

## Substituent Effects in Fluoren-9-one Ketyls. Part 3.<sup>1</sup> An Electron Spin Resonance, ENDOR, and TRIPLE Resonance Study of Sodium Ketyl Solutions in Tetrahydrofuran

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A series of ten fluoren-9-ones substituted in positions 2 or 3 or disubstituted in positions 2 and 7 and unsubstituted fluorenone was reduced by sodium in THF. E.s.r. ENDOR, special TRIPLE, and general TRIPLE resonance spectra of the respective sodium ketyls were recorded in the range 170–300 K and evaluated. The coupling constants thus obtained were used to study the effect of the substituents on electron spin distribution within the radical-anions and spin delocalization to the sodium ion. Linear correlations for the sodium couplings as a function of Hammett's substituent constants were found and discussed in terms of a static ion pair structure.

The location of the metal counter-ion in relation to the fluorenone radical-ion in a monomer ketyl was calculated by McClelland<sup>2</sup> in 1961 to be somewhere above the carbonyl bond. Hirota<sup>3–5</sup> proposed however in 1967 a 'dynamic equilibrium model' assuming two rapidly interconverting structures: that predicted by McClelland and another, which would predominate at lower temperatures, where the metal lies in front of the oxygen atom on the extension of the C–O-axis. Hirota<sup>3</sup> also discussed a 'static vibrational model,' assuming that the metal vibrates around a potential energy minimum above the carbonyl bond. Both models are consistent with the positive slope observed for the metal coupling–temperature plot.

Although McClelland's calculation was criticized for neglecting the solvation of the cation, Lubitz, *et al.*<sup>6</sup> found a similar position by INDO calculations of a ternary complex of fluoren-9-one radical-anion, lithium cation, and dimethoxyethane (Fl<sup>•-</sup>–Li<sup>+</sup>–DME) with a tetrahedral arrangement of the two ether oxygen atoms and the carbonyl group around the lithium ion. This geometry gave the best match of calculated spin populations with their e.s.r., ENDOR (proton, <sup>13</sup>C, <sup>17</sup>O, and alkali-metal), and general TRIPLE resonance data.<sup>6</sup> They modified however the 'classical'<sup>3,7</sup> static vibrational model, where the increase of the metal coupling constant with temperature is explained by a longer average permanence of the metal ion in regions of higher electron spin density at higher temperatures (at lower temperatures the amplitude of vibration around a low electron-spin equilibrium position is smaller). Lubitz *et al.*<sup>6</sup> discussed a different possibility. They assumed that the position of the lithium ion relative to the radical-anion does not change with temperature and explained the increase of the lithium coupling with temperature by an increasing withdrawal of the solvent molecule with rising temperature. This is consistent with the known temperature effects on solvation of most hydrocarbon radical-anions<sup>7</sup> and aromatic metal ketyls,<sup>3</sup> which show that the transformation of a contact ion pair into a solvent-shared structure involves a negative entropy change: higher temperatures favour the contact ion pairs through desolvation of the metal ion. Some exceptions are however known, *e.g.* the positive Li, Na, and K coupling constants in ketyls of 1,2,3,4-tetramesitylbenzene decrease with temperature.<sup>8</sup>

The studies of Screttas *et al.* on paramagnetic solvent n.m.r. shift measurements<sup>9</sup> and e.s.r.<sup>10</sup> in ketyl solutions present

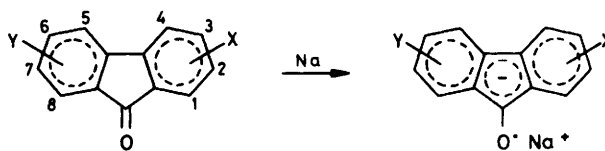
experimental evidence for electron spin delocalization to the solvent in a ternary complex A<sup>•-</sup>–M<sup>+</sup>–(R<sub>2</sub>O)<sub>n</sub> of a radical-anion A<sup>•-</sup> through the mediation of the cation M<sup>+</sup>. This spin delocalization to the solvent should become less effective at higher temperatures as a consequence of desolvation, which would explain the increase of electron spin density at the metal and hence of the metal coupling constant.

In view of this discussion of the effect of temperature on the metal coupling constants, it seemed interesting also to study electronic substituent effects on these constants.

