Radical-anion Intermediates. Part V.[1] Electron Spin Resonance Spectra of Radical Anions and Dianion Radicals of Some 9-Substituted Fluorenes

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The e.s.r. spectra of the radical anions and dianion radicals obtained from eight 9-substituted fluorenes have been studied. The e.s.r. spectra of the radical anions have been satisfactorily interpreted. In many of the spectra a small splitting associated with the substituent is present. The variation of the a_β(H) coupling constant with substituent can be satisfactorily interpreted in terms of either the steric or the polar nature of the substituent. In the case of the dianion radicals the e.s.r. spectra are all fairly similar. However, in three of the dianion radicals studied the e.s.r. spectra are best interpreted in terms of two radicals with g values differing by 0·00006.

THE radical anions of a considerable number of aromatic hydrocarbons have been successfully prepared and studied by both e.s.r. and electronic spectra. The great majority of these radical anions are quite stable and can readily be studied at room temperature by either of the above spectroscopic techniques. However, this is not always the case and a number of radical anions are only relatively stable below room temperature (*i.e.* at *ca.* −70 °C). This is particularly true of the radical anions derived from fluorene and its derivatives.[2]

We have been primarily interested in studying the kinetics of the decay of the radical anions of a variety of fluorene derivatives to form the corresponding anions.[1,2] These anions have also aroused considerable interest, particularly owing to the sensitive nature of their absorption spectra to temperature, solvent, and counter-

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[1] Part IV, B. J. Tabner and T. Walker, *J.C.S. Perkin II*, 1972, 445.

[2] D. Casson and B. J. Tabner, *J. Chem. Soc.* (*B*), 1969, 887; 1970, 1560, 1565.

ion.[3,4] This sensitivity has been successfully interpreted in terms of an equilibrium between contact and solvent-separated ion pairs. Under certain conditions these anions will react further to form a further radical anion usually referred to as the dianion radical.[5]

This paper reports e.s.r. spectra of the radical anions and dianion radicals derived from a number of 9-substituted fluorenes.

EXPERIMENTAL

All operations were performed with standard high-vacuum techniques.

Materials.—Tetrahydrofuran (B.D.H.) was purified as described.[6] 9-Methyl-, 9-ethyl-, 9-n-propyl-, 9-isopropyl-, 9-n-butyl-, 9-t-butyl-, and 9-benzyl-fluorene were prepared and purified as described.[1] 9-Phenylfluorene was prepared by the method of Ullman *et al.*[7] and recrystallised from 95% ethanol. The authenticity of all samples was checked by n.m.r. and purity by t.l.c. or differential scanning calorimetry or both.

Procedure.—Solutions of the 9-substituted fluorenes in tetrahydrofuran, and the corresponding radical anions, were prepared at −70 °C as described.[1] The dianion radicals were prepared from solutions of the corresponding anions by leaving a solution of the anion in contact with a potassium film for several days.

Spectroscopic Measurements.—E.s.r. spectra were recorded on a Varian E3 spectrometer, the temperature of the sample being controlled by a Varian E-4557 variable-temperature unit. Reconstructions of the spectra were performed with the aid of a Digico Micro 16 computer.

RESULTS AND DISCUSSION

The Radical Anions.—The e.s.r. spectrum of each of the 9-substituted fluorene radical anions studied can be satisfactorily interpreted in terms of four (1 : 2 : 1) triplets and a (1 : 1) doublet. These splittings account for all the ring protons and for the C(9) proton. In some of the radical anions the two smallest of the triplets are not resolved and appear in the e.s.r. spectra as a (1 : 4 : 6 : 4 : 1) quintet (see Table 1). In some of the spectra an additional (but rather small) splitting can also be observed and this splitting has been assigned to the substituent.

TABLE 1

A summary of the experimental coupling constants for the 9-substituted fluorene radical anions

	$a_{1,8}$	$a_{2,7}$	$a_{3,6}$	$a_{4,5}$	$a_{9(\beta)}$	a_R	t/°C
9-Me	0·94	5·25	0·94	4·125	4·19	0·15	−70
	1·03	5·00	0·91	4·00	3·95	0·12	+20
9-Et	1·02	5·25	0·88	4·125	4·19	0·15	−70
9-Pr^n	1·00	5·15	0·88	4·10	4·10	0·12	−70
	1·00	5·10	0·88	4·05	3·95	0·12	−20
9-Bu^n	0·97	5·15	0·97	4·09	4·09	<0·15	−70
9-Pr^i	0·95	5·25	0·95	4·00	4·00	0·22	−50
9-Bu^t	0·72	5·25	0·72	3·75	3·875		−70
9-CH$_2$Ph	0·86	5·25	0·86	4·00	4·30	0·20	−70
9-Ph	0·88	5·25	0·88	4·00	5·19	0·00	−70

