

## Substituent Effects on Electron Spin Distribution and Conformation of Radical Ions obtained from 9-Diphenylmethylenefluorenes

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Nine new substituted 9-diphenylmethylenefluorenes were synthesized. The reductions of the unsubstituted hydrocarbon and eleven substituted derivatives were studied by cyclic voltammetry in dimethylformamide solution. E.s.r. and ENDOR spectra of the radical anions obtained by reduction with alkali metal in tetrahydrofuran were recorded. The electron spin distribution as obtained from experiment was compared with the results of Hückel–McLachlan calculations. The conformations of the radical anions were determined from the spectra. The ratio of electron spin densities in the fluorene part of the alkene and in the diphenylmethylene group obeys a linear Hammett correlation. A similar study was performed for the radical cations of six of the twelve alkenes.

The systematic study of substituent effects in aromatic  $\pi$ -radicals<sup>1–4</sup> has shown that for the benzylic radical an empirical linear stabilization energy correlation<sup>3</sup> with a novel  $\sigma_{\alpha}^{\cdot}$  constant<sup>1,2</sup> can be obtained, based on the electron spin density  $C-\alpha$  of substituted benzylic radicals.<sup>1,2</sup>

However, there are cases where Hammett's substitution constant apparently correlates rather well with the magnitudes observed. For example, the <sup>23</sup>Na e.s.r. couplings of substituted fluorenone sodium ketyls in solution<sup>5</sup> and the reduction potentials of substituted benzophenones<sup>6</sup> and fluorenones<sup>7</sup> correlate well with Hammett substituent constants, whereas for  $\pi\pi^*$  triplet energies of substituted benzophenones the classical Hammett plot is scattered and a linear combination of both kinds of substituent constant is reported to give the best correlations [equation (i)].<sup>6</sup> This correlation also improves the

$$\rho\sigma + \rho^{\cdot}\sigma_{\alpha}^{\cdot} \quad (i)$$

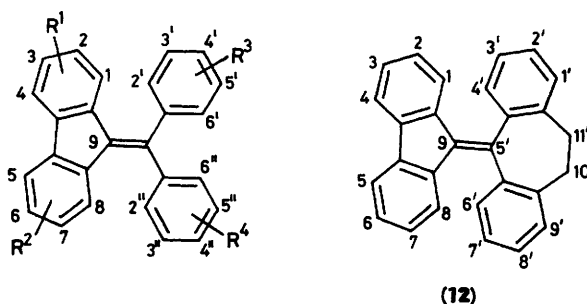
fit in some cases which were initially considered to correlate well with  $\sigma$  alone.<sup>8</sup> This type of extended Hammett equation has also been used to study rates of radical reactions.<sup>1</sup> The relative weight of the first term in relation to the second shows the degree of polarity of the transition state.<sup>1</sup>

On the other hand, e.s.r., ENDOR, and TRIPLE resonance studies on fluorenone ketyls<sup>5,7</sup> have shown that the substituent effect on the overall electron spin distribution is so small, for some substituents which have no formal multiple bonds, that proton couplings can be easily assigned to the various ring positions by introducing into these positions F, Cl, CH<sub>3</sub>, or OCH<sub>3</sub> as substituents instead of the experimentally much more involved specific deuteration of these positions.

The substituted diphenylmethylenefluorenes (1)–(12) were used in this study as substrates for generating radical anions and radical cations. The molecules consist of a fluorene moiety which, as in fluorenone, is not expected to lose its planarity after one-electron reduction or oxidation, and a diphenylmethylene group where restricted rotation of substituted phenyl groups can give rise to rotamers, both in the parent compound and in the radical ions. The olefinic double bond is not expected to be twisted in the parent compound, and the question arises as to how far it is twisted in the radical ions as a result of partial loss of double-bond character and steric repulsion effects.<sup>9</sup>

### Results and Discussion

The substituted diarylmethylenefluorenes (1)–(12) were all synthesized from fluorene and either a benzophenone [for (1)–

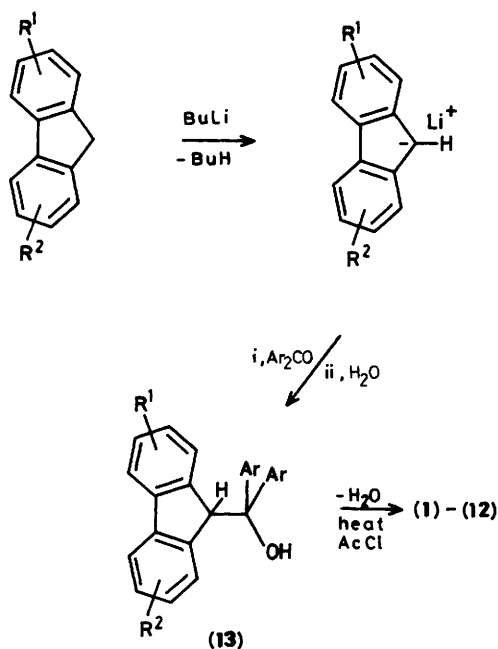


	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>
(1)	H	H	H	H
(2)	H	H	4' - Me	4'' - Me
(3)	H	H	3' - Me	3'' - Me
(4)	H	H	4' - OMe	4'' - OMe
(5)	H	H	4' - Cl	4'' - Cl
(6)	H	H	4' - F	4'' - F
(7)	H	H	3' - F	3'' - F
(8)	H	H	2' - F	2'' - F
(9)	2 - Cl	7 - Cl	H	H
(10)	3 - Me	H	H	H
(11)	2 - Me	H	H	H

(11)] or dihydrodibenzotropone [for (12)] (Scheme), without purification of the intermediate carbinols (13). Three alkenes [(1), (4), and (5)] were already known;<sup>10–12</sup> the other nine [(2), (3), and (6)–(12)] were identified by elementary analysis and <sup>1</sup>H n.m.r. and mass spectroscopy (see Experimental section).

