

ORGANOMETALLIC STUDIES XXIX*. ELECTRON SPIN RESONANCE OF FERROCENE-SUBSTITUTED RADICAL ANIONS

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SUMMARY

ESR spectra of electrochemically generated radical anions of benzoyl-, *p*-toluoyl-, *p*-(methoxycarbonyl)benzoyl-, *p*-nitrophenyl-, *p*-cyanophenyl- and nitroferrocene have been studied in solution. Correlation of the results of Hückel MO calculations with observed hyperfine structure gave a qualitative picture of unpaired spin density distribution in the anion radicals. The ferrocenyl group was found to destabilize radical anions in comparison with the effect exerted by the phenyl group. If both groups are present in one molecule, delocalization of odd electron density into the phenyl group is the more extensive.

INTRODUCTION

Organic radical anions in solution have been studied extensively¹ and several communications³ have described studies in organometallic electrochemistry. Our studies with α -ferrocenyl carbonium ions⁴ prompted us to undertake a parallel investigation of radical anions containing the ferrocene moiety. Whereas metal carbonyl and mixed cyclopentadienylmetal carbonyl anions have been under active study in the last few years there appear to be no reports of anions containing only substituted five- and/or six-membered aromatic ring systems in addition to transition metal atoms. Thus we have examined the synthesis of such anions and the effect of the organometallic substituent on the ESR spectrum. The ESR results provide an experimental test of recent independent-electron MO calculations carried out for substituted ferrocene derivatives. Full details of these MO calculations, carried out in collaboration with Professor E. Heilbronner, will be published elsewhere. Only a very brief outline is given here.

An independent-electron model of the simple Hückel type was constructed for ferrocene and extended for the more complex derivatives. Ferrocene was treated in the usual LCAO approximation by using as basic functions the ten symmetry-determined molecular orbitals of the two cyclopentadienyl moieties and the nine iron

* For Part XXVIII see ref. 1.

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† For an extensive tabulation of results see ref. 2.

$3d4s4p$ atomic orbitals. Overlap integrals between metal AO's and cyclopentadienyl MO's, in units of β , were chosen to parallel values obtained by more sophisticated methods⁵. Coulomb integrals $\alpha_x = \alpha + h_x\beta$, assigned to each of the metal AO's, were in accord with the sequence of valence state ionisation energies (VSIE) of the metal atom. The magnitudes of h_x , however, were adjusted arbitrarily to yield a model with desired charge distribution. In the calculation of resonance integrals the approximation was adopted that the interaction of an atomic orbital of the central metal with a cyclopentadienyl MO of the same irreducible representation is proportional to orbital overlap. The parameters h and k , characterizing heteroatoms in the substituent on ferrocene, were taken from the literature and varied in the range that seemed permissible from previous experience.

EXPERIMENTAL

Acetonitrile and dimethylformamide (FLUKA purum) were refluxed and distilled from calcium hydride in an atmosphere of purified nitrogen. Tetraethylammonium perchlorate was prepared from tetraethylammonium bromide and sodium perchlorate and was dried *in vacuo* at 60°. Benzoylferrocene (I), *p*-Toluoylferrocene (II) and *p*-(methoxycarbonyl)benzoylferrocene (III) were obtained from Friedel-Crafts acylation using methylene chloride as solvent and aluminum chloride as a catalyst. *p*-Nitrophenylferrocene⁶ (IV) and *p*-cyanophenylferrocene⁷ (VI) were prepared from the diazonium salt as previously reported.

