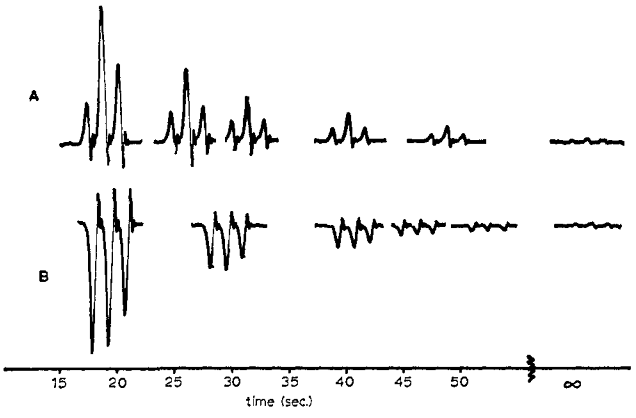

Figure 1. Nmr spectra (δ 4.4–4.8) of H-1 of the 1-chloro-1-phenylpropane produced from the reaction of α,α-dichlorotoluene (0.5 *M*) with ethyllithium (0.6 *M*) in benzene. The time axis indicates the number of seconds after the reagents were mixed; the infinity spectra were taken at times greater than 150 sec. (A) Reagents were mixed in the spectrometer probe. (B) Reagents were mixed outside the spectrometer field, and placed in the probe 12 sec after mixing.

tion of acyl peroxides in the presence of alkyl iodides gives rise to polarization in the protons of both reagent and product iodides.[2c] Such reactions provide an attractive test system for zero field polarization, since they can be thermally initiated and then quenched by cooling, before the sample is introduced into the spectrometer. Figure 2 shows the effect of a magnetic field on the nmr spectrum of 2-iodopropane in *o*-dichlorobenzene taken during (Figure 2A) or following (Figure 2B) the thermal decomposition of benzoyl peroxide in the same solution. In this case also the observed effects are insensitive to temperature and depend only on whether the product was formed in or out of the magnetic field. It should be noted that in this example the methyl protons of 2-iodopropane seem to be unaffected by the magnetic field, and appear in both instances as a doublet with positive and negative enhancements of the high- and low-field lines, respectively.

Although these results bear some resemblance to polarization effects obtained in flowing liquids[7] and in solids subjected to magnetic field changes,[8] the analogy cannot be exact. We have been unable to produce any approximation to these effects in nonreacting samples or in rapid ionic reactions by simply transferring the sample to and from the nmr probe. Possible time-dependent interactions available to a system undergoing a free-radical reaction in zero field include the electron–electron and electron–nuclear scalar and dipolar couplings. Effective operation of these interactions to produce transitions does not require the presence of a magnetic field, although the efficacy of exchange of energy within the spin system and between the spin system and the lattice is, in general, modified by a field. It is therefore at least plausible that transient nonequilibrium populations of the zero-field spin levels arising from electron–electron and electron–nuclear interactions may occur during a free-radical reaction in solution. The mechanisms by which these zero-field relaxation processes can affect spin level populations after quantization in the field of the spectrometer have yet to be detailed.

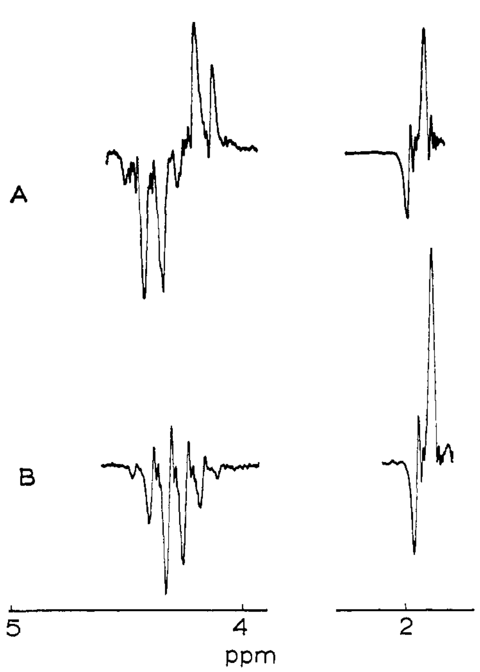

Figure 2. Nmr spectra of 2-iodopropane (1.48 *M*) in *o*-dichlorobenzene solution containing 0.61 *M* benzoyl peroxide. (A) Spectrum taken at 140° during decomposition of the benzoyl peroxide. (B) Spectrum taken approximately 5 sec after quenching the thermal decomposition, which was conducted at 140° outside the spectrometer field.