In the interpretation of the e.s.r. spectrum of the fluorene radical anion reported previously[2] it was not possible to give a complete assignment of the splitting constants. The difficulty concerned the values for the C(4, 5) and C(9) protons which were similar in magnitude and both of which gave triplets in the spectrum. However, in the 9-substituted fluorenes this difficulty does not arise as the C(4, 5) splitting is a triplet in contrast to the doublet from the single C(9) proton. The remaining coupling constants in the 9-substituted fluorene radical anions have been assigned by comparison with those for the fluorene radical anion.

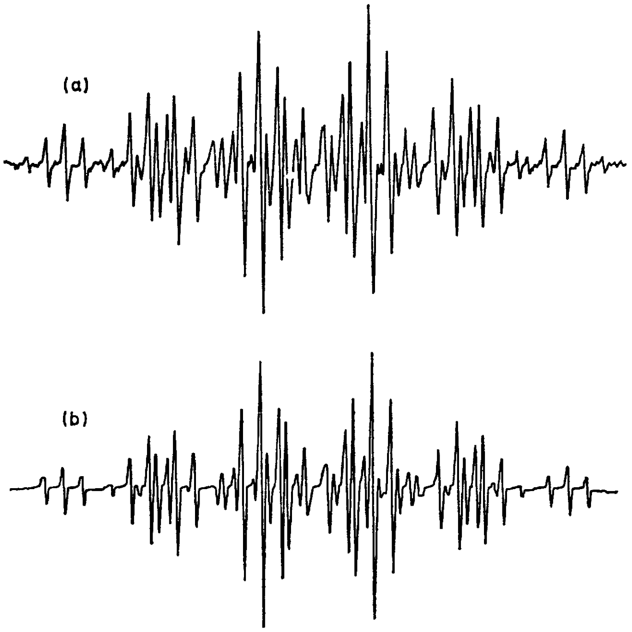

FIGURE 1 (a) The e.s.r. spectrum of the 9-phenylfluorene radical anion in tetrahydrofuran at −70 °C with lithium as the counterion; (b) a reconstruction based on the coupling constants given in Table 1

The interpretation of each of the spectra was checked with a computer reconstruction. A typical spectrum, that of the 9-phenylfluorene radical anion, together with the computer reconstruction, is shown in Figure 1. The linewidth in the spectra of the 9-n-butyl- and 9-t-butyl-fluorene radical anions is much greater than in the other spectra. It was not possible therefore to measure the coupling constants with the same accuracy in these two spectra and so it was not possible to detect the expected a_R coupling constant in the spectrum of the 9-n-butyl-fluorene radical anion (except that a_R must be less than 0·15 G). Despite this difficulty, however, there is no doubt that apart from the value of $a_{2,7}$ the coupling constants in the spectrum of the 9-t-butylfluorene radical

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[3] T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, 1966, **88**, 307, 318.

[4] E. de Boer, A. M. Grotens, and J. Smid, *J. Amer. Chem. Soc.*, 1970, **92**, 4742.

[5] E. G. Janzen, J. G. Pacifici, and J. L. Gerlock, *J. Phys. Chem.*, 1966, **70**, 3022.

[6] D. Casson and B. J. Tabner, *J. Chem. Soc.* (*B*), 1969, 572.

[7] F. Ullman and R. von Wurstemberger, *Ber.*, 1904, **37**, 73.

anion are all smaller than for any of the other radical anions.

One interesting feature which emerged from the study of the 9-methyl- and 9-n-propyl-fluorene radical anions was a small temperature-dependence in some of the coupling constants. At temperatures above —70 °C the total width of the spectra of these two derivatives was found to decrease. A decrease in the larger coupling constants was found to be primarily responsible for this effect. Although the $a_{4,5}$ and $a_{9(\beta)}$ coupling constants are very similar, the best fit was found with $a_{9(\beta)}$ just slightly smaller than $a_{4,5}$.

