ESR OF THE ELECTRONEUTRAL ARENECYCLOPENTADIENYLIRON DERIVATIVES

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Summary

ESR spectra of the electroneutral arenecyclopentadienyliron complexes have been measured at 77—300 K. The g-factors are slightly anisotropic. The values of the splitting of the $e_{1g}^{\star}$ level are determined on the basis of g-factor anisotropy. The temperature dependence of the naphthalenecyclopentadienyliron spectra is discussed in terms of the Jahn—Teller effect. Optical spectra of the benzene and naphthalene derivatives are obtained.

The polarographic reduction of arenecyclopentadienyliron cations [1] and preliminary ESR investigation [2] show the formation of electroneutral paramagnetic arenecyclopentadienyliron.

In the present report we give a full account of our ESR measurements on several arene—FeC$_5$H$_5$ complexes. The electroneutral arenecyclopentadienyliron derivatives were obtained by reduction of the corresponding BF$_4^-$ salts by sodium mirror in 1,2-dimethoxyethane at ~200 K in vacuum. All samples were measured in quartz tubes at 77 K with a Varian E12 X-band spectrometer, using 100 kHz field modulation.

In Table 1 we have collected $g_{\parallel}$ values, $g_{\perp}$ for all compounds being very near to 2 ($\bar{g}_{\perp}$ 2.006). The data is given in Table 1 clearly demonstrate the decrease in anisotropy of $g_{\parallel}$ values for benzene, naphthalene and phenanthrene derivatives. The substituted benzene derivatives have approximately the same g-factor anisotropy.

In accordance with the electronic structure of d^n cyclopentadienyl complexes [3—5] the unpaired electron occupies the $e_{1g}^{\star}$ level in the complexes with low-spin $a_{1g}^2 e_{2g}^4 e_{1g}^{\star 1}$ configuration.

The doubly degenerate $e_{1g}^{\star}$ level is apparently split by low symmetry distortion caused by the arene ligands.

As a first approximation, we assume that the unpaired electron occupies one of the two split orbitals d_{xz} or d_{yz}, then for the g-values one obtains:

$$g_z = g_{\parallel} = 2\left(1 - \frac{\lambda_0}{\Delta E}\right) \; ; \; g_x = g_y = g_{\perp} = 2 \; , \tag{1}$$

where $\Delta E = E_{dxz} - E_{dyz}$; and λ_0 = spin-orbital coupling parameter.

The ΔE values listed in Table 1 have been calculated where $\lambda_0(Fe^+) = -350$ cm^{-1} [3,6].

The ΔE values increase along the series of benzene, naphthalene and phenanthrene derivatives.

We have also used another way to estimate the parameters, by determining energy level splitting. It known that energy levels of the ligands are situated lower than the $3d$ levels of the iron atom. The Hückel molecular orbital schemes of benzene, naphthalene and phenanthrene and the cyclopentadienyl anion are shown in Fig. 1. The energy of the levels is given in exchange integral units. The relative positions of the ligand levels and $3d$ levels of the iron atom are arbitrary (Fig. 1) but it is clear that the highest filled and lowest unoccupied orbitals along the series benzene, naphthalene and phenanthrene approach $3d$ levels.

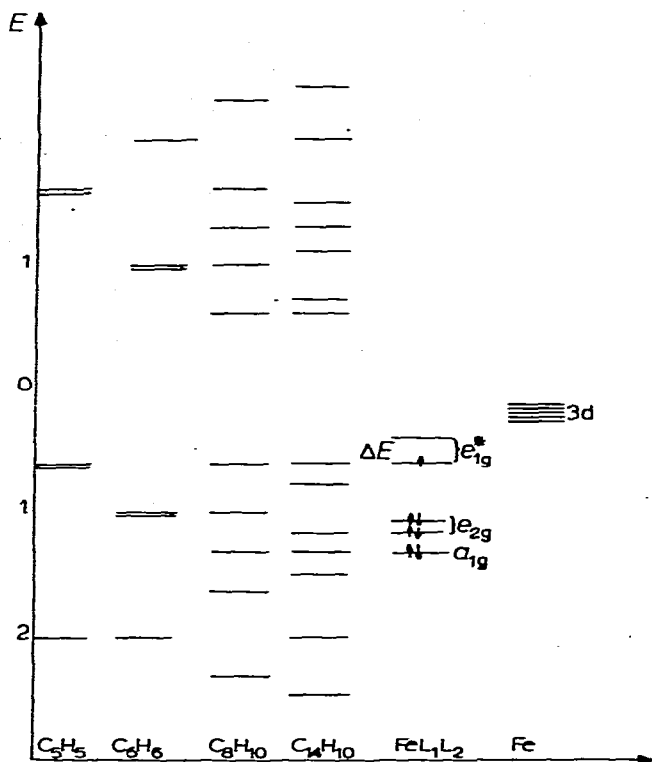Having assumed that ΔE depends on the relative positions of the highest