Zero-field polarization has been observed in every rapid radical reaction (*i.e.*, reactions complete in times less than T_1 of the products) that we have examined.[9] If it proves to be a general phenomenon, it may be utilized beneficially in CIDNP investigations of reaction mechanisms. Radical reactions can be conducted outside the spectrometer field, thus facilitating the introduction of energy (as light or heat, for example) into the sample. Experiments providing examples of such applications are in progress.

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[7] A. J. Zhernovoi and G. D. Latyshev, "Nuclear Magnetic Resonance in a Flowing Liquid," Consultants Bureau, New York, N. Y., 1965.

[8] R. V. Pound and E. M. Purcell, *Phys. Rev.*, **81**, 279 (1951); A. Abragam and W. G. Proctor, *ibid.*, **109**, 1441 (1958).

(9) H. Fischer has observed a field effect on the polarization in the products of peroxide pyrolysis and photolysis (personal communication).

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Electron Spin Resonance of the Cation of Ferrocene

Sir:

The chemical bonding in ferrocene ($FeCp_2$) has attracted much theoretical interest.[1-3] Although in checking bonding theories esr data are very useful, it is only for a few sandwich complexes that the esr spectra have been measured, and for the cation of ferrocene

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(1) G. Wilkinson and F. A. Cotton, *Progr. Inorg. Chem.*, **1**, 1 (1959).

(2) M. Rosenblum, "Chemistry of the Iron Group Metallocenes," Part I, Interscience Publishers, New York, N. Y., 1965, Chapter 2.

(3) R. Prins and J. D. W. van Voorst, *J. Chem. Phys.*, **49**, 4665 (1968).

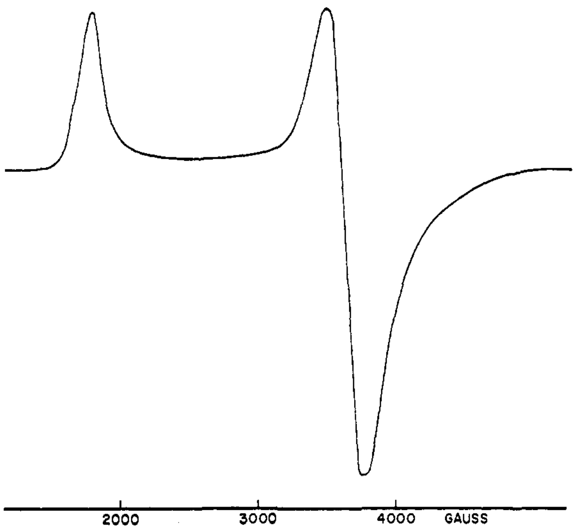

Figure 1. Esr spectrum of $Fe(C_6H_5C_5H_4)_2I_3$ in acetone at 20 °K: modulation 100 kHz, 2.5 G; microwave frequency 9144 MHz.

($FeCp_2^+$), which has a low-spin d^5 ground-state configuration with one unpaired electron,[4,5] it has never been determined. Despite the fact that several attempts have been made at temperatures above 78 °K,[6–11] no signals which could be attributed to $FeCp_2^+$ have been found. This failure is probably due to the relaxation time T_1 being very short, for which evidence has indeed been obtained from nmr measurements of $FeCp_2^+$.[11]

On the basis of its magnetic susceptibility, which significantly differs from the spin-only value, the orbitally degenerate configuration $^2E_{2g}[(a_{1g})^2(e_{2g})^3]$ has been assigned to the ground state of $FeCp_2^+$.[4,5,12] The expectation values of the spin–orbit and orbital momentum operators for the wave functions of an orbitally degenerate configuration may differ strongly from zero, and this explains both the magnetic susceptibility result and the fast relaxation.