The alkenes were reduced to their radical anions by alkali metal in tetrahydrofuran (THF), and oxidized to their radical cations with aluminium trichloride in dichloromethane. Both types of radical ion were studied by e.s.r., ENDOR, and TRIPLE resonance.

To confirm that the one-electron reduction was reversible without secondary alteration of the molecular structure, the reductions were also studied for the alkenes (1)–(11) by cyclic voltammetry in *N,N*-dimethylformamide (DMF), using tetraethylammonium perchlorate as supporting electrolyte. The experiments showed a first reversible wave with half-wave



Scheme.

reduction potentials ( $E_{\frac{1}{2}}$ ) relative to a saturated calomel electrode (Table 1) dependent on the electron-attracting capacity of the substituent. The reduction is energetically favoured for the alkenes bearing an electron-attracting substituent. These alkenes showed lower  $E_{\frac{1}{2}}$  values than the unsubstituted material.

The values shown in Table 1 exhibit a correlation between  $E_{\frac{1}{2}}$  and the Hammett substituent constants  $\sigma$  for the alkenes with substituted phenyl rings [equation (ii), with  $n = 8$  and  $R =$

$$\delta E_{\frac{1}{2}} = -0.01 + 0.157\sigma \quad (\text{ii})$$

0.984;  $\delta$  is the Leffler–Grunwald operator,  $n$  the number of experimental points, and  $R$  the correlation coefficient].

Reduction of the alkenes (1)–(12) with alkali metals in THF led to long-lived (several weeks) solutions of radical anions, even at room temperature, and well resolved e.s.r. spectra were obtained (Figure 1). Table 2 shows the hyperfine splitting constants (h.s.c.s) of the radical anions (1) $^{\cdot-}$  to (11) $^{\cdot-}$  obtained by reduction of (1)–(11) with sodium in THF and by reduction of (1) with caesium in THF. The values result from the simulation of e.s.r. spectra using the values obtained from ENDOR spectroscopy as initial trials. The relative signs of the h.s.c.s were obtained experimentally by TRIPLE resonance spectroscopy.

The assignment of the h.s.c.s to positions in the molecule (except those for positions 1,8 and 4,5 which were obtained exclusively by spin density calculations) was studied by substitution of hydrogen atoms of the alkene (1) by methyl, methoxy, and halogen independently of theoretical calculations.

In order to use this method instead of deuterium substitution one has to be sure that the overall spin distribution in the radical anion is so little affected by the introduction of substituents that the relative order of spin densities in the position of highest positive spin density is not reversed. This is a reasonable assumption for the substituents chosen.<sup>5,7</sup> The h.s.c. value of the *para* ring protons was thus assigned by comparing the spectrum of (1) $^{\cdot-}$  with that of either (2) $^{\cdot-}$  or (4) $^{\cdot-}$ . The h.s.c. values for positions 3 and 6 were assigned by comparing the spectrum of (1) $^{\cdot-}$  with that of (10) $^{\cdot-}$ . The h.s.c. of positions 2 and 7 were

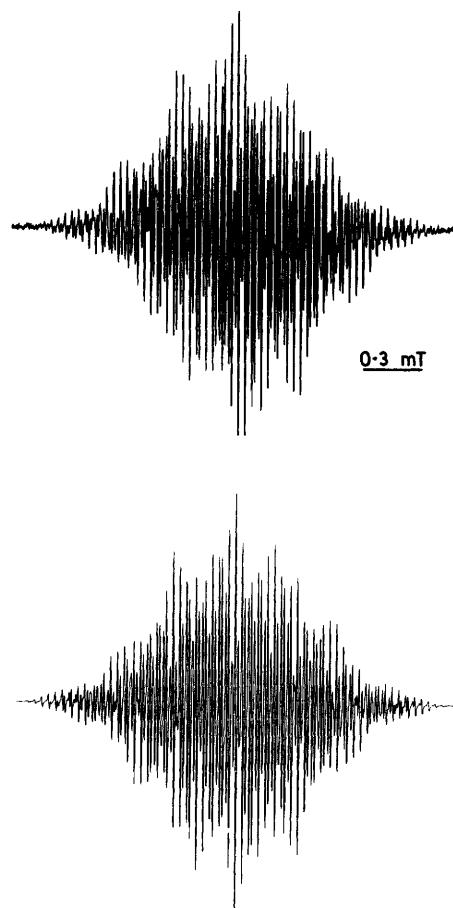


Figure 1. E.s.r. spectrum of the radical anion (9) $^{\cdot-}$  of 2,7-dichloro-9-diphenylmethylenefluorene in THF

assigned by comparing the spectrum of (1) $^{\cdot-}$  either with that of (9) $^{\cdot-}$  (Figure 1) or with that of (11) $^{\cdot-}$ .

In the various e.s.r. spectra two different values were obtained for the *ortho*-protons and also two different values for the *meta*-protons of the phenyl rings. This shows that two non-equivalent sets of *ortho*-protons and of *meta*-protons exist; therefore the rotations around the bonds C( $\alpha$ )–C(1') and C( $\alpha$ )–C(1'') [Figure 2(a)] are frozen on the e.s.r. time scale.

The interaction of the hydrogen atoms in positions 1 and 8 of the alkenes (1)–(12) with the  $\pi$  electrons of the phenyl rings, which are twisted out of the plane of the fluorene ring, is shown by their n.m.r. spectra: a peak can always be seen which can be assigned to protons 1 and 8, with chemical shifts between  $\delta$  6.4 and 6.6, *viz.* at a higher field than the other aromatic protons.

In the ENDOR spectrum of (3) $^{\cdot-}$  [Figure 3(a)] a strong signal appears which corresponds to h.s.c. 63.8  $\mu$ T. In the special TRIPLE resonance experiment the signal appearing at this frequency is three times stronger than the others [Figure 3(b)]. As shown in Table 2, the value 63.8  $\mu$ T can therefore be assigned to the methyl protons. The existence of only one signal for both methyl groups shows that of the three possible conformational isomers only one is present, which means that *meta*-methyl groups lock the conformation.