### Experimental

**Materials.**—The fluoren-9-ones (1)–(11) used in this study were synthesized and purified as described elsewhere.<sup>1</sup>

Tetrahydrofuran (THF) was either purified (in Cardiff) as described earlier<sup>11</sup> or (Lisbon) dried successively by refluxing with LiAlH<sub>4</sub> under dry atmosphere, distilled, dried, and deoxygenated by refluxing over sodium wire and benzophenone, until the colour of the blue ketyl becomes visible, stored over ketyl



- |                                |            |
|--------------------------------|------------|
| (1) X = H,                     | Y = H      |
| (2) X = 2 - OCH <sub>3</sub> , | Y = H      |
| (3) X = 3 - OCH <sub>3</sub> , | Y = H      |
| (4) X = 2 - CH <sub>3</sub> ,  | Y = H      |
| (5) X = 3 - CH <sub>3</sub> ,  | Y = H      |
| (6) X = 3 - F,                 | Y = H      |
| (7) X = 3 - Cl,                | Y = H      |
| (8) X = 2 - F,                 | Y = H      |
| (9) X = 2 - F,                 | Y = 7 - F  |
| (10) X = 2 - Cl,               | Y = H      |
| (11) X = 2 - Cl,               | Y = 7 - Cl |

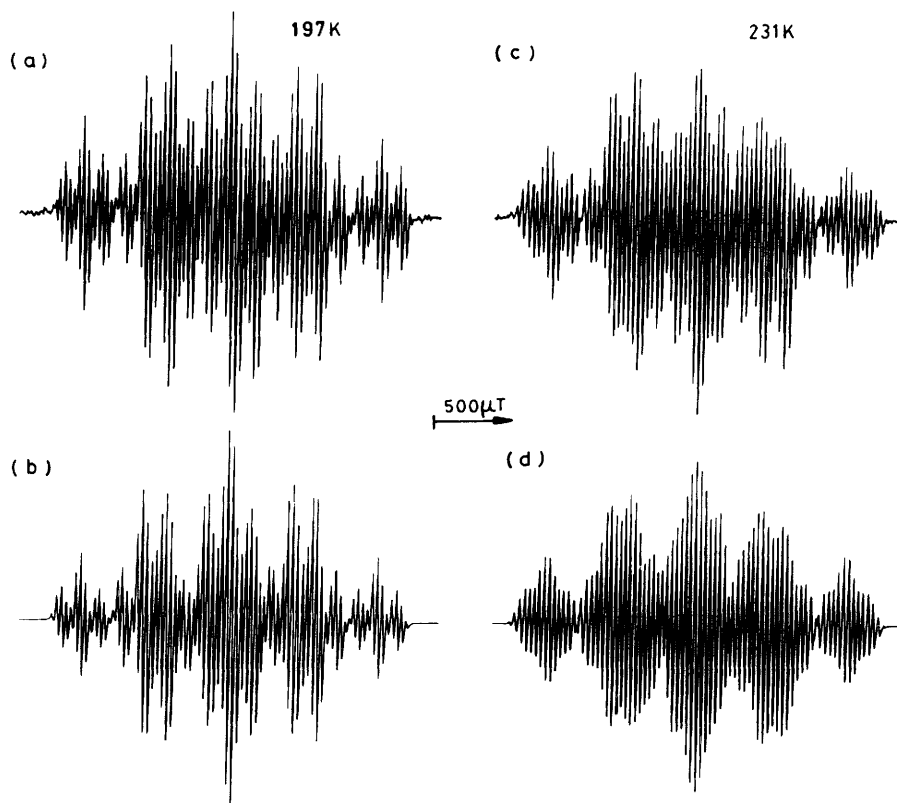


Figure 1. E.s.r. spectra of 2-methylfluoren-9-one-sodium ( $4^{\cdot-}\text{-Na}^+$ ) in THF at: (a) 197 K, (c) 231 K, and corresponding simulations (b) and (d)

solution, distilled in a vacuum line into a vessel containing sodium-potassium alloy (1:4), and subjected to a series of freeze-thawing cycles and distilled into the sample tube.

