E.s.r., ENDOR, and Triple Resonance of Fluoro-substituted Fluorenone Ketyls

Jeffrey C. Evans * and Christopher C. Rowlands
Chemistry Department, University College Cardiff, P.O.Box 78, Cardiff CF1 1XL
Bernardo J. Herold and Jose M. A. Empis
Laboratório de Química Orgânica, Instituto Superior Técnico, Avenida Rovisco Pais, 1096 Lisboa Codex, Portugal

Electron spin resonance (e.s.r.) and electron nuclear double resonance (ENDOR) spectra have been observed from dilute solutions of the radical anions of 1-, 2-, 3-, and 4-fluoro- and 2,7-difluoro-fluorenone in tetrahydrofuran (THF) at temperatures below −70 °C with sodium as gegenion. For all the radical anion pairs, both general and special triple resonance experiments were carried out. Similar e.s.r. spectra were obtained for each compound by electrolytic reduction in dimethylformamide (DMF), at room temperature. The e.s.r. spectra have been analysed using coupling constants obtained from the ENDOR experiments. In the cases of the 1-, 2-, and 4-fluoro- and 2,7-difluoro-fluorenone, both ^{1}H and ^{19}F absorptions were clearly seen in their multiple resonance spectra. However for 3-fluorofluorenone no ^{19}F ENDOR absorptions were evident. The ^{1}H hyperfine couplings are in every case similar to the values determined for the parent unsubstituted fluorenone and were assigned according to the results of Hückel–McLachlan calculations.

Proton ENDOR of radicals in solution has proved to be a valuable spectroscopic technique for the elucidation of electronic structure. Since ^{19}F nuclei have a gyromagnetic ratio similar to that of ^{1}H, the ENDOR technique should be applicable to the case of fluorinated organic radicals, and the unravelling of complex hyperfine patterns should become easy and accurate.

Allendoerfer and Maki [1] studied a series of methyl- and fluoro-substituted triphenylmethyl radicals in toluene at −70 °C using e.s.r. and ENDOR spectroscopy. In all cases they were able to observe proton ENDOR but not ENDOR signals arising from the ^{19}F nucleus, although the ^{19}F hyperfine coupling constants could be determined from the e.s.r. spectra and from these constants the frequency of the ENDOR absorptions could be easily calculated. Their reason for not detecting ^{19}F ENDOR is the broadening of the signal at low temperature caused by the contribution of the unaveraged anisotropic part of the coupling. This, as shown by Freed,[2] enters quadratically into the relaxation rates originating from electron–nucleus dipolar interaction. Since the anisotropy of the fluorine nucleus is four times larger than that of a proton, at constant isotropic coupling, the saturation of the n.m.r. transitions can become quite difficult. The short-circuiting of the n.m.r. transition as required by ENDOR may no longer be achieved with the available radiofrequency power.

Lubitz *et al.*[3] have carried out ENDOR experiments on fluorinated benzophenone radical anions and have detected both fluorine and proton ENDOR. They have shown that with an n.m.r. radiofrequency field of 4 mT (rotating frame), detectable fluorine absorption can only be expected for fluorine couplings not much larger than 14 MHz.

In a study of a fluorine substituted bipyridylium radical cation, Evans *et al.*[4] reported fluorine ENDOR enhancements where the fluorine coupling constant is of the order of 3 MHz.

In this paper we describe an ENDOR and general and special triple resonance [5–7] study of fluorofluorenone radical anions in THF with sodium as gegenion. We have observed ^{19}F absorption in the ENDOR experiments at low temperature when the fluorine coupling was smaller than 8 MHz, but with a ^{19}F coupling in excess of 17 MHz (obtained from the e.s.r. spectrum) no ENDOR absorption was detected.

In comparing the experimentally obtained coupling constants with the results of calculations, the Hückel–McLachlan method was used. It is generally recognized [8] that for planar aromatic systems satisfactory agreement can usually be obtained between experimental and calculated isotropic ^{1}H coupling constants. The use of more involved methods like INDO [9] does not lead to more accurate predictions and consumes much more computational time. Fluorine-19 isotropic coupling constants, however, cannot be as accurately predicted from spin populations calculated by the Hückel–McLachlan methods as for ^{1}H. The various approaches described in the literature [10–12] have been used and commented on recently by Lubitz *et al.*[3]

In a recent review [13] it has been recognized that several of the reported attempts lead to widely differing values for McConnell constants or use different models. The authors conclude that, considering the complexity of the problem, this is not surprising.