Although above 78 °K T_1 is very short, it may, at lower temperatures, be long enough to give an observable esr spectrum. At 20 °K we have indeed found a very broad signal in solid solutions of $FeCp_2^+ \cdot BF_4^-$ and $FeCp_2^+ \cdot I_3^-$ in DMF and acetone. We did not succeed in detecting this signal at 78 °K. Of the cation radicals of phenylferrocene and 1,1′-diphenylferrocene, we have measured esr signals in acetone both at 20 and 78 °K. The signals at 78 °K were broader and less intense, however. In all three cases the observed polycrystalline line shape can be fitted with an axial g tensor. The g values obtained are given in the table and a characteristic esr spectrum is shown in Figure 1.

The strong deviation of the g values from 2.0023 indicates that the orbital contribution to the g values is large. For the lower of the two Kramers doublets belonging to the $^2E_{2g}[(a_{1g})^2(e_{2g})^3]$ configuration, one calculates (including spin–orbit coupling) $g_{\parallel} = 2 + 4k$ and $g_{\perp} = 0$, where k is the orbital reduction factor. At the same time, however, one calculates that the probability of observing the esr transition is zero when the magnetic field is parallel to the z axis of the molecule. A nonzero $g_{\perp}$ value and a nonzero z-transition probability can only be obtained by introducing a lower than axial symmetry by a crystal field H′, which may have either an external or an internal origin. The perturbation treatment of the spin–orbit coupling and the low-symmetry crystal field H′ yields g values which are a function of the orbital reduction factor k, the spin–orbit coupling parameter ζ, and the parameter δ, which is a measure of the strength of H′.[9,10] Values obtained for k and δ are given in Table I. From the reduction factor k we can evaluate the coefficient of the $3d_2$ orbital in the e_{2g} molecular orbital. With proper account for the overlap between metal and π-cyclopentadienyl ring orbitals and the quenching of the orbital momentum in the rings,[13] a value of about 0.80 is obtained for $FeCp_2^+$. This value is in accord with theoretical predictions.[1–3]

Table I. g Values and Molecular Parameters for the Cations of Arylferrocenes

Compound	$g_{\parallel}$	$g_{\perp}$	k	δ, cm^{-1}
$Fe(C_5H_5)_2^+$	4.36	1.30	0.80	200
$Fe(C_5H_5)(C_6H_5C_5H_4)^+$	3.98	1.62	0.86	380
$Fe(C_6H_5–C_5H_4)_2^+$	3.62	1.75	0.84	460

The energy difference between the two Kramers doublets belonging to the $^2E_{2g}$ configuration is $2(\zeta^2 + \delta^2)^{1/2}$ and is predicted to be 610 cm^{-1} in $FeCp_2^+$ and 930 and 1060 cm^{-1} in the mono- and diphenylferricenium cations. The fact that the second doublet occurs not far above the ground-state doublet is the reason for the fast spin–lattice relaxation. In agreement with the predicted energy differences, the narrowest esr lines were obtained for $Fe(C_6H_5C_5H_4)_2^+$ and the esr signal of $FeCp_2^+$ was too broad to be detectable at 78 °K.

Notwithstanding the predicted low symmetry of the compounds, the esr spectra of glassy solutions display axial symmetry. This is understandable since in first order, within the $^2E_{2g}$ configuration, $g_x = g_y$, and one has to go to second order and mix in higher excited states to obtain $g_x \neq g_y$. The difference $g_x - g_y$ will then be of the order of magnitude of $\zeta/\Delta E$ and will be too small to split the x,y esr peak, since the line width is very large owing to the large g tensor anisotropy.

The results for the phenylferricenium cations show that at least part of the lowering of the axial symmetry has an internal origin, while the result for $FeCp_2^+$ indicates that also external perturbations are effective. Our approach to the problem of the lowered symmetry has been to assume a static distortion, but it may be better to describe the experimental results in terms of a dynamic Jahn–Teller effect.[14] A more detailed dis-

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(4) R. E. Robertson and H. M. McConnell, *J. Phys. Chem.*, **64**, 70 (1960).