*Nitroferrocene (V)**

To 1.75 ml (1.45 g, 12.5 mmoles) of *N, N, N', N'*-tetramethylethylenediamine in 10 ml of dry cyclohexane were added under an atmosphere of dry nitrogen 15.5 ml of a 0.8 molar solution of *n*-butyllithium in cyclohexane. After 10 min stirring a solution of 0.93 g (5 mmoles) of ferrocene in 20 ml of cyclohexane was added during 20 min. The mixture was stirred at room temperature overnight, then cooled to -70°, and 1.5 ml (15 mmoles) of *n*-propyl nitrate⁹ in 2 ml of cyclohexane was added dropwise. The mixture was allowed to warm to room temperature during one h and 20 ml of water and 15 ml of benzene were added. The orange-brown organic layer was dried over MgSO₄, concentrated and chromatographed on neutral alumina. Ferrocene was eluted with benzene/ether (5/1), and the violet-red zone of nitroferrocene with benzene/ether (4/1). After a repeated chromatography the residue was sublimed (10⁻³ mm, 60°); yield: 50 mg violet-red crystals, m.p. 116-118° (lit. 130°). IR absorptions identical with reported spectrum.

Radical anions were generated in a slightly modified VARIAN electrolytic cell, the part extending into the microwave cavity being of the flat cell type. The cell was evacuated and flushed with nitrogen several times before use. Mercury, serving as the cathode material, was filled into the cell until its level reached the flat part of the cell, the solution of the substrate to be reduced was then added and the cell closed under nitrogen. All experiments were carried out at room temperature. A potential was applied to the cell from a simple potentiometer circuit. To avoid contamination

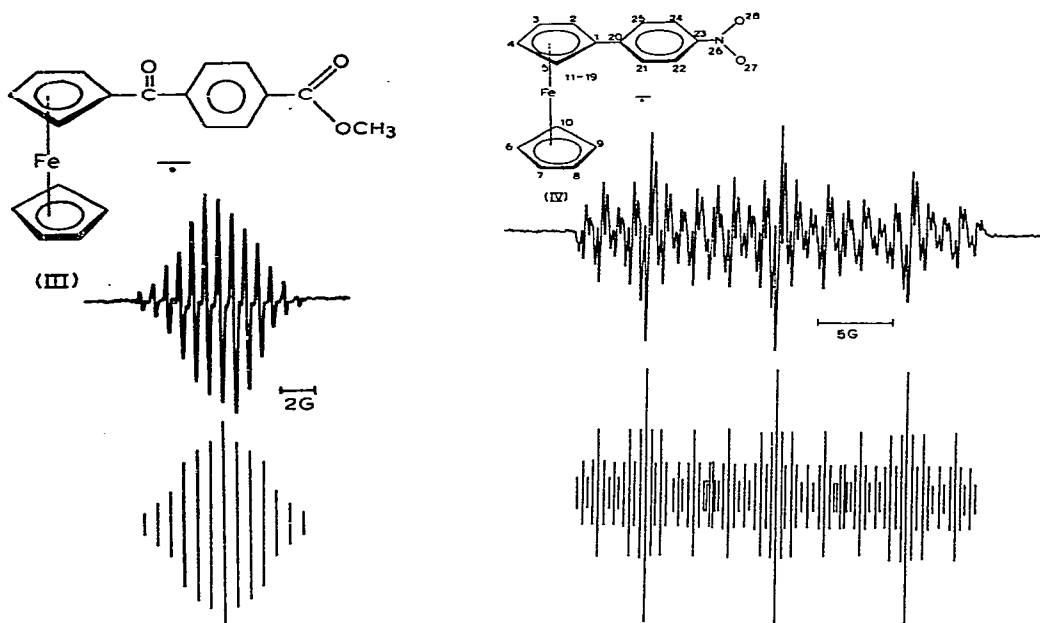
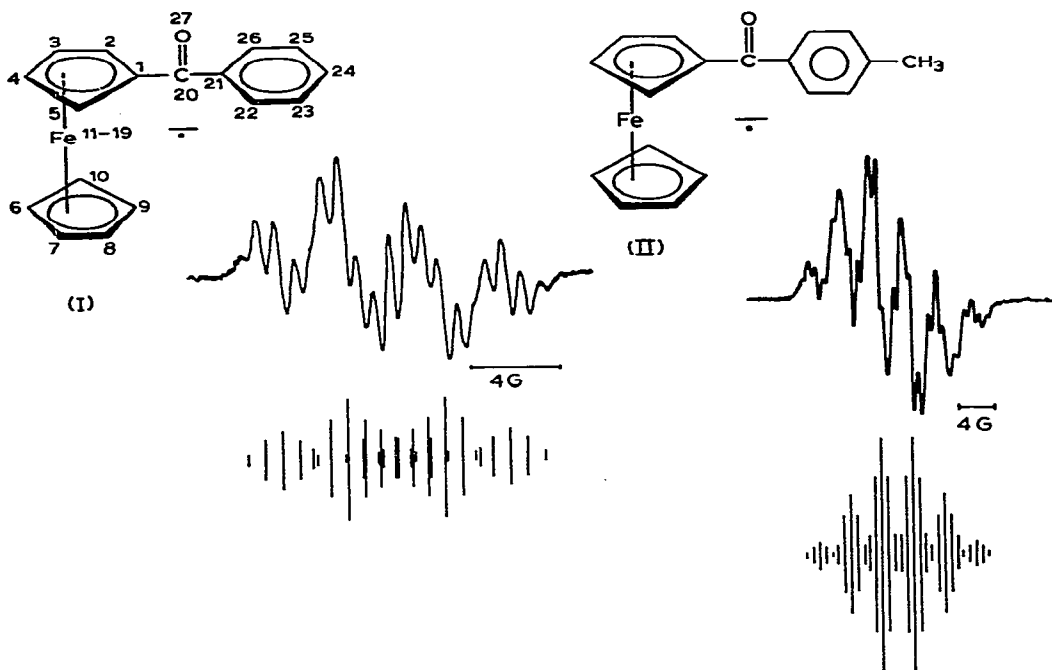
* Compare ref. 8, in which no experimental details of this preparation are given.