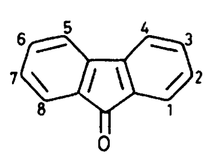
In view of the fact that ^{19}F coupling constants are not always easily predictable with the theoretical tools currently used, it seemed worthwhile to enlarge the already existing body of data with some new experimental determinations of isotropic ^{19}F coupling constants, especially if these data were obtained with the accuracy offered by ENDOR and the reliability of the sign determination offered by general triple resonance.[14]

Experimental

Materials.—2-Fluorofluorenone (K and K Laboratories Inc.) was used as supplied without further purification; 1-, 3-, and 4-fluorofluorenone and 2,7-difluorofluorenone were prepared by methods previously described.[15] Tetrahydrofuran (THF) was purified as described earlier.[16] Sodium metal (B.D.H.) was purified by refluxing under dinitrogen in toluene. Dimethylformamide (DMF) (B.D.H.) spectroscopic grade was stored over and distilled from molecular sieves. Tetrabutylammonium perchlorate (B.D.H.) was used as supplied.

Procedure.—The radical anions were made, either (a) by passing a solution in THF over a freshly prepared sodium film under vacuum as described earlier,[16] or (b) by electrolytic reduction in the e.s.r. cavity using DMF as solvent and 10^{-1}M-tetrabutylammonium perchlorate as supporting electrolyte with platinum wires as cathode and anode.

The e.s.r./ENDOR/triple resonance spectra were recorded



(I) Fluorenone

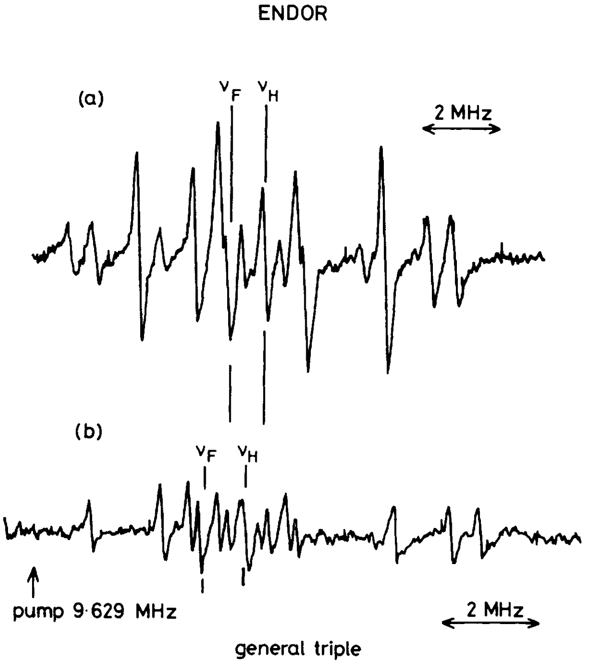


Figure 1. ENDOR (a) and general triple resonance (b) of 1-fluorofluorenone sodium ketyl; solution in THF at −100 °C

with a Varian E109 spectrometer interfaced with a Bruker ENDOR/triple resonance system. The variable temperature measurements were made using a Varian E1001 temperature controller. Computer simulations of the e.s.r. spectra were carried out using a fast Fourier transform program previously described,[17] based on the splitting constants obtained from the ENDOR experiments.

Results

The structure of fluorenone and the numbering system are shown in formula (I).

Brown [18] has shown that when highly fluorinated aromatic compounds are reduced by alkali metals in THF, no radical anions are produced, and that abstraction of fluorine by the alkali metal occurs. To investigate whether the radicals produced in our system are subject to fluorine abstraction, we have prepared the radical anions electrolytically in DMF, and find that in each case the e.s.r. spectra are similar to the sodium ion spectra at about −70 °C. This shows that fluorine abstraction is not a problem. To make certain that there had been no fluorine abstraction from the ion pairs, samples of the sodium-reduced fluorofluorenones which had been used to record the spectra were reoxidised with dry dioxygen. The reaction products, left after evaporation of the solvent, were analysed by h.p.l.c. on a LiChrosorb SI/60 column, using hexane with 1% of dioxane as eluant. Under these conditions, previously prepared mixtures of fluorenone and the fluorofluorenone can be easily separated. Fluorine abstraction does indeed occur eventually, as shown by h.p.l.c. of old (typically one week or more) samples, in which various percentages of the fluorofluorenone and the parent fluorenone were detected.