Fig. 1. The Hückel molecular orbital schemes of benzene, naphthalene, phenanthrene and the cyclopentadienyl anion.

filled or lowest unoccupied orbitals compared to the iron orbitals in naphthalene and phenanthrene derivatives, we may describe ΔE by eq. 2.

$$\Delta E = \Delta E_{benzene} + \Delta E_i \cdot K \tag{2}$$

($\Delta E_{benzene}$ is the splitting of e_{1g}^* level for benzene derivatives, ΔE_i is the distance between naphthalene (or phenanthrene) and benzene levels, K is a coefficient.)

$$\Delta g_{\|} = \frac{2\lambda}{\Delta E} = \frac{2\lambda}{\Delta E_{benzene} + \Delta E_i \cdot K} \tag{3}$$

$$\frac{1}{\Delta g_{\|}} = \frac{\Delta E_{benzene} + \Delta E_i \cdot K}{2\lambda} = \frac{\Delta E_{benzene}}{2\lambda} + \frac{K}{2\lambda} \cdot \Delta E_i$$

Then for $\Delta g_{\|}$ values eq. 3 is obtained where $\lambda = \lambda_0 \cdot C_1^2$ (C_1 is a coefficient for the d_{xz} orbital in the unpaired electron molecular orbital). We have calculate λ/K from this equation and compare it with λ_0.

We have applied two different methods for the rough estimation of ΔE_i: one using the ionisation potentials and the other using long wave absorbtion band energy in the optical spectra of the ligands.

The ionisation potentials are (9.4 eV; 75800 cm^{-1}) for benzene, (8.2 eV; 66100 cm^{-1}) for naphthalene and (8.03 eV; 64700 cm^{-1}) for phenanthrene. ΔE_i is 9700 cm^{-1} for naphthalene and 11100 cm^{-1} for phenanthrene.

The absorption band energy is 38000 cm^{-1} for benzene, 32000 cm^{-1} for naphthalene and 29000 cm^{-1} for phenanthrene. ΔE_i is 6000 cm^{-1} for napthalene and 9000 cm^{-1} for phenanthrene.

The plot of $1/\Delta g_{\|}$ versus ΔE_i is given in Fig. 2. Plot I is derived from the ionisation potentials correlation, and plot II from the absorption band correlation. The values $2\lambda/K$ are 1200 cm^{-1} (I) and 860 cm^{-1} (II). It is noteworthy that this rough treatment gives $2\lambda/K$ close to $2\lambda_0$. If $K \approx 1$, then $\lambda \approx \lambda_0$ and $c_I \approx 1$. This result may be regarded as a confirmation of the supposition that the unpaired electron is located mainly on the iron atom [2]. It was proved on the basis of NMR investigation [4] that the unpaired electron is located mainly on the iron atom in the isoelectronic bis(hexamethylbenzene)iron(I) cation. Here the g-factor anisotropy [7] is of the same order as in the complexes under investigation.

The qualitative estimation of the change in the unpaired electron level position may be obtained from the polarographic reduction potentials [1].

The ESR spectra of toluene, p-xylene, phenanthrene, fluorene and naphthalene derivatives were investigated at 77—300 K. The appearance of these spectra is as expected with exception of the naphthalene cyclopentadienyliron spectrum. The anisotropic spectrum turns into the isotropic one near the melting point of 1,2-dimethoxyethane (~200 K).

The unusual temperature dependence of the spectra is observed in the case of the naphthalene cyclopentadienyliron complex [2]. The anisotropic spectrum is recorded at 77 K. There are also two spectra at 100—150 K, one of which has an anisotropic g-factor, while the other has an isotropic one with $g_{iso} = \frac{1}{3} (g_{\|} + 2g_{\perp})$. The intensity of the anisotropic spectrum decreases and that of the isotropic one increases through this temperature range. The appearance
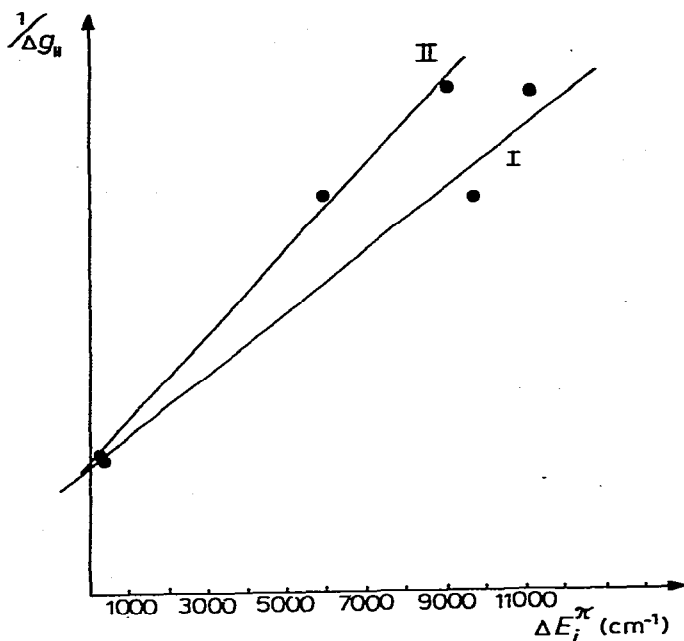
Fig. 2. Plot $1/\Delta g_{\parallel}$ versus ΔE_i. I: ΔE_i from ionisation potentials of the ligands; II: ΔE_i from optical spectra of the ligands.