by traces of water from the calomel reference electrode a two electrode arrangement was usually used (Hg-pool cathode, Pt-net anode) and the applied voltage was slowly increased, within the range of approx. -0.8 volts to -2.0 volts (*vs.* SCE), until radicals could be detected spectrometrically. The electrolysis current was usually between 1 and 3 mA. Solutions to be investigated contained varying amounts of substrate, but were always 0.1 molar in the supporting electrolyte, Et_4NClO_4 .

The electron spin resonance spectra were recorded with a Varian V-4502 EPR Spectrometer operating with 100 kc/sec field modulation. The field sweep was calibrated by recording the signal of the peroxyaminedisulfonate ion (hfs constant = 13.0 ± 0.1 G) simultaneously with the spectra of the radical anion employing a dual sample cavity. g -Values were accurately determined by measuring the field difference relative to peroxyaminedisulfonate ($g = 2.0057$). Approximate radical half-lives could be inferred from observation of the decrease in signal intensity after switching off the electrolysis current.

RESULTS

In all cases, the observed spectra were symmetrical with respect to their centre, so it is reasonable to conclude that only one type of radical was formed in each case during electrochemical reduction and that other radicals, generated through secondary reactions of the radical anion with solvent molecules, are too short-lived to be observed in the static system employed. The spectra resulting from electrochemical reduction are given in Fig. 1 [(I)–(VI)]. Stick diagrams were constructed by using the appropriate isotropic proton hyperfine coupling constants. The latter, together with other characteristic spectral parameters, are listed in Table 1. The diagrams agree satisfactorily with the experimental spectra although in the cases of large line widths there is a corresponding uncertainty in the hyperfine splitting constants. The choice of either acetonitrile (AN) or dimethylformamide (DMF) as a solvent was dictated by the lifetime of the respective radical anion; the lifetime is slightly greater in AN but better resolution could be obtained in DMF. The problem of recording the spectra satisfactorily increased with decrease in the half life of the paramagnetic species. Whereas the *p*-nitrophenylferrocene anion radical (IV)⁻ ($\tau_{\frac{1}{2}} > 10$ min) could be observed for unlimited periods of time after potential was applied to the cell, the signal of the nitroferrocene anion radical (V)⁻ ($\tau_{\frac{1}{2}} = 4$ min) showed only fair stability during electrolysis and the spectrum of the radical derived from benzoylferrocene (I)⁻ ($\tau_{\frac{1}{2}} = 1.5$ min) disappeared within 7 min from switching on of the electrolysis current. *p*-Cyanophenylferrocene anion radical (VI)⁻ ($\tau_{\frac{1}{2}} < 30$ sec) could only be observed during the first 3 min of electrolytic reduction. After about 20 min spectra could again be recorded upon application of voltage. In the case of the shorter lived species, with which radical decay is faster than diffusion of new unreduced material to the mercury surface, the concentration of anion radicals rapidly becomes unmeasurably small. No paramagnetic species could be detected with cyanoferrocene, acetylferrocene and ferrocenealdehyde although the measured current indicated that an electrochemical reaction did take place. By comparison to *p*-cyanophenylferrocene, it can be concluded that the half lives of the radical anions generated from cyano-, acetyl- and formylferrocene are considerably less than 30 seconds. The corresponding benzene derivatives were reduced electrochemically under analogous conditions, in order to