Table 1. Hyperfine coupling constants (^1H and ^{19}F) determined by ENDOR and triple resonance of dilute solutions of the sodium ion pairs in THF at −72 °C

Substituents	a/MHz [a,b]		
1-Fluoro	−9.77	+0.65	+1.63
	−8.56	+1.05	
	−6.56	−1.26	+1.78 (^{19}F)
2-Fluoro	−9.25	−5.99	+2.50
	−9.09	+0.58	−3.37 (^{19}F)
	−6.14	+1.90	
2,7-Difluoro	−8.40		
	−6.87		−3.70 (^{19}F)
	+2.02		
3-Fluoro	−8.78	+1.59	
	−5.51 (2^1H)	+1.70	+17.71 (^{19}F) [c]
	+0.63		
4-Fluoro	−8.83	+0.24 (2^1H)	
	−8.23	+1.64	
	−5.46 (2^1H)		−7.50 (^{19}F)

[a] ±0.01 MHz. [b] Sign of largest a_H assumed negative; in every case, multiplicities from special triple resonance. [c] Determined from the e.s.r. spectrum at room temperature; sign from asymmetric line-broadening effect (see text).

1-Fluorofluorenone.—The ENDOR and general triple resonance spectra are shown in Figure 1. In the ENDOR spectrum [Figure 1(a)] there are pairs of lines centred at 13.875 MHz and a pair of lines centred at 13.228 MHz. The assignment of the ENDOR lines to protons or fluorine nuclei can be determined from the ENDOR resonance condition $\nu_{ENDOR} = \nu_N \pm a_N/2$, where ν_N = free nuclear Larmor frequency and a_N = hyperfine coupling constant.

At 326 mT ν_H = 13.875 MHz and ν_F = 13.228 MHz. The coupling constants obtained are shown in Table 1. The linewidths of the fluorine and proton ENDOR are comparable. The relative signs of all the coupling constants were obtained from the general triple resonance experiment [Figure 1(b)].

2-Fluoro- and 2,7-Difluoro-fluorenone.—Figures 2 and 3 show the multiple resonance spectra of the 2-fluoro- and 2,7-difluoro-fluorenone radical anion pairs. Both ^{19}F and proton ENDOR are clearly observed. The linewidth of ^{19}F ENDOR is only slightly greater than that of the proton ENDOR lines.

The insets [Figure 2(a)] show the effect of lower radiofrequency modulation and cooling the sample to −100 °C; under these conditions peaks 3 and 4 can be further split into two peaks; this is also true of peaks 1 and 2 but the resolved lines are not shown.

The ENDOR spectrum obtained at −100 °C from 2,7-difluorofluorenone shown in Figure 3(a) comprises two sets of absorptions, the proton absorptions centred at 13.875 MHz (the free proton frequency), and a pair of lines symmetrical around 13.23 MHz (the free ^{19}F frequncy). The high-field member of this pair is coincident with a high-field proton line. The coupling constants obtained are shown in Table 1.

The multiplicities and relative signs were determined by special and general triple resonance techniques for both radical anions.

From the special triple resonance experiment [Figure 2(b)] the multiplicity of the ENDOR absorption lines was ascertained. Peaks B and D in Figure 2(b) arise from the ^{19}F nucleus and are therefore centred at ν_F and not at ν_H; hence