(5) E. M. Shustorovich and M. E. Dyatkina, *Zh. Neorg. Khim.*, **6**, 493 (1961); *Russ. J. Inorg. Chem.*, **6**, 249 (1961).

(6) H. Nöth, J. Voitländer, and M. Nussbaum, *Naturwiss.*, **47**, 57 (1960).

(7) A. N. Nesmeyanov, *et al.*, *Dokl. Akad. Nauk SSSR*, **137**, 1370 (1961); *Proc. Acad. Sci. USSR, Chem. Sect.*, **137**, 411 (1961).

(8) R. M. Golding and L. E. Orgel, *J. Chem. Soc.*, 363 (1962).

(9) M. Nussbaum and J. Voitländer, *Z. Naturforsch.*, **20a**, 1417 (1965).

(10) A. H. Maki and T. E. Berry, *J. Am. Chem. Soc.*, **87**, 4437 (1965).

(11) H. P. Fritz, H. J. Keller, and K. E. Schwarzhans, *J. Organometal. Chem.*, **6**, 652 (1966).

(12) D. A. Levy and L. E. Orgel, *Mol. Phys.*, **4**, 93 (1961).

(13) D. M. Bishop and T. W. Dingle, *J. Chem. Phys.*, **48**, 541 (1968).

(14) R. M. MacFarlane, J. Y. Wong, and M. D. Sturge, *Phys. Rev.*, **166**, 250 (1968).

cussion of this and other questions will be presented in a further report.

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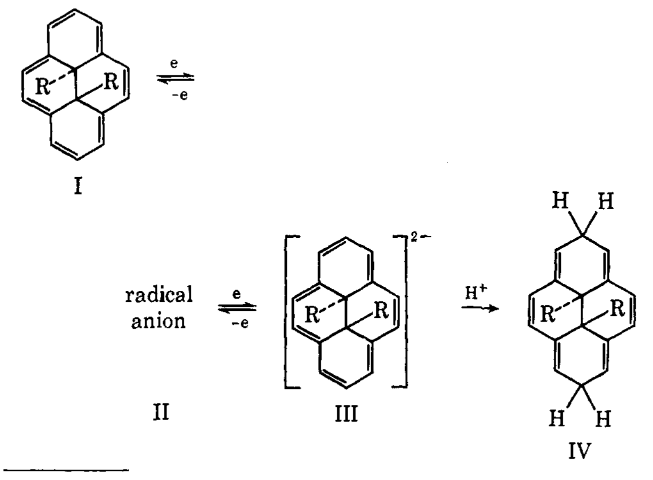
The Dianions of *trans*-15,16-Dialkyldihydropyrenes. Paramagnetic Ring Current Effects

Sir:

Sondheimer and his colleagues have discovered that annulenes having $4n$ π electrons display proton resonance signals in which the chemical shifts of protons internal to the ring are displaced downfield and those peripheral to the ring are displaced toward higher field.[1,2] This has been termed a "paramagnetic ring current effect," and theoretical explanations for it have been provided.[3–5]

It is obvious that, when a neutral hydrocarbon is converted to the corresponding dianion, this corresponds to a change from a $4n$ to a $4n + 2$ system or, alternatively, a $4n + 2$ to a $4n$ system. Thus, it would be predicted that there would be a sharp reversal in ring current effects on interior and exterior protons as a neutral hydrocarbon is converted to its dianion. Oth, Anthoine, and Gilles have recently reported such a result when [16]annulene is converted to its corresponding dianion.[6] We have now studied the conversion of our three *trans*-15,16-dialkyldihydropyrenes to their corresponding dianions. In each case this represents a conversion from a $4n + 2$ π electron system, as in I, to a $4n$ system, as illustrated by III. In contrast to [16]annulene, the dihydropyrenes are fairly rigid molecules and the magnetic properties of the dianions should be informative in defining the nature of the so-called paramagnetic ring current. Also, the availability of dihydropyrenes having differing interior alkyl groups allows partial mapping of the magnetic effects due to the paramagnetic ring current.