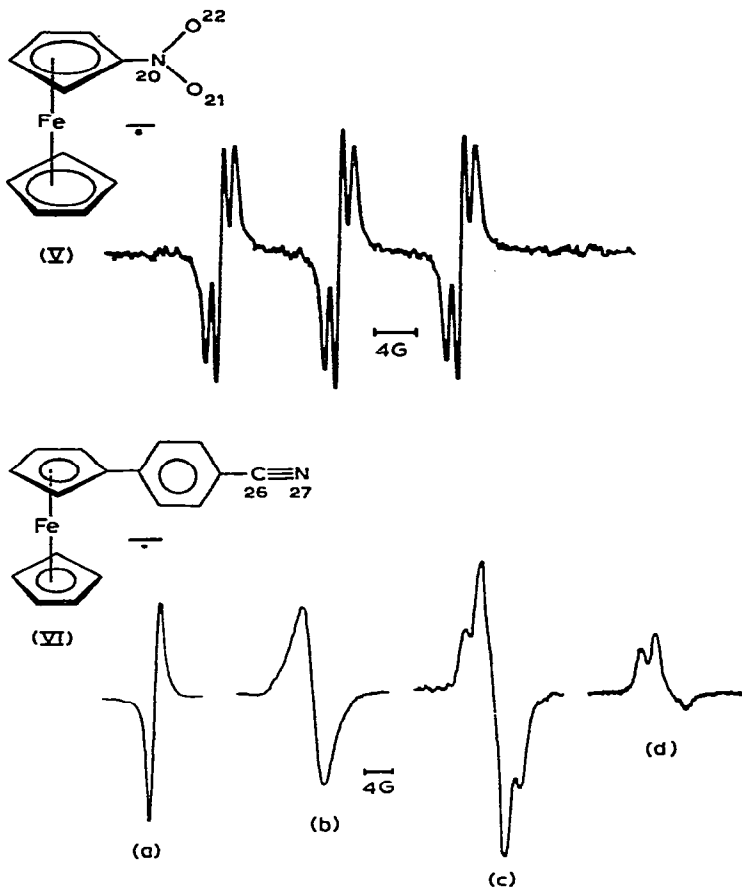


Fig. 1. ESR spectra of ferrocenyl containing radical anions; (a) 5×10^{-1} molar in (VI); (b) 5×10^{-3} molar in (VI); (c) 1×10^{-3} molar in (VI), field sweep time 20 G/min; (d) 1×10^{-3} molar in (VI), field sweep time 5 G/min.

check the experimental procedure. ESR spectra of benzonitrile, acetophenone and benzaldehyde anion radicals, identical with those in the literature were easily obtained.