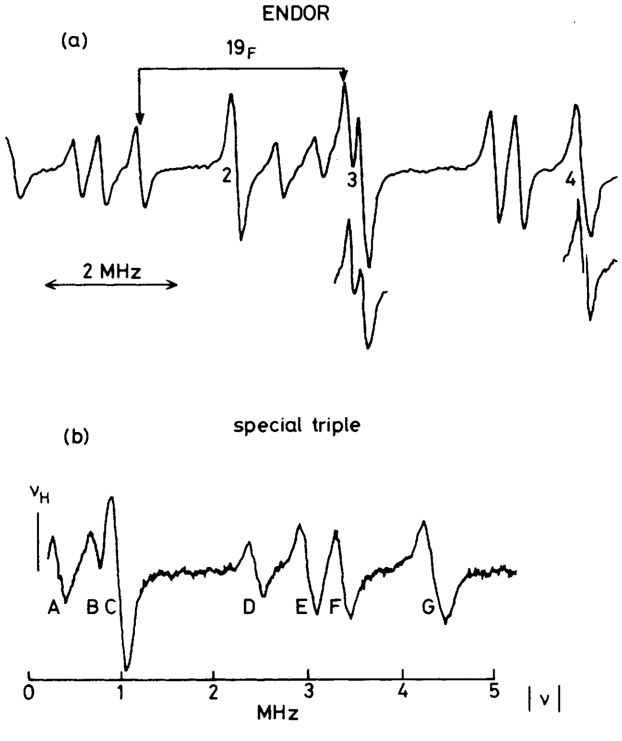


Figure 2. ENDOR (a) and special triple resonance (b) of 2-fluorofluorenone sodium ketyl; solution in THF at −100 °C

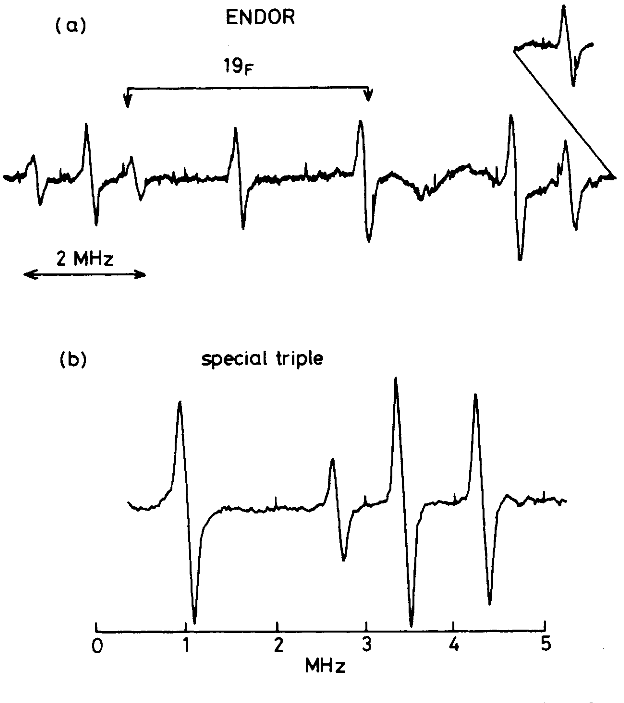


Figure 3. ENDOR (a) and special triple resonance (b) of 2,7-difluorofluorenone sodium ketyl; solution in THF at − 100 °C

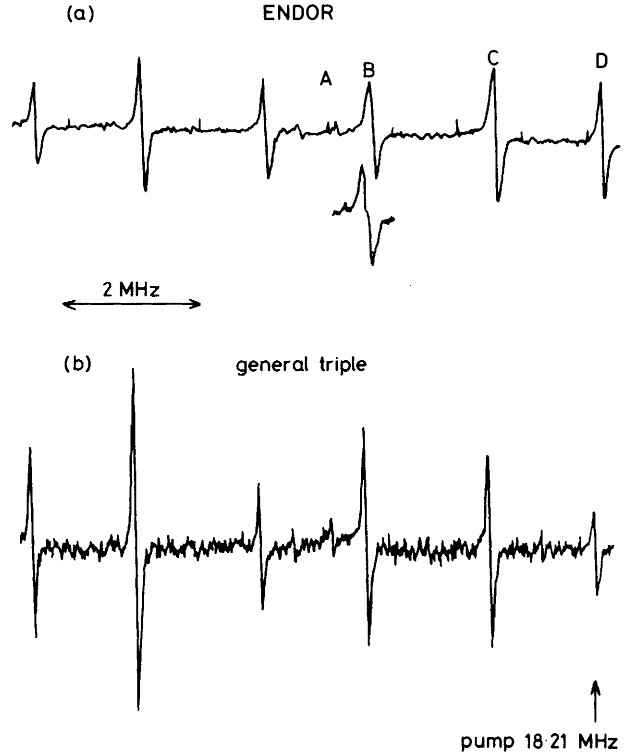


Figure 4. ENDOR (a) and general triple resonance (b) of 3-fluorofluorenone ketyl; solution in THF at −93 °C

they are not coincident. Peak C is approximately twice as intense as the remaining peaks, A, E, F, and G, because it is due to two accidentally almost equivalent protons.