**Procedure.**—The fluorenone ketyls were made by passing a solution in THF over a freshly prepared sodium film under vacuum as described earlier.<sup>1</sup> Some e.s.r. spectra were recorded on a Bruker 200tt (by courtesy of Universidade Nova de Lisboa) and later on a Bruker 200D spectrometer (at Instituto Superior Técnico) and some on a Varian E109 spectrometer (University College Cardiff), all three equipped with a variable-temperature unit based on blowing cold dinitrogen gas on the sample tube. ENDOR and TRIPLE resonance spectra were recorded on the same Varian E109 spectrometer interfaced with a Bruker ENDOR-TRIPLE resonance system.

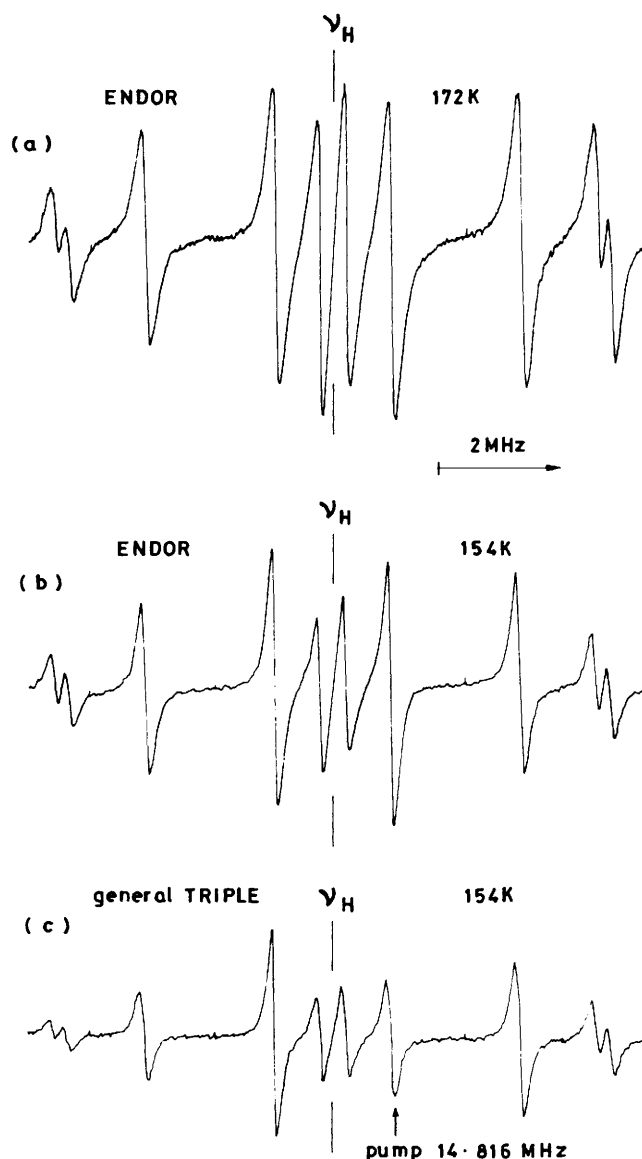
Computer simulation of the e.s.r. spectra were carried out using a fast Fourier transform program previously described,<sup>12</sup> based in most cases on fine adjustments of splitting constants obtained from the ENDOR experiments, also taking advantage of the multiplicities determined through special TRIPLE resonance experiments.

## Results

The e.s.r. spectra of dilute (*ca.*  $10^{-4}$  M) solutions of the sodium ketyls of the fluoren-9-ones (1)–(11) in tetrahydrofuran (THF) were recorded at various temperatures ranging from 190 to 300 K. Examples of such spectra and their simulations are shown in Figure 1. ENDOR and general TRIPLE resonance spectra were also recorded at an overlapping range 160–220 K as exemplified in Figure 2. An exception had to be made for the ketyl of 2-chlorofluoren-9-one (10), which eliminates sodium

chloride at room temperature. In this case the measuring range went up only to 240 K. The values of the coupling constants at 295 K were linearly extrapolated. The proton coupling constants  $a_i$  ( $i = 1-8$ ) determined from ENDOR and special TRIPLE resonance were used as initial data for the computer simulations<sup>12</sup> of the e.s.r. spectra.