of the naphthalene cyclopentadienyliron spectrum may be attributed to Jahn—Teller effect. The temperature dependence may be caused by transition from the static to a dynamic Jahn—Teller effect [8,9].

We have carried out preliminary investigations of optical spectra of the benzene and naphthalene derivatives to obtain additional energy data. The optical
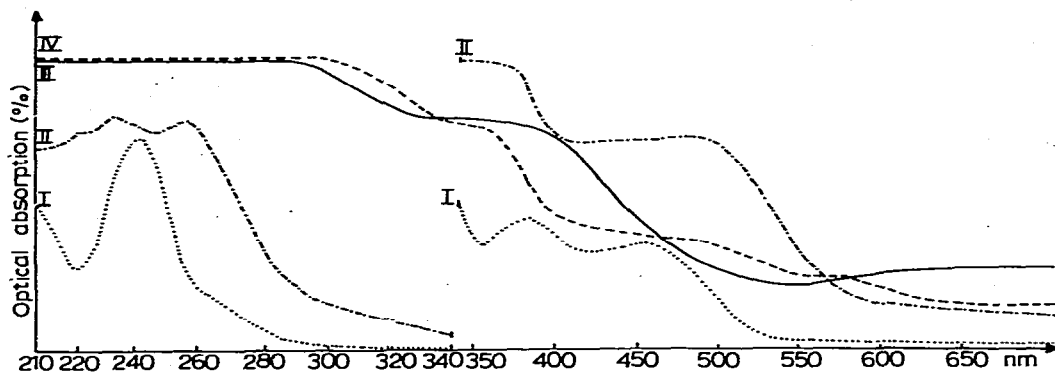

Fig. 3. The electronic absorbtion spectra of the benzene cyclopentadienyliron (I) and naphthalene cyclopentadienyliron (II) cations and their reduced forms III and IV. I $\cdots\cdots$ [$C_6H_6FeC_5H_5$]BF_4 $c = 10^{-4}$ mol l^{-1}, 220—340 nm, 1 mm; $c = 10^{-3}$ mol l^{-1}, 350—700 nm, 10 mm. II $\cdot-\cdot-\cdot$ [$C_{10}H_8FeC_5H_5$]BF_4 $c = 10^{-4}$ mol l^{-1}, 220—340 nm, 1 mm; $c = 10^{-3}$ mol l^{-1}, 350—700 nm, 10 mm. III ———— $C_6H_6FeC_5H_5$ $c = 10^{-3}$ mol l^{-1}. IV $------$ $C_{10}H_8FeC_5H_5$ $c = 10^{-3}$ mol l^{-1}.

TABLE 1

THE $g_{\|}$ VALUES OF THE ELECTRONEUTRAL ARENECYLOPENTADIENYLIRON COMPLEXES

	Arene ligand	$g_{\|}$	$1/\Delta g_{\|}$	ΔE (cm^{-1})
1	Benzene	2.26	3.8	2700
2	Toluene	2.25		
3	Biphenylmethane	2.24		
4	p-Xylene	2.25		
5	Tetralin	2.21		
6	Dihydroanthracene	2.22		
7	Mesitylen	2.24		
8	Durene	2.21		
9	Fluorene [a]	2.10		
10	Naphthalene	2.09	11.1	7700
11	Phenanthrene	2.07	14.2	10000

[a] Axial symmetry in the fluorene derivative spectrum is distorted: $g_x = 2.00$; $g_y = 1.99$.

spectra of the benzene- and naphthalene-cyclopentadienyliron cations and their reduced forms in 1,2-dimethoxyethane are shown in Fig. 3, The spectra of the electroneutral complexes were recorded at room temperature immediately after reduction at ~200 K. There are new bands in a long wave spectral region for these electroneutral complexes in comparison to the spectra of the corresponding cations.

The bands corresponding to ΔE transitions must be located in the red and near infrared ragion.

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