3-Fluorofluorenone.—Figure 4(a) shows the ENDOR spectrum obtained at −93 °C. The ENDOR spectrum is symmetrical, with peaks centred at the value of the free proton frequency. Examination of the region where ^{19}F would occur as calculated from the e.s.r. spectrum showed no sign of ^{19}F absorptions, the linewidth of this absorption being so great that it is not detected. Lubitz [3] has shown that the linewidths for fluorine and proton ENDOR transitions are different and that the difference depends on the magnitude of the ^{19}F coupling in such a way that a ^{19}F coupling constant of 0.75 mT could barely be detected in the ENDOR spectrum. We were unable to detect the fluorine ENDOR absorption (a_F = 0.632 mT from e.s.r.) in our system by increasing the radiofrequency modulation to 400 kHz, this value completely over-modulates the proton lines.

The insert in Figure 4 shows that peak B can be further resolved into two components by lowering the temperature to below −100 °C and using very low radiofrequency field levels. This is true also for its mirror image peak below the spectrum centre (not shown), but none of the other peaks could be further resolved. The multiplicities and relative signs again were determined by special and general triple resonance experiments. The proton coupling constants are shown in Table 1. The ENDOR intensity of the central lines (A) is greatly reduced in comparison with the other lines because the e.s.r. linewidth is comparable to the hyperfine coupling constant, and therefore adjacent e.s.r. transitions cannot be saturated separately. We have not used the formula given by Allendoerfer and Maki [19] to correct the observed intensities because of the larger proton ENDOR linewidths due to the fluorine nucleus in the molecules. The large pseudosecular term for the fluorine contributes to the proton linewidth (see ref. 3).

In Figure 5(a) the e.s.r. spectrum of the DMF solution of 3-fluorofluorenone electrolytically reduced is shown. That the observed broadening of the highfield lines of this spectrum, apparent from comparison with the isotropic simulation in