In order to analyse the set of e.s.r. spectra of a given ketyl, recorded at various temperatures, the one recorded at temperature  $T_0$  where the sodium coupling constant  $a_{\text{Na}}$  is zero (Figure 1a) was selected. Once the proton coupling constants  $a_i$  had been adjusted in such a way that the simulation of this e.s.r. spectrum became satisfactory, they were used to simulate e.s.r. spectra at temperatures where  $a_{\text{Na}}$  is different from zero. A value for  $a_{\text{Na}}$  had then to be introduced and  $a_i$  had to be again adjusted. Table 1 lists the values of  $a_i$  for the ketyls of (1)–(11) at  $T_0$  for which  $a_{\text{Na}}$  equals zero. Table 2 lists the values of  $a_i$  and  $a_{\text{Na}}$  for 295 K, which led to the best simulation of e.s.r. spectra at that temperature. The sets of proton coupling constants  $a_i$  reported were found to be similar to the corresponding values for the radical-anions of the same fluoren-9-ones, generated by electrolysis in dimethylformamide with tetrabutylammonium as counter-ion, reported elsewhere.<sup>1</sup> They were, however, sufficiently different to allow the conclusion that, even at temperatures for which  $a_{\text{Na}}$  is zero, the sodium ketyls of the substituted fluoren-9-ones are present as ion pairs. The variations of aromatic proton coupling constants  $a_i$  with temperature were found to be quite near to the experimental error for  $a_i$  ( $i = 2-7$ ).  $a_1$  and  $a_8$ , however, changed measurably with temperature, but not in a significantly different way from unsubstituted fluorenone. For this reason it was considered sufficient to report the experimental values of  $a_i$  for  $T = T_0$  and  $T = 295$  K in this publication. It may, however, be worthwhile mentioning an exception: the ketyl of 2,7-difluorofluoren-9-one



**Figure 2.** ENDOR and general TRIPLE resonance spectra of 2-methylfluoren-9-one-sodium ( $4^{-}\text{-Na}^{+}$ ) in THF at various temperatures: (a) ENDOR spectrum at 172 K; (b) ENDOR spectrum at 154 K; (c) general TRIPLE resonance spectrum at 154 K, irradiating at 14.816 MHz

(9) shows no variation of  $a_1 = a_8$  within experimental error between 180 and 295 K.

The signs of the coupling constants reported in Tables 1 and 2 were already known in the cases of fluoren-9-one-sodium<sup>13</sup> and the three isomers of fluorofluoren-9-one-sodium.<sup>14</sup> In the remaining cases the relative signs were determined experimentally by ENDOR and general TRIPLE resonance,<sup>15</sup> as exemplified in Figure 2b for 2-methylfluoren-9-one-sodium ( $4^{-}\text{-Na}^{+}$ ). It was assumed as usual that the proton coupling  $a_i$  with the largest absolute value is negative. It was assumed that for any substituted fluorenone-sodium ketyl the sodium coupling constant  $a_{\text{Na}}$  has the same sign as in unsubstituted fluorenone-sodium, *i.e.* negative at low temperature changing to positive as the temperature increases.<sup>3,13</sup>

No  $^{35}\text{Cl}$  couplings are reported in Tables 1 and 2. They were not observed, presumably because of ENDOR-line broadening caused by the large nuclear quadrupole moment and the

presence of the two isotopes of chlorine.<sup>16</sup> In other cases, where no coupling is mentioned in the Tables, it was too small to be measured or even to be detected at all.

### Discussion

The values of the coupling constants  $a_i$  ( $i = 1-8$ ) of ketyls of (1)–(11) reported in Tables 1 and 2 were compared with those of coupling constants obtained from the e.s.r. spectra of the corresponding radical-anions of (1)–(11) generated electrolytically.<sup>1,14</sup> The tentative assignments of the latter couplings to positions 1–8 had been made by matching them with the magnitude of calculated spin densities.<sup>1</sup>

In the present case of sodium ketyls, the relative signs of the couplings were available from general TRIPLE resonance experiments. Therefore, not only the magnitudes, but also the relative signs of the couplings and the spin densities had to be matched. Whereas for the larger couplings there had been no doubts about their signs (higher reliability of spin density calculation), this had not been the case for the smaller ones in some cases. The assignments thus become more reliable. As the absolute values of the couplings of the electrolytically generated radical-anions closely resemble those of the respective sodium ketyls, care was taken to make both assignments consistent with each other.<sup>1,14</sup>