Alkyl proton coupling constants. One of the most interesting aspects of a number of studies of alkyl-substituted radical anions has been the structural information which can be obtained from the magnitude of the alkyl proton coupling constant.[8] It is usual in this context to refer to a hydrogen atom bonded to a carbon atom forming part of the π-system as an α-proton. A hydrogen atom bonded to an sp^3 carbon atom which is itself bonded to a carbon atom forming part of the π-system is referred to as a β-proton. The corresponding coupling constants are a_α and a_β respectively, and it is the latter which are of importance in obtaining the structural information.

A large number of studies have successfully used the relationship [9] (1) to represent the β-proton coupling

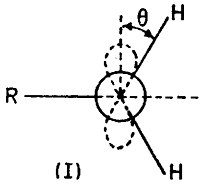
$$a_\beta = \rho^\pi(B_0 + B\cos^2\theta) \qquad (1)$$

constant, where ρ^π is the π-electron spin density on the carbon atom to which the alkyl group is bonded, B_0 and B are splitting parameters which define the contribution from spin polarisation and hyperconjugation respectively, and θ is the angle between the carbon–hydrogen bond and the axis of the p_z orbital on the carbon atom to which it is bonded (and which forms part of the π-system). B_0 Is usually taken to be small in comparison with B which itself is taken to be constant for a series of related radical anions. In addition, for ease of comparison the ratio, R [equation (2)], of the β-alkyl proton coupling constant (a_β) to the corresponding methyl proton coupling constant (a_{Me}) is introduced.

$$R = a_\beta/a_{\mathrm{Me}} \qquad (2)$$

In the case of the free rotation of a methyl group a time-average value for a_{Me} will be obtained. If, however, the substituent is ' locked ' in a particular conformation the value of θ and hence R will depend upon the conformation. The value of R has therefore caused some interest in a number of alkyl-substituted radicals and radical anions.

In the fluorene radical anion the C(9β) protons are ' locked ' by the planar nature of the molecule into a conformation (I) with θ = 30°. A number of ' locked ' conformations of this type have been reported, for example the cyclobutyl radical (R = 1·36) [10] and the 4-nitroindane radical anion (R = 1·58).[11] Clearly both these values are close to the value predicted in the above discussion. Unfortunately, whilst there appear to be obvious models to choose for fluorene (say the *oo*′-bitolyl radical anion, a_{Me}= 2·20 G or the 2-methylbiphenyl radical anion, a_{Me} = 2·41 G [12]), an added difficulty arises from the non-planar nature of biphenyl and its derivatives. Ishizu [12] has suggested that in the *oo*′-bitolyl radical anion the angle of twist between the two phenyl groups lies between 30 and 45°. Molecular orbital calculations show that the value of ρ_2^π should increase as the angle of twist decreases and there therefore seems to be reasonable agreement with prediction for the fluorene radical anion (R = 1·57—1·85, based on the experimental results for a twisted biphenyl).



(I)

Variation of a$_\beta$ *with substituent.* The variation of a_β(H) with substituent will be principally influenced by polar and steric factors. It is interesting to discuss the effect the steric nature of the substituent will have on the conformation of the remaining C(9) proton. The steric interaction in, for example, the t-butyl group will be reduced if θ >30°. In the case of the alkyl substituents one would therefore expect a decrease in the magnitude of a_β(H) as the size of the substituent increases. The observed trend is in this direction. The phenyl group, however, provides an interesting exception. In this case stabilisation can be found in a structure approaching that of triphenylmethane, *i.e.*, θ < 30°. Consequently one would expect, and does indeed observe, the largest value of a_β(H) in the 9-phenylfluorene radical anion. In both these two extreme examples the interannular bond would no longer hold the aromatic part of the molecule coplanar.

The effect of the polar nature of the substituent on a_β(H) is also interesting. Bowden *et al.*[13] found a good correlation between the Taft polar substituent constant, σ* and the pK_a values of some 9-substituted fluorenes. When the σ* values are used as an indication of the electron-donating or -withdrawing properties of the substituent, good agreement with the changes in a_β(H) is found. For example, the largest coupling constant would be expected for the phenyl group and the smallest for the Bu^t group. The intermediate coupling constants

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[8] D. H. Geske, *Progr. Phys. Org. Chem.*, 1967, **4**, 125.

[9] C. Heller and H. M. McConnell, *J. Chem. Phys.*, 1960, **32**, 1535.

[10] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147.

[11] T. M. McKinney and D. H. Geske, *J. Amer. Chem. Soc.*, 1967, **89**, 2806.

[12] K. Ishizu, *Bull. Chem. Soc. Japan*, 1964, **37**, 1093.