The result is verified by *ortho*-fluorine substitution: in the ENDOR spectrum of (8) $^{\cdot-}$  only one h.s.c. corresponding to 204.5  $\mu$ T appears.

In both cases where there is a choice between two pairs of either *ortho*- or *meta*-positions, the aromatic hydrogen h.s.c. of (1) $^{\cdot-}$ , which is missing in the ENDOR spectra of (7) $^{\cdot-}$  and (8) $^{\cdot-}$ ,

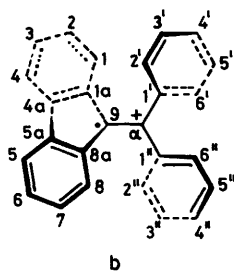
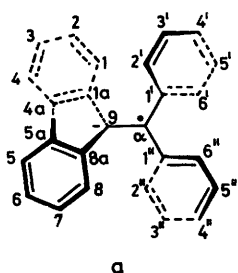
**Table 1.** Experimental half-wave reduction potentials (*versus* saturated calomel electrode) of the alkenes (1)–(11) in DMF

$E_{1/2}/V$	Alkene									
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(9)	(10)	(11)
	-1.53	-1.6	-1.57	-1.62	-1.49	-1.52	-1.42	-1.55	-1.59	-1.55

**Table 2.** Experimental h.s.c.s ( $a_H/\mu T$ ) for radical anions (1)<sup>-•</sup> to (11)<sup>-•</sup> in THF and calculated values for (1)<sup>-•</sup>

		Ring positions								
		1,8	2,2	3,6	4,5	2',2'	3',3''	4',4''	5',5''	6',6''
(1)	Na	-84.5	11.2	-135.0	39.9	-198.2	67.0	-260.0	104.4	-220.6
	Cs	-83.9	8.9	-134.8	36.6	-205.3	70.5	-262.5	108.0	-224.0
	(Calc. <sup>a</sup> )	-75.0	10.4	-158.9	56.7	-221.8	71.8	-251.1	176.8	-231.1
(2)	Na	-74.5	8.9	-127.6	37.5	-205.3	74.5	272.3	106.2	-225.9
(3)	Na	-83.0	11.0	-131.2	39.0	-196.2	-63.8	-255.6	105.3	-215.0
(4)	Na	-69.6	7.7	-120.0	34.8	-217.8	75.0	22.0 <sup>b</sup>	107.0	-237.5
(5)	Na	-95.5	17.0	-143.8	44.0	-190.6	65.9		104.0	-216.0
(6)	Na	-89.6	14.3	-139.5	40.0	-210.7	75.3	540.0 <sup>b</sup>	109.6	-223.0
(7)	Na	-98.2	18.7	-144.6	43.8	-194.6	53.5	-245.5	-160.7 <sup>b</sup>	-212.5
							-134.8 <sup>b</sup>		98.2	
(8)	Na	-101.7	16.0	-148.0	43.0	293.9 <sup>b</sup>	62.5	-246.0	101.7	-204.5
(9)	Na	-75.0		-123.2	36.6	-211.6	75.0	-267.8	110.7	-230.0
(10)	Na	-87.0	11.4	-136.6	40.0	-193.7	64.3	-256.2	101.7	-214.0
(11)	Na	-86.0	-11.0	-136.0	40.0	-195.0	66.1	-257.8	103.9	-217.8

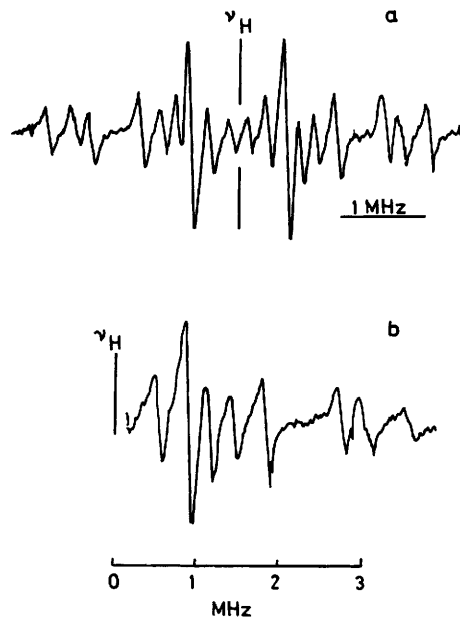
<sup>a</sup> Calculated h.s.c.s ( $a_H/\mu T$ ) for (1)<sup>-•</sup> with  $Q_{CH}^H = -3400 \mu T$  and  $\gamma_{9,1a} = \gamma_{9,8a} = \gamma_{9,\alpha} = 0.9$ ;  $\gamma_{4a,5a} = 0.7$ ;  $\gamma_{\alpha,1'} = \gamma_{\alpha,1''} = 0.85$ ;  $\delta_{C-2'} = \delta_{C-2''} = -0.05$ ;  $\delta_{C-1} = -0.1$ . <sup>b</sup> Values not corresponding to aromatic protons but to <sup>1</sup>H couplings of OCH<sub>3</sub> or CH<sub>3</sub>, or <sup>19</sup>F couplings.

**Figure 2.** (a) Radical anion (1)<sup>-•</sup> and (b) radical cation (1)<sup>+•</sup> of 9-diphenylmethylenefluorene with indication of preferential conformations

is the one with the lower value, showing that in the two radical anions the same kind of conformational isomer is energetically favoured.

If one assumes a helicoid arrangement of the phenyl groups, such as shown in Figure 2(a), and if one also compares the spectra of the radical anions (1)<sup>-•</sup> to (11)<sup>-•</sup> with that of (12)<sup>-•</sup> (Table 3) the evidence is in favour of the methyl substituents in (3)<sup>-•</sup> and the fluorine substituents in (8)<sup>-•</sup> lying in the *exo*-positions [3',3''-dimethyl and 2',2''-difluoro for the conformation shown in Figure 2(a)].