Further support for these assignments stems from the study of variation with temperature of the couplings of the sodium ketyls. As can be seen by comparing Tables 1 and 2, the sodium couplings  $a_{\text{Na}}$  are most sensitive to changes in temperature. They are followed first by  $a_1$  and  $a_8$ , and second by  $a_2$  and  $a_7$ . Couplings  $a_3-a_6$  change very little with temperature. This pattern was observed for sodium ketyls of both unsubstituted and substituted fluoren-9-ones (by completing with new experiments earlier data for fluoren-9-one<sup>6,13,17</sup> and several isomeric fluorofluoren-9-ones<sup>14</sup>). There is, however, one exception: in 2,7-difluorofluoren-9-one-sodium ( $9^{-}\text{-Na}^{+}$ )  $a_1 = a_8$  do not change measurably with temperature within the range of measurements.

These patterns, once recognized, helped to amend one assignment and to confirm the others, made by matching with electron spin density calculations. The case where the pattern of variation with temperature led to reversing the initial assignment was the sodium ketyl of 2-methoxyfluoren-9-one (2): Although the spin density calculation<sup>1</sup> pointed to  $|a_3| < |a_1|$ , the magnitude  $|-288 \mu\text{T}|$  (identical for  $T = T_0 = 190 \text{ K}$  and  $T = 295 \text{ K}$ ) was assigned to position 3 instead of 1, although larger than  $|-247 \mu\text{T}|$  (190 K) and  $|-251 \mu\text{T}|$  (295 K), which were eventually assigned to position 1.

Other conclusions, which could be extracted from the values of the aromatic proton coupling constants, were obtained by examining the difference  $|a_1| - |a_8|$  for the radicals obtained from 3-substituted fluoren-9-ones. The values of the difference  $|a_1| - |a_8|$  are practically identical for the radical-anion generated electrolytically in dimethylformamide<sup>1</sup> and the sodium ketyl in THF of each 3-substituted fluoren-9-one. As the tetrabutylammonium ion in DMF interacts much more weakly with the radical-anion than the sodium ion in THF, one can conclude that the introduction of a substituent in position 3 does not shift the sodium ion noticeably out of the plane perpendicular to the plane of the ring system (Figure 3,  $y = 0$ ), containing the carbonyl bond.

No alternating line-width effects throughout the temperature range used for the e.s.r. experiments were observed in any case, which might give evidence for a dynamic equilibrium between two positions of the sodium ion relatively to the radical-anion. This supports a static vibrational model for these ketyls, with the geometry used for the INDO calculations of Lubitz *et al.*<sup>6</sup> and the earlier calculation of McClelland.<sup>2</sup>

**Table 1.** Hyperfine couplings of fluorenone-sodium ( $1^{--}\text{-Na}^+$ )—( $11^{--}\text{-Na}^+$ ) in the THF from e.s.r. spectra:  $^1\text{H}$  and  $^{19}\text{F}$  couplings  $a_i$  at positions  $i = 1$ —8 and at temperature  $T_0$  for which  $a_{\text{Na}} = 0$ 

