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High resolution EPR spectra of ferrocenyl(nitrophenyl)ethylene anion-radicals

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Abstract

The anion-radicals of the titled compounds were generated in DMSO by treatment of the appropriate precursors with ^{t}BuOK, and their high resolution EPR spectra were recorded. The spectroscopic parameters indicate that the unpaired electron is delocalized on the ferrocenyl cyclopentadienyl ring and to some extent on the iron key-atom, in the *ortho* and *para* but not in the *meta* nitrophenyl derivatives.

1-Ferrocenyl-2-(nitrophenyl)ethylenes (**1**) contain two conjugated donor and acceptor groups and push–pull effects seem possible. This effect is necessary for large hyperpolarizability and is important in the search for new non-linear optic materials and compounds with biological activity [1,2].

The anion-radicals of these compounds are of particular interest since the distribution of the unpaired electron on the ferrocenyl and nitrophenyl groups can be easily determined from EPR spectra. The nitrophenyl group has a pronounced electron affinity and the ferrocenyl group has a strong affinity for cells of organisms. Hence, the capability of the ferrocenyl group to delocalize the unpaired electron in anion-radicals may be of some relevance to the possibility of nitrophenyl ferrocenyl ethylenes taking part in electron transport processes.

Literature data on similar systems do not allow an unambiguous prediction of whether or not some spin density will be delocalized upon the ferrocenyl fragment in these anion-radicals. In fact, the unpaired electron essentially resides on the nitro substituent in the anion-radical of 1-ferrocenyl-2-nitroethylene and no evidence has been found of delocalization of spin density on the ferrocenyl group [3]. However, in the anion-radical of *p*-nitrophenylferrocene, hyperfine coupling has

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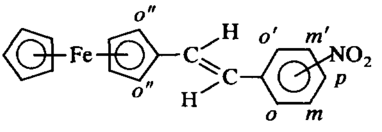
Table 1

EPR Spectral parameters (a in Gauss) of the anion-radicals of 1-ferrocenyl-2-(nitrophenyl)ethylenes (**1**) measured in DMSO at room temperature



(**1**)

Parameter	Position of the NO_2-group (g-factor)		
	para (2.0056)	*meta* (2.00466)	*ortho* (2.0054)
a_N	8.263	10.050	9.190
a_H^p	0	3.920	1.120
a_H^m	3.218	1.069	3.703
$a_H^{m'}$	3.218	0	2.992
a_H^o	1.162	3.930	1.120
$a_H^{o'}$	1.162	3.370	0
a_H^1	2.654	0.390	1.860
a_H^2	1.496	0.510	1.860
$a_H^{o''}$	0.213	0	0.145

been detected at the cyclopentadienyl ring protons, indicating that delocalization of spin density on the ferrocenyl group takes place [4,5].

We generated the anion-radicals of the *para*, *ortho* and *meta* nitrophenyl derivatives of ferrocenyl ethylene by reduction of the neutral precursors with potassium *tert*-butylate in DMSO. The anion-radicals were stable for several hours in solution and gave rise to complex but well resolved EPR spectra which were interpreted in terms of the spectral parameters reported in Table 1, with the aid of computer simulation. The data for the anion-radicals of the *para* and *ortho* derivatives suggest that some spin density is delocalized on the ferrocenyl fragment. This conclusion comes from the observation of hyperfine coupling at the *ortho* position of the C_5H_4 ring and also from the unusually large g-factors (2.0056 and 2.0054) compared with that of the nitrobenzene anion-radical (2.00479). Higher than expected values of the g-factor have been observed previously in the anion-radicals of other substituted ferrocenes [4–6] and have been taken as good evidence for a significant degree of participation of the iron atomic orbitals in the π-system, in particular in the singly occupied molecular orbital. A comparison of the data for the *ortho* and *para* nitroanion-radicals shows that, in the former, both the splitting at the cyclopentadienyl protons and the g-factor are smaller, thus suggesting a reduced delocalization of spin density into the ferrocenyl group in the *ortho* isomer, presumably because of deviation from co-planarity of the π-system due to steric crowding.

This is also evident from the nitrogen splitting which is larger in the *ortho* (9.19 G) than in the *para* nitroanion-radical (8.26 G). In fact, it is known that the nitrogen constant in the anion-radicals of substituted nitrobenzenes is greatly affected by the nature of the substituent, becoming larger than that in nitrobenzene with electron donors and smaller with electron acceptors [7].

These results clearly indicate that the ferrocenyl group acts as an electron acceptor, in anion-radicals, while in neutral molecules it plays the role of donor with a substituent constant $\sigma_p = -0.18$ (*cf.* $\sigma_p = -0.66$ for NH_2) [8].

It is worthwhile pointing out that any participation of the ferrocenyl group in the π-system is absent in the meta isomer of 1-ferrocenyl-2-(nitrophenyl)ethylene. In fact the spectral parameters of the corresponding anion-radical are very similar to those of the nitrobenzene anion-radical. Therefore, the conjugation laws are similar for ferrocenyl(nitrophenyl)ethylenes in their neutral or reduced form, but the sign of this interaction is opposite in the two cases.

References

1 M.L.H. Green, S.R. Marder, M.E. Tompson, Ju.A. Bandy, D. Bloor, P.V. Kolinsky and R.J. Jones, Nature, 330 (1987) 360.
2 K.P. Park and J.H. Jeong, Acta Crystallogr. C, 16 (1990) 1657.
3 Z.V. Todres and T.M. Tsvetkova, Bull. Acad. Sci. USSR, Division Chem. Sci., 36 (1987) 1433.
4 W.C. Danen and C.T. West, Tetrahedron Lett., (1970) 219.
5 G.R. Underwood, D. Jurkowitz and S.C. Dickerman, J. Phys. Chem., 74 (1970) 544.
6 G. Bigan, J. Hooz, S. Linke, R.E.D. McClung, M.W. Mosher and D.D. Tanner, Can. J. Chem., 50 (1972) 1825.
7 F. Bernardi, A. Mangini, M. Guerra and G.F. Pedulli, J. Phys. Chem., 83 (1979) 640.