In the ENDOR spectrum of (7)<sup>-•</sup> two different h.s.c.s for the *meta*-fluorine atoms can be seen (160.7 and 134.8  $\mu T$ ), together with two different *meta*-hydrogen h.s.c.s (53.5 and 98.2  $\mu T$ ), showing that this radical anion can exist in any of the predictable conformations, which might be expected to have nearly equal energies and therefore nearly equal populations. X-Ray diffraction studies have shown that the alkene (7) is a mixture of two rotamers even before reduction to its radical anion.<sup>13</sup> The fact that the signal corresponding to the *meta*-hydrogen h.s.c. of 98.2  $\mu T$  is stronger than the one corresponding to the value of 53.5  $\mu T$  leads to the conclusion

**Figure 3** (1) ENDOR Spectrum and (b) special TRIPLE spectrum of the radical anion (3)<sup>-•</sup> of 9-di-*m*-tolylmethylenefluorene in THF

that the more stable conformation is that where the fluorine substituents are in the 3'- and 3''-positions [*exo,exo*; see Figure 2(a)].

No chlorine splittings were detected for (5)<sup>-•</sup> and (9)<sup>-•</sup>. The ratios of fluorine splittings in (6)<sup>-•</sup>, (7)<sup>-•</sup>, and (8)<sup>-•</sup> to the splittings of the protons which in (1)<sup>-•</sup> occupy the same positions are the following: 2.08 for (6)<sup>-•</sup>; 1.5 and 2.01 for (7)<sup>-•</sup>; and 1.5 for (8)<sup>-•</sup>. These ratios are in reasonable agreement with those reported.<sup>14</sup>

**Table 3.** Experimental and calculated h.s.c.s ( $a_{\text{H}}/\mu\text{T}$ ) for  $(12)^{-\cdot-} \text{Na}^+$  in THF. The h.s.c.s were calculated by McLachlan's method with  $Q_{\text{CH}}^{\text{H}} = -3\,400 \mu\text{T}$  and  $Q_{\text{C-CH}_3}^{\text{H}} = 3\,400 \mu\text{T}$ 

		Ring positions									
		1,8	2,7	3,6	4,5	4',6'	3',7'	2',8'	9',1'	10',11' (ax)	10',11' (eq)
(12)	Exp.	-66.0	20.0	-110.0	44.0	-264.0	88.0	-320.0	110.0	286.0	88.0
	Calc. <sup>a</sup>	-61.4	7.2	-125.8	44.2	-272.0	88.0	-292.0	91.8	282.0	

<sup>a</sup>  $\gamma_{9,1a} = \gamma_{9,8a} = 0.9$ ;  $\gamma_{4a,5a} = 0.8$ ;  $\gamma_{9,5'} = 0.8$ ;  $\gamma_{5',4'a} = \gamma_{5',5'a} = 0.95$ .

**Table 4.** Experimental *versus* calculated h.s.c.s ( $a_{\text{H}}/\mu\text{T}$ ) for radical cation  $(1)^{+\cdot}$  and experimental h.s.c.s for  $(2)^{+\cdot}$  to  $(4)^{+\cdot}$ ,  $(10)^{+\cdot}$  and  $(11)^{+\cdot}$ 

		Ring positions									
		1,8	2,7	3,6	4,5	2',2''	3',3''	4',4''	5',5''	6',6''	
(1)	Exp.	-265.0	75.0	246.0		-110.7	24.5	-143.9	55.3	-120.7	
	Calc. <sup>a</sup>	-266.0	78.9	218.0	18.9	-117.8	43.4	-138.2	57.8	-131.0	
(2)	Exp.	-275.0	68.9	-255.7		-85.0	14.3	185.7	53.9	-94.3	
(3)	Exp.	-268.9	73.9	246.1		-97.8	-22.8	146.8	56.0	-100.0	
(4)	Exp.	-285.7	63.9	-268.9	12.1	-39.2	19.6	39.3	26.1	57.9	
(10)	Exp.	-245.7	78.9	195.0		-107.8	29.6	-145.0	79.9	-112.8	
(11)	Exp.	-257.1	-77.8	-236.0		-107.0	26.0	-143.9	75.0	101.8	

<sup>a</sup>  $\gamma_{9,1a} = \gamma_{9,8a} = \gamma_{4a,5a} = 0.8$ ;  $\gamma_{9,2} = 0.9$ ;  $\gamma_{2,1'} = \gamma_{2,1''} = 0.65$ ;  $\delta_{\text{C-2}'} = \delta_{\text{C-2}''} = 0.1$ .

Theoretical values for h.s.c.s of  $(1)^{-\cdot-}$  to  $(11)^{-\cdot-}$  were calculated by the Hückel-McLachlan spin density method using  $\lambda = 1.2$ , McConnell constants  $Q_{\text{CH}}^{\text{H}} = -3\,400 \mu\text{T}$ ,  $Q_{\text{C-CH}_3}^{\text{H}} = 3\,400 \mu\text{T}$ , and the usual correction parameters for the substituents. For the sake of brevity only the calculations referring to  $(1)^{-\cdot-}$  are included in Table 2; a similar degree of agreement was found for  $(2)^{-\cdot-}$  to  $(11)^{-\cdot-}$ .