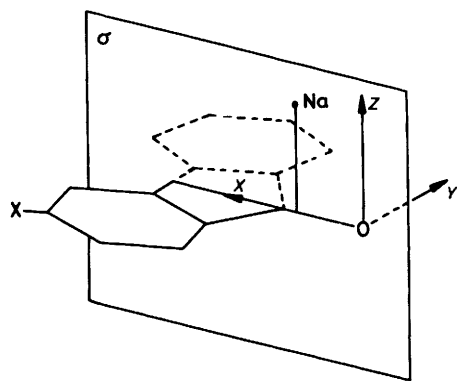
Ketyl	Substituent(s)	$a_i/\mu\text{T}$ for position $i$ at $T_0$								$T_0/\text{K}$
		1	2	3	4	5	6	7	8	
( $2^{--}\text{-Na}^+$ )	2-OCH <sub>3</sub>	-247.0	+42.7	-288.0	+68.0	+68.8	-321.0	+24.0	-221.5	190
( $3^{--}\text{-Na}^+$ )	3-OCH <sub>3</sub> †	-183.5	-16.2*	+23.4*	+33.3	+61.2	-324.6	-11.5	-196.0	170
( $4^{--}\text{-Na}^+$ )	2-CH <sub>3</sub>	-218.8	+20.8	-303.1	+68.2	+68.2	-320.8	+16.2	-215.8	197
( $5^{--}\text{-Na}^+$ )	3-CH <sub>3</sub>	-201.2	+21.4	+317.5*	+60.7	+66.1	-313.5	+3.6	-205.4	195
( $6^{--}\text{-Na}^+$ ) <sup>14</sup>	3-F	-192.5	+11.6	+623.7*	+57.8	+59.8	-312.8		-192.5	203
( $1^{--}\text{-Na}^+$ )	H	-207.5	+7.2	-313.2	+65.8	+65.8	-313.2	+11.6	-207.5	195
( $7^{--}\text{-Na}^+$ )	3-Cl	-194.3	-113.0*		+58.6	+72.8	-298.7		-202.6	214
( $8^{--}\text{-Na}^+$ ) <sup>14</sup>	2-F	-240.6	-136.3*	-310.2	+70.0	+70.0	-311.8	+21.4	-214.0	208
( $9^{--}\text{-Na}^+$ ) <sup>14</sup>	2,7-F <sub>2</sub>	-250.0		-313.3	+73.0	+73.0	-313.3	-136.3*	-250.0	207
( $10^{--}\text{-Na}^+$ )	2-Cl	-221.6		-286.1	+61.6	+72.2	-341.8	+16.0	-209.2	198
( $11^{--}\text{-Na}^+$ )	2,7-Cl <sub>2</sub>	-213.5		-319.5	+69.5	+69.5	-319.5		-213.5	218

\*  $a_i$  Values not corresponding to aromatic protons but to  $^1\text{H}$  couplings of either OCH<sub>3</sub> or CH<sub>3</sub> or  $^{19}\text{F}$  couplings. † Values obtained from general TRIPLE resonance spectra.

**Table 2.** Hyperfine couplings of fluorenone-sodium ( $1^{--}\text{-Na}^+$ )—( $11^{--}\text{-Na}^+$ ) in THF from e.s.r. spectra:  $^1\text{H}$  and  $^{19}\text{F}$  couplings  $a_i$  at positions  $i = 1$ —8 and  $a_{\text{Na}}$  at 295 K,  $da_{\text{Na}}/dT$ , Hammett's  $\sigma_m$  and  $\sigma^-$  (or  $\sigma_p$ ) constants<sup>18,19</sup>

Ketyl	$a_i/\mu\text{T}$ for position $i$ at 295 K								$a_{\text{Na}}/\mu\text{T}$	$da_{\text{Na}}/dT/\mu\text{T K}^{-1}\dagger$	$\sigma_m$	$\sigma^-$ (or $\sigma_p$ )
	1	2	3	4	5	6	7	8				
( $2^{--}\text{-Na}^+$ )	-251		-288	+69	+74	-327	+32	-232	+48.5	0.47	0.115	0.2
( $3^{--}\text{-Na}^+$ )	-193	+47	+24*	+37	+66	-326	-4	-203	+47.0	0.37	0.115	0.2
( $4^{--}\text{-Na}^+$ )	-228	-22*	-308	+69	+70	-326	+20	-222	+45.5	0.46	-0.069	-0.17
( $5^{--}\text{-Na}^+$ )	-211	+28	+317*	+67	+69	-323	+12	-212	+44.3	0.45	-0.069	-0.17
( $6^{--}\text{-Na}^+$ ) <sup>14</sup>	-204	+28	+645*	+60	+63	-316	+4	-203	+42.5	0.47	0.337	-0.02
( $1^{--}\text{-Na}^+$ )	-215	+17	-320	+68	+68	-320	+17	-215	+42.1 <sup>15</sup>	0.446 <sup>15</sup>	0.000	0.000
( $7^{--}\text{-Na}^+$ )	-197	+13		+62	+76	-300		-205	+40.5	0.47	0.373	0.227
( $8^{--}\text{-Na}^+$ ) <sup>14</sup>	-247	-118*	-311	+71	+72	-316	+27	-222	+38.7	0.43	0.337	-0.02
( $9^{--}\text{-Na}^+$ ) <sup>14</sup>	-248	-139*	-313	+73.5	+73.5	-313	-139*	-248	+36.1	0.42	0.674	-0.04
( $10^{--}\text{-Na}^+$ )	-219		-299	+62	+72	-350	+16	-203	+31	0.41‡	0.373	0.227
( $11^{--}\text{-Na}^+$ )	-225		-316	+72	+72	-316		-225	+28.0	0.40	0.746	0.454

\*  $a_i$  Values not corresponding to aromatic protons but to  $^1\text{H}$  couplings of either OCH<sub>3</sub> or CH<sub>3</sub> or  $^{19}\text{F}$  couplings. † The slopes of  $a_{\text{Na}}$  versus temperature were obtained from at least five values of  $a_{\text{Na}}$  at different temperatures ranging from 190 to 300 K. ‡ Measuring range in this case went up only to 240 K,  $a_i$  values obtained by linear extrapolation.