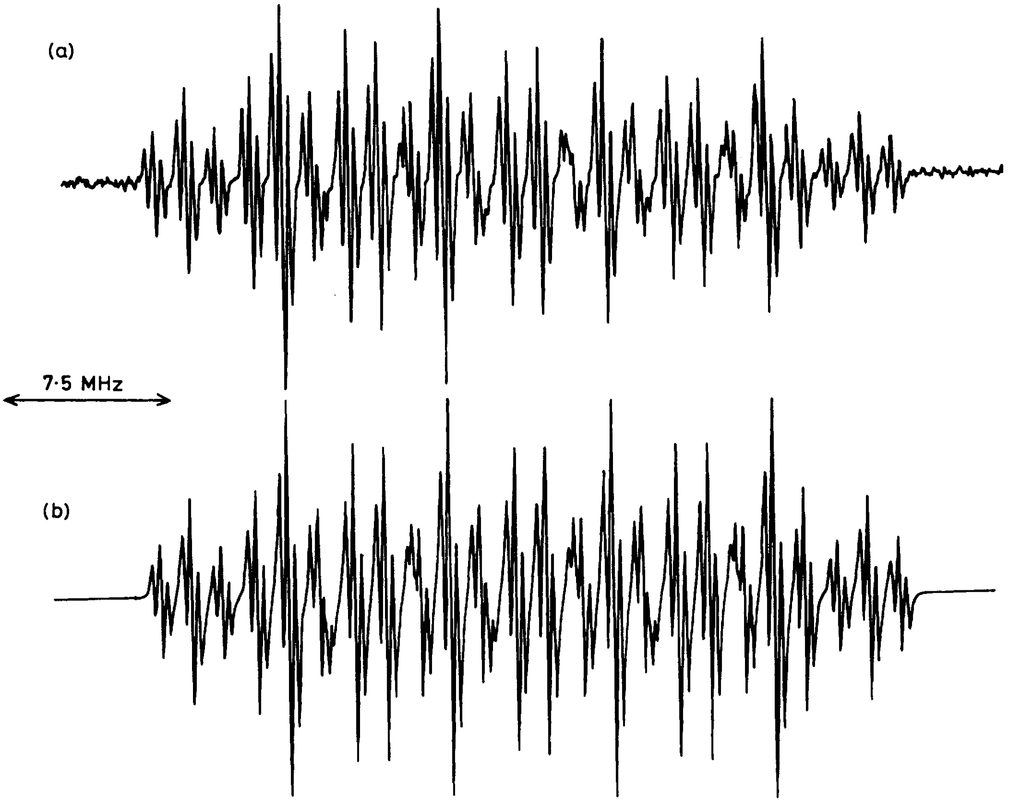


Figure 5. E.s.r. spectrum of electrolytically generated 3-fluorofluorenone radical anion solution in DMF (a) and its computer simulation (b)[17,*]

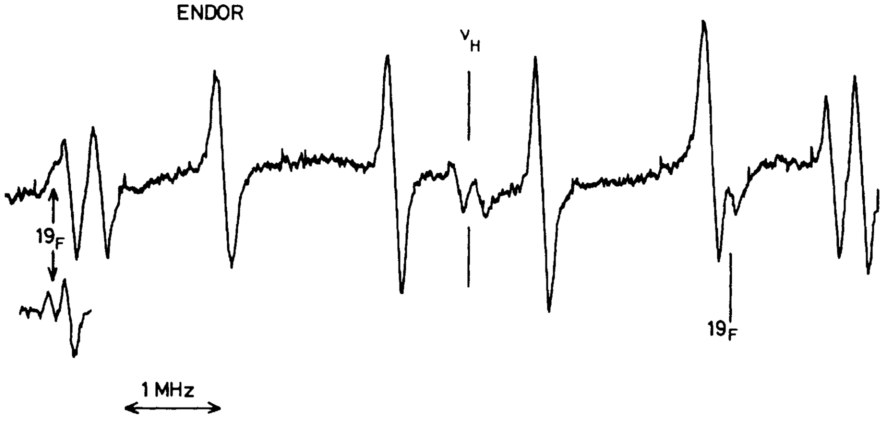


Figure 6. ENDOR of 4-fluorofluorenone sodium ketyl; solution in THF at −100 °C

Figure 5(b), can be used to determine the sign of the ^{19}F coupling will be demonstrated later.

4-Fluorofluorenone.—The ENDOR spectrum is shown in Figure 6. The linewidth of the ^{19}F absorptions is greater than that of the proton signals. Table 1 gives the hyperfine coupling constants. The multiplicity and relative signs of the coupling constants were determined from special and general triple resonance, respectively.

Discussion

Table 1 summarizes the ^1H and ^{19}F coupling constants measured from ENDOR and general and special triple resonance spectra. The experimental hyperfine couplings determined in this way were found to yield accurate simulations of the experimental e.s.r. spectra in every case except for 1-fluorofluorenone. For this compound a broad e.s.r. spectrum is obtained which varies only slightly with temperature, suggesting a chelate-type structure.

The results of Hückel–McLachlan calculations of spin densities were plotted against the experimental coupling constants, and a least-squares analysis was performed in order to determine the best value of the McConnell parameter Q_{CH}^{H} in every case. This Q_{CH}^{H} value was used to convert spin

---

[*] Simulation parameters were $|a_F| = 0.6125$ mT, $|a_H| = 0.0140$; 0.0144; 0.0570; 0.0590; 0.1817 (2); 0.306 mT; linewidth 550 μT; modulation amplitude 320 μT; sweep time 500 s; time constant 0.2 s.