The best fit in the calculations was achieved by assuming an angle of rotation  $\theta$  for the phenyl groups relative to the plane of the three bonds around C- $\alpha$  [Figure 2(a)] of  $32^\circ$  ( $\beta_{\alpha,1'} = \beta_{\alpha,1''} = \beta_{\text{CC}} \cos \theta = 0.85$ ), and an angle  $\theta'$  between this plane and the fluorene plane of  $25^\circ$  ( $\beta_{9,1a} = \beta_{\text{CC}} \cos \theta' = 0.9\beta$ ). The bonds between C-9 and C-1a, C-4a and C-5a, and C-8a and C-9 of the fluorene ring were considered to be longer than the bonds in the phenyl rings, according to the values from X-ray diffraction for the fluorene molecule.<sup>15</sup>

The non-equivalence of the two pairs of *ortho*-protons and of the two pairs of *meta*-protons was taken into account in the calculations by using a Coulomb adjusting parameter  $\delta_{\text{C}} = -0.05$  for the C-2' and -2''.

The rotation angle  $\theta$  is considered to be approximately the same for the radical anions of the various alkenes regardless of the substituents because a slight variation is observed in the ratio between the couplings of two non-equivalent pairs of *ortho*-protons attached to the same phenyl ring ( $1.09 < a_{2'}/a_{6'} = a_{2''}/a_{6''} < 1.12$ ). The same applies to the *meta* positions ( $1.43 < a_{3'}/a_{5'} = a_{3''}/a_{5''} < 1.65$ ).

A slight decrease is observed in the overall spin density of the fluorene ring system with increasing radius of the alkali cation (from lithium to caesium), *i.e.* the tighter the ion pair, the smaller the spin density in the fluorene ring system. This is to be expected because the higher the negative excess of charge density in the fluorene moiety the lower the electron spin density in that region.

The h.s.c.s of the radical anions do not change with temperature, except those of the methoxy-protons in  $(4)^{-\cdot-}$  which increase as the temperature decreases [ $a_{\text{H}(\text{OCH}_3)} = 0.332 - 0.0004 T$ ].

The increase in spin density in the phenyl rings of  $(12)^{-\cdot-}$  (Table 3) shows a change in the values of  $\theta$  and  $\theta'$ , in accord with

the results of the calculations, since the best fit was achieved for  $\theta = 18^\circ$  and  $\theta' = 36^\circ$ . The more stable conformation of  $(12)^{-\cdot-}$ , corresponding to a more extensive planarity of the  $\pi$  system, leads to the appearance of two equatorial protons and two axial protons connected to the C-10' and C-11'. In this conformation the larger coupling ( $a_{10'} = a_{11'} = 286.0 \mu\text{T}$ ) corresponds to the axial protons.

Table 4 shows the h.s.c.s of the radical cations  $(1)^{+\cdot}$  to  $(11)^{+\cdot}$  [Figure 2(b)] obtained by oxidation of the alkenes  $(1)$ – $(11)$  with aluminium trichloride in dichloromethane. Since there is no simple relationship between the energies and the orbital coefficients of the bonding and antibonding molecular orbitals in non-alternant hydrocarbons, the assignment of the h.s.c. to each position results from the examination of the effects of the introduction of substituents independently of the assignment for the radical anions and of the results of the theoretical calculations. The h.s.c. of the *para* ring protons was determined by comparing the spectrum of  $(1)^{+\cdot}$  with that of either  $(2)^{+\cdot}$  or  $(4)^{+\cdot}$ . The h.s.c. for the 3- and 6-protons was determined by comparing the spectrum of  $(1)^{+\cdot}$  with that of  $(10)^{+\cdot}$ . The h.s.c. for positions 2 and 7 was determined by comparing the spectrum of  $(1)^{+\cdot}$  with that of  $(11)^{+\cdot}$ , and the h.s.c. of the *meta*-protons by comparing the spectrum of  $(1)^{+\cdot}$  with that of  $(3)^{+\cdot}$ .

The theoretical values calculated by the Hückel-McLachlan spin density method are shown for  $(1)^{+\cdot}$  in Table 4. Those for the remaining radical cations displayed the same degree of agreement when the usual correction parameters for the substituents and the McConnell constants were used. The best fit in the calculations was achieved for an angle  $\theta = 50^\circ$ .

From Tables 2 and 4 we can conclude that, for the alkenes  $(1)$ – $(12)$ , the spin density in the radical anions is mainly localized in the diphenylmethyl group, but for the radical cations it is mainly localized in the fluorene portion. These results are consistent with a larger contribution of the valence bond structure shown in Figure 2(a) to the resonance hybrid  $(1)^{-\cdot-}$  and a larger contribution of the structure in Figure 2(b) to the hybrid  $(1)^{+\cdot}$ .

Examination of the values shown in Tables 2 (radical anions) and 4 (radical cations) reveals relatively small changes in h.s.c.s for different substituted alkenes as a result of the introduction of

**Table 5.** Numerical values for the expression (iii)

	Substituent	$10^2a$	$\rho$	$n^c$	$R^d$	$F^e$
Radical anion <sup>a</sup>	In the aryl groups	-0.7	0.147	7	0.989	227.59
	In the fluorene moiety	-0.23	-0.183	4	0.999	1 318
Radical cation <sup>b</sup>	In the aryl groups	0.6	-0.269	4	0.999	1 561
	In the fluorene moiety	-0.32	0.311	3	0.996	125.6

<sup>a</sup> Versus  $\sigma$ . <sup>b</sup> Versus  $\sigma^+$ . <sup>c</sup> Number of experimental points. <sup>d</sup> Correlation coefficient. <sup>e</sup> Fisher parameter.

electron-withdrawing and electron-donating substituents. These variations of the spin distribution were studied by regression analysis versus Hammett's substituent constants  $\sigma$ .

If we consider  $\Sigma|a_{F1}|$  the sum of the h.s.c.s of the fluorenyl protons and  $\Sigma|a_{Ph}|$  the sum of the h.s.c.s of the protons in the diphenylmethyl group (except the 4'- and 4''-positions), correlations are obtained which describe the influence of substituents on the spin density distribution. The general expression is equation (iii) ( $s$  = substituted;  $o$  = unsubstituted). The numerical values are shown in Table 5.

$$\log(\Sigma|a_{F1}|/\Sigma|a_{Ph}|_s)/(\Sigma|a_{F1}|/\Sigma|a_{Ph}|_o) = a + \rho\sigma \quad (\text{iii})$$

From the  $\rho$  values we can conclude that the influence of substitution in the diphenylmethyl group is opposite in sign to that for the same substitution in the fluorene moiety. The sensitivity to substitution is larger in the fluorene moiety for radical anions (larger negative charge density), whereas in the radical cations the diphenylmethyl moiety is the more sensitive (larger positive charge density).