The results in Table 1 show that there is a pronounced increase in line width as the half life of the radical anion decreases. This effect, inherent in the method of electrochemical reduction under static conditions, may be explained by the contribution of electron-exchange interaction between radical anion and parent neutral compound to the linewidth^{10,11}. If the rate of linear diffusion to the cathode and the rate of radical decay are of comparable magnitude, an equilibrium concentration of radical anion will build up which will not change greatly during electrolysis. If, however, radical decay is much faster than diffusion, the concentration ratio of the parent compound to the radical anion will gradually increase during electrochemical reduction, favouring electron exchange and causing broadening of the lines. In the case of *p*-cyanoferrocene, this effect could be observed during the period of time it took to record the signal. Within the sweep time of 2.5 min the signal broadened consider-

TABLE 1

ESR-SPECTRAL PARAMETERS FOR ORGANOMETALLIC FERROCENYL CONTAINING RADICAL ANIONS

Substrate	g_{AN}	Total width of spectrum (G)	hfs constants (G)				Solv.	Concn.	Line width (G)	τ_1 (min)	
			a^N	a_1^H	a_2^H	a_3^H					
Benzoylferrocene (I)	2.0069	13.6		4.5	3.0	0.8	DMF	$1.5 \cdot 10^{-3}$	0.40	≈ 1.5	
Toluoylferrocene (II)	2.0066	22.2		3.95	0.8		DMF	$1.5 \cdot 10^{-3}$	0.40		
<i>p</i> -(methoxycarbonyl)-Benzoylferrocene (III)	2.0041	9.4		2.4	1.6	0.8	DMF	$2.0 \cdot 10^{-3}$	0.17		
<i>p</i> -Nitrophenylferrocene (IV)	2.0064	34.8		9.6	3.5	1.15	(0.3)	AN ^a	$1.0 \cdot 10^{-3}$		> 10
				9.2	3.36	1.12	0.27	DMF	$0.8 \cdot 10^{-3}$	0.16	≈ 8
Nitroferrocene (V)	2.0133	26.2		12.2	1.1			AN ^a	$1.5 \cdot 10^{-3}$	0.50	≈ 4
								DMF		0.50	
<i>p</i> -Cyanophenylferrocene (VI)	2.0071			2.3				AN ^a	$1.0 \cdot 10^{-3}$	4.2	< 0.5
									$5.0 \cdot 10^{-3}$	2.9	
									$1.0 \cdot 10^{-2}$	3.2	
									$5.0 \cdot 10^{-1}$	1.4	

^a Acetonitrile.

ably so that the high field component of the triplet splitting could no longer be observed.

DISCUSSION

Benzoylferrocene, (I)

Whereas the ESR spectrum of the electrochemically generated benzophenone anion radical was obtained in high resolution, with almost all of the expected lines being observed, the radical anion derived from benzoylferrocene showed only 19 rather broad lines, the full hyperfine structure being obscured by the linewidth (350 mG). At first glance the spectrum seems to consist of a basic quartet of lines, indicating three equivalent protons in the molecule. Closer inspection of the intensity ratios, however, suggests a basic doublet ($a_1^H = 4.5$ G) each component of which is split into triplets ($a_2^H = 3.0$ G) and quintets ($a_3^H = 0.8$ G). Attempts were made to correlate these coupling constants with positions in the molecule by looking at the LCAO coefficients of the lowest empty molecular orbital obtained from the MO calculation of the parent benzoylferrocene*. Using McConnell's relation¹³ but without specifying the exact magnitude of Q , it turns out that a large fraction of the calculated spin density resides on nuclei which do not contribute to observable splittings (C_1 and C_{21} which do not have hydrogen atoms attached, carbonyl-carbon, -oxygen and non-magnetic ^{56}Fe). This is in qualitative agreement with the much smaller total width of the spectrum of benzoylferrocene anion radical (13.6 G) compared to benzophenone (24.5 G). Spin densities that cause observable splittings are calculated to be largest on the *para*-position of the benzoyl substituent, somewhat smaller on the benzoyl *ortho*-positions and considerably smaller on the benzoyl *meta*- and the "ortho" (2.5) positions of the substituted cyclopentadienyl ring. How-