Table 2. Experimental *versus* calculated ^{1}H coupling constants (a_H/MHz) and optimized McConnell constants ($Q_{CH}{}^{H}$) for radical anions from fluorofluorenones

Substituent		a_H/MHz at position 1	2	3	4	5	6	7	8	$Q_{CH}{}^{H}$ [a]
Unsubstituted	exp.[3]	−5.93	+0.37	−8.88	+1.87	+1.87	−8.88	+0.37	−5.93	
	calc.[2]	−5.38	+0.35	−9.35	+1.94	+1.94	−9.35	+0.35	−5.38	
1-Fluoro	exp.		+0.65	−8.56	+1.26	+1.63	−9.77	+1.05	−6.26	
	calc. [b]		−0.58	−8.94	+1.80	+2.25	−9.24	+0.16	−6.58	−83.7
2-Fluoro	exp.	−6.14		−9.09	+1.90	+2.00	−9.25	+0.59	−5.99	
	calc. [b]	−7.09		−8.12	+2.07	+2.29	−8.84	+0.43	−6.43	−79.0
2,7-Difluoro	exp.	−6.87		−8.40	+2.02	+2.02	−8.40		−6.87	
	calc. [b]	−7.04		−8.07	+2.14	+2.14	−8.07		−7.04	−77.1
3-Fluoro	exp.	−5.51	+0.63		+1.59	+1.70	−8.78		−5.51	
	calc. [b]	−5.75	+0.70		+1.49	+2.03	−8.18	+0.18	−5.80	−72.8
4-Fluoro	exp.	−5.46	+0.24	−8.83		+1.67	−8.23	+0.24	−5.46	
	calc. [b]	−6.03	−0.34	−8.24		+1.99	−7.81	+0.33	−5.69	−70.9

[a] $Q^{H}{}_{CH}$ in MHz, calculated for best fit by least-mean-squares method. [b] McLachlan parameters: $\lambda = 1.2$, $\delta_O = 1.45$, $\gamma_{CO} = 1.6$, $\gamma C(9)C(10) = \gamma C(9)C(13) = 1.3$, $\gamma C(11)C(12) = 0.8$, $\delta C(9) = -0.1$, $\delta_F = -2.5$, $\gamma_{CF} = 0.62$.[20,22]

densities into calculated coupling constants. In Table 2, a comparison of experimental and calculated coupling constants is presented.

The parameters used in the Hückel–McLachlan calculations were as recommended in the literature for fluorenone,[20] with a correction of 0.3β for the oxygen Coulomb integral to account for the gegenion electrostatic field. Parameters recommended in the literature [21,22] were used for fluorine.

The analysis of the correlation of calculated *versus* experimental ^{1}H coupling constants shows a level of significance which is in every case greater than 99.9%. Except for the small coupling constants assigned to the proton in position 2 in 1-fluorofluorenone radical anion, the signs of the calculated ^{1}H couplings agree with those determined by general triple resonance experiments.

The discrepancy for position 2 in 1-fluorofluorenone radical anion is probably due to the fact that the influence of the gegenion field upon the fluorine was not taken into account in the calculations.

Both signs and magnitudes of the ^{19}F couplings were apparent from general triple resonance spectra for every compound except 3-fluorofluorenone. For this compound, fluorine is substituted into a high spin position in the aromatic ring; hence a local positive spin density is expected, and the observed preferential broadening of the high field e.s.r. absorptions can be taken to mean that the ^{19}F coupling constant is also positive.[3,23]

The signs of the ^{19}F hyperfine couplings are therefore, as expected,[3] opposite to the signs of proton couplings in the corresponding positions in the fluorenone ion pair solutions.[24]

The magnitudes of the ^{19}F hyperfine couplings are not accountable for by any of the various single- or multi-parameter-type equations which have so far been proposed.[11,12] In fact, a single McConnell-type relation with $Q_{CF}{}^{F} = 152.6$ MHz [12] works well for the ^{19}F coupling in 3-fluorofluorenone [a_F(calc) = 15.9 MHz]; the deviation found for 4-fluorofluorenone [a_F(calc) = −4.1 MHz] might be assigned to deviation from planarity, arising from the steric requirements of a fluorine substituent in position 4. For 1-fluorofluorenone, an ' *ortho* effect ' [25] and gegenion proximity, enhancing charge delocalization to the substituent, are probably at least partly responsible for the very low a_F/a_H value * observed (0.33), but a broadening of the e.s.r. features which is only slightly temperature dependent leads us to think a chelate-type structure might be involved.

On the other hand, in 2-fluoro- and 2,7-difluoro-fluorenone ion pairs a_F/a_H is very large,[10] although fluorine substitution does not appear to perturb severely the ^{1}H couplings.