In the regression analysis, the substituent effect in the positions lacking hydrogen could not be considered; nevertheless analogous trends were obtained with the calculated values for all positions. The ratio  $\rho_o/\rho_s$  for the radical anion increases with decrease in the electron-donating effect of the substituent in the diphenylmethyl group.

In order to estimate quantitatively the relative importance of the radical stabilization vs. charge stabilization a Hammett diparametric relationship (iv) was studied using the  $\sigma^+$  values

$$\log(\Sigma|a_{F1}|/\Sigma|a_{Ph}|_s)/(\Sigma|a_{F1}|/\Sigma|a_{Ph}|_o) = a + \rho\sigma + \rho^+\sigma^+ = -0.007 + 0.145\sigma - 0.052\sigma^+ \quad (\text{iv})$$

$n = 7$ ;  $R = 0.989$

from Dust and Arnold.<sup>1</sup> The relative contributions of  $\rho$  and  $\rho^+$  are, respectively, 98 and 2%; this confirms the dominant importance of charge stabilization on electron spin distribution in radical ions.

We also conclude that, contrary to the alkenes, which have an untwisted olefinic bond [shown e.g. for (7)], the radical ions have twist angles  $\theta'$  estimated to be 25° for (1)<sup>-•</sup> to (11)<sup>-•</sup>, (1)<sup>+•</sup> to (4)<sup>+•</sup>, (10)<sup>+•</sup>, and (11)<sup>+•</sup>, and 36° for (12)<sup>+•</sup>. This is in accord with earlier results e.g. on the radical anion of tetraphenylethylene.

## Experimental

Solvents supplied by B.D.H. were dried and freed from oxygen as follows. Tetrahydrofuran (THF) (reagent grade) was dried

with LiAlH<sub>4</sub>, distilled from sodium benzophenone ketyl in a vacuum line and stored over Na-K alloy (1:4) under vacuum. Analytical grade *N,N*-dimethylformamide (DMF) and dichloromethane were dried over 3 Å molecular sieves (Fluka).

Benzophenone, fluorene (B.D.H.), 4,4'-dichlorobenzophenone, 4,4'-difluorobenzophenone, 4,4'-dimethoxybenzophenone, dibenzosuberone, and dibenzotropone (Ega Chemie) were recrystallized before use. 1-Bromo-2-fluorobenzene (Ega Chemie) was used as supplied.

<sup>1</sup>H N.m.r. spectra were determined with JEOL JNM PS 100 and Bruker 300 CXP instruments, with Me<sub>4</sub>Si as internal standard.

**Synthetic Procedures.**—The alkenes (1)–(12) were synthesized according to a procedure described in detail for 9-di-*p*-tolylmethylenefluorene (2), which can be used for the alkenes (1) and (3)–(12) with the adaptations quoted. For 9-bis-(3-fluorophenyl)methylenefluorene (6) and 9-bis-(2-fluorophenyl)methylenefluorene (7) the corresponding fluorinated benzophenones<sup>16</sup> were not commercially available. They were synthesized by different procedure described later.

**3,3'-Difluorobenzophenone.** A mixture of 3,3'-diaminobenzophenone<sup>17</sup> (18 g, 0.085 mol) and 38% tetrafluoroboric acid (400 ml) was heated to form a salt and cooled to 5 °C. A saturated solution of sodium nitrite (20 g, 0.29 mol) was added dropwise with stirring. After a further 30 min stirring the diazonium salt was filtered off and washed with cold 5% tetrafluoroboric acid, methanol, and ether, and dried. The salt was decomposed by gently heating a suspension in toluene (3 l) to give the expected ketone (13 g, 70%), m.p. 61–61.5 °C (from light petroleum) (lit.,<sup>16</sup> 61.5 °C).

**2,2'-Difluorobenzophenone.** To a solution of 1-bromo-2-fluorobenzene (8.8 g, 0.05 mol) in THF (100 ml) at -70 °C, butyllithium (0.05 mol) in hexane (38 ml) was slowly added. At the same temperature, ethyl formate (1.85 g, 0.025 mol) was added. The carbinol thus obtained was oxidized with potassium dichromate, giving the expected ketone, which was purified by reduced-pressure distillation; yield 5.4 g [(60%); b.p. 119 °C at 1.5 mmHg] (lit.,<sup>16</sup> 158–159 °C at 8.1 mmHg);  $n_D^{23}$  1.569 (lit.,<sup>16</sup>  $n_D^{23.5}$  1.5685).

**9-Di-*p*-tolylmethylenefluorene (2)** [general procedure for alkenes (1)–(12)]. A four-necked flask (250 ml) fitted with a stirrer, a low-temperature thermometer, an argon inlet, and a rubber septum was thoroughly cleaned, dried, flamed-out, and cooled under a stream of dry argon immediately before use. Pure, dry THF (100 ml) and fluorene (1.66 g, 0.01 mol) were introduced. The solution was cooled to -100 °C and *n*-butyllithium in hexane (7.8 ml, 0.01 mol) (supplied by Merck and titrated by the method of Gilman and Haubein<sup>18</sup>) was slowly added over 15 min. After 30 min at -100 °C, a solution of 4,4'-dimethylbenzophenone<sup>19</sup> (1.47 g, 0.007 mol) in THF (10 ml) was added. The temperature was kept at -100 °C for 1 h, then the mixture was allowed to warm up slowly. At room temperature it was added to half-saturated ammonium chloride solution; the organic layer was extracted with ether and dried (MgSO<sub>4</sub>). The alcohol obtained was converted into the alkene (2) by heating with an excess of acetyl chloride, giving yellow crystals (1.5 g, 60%), m.p. 137 °C (from ethyl acetate) (Found: C, 93.75; H, 6.15. C<sub>28</sub>H<sub>22</sub> requires C, 93.8; H, 6.1%);  $\delta$ (CD<sub>3</sub>COCD<sub>3</sub>) 2.74 (6 H, s, CH<sub>3</sub>), 6.713 (2 H, d, *J* 7.5 Hz), 6.95 (2 H, t, *J* 7.5 Hz), 7.3 (10 H, m), and 7.82 (2 H, d, *J* 7.5 Hz); *m/z* 358 (*M*<sup>+</sup>, 100%), 343 (33), 328 (22.2), and 266 (27.7).