* The parameters in this calculation were those reported¹² for benzophenone: $\alpha(\text{O}) = \alpha + 1.4\beta$; $\beta(\text{CO}) = 1.5\beta$; $\beta(\text{C}_1, \text{C}_{20}) = 0.9\beta$.

ever, the spin densities at the *meta*-positions may well be negative, a fact that cannot be accommodated by the HMO method. In fact, these calculations show, not unexpectedly, that one cannot attach much significance to the quantitative aspect of the calculated data. At the same time, the calculations may have a limited value for forming a qualitative picture about the relative magnitudes of the large coupling constants. Thus, assuming that the calculated results are indicative qualitatively, one is led to the result that the proton hyperfine structure stems mainly from interaction of the unpaired electron with protons of the benzene ring, the interaction with the cyclopentadienyl ring protons being much smaller. With this assumption, the experimental coupling constants would be assigned to the protons attached to C₂₄ (doublet, $a_1^H = 4.5$ G), protons at C₂₂ and C₂₆ (triplet, $a_2^H = 3.0$ G) and protons at C₂, C₅, C₂₃, C₂₅ (quintet, $a_3^H = 0.8$ G).

Such an assignment would then lead to the conclusion that if the ferrocenyl and phenyl moieties have to compete for delocalization of electronic charge, the unpaired electron will tend to occupy the phenyl ring rather than the ferrocenyl group. In other words, the ferrocenyl group appears to be more electron-releasing than the phenyl ring, a conclusion which is well supported by the well known stability of α -ferrocenylcarbonium ions⁴ and the enhanced reactivity of the ferrocene system in electrophilic aromatic substitution¹⁴.

p-Toluoylferrocene, (II)

The spectrum of *p*-toluoylferrocene radical anion (II)⁻ was recorded in order to further clarify the spectral assignment in (I)⁻. Substitution of a hydrogen atom on an aromatic carbon center by a methyl group usually yields hyperfine structure arising from the three methyl protons, the coupling constant being equal to, or slightly smaller than the original proton coupling constant. It is therefore not surprising to find in the spectrum of (II)⁻ a basic sextet of lines ($a_1^H = 3.95$ G, intensities approximately 1/5/10/10/5/1). This can be interpreted as arising from the three methyl protons and the two *ortho* protons on the *p*-toluoyl group, displaying accidental degeneracy within the limitations imposed by the linewidth (400 mG). Additional, not wholly resolved, hyperfine structure ($a_2^H = 0.8$ G) as in (I)⁻ most probably reflects interactions with protons on C₂, C₅ and C₂₃, C₂₅. Again, total spectral width (22.2 G) is markedly smaller than in *p*-methylbenzophenone anion radical¹⁵ (29.1 G) demonstrating small interaction with protons on the cyclopentadienyl rings and considerable spin density on non magnetic ⁵⁶Fe.

p-(Methoxycarbonyl)benzoylferrocene, (III)

The anion radical shows a deceptively simple 13-line ESR spectrum. However, measurement of the intensity ratios shows that this cannot be caused by 12 equivalent protons. Consideration of the structure of (III) reveals that the protons responsible for the observable splitting must occur in three pairs. This, together with total spectral width (9.4 G) leads to the magnitudes of triplet splitting constants $a_1^H = 2.4$ G, $a_2^H = 1.6$ G, $a_3^H = 0.8$ G. Thus, the simple appearance of the spectrum must be due to the ratio 3/2/1 of the coupling constants. Whereas the smallest splitting may safely be assigned to the "ortho" 2,5-protons on cyclopentadienyl, no unequivocal decision is possible as to the assignment of a_1^H and a_2^H to protons on C₂₂, C₂₆ and C₂₃, C₂₅.

p-Nitrophenylferrocene, (IV)