**Figure 3.** Approximate geometry of a sodium ketyl of a substituted fluorenone

As to the influence of substituents on spin distribution within the radical-anion, the values of  $a_i$  ( $i = 1$ —8) reported in Tables 1 and 2 do not allow us to draw conclusions further than those, which could be drawn from e.s.r. data of electrolytically reduced substituted fluorenone-9-ones.<sup>1</sup> The substituents studied affect but slightly the overall spin distribution within the radical-anions.

The differences between the coupling constants  $a_i$  in the

sodium ketyls and the respective electrolytically generated radical-anions are sufficiently important to allow us to conclude that the sodium ketyls of (1)—(11) always present as ion pairs, including the temperature range where no sodium coupling can be observed.

The small differences in spin distribution within the radical-anion among the different sodium ketyls of (1)—(11) and the similar behaviour towards variation of temperature are evidence for the great similarity of the sodium ion-pair structures, regardless of the nature of the substituent.

Apparently there is also no simple relation between any aromatic proton couplings  $a_i$  and Hammett or similar substituent constants.<sup>18,19</sup>

As for the sodium couplings  $a_{\text{Na}}$  and  $da_{\text{Na}}/dT$ , diparametric regression analyses were, however, successful. The approach used is the same as in the analysis of reduction potentials of substituted fluorenone-9-ones.<sup>1</sup> The variable  $Y$  was assumed to feel the electronic substituent effect *via* two additive contributions, a 'direct' contribution through the substituted benzene ring and an 'indirect' contribution through the other benzene ring, in the form (1). For substituents in positions 2 or 2 and 7 we took

$$Y = A + \rho_d \sigma_d + \rho_i \sigma_i \quad (1)$$

$\sigma_d = \sigma_m$  and  $\sigma_i = \sigma^-$  (or  $\sigma_p$ , when no special  $\sigma^-$  values were

**Table 3.** Results of diparametric and monoparametric linear regression analyses of  $a_{Na}$  and  $da_{Na}/dT$  versus Hammett's substituent constants,<sup>18,19</sup>  $\sigma_m$ ,  $\sigma^-$ , or  $\sigma_p$ :  $Y = A + \rho_d \sigma_d + \rho_i \sigma_i$  or  $Y = A + \rho \sigma$  for ketyls (1<sup>-</sup>-Na<sup>+</sup>)—(11<sup>-</sup>-Na<sup>+</sup>) from substituted fluoren-9-ones (1)—(11)

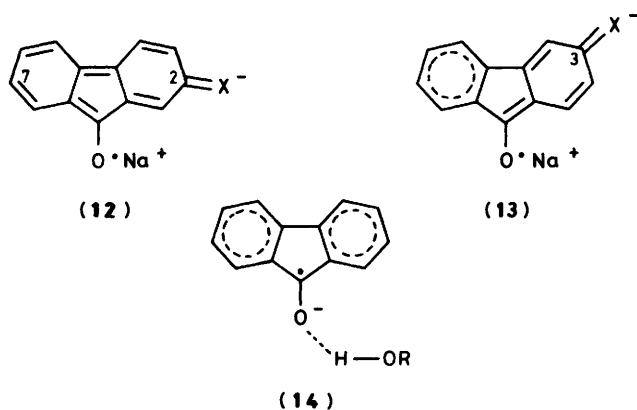
## Diparametric correlations

Variable Y	Substituted fluoren-9-one	$\rho_d$	$\rho_i$	$\epsilon(\rho_d)^a$	$\epsilon(\rho_i)^a$	r	$\epsilon(Y)^b$	A
$a_{Na}/\mu T$	(1)—(11)	-14.55	-9.86	3.3	4.7	0.9023	3.1	43.9 $\mu T$
	(1), (2), (4), (8)—(11)	-8.15	-22.3	4.4	6.1	0.9611	2.5	41.9 $\mu T$
	(1), (3), (5)—(7)	-15.8	+3.2	5.2	4.5	0.928 91	1.3	42.3 $\mu T$
$da_{Na}/dT/\mu T K^{-1}$	(1), (2), (4), (8)—(11)	-0.037	-0.064	0.013	0.007	0.9508	0.01	0.447 $\mu T K^{-1}$