**9-Diphenylmethylenefluorene (1).** Benzophenone (1.27 g, 0.007 mol) in THF (10 ml) was added to fluorene (1.66 g, 0.01 mol) according to the general procedure. The alkene (1) was obtained as white crystals (1.62 g, 70%), m.p. 235 °C (from ethyl acetate) (lit.,<sup>10</sup> 235–236 °C) (Found: C, 94.5; H, 5.5. Calc. for C<sub>26</sub>H<sub>18</sub>: C, 94.5; H, 5.45%);  $\delta$ (CD<sub>3</sub>COCD<sub>3</sub>) 6.565 (2 H, d, *J* 9

Hz), 6.93 (2 H, t, *J* 6 Hz), 7.27 (2 H, t, *J* 9 Hz), 7.48 (10 H, m), and 7.805 (2 H, d, *J* 9 Hz).

**9-Di-*m*-tolylmethylenefluorene (3).** 3,3'-Dimethylbenzophenone<sup>20</sup> (1.47 g, 0.007 mol) in THF (10 ml) was added to the fluorene solution according to the general procedure. The alkene (3) was obtained as white crystals (1.38 g, 55%), m.p. 224 °C (from ethyl acetate) (Found: C, 93.6; H, 6.15. C<sub>28</sub>H<sub>22</sub> requires C, 93.8; H, 6.1%; δ(CD<sub>3</sub>COCD<sub>3</sub>) 2.417 (6 H, s, CH<sub>3</sub>), 6.58 (2 H, d, *J* 9.5 Hz), 6.95 (2 H, t, *J* 9.5 Hz), 7.28 (10 H, m), and 7.827 (2 H, d, *J* 8.3 Hz); *m/z* 358 (*M*<sup>+</sup>, 100%), 343 (35.8), 328 (10.25), and 266 (35.8).

**9-Bis-(4-methoxyphenyl)methylenefluorene (4).** 4,4'-Dimethoxybenzophenone (1.67 g, 0.007 mol) in THF (10 ml) was added to the fluorene solution according to the general procedure. The alcohol obtained was heated with H<sub>2</sub>SO<sub>4</sub>-benzene (50%) yielding the alkene (4) (1.77 g, 65%) as yellow crystals, m.p. 152 °C (from ethyl acetate) (lit.,<sup>11</sup> 153–154 °C) (Found: C 86.2; H, 5.7. Calc. for C<sub>28</sub>H<sub>22</sub>O<sub>2</sub>: C, 86.15; H, 5.6%; δ(CD<sub>3</sub>COCD<sub>3</sub>) 3.872 (6 H, s, CH<sub>3</sub>), 6.575 (2 H, d, *J* 7.3 Hz), 7.055 (6 H, m), 7.231 (6 H, m), and 7.797 (2 H, d, *J* 7.8 Hz).

**9-Bis-(4-fluorophenyl)methylenefluorene (6).** 4,4'-Difluorobenzophenone (1.53 g, 0.007 mol) in THF (10 ml) was added to the fluorene solution according to the general procedure. The alkene (6) (1.9 g, 75%) was obtained as pale yellow crystals, m.p. 217 °C (from ethyl acetate) (Found: C, 85.45; H, 4.3. Calc. for C<sub>26</sub>H<sub>16</sub>F<sub>2</sub>: C, 85.2; H, 4.4%; δ(CDCl<sub>3</sub>) 6.66 (2 H, d, *J* 8.3 Hz), 7.250 (12 H, m), and 7.69 (2 H, d, *J* 6.9 Hz).

**9-Bis-(3-fluorophenyl)methylenefluorene (7).** 3,3'-Difluorobenzophenone (1.53 g, 0.007 mol) in THF (10 ml) was added to the fluorene solution. The alkene (7) (1.9 g, 75%) was obtained as white crystals, m.p. 181 °C (from ethyl acetate) (Found: C, 85.1; H, 4.3. C<sub>26</sub>H<sub>16</sub>F<sub>2</sub> requires C, 85.2; H, 4.4%; δ[(CD<sub>3</sub>)<sub>2</sub>CO] 6.575 (2 H, d, *J* 9 Hz), 6.99 (2 H, t, *J* 9 Hz), 7.31 (10 H, m), and 7.825 (2 H, d, *J* 9 Hz); *m/z* 366 (*M*<sup>+</sup>, 100%) and 272 (82.3).

**9-Bis-(2-fluorophenyl)methylenefluorene (8).** 2,2'-Difluorobenzophenone (1.53 g, 0.007 mol) in THF (10 ml) was added to the fluorene solution according to the general procedure. The alkene (8) (1.28 g, 50%) was obtained as white crystals, m.p. 232 °C (from ethyl acetate) (Found: C, 85.3; H, 4.45. C<sub>26</sub>H<sub>16</sub>F<sub>2</sub> requires C, 85.2; H, 4.4%; δ(CD<sub>3</sub>COCD<sub>3</sub>) 6.495 (1 H, d, *J* 7 Hz), 6.645 (1 H, d, *J* 7 Hz), 7 (2 H, t, *J* 7 Hz), 7.33 (10 H, m), and 7.825 (2 H, d, *J* 9 Hz); *m/z* 366 (*M*<sup>+</sup>, 100%), 265 (13), and 191 (43.4).