Electrochemical reduction of (IV) yielded the most stable and best resolved ESR spectrum in the series under investigation. Therefore, interpretation was straightforward. The basic triplet of lines (intensities 1/1/1, $a^N = 9.2$ G) is further split into triplets (1/2/1, $a_1^H = 3.36$ G, $a_2^H = 1.12$ G, $a_3^H = 0.27$ G). a^N , a_1^H and a_2^H closely resemble the coupling constants in nitrobenzene radical anion NB^- ($a^N = 10.32$, $a_0^H = 3.39$, $a_m^H = 1.09$ G)¹⁶ indicating that the influence of the strongly electron-accepting nitrogroup predominates and the *p*-ferrocenyl group only acts as a small perturbation on the nitrobenzene system. The almost identical total spectral widths ($\text{IV}^- = 34.8$ G, $\text{NB}^- = 33.6$ G) point in the same direction. The ratio of experimental proton-coupling constants was found to be in satisfactory agreement with the ratio of calculated spin densities*. Correlation of calculated spin densities with experimental ¹⁴N-splitting was attempted by using a modified McConnell relation as given by Rieger and Fraenkel¹⁸. As in the case of proton coupling constants, agreement with experiment was rather poor.

Nitroferrocene, (V)

Whereas in (IV)⁻ unpaired spin remained distributed mainly over the substituent of the ferrocene molecule, it was hoped that the spectrum of (V)⁻ would reveal something about the spin distribution on the ferrocene system itself. The spectrum of (V)⁻ consists of a ¹⁴N-triplet with a splitting ($a^N = 12.2$ G) considerably larger than in nitrobenzene. Thus it seems that the ferrocenyl group delocalizes the additional electron less effectively than the phenyl group, a conclusion already mentioned above. It would appear that in the nitroferrocene case the electron is delocalized mainly by placing spin density on Fe rather than over the cyclopentadienyl rings, as demonstrated by the small triplet splitting of the "ortho" protons (1.1 G vs. 3.39 in NB^-) and the smaller spectral width. This case showed the greatest discrepancies between the MO calculated results and the experimental data. The spin density on nitrogen in (V)⁻ was calculated to be smaller than in (IV)⁻, whereas experimentally it was found to be larger and for spin densities on C₂ and C₅ a negligibly small value was obtained. This situation could not be improved by varying the nitro group parameters without simultaneously impairing the results for (IV)⁻.

p-Cyanophenylferrocene, (VI)

As previously mentioned, the radical anion (VI)⁻ was the least stable in the series and showed indication for resolution into hyperfine components only if the initial concentration of (VI) was kept below 10⁻³ molar. In the latter case, the signal displays a barely resolved triplet ($a = 2.3$ G, intensities 1/2/1 more likely than 1/1/1) pointing at splitting by two equivalent protons. The MO calculation* was in qualitative agreement with this finding.

g-Factor variation

Deviations of g_{av} from "free spin value" ($g_{fs} = 2.0023$) by heteroatom sub-

* The MO parameters used for the nitro group, $h(\text{N}) = 1.0$, $h(\text{O}) = 1.0$, $k(\text{CN}) = 1.41$, $k(\text{NO}) = 1.41$ were those employed by Trotter¹⁷.

* Parameters employed were $k(\text{C}'\text{C}) = 0.9$, $k(\text{CN}) = 1.35$, $h(\text{O}) = 1.0$.

stitution are considered to be caused by two effects¹⁹: large values of ζ , the spin orbit coupling constant of the heteroatom under consideration, furnishing the unpaired electron with some orbital angular momentum, and inclusion into the molecule of groups ($-\text{N}=\text{O}$, $\text{C}=\text{O}$) containing nonbonding $n(\sigma)$ electrons with low energy $n \rightarrow \pi$ transitions rendering mixing of configurationally excited states with the ground state more important. Both effects are proportional to the odd electron density on the heteroatom. It is thus not surprising to find that the experimentally determined g_{av} -values of the radical anions (I)⁻ to (VI)⁻ deviate from 2.0023 by an amount approximately proportional to the calculated spin densities on the heteroatoms.

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