I II III IV

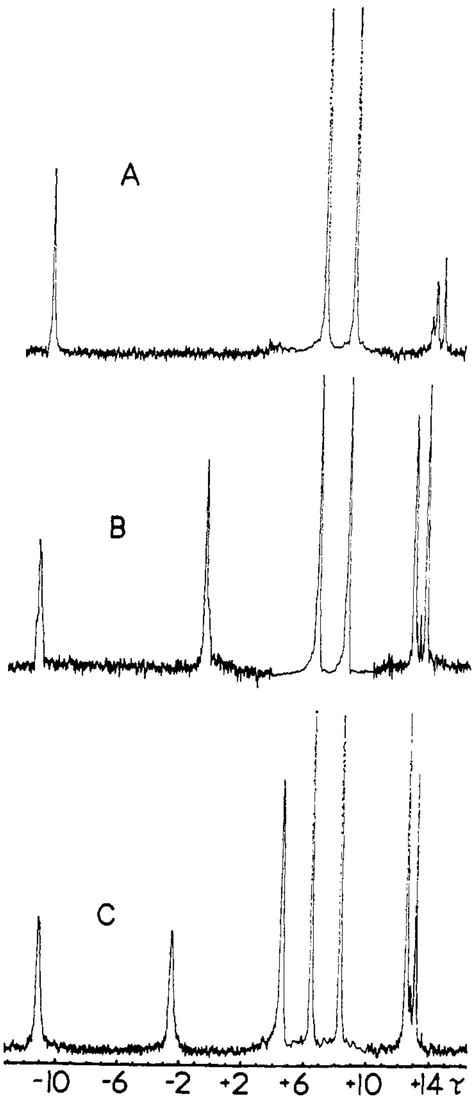


Figure 1. The nmr spectra of the dianions III in tetrahydrofuran-d_8 at −65°. Spectrum A is that of the dianion of *trans*-15,16-dimethyldihydropyrene; B is that of *trans*-15,16-diethyldihydropyrene; and C is that of *trans*-15,16-*n*-propyldihydropyrene. The signals at τ 6.4 and 8.2 are due to the presence of ordinary tetrahydrofuran. Recorded with a Varian HA-100 MHz spectrometer.

The reduction of 15,16-dimethyldihydropyrene (I, R = CH_3) to the corresponding radical anion II (R = CH_3) has been presented previously.[7] Further reduction of the radical-anion II gives the dianion III. As illustrated, the dianion III, on treatment with a proton donor, gives the known bis-triene IV in high yield, providing independent chemical evidence for the formation of the dianion.

The nmr spectra of the three dianions are presented in Figure 1 with the chemical shifts of the relevant protons summarized in Table I. As predicted, there is a very strong paramagnetic ring current effect. The signal for the interior protons at the α carbon, which occurs at τ 13.25–14.25 in the neutral hydrocarbons, now appears in the range of τ −11.0 to −11.24 for the corresponding dianions, a remarkable downfield shift of 25 ppm. Again, in accord with prediction, the signals for the exterior protons, which appear in the range of τ 1.33–2.05

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(1) For a summary, see F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garrat, K. Grohmann, G. Di Maio, J. Mayer, M. V. Sargent, and R. Wolovsky, Special Publication No. 21, The Chemical Society, London, 1967, p 75.

(2) K. G. Untch and D. C. Wysocki, *J. Amer. Chem. Soc.*, **89**, 6386 (1967).

(3) G. Wagniere and M. Gouterman, *Mol. Phys.*, **5**, 621 (1962).

(4) H. C. Longuet-Higgins, Special Publication No. 21, The Chemical Society, London, 1967, p 109.

(5) J. A. Pople and K. G. Untch, *J. Amer. Chem. Soc.*, **88**, 4811 (1966).

(6) J. F. M. Oth, G. Anthoine, and J.-M. Gilles, *Tetrahedron Letters*, 6265 (1968).

(7) F. Gerson, E. Heilbronner, and V. Boekelheide, *Helv. Chim. Acta*, **47**, 1123 (1964).