. The response of the IE's of metal d levels on the bridge length parallels the changes in oxidation potentials.

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