[13] K. Bowden, A. F. Cockerill, and J. R. Gilbert, *J. Chem. Soc.* (*B*), 1970, 179.

(*i.e.*, 9-Me, 9-Et, 9-Pr^n, *etc.*) are also in good agreement with prediction.

A satisfactory explanation can therefore be found for the variations in a_β(H) with substituent from consideration of either the steric or the polar nature of the substituent.

The Dianion Radicals.—Dianion radicals obtained from 9-*methyl-*, 9-*ethyl-*, 9-*isopropyl-*, 9-*phenyl-*, *and* 9-*benzyl-fluorene*. The dianion radicals were obtained by the addition of an electron to the corresponding 9-fluorenyl anions [*i.e.*, reaction (3)]. In all the reactions studied this further reduction was only possible (in tetrahydrofuran solution at least) when potassium was used as the reducing metal. The e.s.r. spectra of three of the dianion radicals (9-Me, 9-Et, and 9-Pr^i) were all very similar and could be satisfactorily interpreted in terms of a quintet and two triplet splittings [see Figure 2(a) and Table 2]. In the e.s.r. spectrum of the dianion radical obtained from 9-methylfluorene additional splitting was present at temperatures below −40 °C owing to interaction with at least one of the alkali-metal counterions.

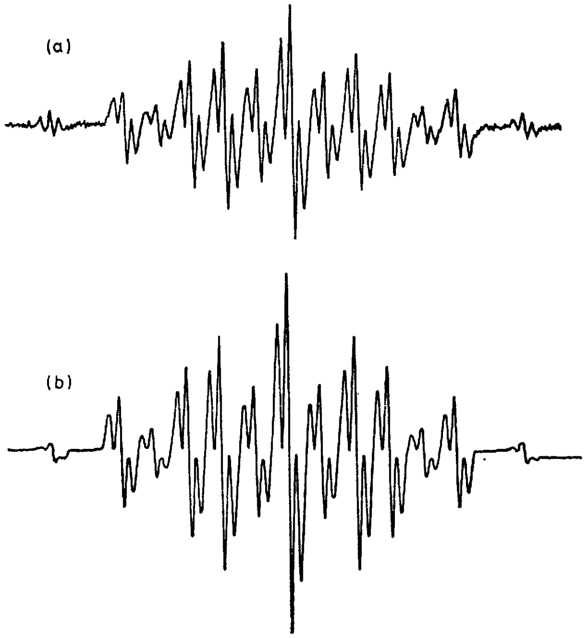
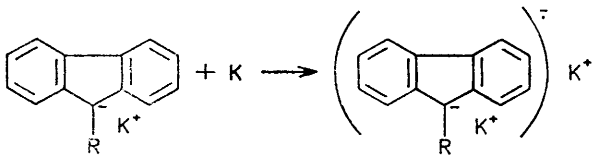


FIGURE 2 (a) The e.s.r. spectrum of the dianion radical obtained from 9-isopropylfluorene in tetrahydrofuran at +20 °C with potassium as the counterion; (b) a reconstruction based on the coupling constants given in Table 2



(3)

The e.s.r. spectra of the 9-benzyl and 9-phenyl derivatives were best interpreted in terms of four triplet splittings (see Table 2). The coupling constants were assigned by comparison with the calculated values for the fluorene dianion radical. For the latter dianion radical the agreement between the experimental coupling constants[5] and those calculated by use of McLachlan's self-consistent field method[14] (λ = 0·55) was very good

TABLE 2

A summary of the experimental coupling constants for the dianion radicals obtained from the 9-substituted fluorenes and of the experimental and calculated coupling constants for the dianion radical obtained from fluorene

	$a_{1,8}$	$a_{2,7}$	$a_{3,6}$	$a_{4,5}$	a_9
9-Me	3·19	3·19	0·40	4·85	
9-Et	3·13	3·13	0·40	4·75	
9-Pr^i	3·13	3·13	0·40	4·69	
9-CH_2Ph	3·30	2·97	0·40	4·75	
9-Ph	3·50	2·87	0·65	4·69	
9-Pr^n	3·19	3·19	0·40	4·75	
9-Bu^n	3·13	3·13	0·40	4·75	
9-Bu^t	3·10	3·10	0·40	4·75	
Fluorene [a]	3·05	3·05	0·35	4·53	0·35
Fluorene [b]	3·48	3·33	0·14	4·56	0·59
Fluorene [c]	3·08	3·08	−0·46	4·51	0·44

[a] See ref. 5 (experimental values). [b] $Q = |27{\cdot}5|$ (Hückel). [c] $Q = |23{\cdot}5|$, $\lambda = 0{\cdot}55$ (McLachlan).