**2,7-Dichloro-9-diphenylmethylenefluorene (9).** A solution of benzophenone (1.27 g, 0.007 mol) in THF (10 ml) was added to a solution of 2,7-dichlorofluorene<sup>21</sup> (2.35 g, 0.01 mol) according to the general procedure. The alkene (9) (1.67 g, 60%) was obtained as white crystals, m.p. 215 °C (from ethanol) (Found: C, 78.0; H, 4.0. C<sub>26</sub>H<sub>16</sub>Cl<sub>2</sub> requires C, 78.2; H, 4.0%; δ(CD<sub>3</sub>COCD<sub>3</sub>) 6.5 (2 H, s), 7.225 (2 H, d, *J* 9 Hz), 7.575 (10 H, m), and 7.88 (2 H, d, *J* 10.5 Hz); *m/z* 398 [*M*<sup>+</sup>(<sup>35</sup>Cl), 100%], 400 (<sup>37</sup>Cl; 77), 363 (22.2), and 328 (100).

**9-Diphenylmethylene-3-methylfluorene (10).** Benzophenone (1.27 g, 0.007 mol) in THF (10 ml) was added to a solution of 3-methylfluorene<sup>22</sup> (1.8 g, 0.01 mol) according to the general procedure. The alcohol obtained was heated for 2 h with an excess of acetic anhydride and a few drops of sulphuric acid, yielding the alkene (10) (1.68 g, 70%) as white crystals, m.p. 205 °C (from ethyl acetate) (Found: C, 94.2; H, 5.8. C<sub>27</sub>H<sub>20</sub> requires C, 94.2; H, 5.8); δ(CDCl<sub>3</sub>) 2.37 (3 H, s, CH<sub>3</sub>), 6.487 (1 H, d, *J* 7.9 Hz), 6.61 (1 H, d, *J* 7.9 Hz), 6.75 (1 H, d, *J* 7.9 Hz), 6.91 (1 H, t, *J* 7.9 Hz), 7.39 (11 H, m), 7.5 (1 H, s), and 7.67 (1 H, d, *J* 7.9 Hz); *m/z* 344 (*M*<sup>+</sup>, 86.4%), 329 (36), 267 (18), 207 (35.6), 69 (100), and 57 (87.9).

**9-Diphenylmethylene-2-methylfluorene (11).** Benzophenone (1.27 g, 0.007 mol) in THF (10 ml) was added to 2-methylfluorene<sup>22</sup> (1.8 g, 0.01 mol) in THF according to the general procedure. The alcohol thus obtained was heated for 2 h with an excess of acetic anhydride and a few drops of H<sub>2</sub>SO<sub>4</sub>,

yielding the alkene (11) (1.65 g, 70%) as white crystals, m.p. 208 °C (from ethyl acetate) (Found: C, 94.0; H, 6.0. C<sub>27</sub>H<sub>20</sub> requires C, 94.2; H, 5.8%; δ(CDCl<sub>3</sub>) 2.094 (3 H, s, CH<sub>3</sub>), 6.4 (1 H, s), 6.59 (1 H, d, *J* 8.3 Hz), 6.88 (1 H, t, *J* 6.95 Hz), 7.089 (11 H, m), 7.392 (1 H, s), and 7.64 (1 H, d, *J* 7.8 Hz); *m/z* 344 (*M*<sup>+</sup>, 100%), 329 (47), 267 (20), 179 (18), and 163 (24).

**9-(10,11-Dihydrodibenzo[*a,d*]cycloheptadien-5-ylidene)-fluorene (12).** Dibenzosuberone (1.46 g, 0.007 mol) in THF (10 ml) were added to the fluorene solution according to the general procedure. The alcohol thus obtained was refluxed with an excess of acetic anhydride and a few drops of H<sub>2</sub>SO<sub>4</sub>, yielding the alkene (12) (1.49 g, 60%) as white crystals, m.p. 296 °C (from ethyl acetate) (Found: C, 94.3; H, 5.7. C<sub>28</sub>H<sub>20</sub> requires C, 94.4; H, 5.6%; δ(CDCl<sub>3</sub>) 2.87 (2 H, m), 3.48 (2 H, m), 6.855 (2 H, d, *J* 9 Hz), 6.96 (2 H, t, *J* 7.5 Hz), 7.28 (10 H, m), and 7.7 (2 H, d, *J* 9 Hz); *m/z* 356 (*M*<sup>+</sup>, 100%), 265 (13), and 191 (43.4).

*Study of the Radical Ions obtained from the Alkenes (1)–(12).—Cyclic voltammetry.* Reduction experiments were performed in dry DMF (10<sup>-3</sup>M) using as supporting electrolyte tetrabutylammonium perchlorate; saturated calomel was used as reference electrode, dropping mercury as working electrode, and platinum wire as a counter electrode. A Princeton Applied Research 173 potentiostat-galvanostat with 176 current follower and 175 universal programmer was used.

*E.s.r., ENDOR, and TRIPLE Resonance.* The radical anion solutions were prepared under high vacuum by standard techniques. The oxidation was carried out in a double Schlenk tube with one arm containing anhydrous aluminium chloride and the other the compound to be oxidized. This tube was connected to a vacuum line, the aluminium chloride was sublimed, and dichloromethane was distilled into the reaction mixture. The reaction was carried out at room temperature.

E.s.r. spectra were run with a Bruker ER 200D spectrometer equipped with a variable-temperature unit ER 400 VT (Lisbon). ENDOR and TRIPLE spectra were recorded with a Varian E109 spectrometer interfaced with a Bruker ENDOR-TRIPLE resonance system (Cardiff).

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