Although the magnitudes of ^{19}F couplings are not predictable from the results of the Hückel–McLachalan calculations, their signs, as determined by general triple resonance and e.s.r. linewidth analysis, agree with the signs of the calculated ^{19}F spin densities, suggesting that, at least in this type of radical anion, overlap is the dominant spin transmission mechanism, irrespective of whether the attached carbon atom is in a high or a low spin position.

Acknowledgements

A grant from the Royal Society to purchase computer equipment and a grant from S.E.R.C. towards the purchase of an ENDOR spectrometer (both for the University College Cardiff) are gratefully acknowledged, as well as financial support by the Instituto Nacional de Investigacão Cientificia (through the Centro de Processos Quimicos da Universidade Técnica de Lisboa). J. M. A. E. thanks the British Council for a travel grant. The last stages of this work were also supported by a NATO co-operative research grant, for which we also express our gratitude.

References

1 R. D. Allendoerfer and A. H. Maki, *J. Am. Chem. Soc.*, 1969, **91**, 1088.

2 J. H. Freed, in ' Electron Spin Relaxation in Liquids,' ed. L. T. Muns and P. W. Atkins, Plenum Press, New York, 1972.

3 W. Lubitz, K. P. Dinse, K. Möbius, and R. Biehl, *Chem. Phys.*, 1975, **8**, 371.

4 J. C. Evans, M. H. Nouri Sorkhabi, and C. C. Rowlands, *Tetrahedron*, 1982, **38**, 2581.

5 R. Biehl, M. Plato, and K. Möbius, *J. Chem. Phys.*, 1975, **63**, 3515.

6 K. P. Dinse, R. Biehl, and K. Möbius, *J. Chem. Phys.*, 1974, **61**, 4335.

7 K. Möbius and R. Biehl, in ' Multiple Electron Spin Resonance Spectroscopy,' ed. M. M. Dorio and J. H. Freed, Plenum Press, New York, 1979.

8 N. M. Atherton, in ' Electron Spin Resonance,' Ellis Horwood, Chichester, 1973.

9 W. Lubitz, M. Plato, K. Möbius, and R. Biehl, *J. Phys. Chem.*, 1979, **83**, 3402.

---

* a_H is the proton coupling constant for the same position as the unsubstituted fluorenone ketyl.

10 D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Mol. Phys.*, 1962, **5**, 407.

11 A. Hinchcliffe and J. N. Murrell, *Mol. Phys.*, 1968, **14**, 147.

12 P. H. H. Fischer and J. P. Colpa, *Z. Naturforsch.*, *Teil A*, 1969, **24**, 1980.

13 W. Gordy, in 'Theory and Applications of Electron Spin Resonance,' Wiley, New York, 1980.

14 W. Lubitz and T. Nyrönen, *J. Magn. Reson.*, 1980, **41**, 17.

15 T. L. Fletcher, M. J. Namkung, W. H. Wetzel, and H. L. Pan, *J. Org. Chem.*, 1960, **25**, 1342.

16 J. E. Bennett, A. G. Evans, J. C. Evans, E. D. Owen, and B. J. Tabner, *J. Chem. Soc.*, 1963, 3954.

17 J. C. Evans, P. H. Morgan, and R. H. Renaud, *Anal. Chim. Acta*, 1978, **103**, 175.

18 J. K. Brown and W. G. Williams, *Trans. Faraday Soc.*, 1968, **64**, 298.

19 R. D. Allendoerfer and A. H. Maki, *J. Magn. Reson.*, 1970, **3**, 396.

20 T. Takeshita and N. Hirota, *J. Am. Chem. Soc.*, 1971, **93**, 6421.

21 A. Streitwieser, in 'Molecular Orbital Theory for Organic Chemistry,' Wiley, New York, 1961.

22 F. Nemoto, K. Ishizu, and F. Shimoda, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 570.

23 A. Hudson and G. R. Luckhurst, *Chem. Rev.*, 1969, **69**, 191.

24 W. Lubitz, R. Biehl, and K. Möbius, *J. Magn. Reson.*, 1977, **27**, 411.

25 R. V. Cloyd and D. E. Wood, *J. Am. Chem. Soc.*, 1974, **96**, 559, and references therein.

Received 13*th June* 1983; *Paper* 3/984