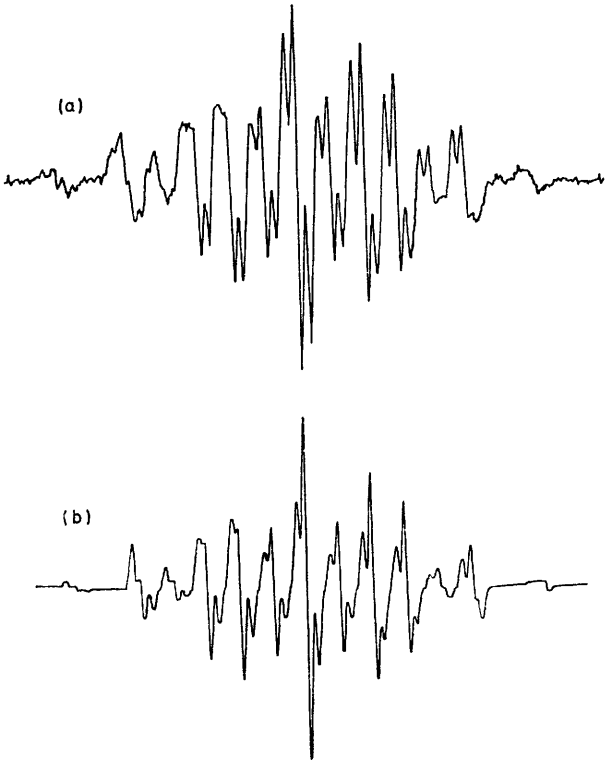


FIGURE 3 (a) The e.s.r. spectrum of the dianion radical obtained from 9-n-propylfluorene in tetrahydrofuran at +20 °C with potassium as the counterion; (b) a reconstruction for two species with *g* values differing by 0·00006 based on the coupling constants given in the text

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[14] A. D. McLachlan, *Mol. Phys.*, 1960, **3**, 233.

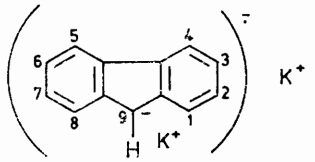
(see Table 2). In the case of the dianion radical obtained from 9-phenylfluorene our interpretation of the spectrum differs from that previously reported.[5] Although the two computer reconstructions are quite similar we feel that our interpretation of this spectrum gives better agreement with the experimental spectrum, particularly with respect to line intensities. We feel that the very similar interpretation for the 9-benzylfluorene dianion radical supports this conclusion.

In none of the e.s.r. spectra of the dianion radicals reported in Table 2 was any splitting observed from interaction with the substituent.

Dianion radicals obtained from 9-*n-propyl-*, 9-*n-butyl-*, *and* 9-*t-butyl-fluorene.* The interpretation of the e.s.r. spectra of the dianion radicals obtained from the above fluorene derivatives presented a more difficult task. The e.s.r. spectra of these three dianion radicals are unsymmetrical; a typical example (that of the dianion radical obtained from 9-n-propylfluorene) is shown in Figure 3(a). The lack of symmetry is best noted by a comparison of the five outer groups of lines on either side of the spectrum. Many different computer reconstructions of these unsymmetrical spectra have been tried. The most successful have been based on the presence of two different free radicals having slightly different g values. Figure 3(b) shows such a reconstruction obtained for two species, one species (55%) having a quintet (3·19 G) and two triplet (4·75 and 0·40 G) splittings, and the second (45%) species having a quintet (3·29 G) and a triplet (4·85 G) and a g value differing from that of the first species by 0·00006. Whilst the agreement between the experimental spectrum and the reconstructed spectrum is not perfect, it is the best we have been able to obtain.

The interpretation of the first species is consistent with the expected dianion radical (see Table 2). However, the nature of the second species is more doubtful. It is tempting to assign to it structure (II) formed by loss of the substituent. This explanation however would require the interpretation to agree with that for the fluorene dianion radical which has an additional quartet splitting. It is clear that it should be possible to improve the computer reconstruction from that given in Figure 3(b) but the inclusion of a quartet splitting did not result in any further improvement. This observation, however, does not eliminate the possibility of this reaction particularly as the unsymmetrical spectra are, in general, obtained for the more bulky of the substituents.

(II)



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