## Monoparametric correlations

Variable Y	Substituted fluoren-9-one	$\rho$	$\epsilon(\rho)$	r	$\epsilon(Y)$	A
$a_{Na}/\mu T$	(1), (3), (5)—(7)	-13.3	3.5	0.909 2	1.2	42.8 $\mu T$

<sup>a</sup>  $\epsilon(\rho_d)$  and  $\epsilon(\rho_i)$  are standard deviations of independent variables  $\rho_d$  and  $\rho_i$ . <sup>b</sup>  $\epsilon(Y)$  is the standard deviation of the dependent variable Y.



available) and for substituents in position 3  $\sigma_d = \sigma^-$  (or  $\sigma_p$ ) and  $\sigma_i = \sigma_m$ . The substituent constants used were those listed in Table 2.<sup>18,19</sup>

Examining  $a_{Na}$  values in Table 3 and comparing the values of standard deviations with the values of the respective magnitudes of parameters, one can see that the best correlation for  $a_{Na}$  was found for 2- and 2,7-substituted fluoren-9-one ketyls, leading to equation (2) (in  $\mu T$ ) which means that a direct effect

$$a_{Na} = 41.9 - 8.15 \sigma_m - 22.3 \sigma^- \quad (2)$$

is responsible for only 33.4% of the total effect,\* whereas an indirect effect through the unsubstituted ring is responsible for the remaining 66.6% of the total effect. This means that the substituent effect is mainly a mesomeric effect through the unsubstituted ring according to the valence bond formula (12), besides a smaller direct *meta*-effect through the substituted ring.

The diparametric correlation for substituents in position 3 is unsatisfactory [a positive  $\rho_i$  is nonsensical and a standard deviation  $\epsilon(\rho_i)$  larger than  $\rho_i$  itself is sufficient to discard this result]. It points however to a predominantly 'direct' influence of the substituent. Therefore a monoparametric linear regression analysis was carried out. As can be seen from Table 3, the results are more satisfactory and can be expressed by equation (3), confirming that the 'indirect' effect through the unsub-

$$a_{Na} = 42.8 - 13.3 \sigma^- \quad (3)$$

\* For more detailed information on the calculation of the percentage see ref. 1, footnotes, Table 2.

stituted ring can be entirely discarded. The mesomeric 'para'-effect, according to the valence-bond formula (13), dominates therefore.

These correlations both show that a decrease in negative charge density at the carbonyl group causes a decrease of the value of  $a_{Na}$ , which obviously cannot be caused by the slight alteration of the spin density distribution within the radical-anion by the influence of the substituent.

This effect of a change of charge density on the sodium coupling  $a_{Na}$  can be explained, in principle, in two ways, or a combination of both. (a) One considers that, through weakening of the Coulomb attraction, the distance along the z axis between the sodium ion and the C—O-bond (Figure 3) is lengthened, as the negative charge density at the carbonyl group decreases, which causes  $a_{Na}$  to become smaller. (b) The distance between the sodium ion and the nearest oxygen atom of a solvent molecule in the ternary complex  $Fl^{--}Na^+(OR)_n$  is shortened, as the negative charge density at the carbonyl group decreases. The shortening of the distance would be the consequence of less effective competition of the radical-anion for the sodium ion. In this case the decrease of  $a_{Na}$  would be explained by an increase of cation-mediated spin delocalization to the solvent.

The first of these explanations seems to us more plausible, although one has to admit that better molecular orbital calculations and experiments on the influence of substituents on n.m.r. paramagnetic solvent shifts<sup>9</sup> may reveal a more complex situation.

If the first of these two explanations is correct, it is also easy to rationalize the influence of substituents on the slope of  $a_{Na}$  versus temperature for 2- and 2,7-substitution (in  $\mu T K^{-1}$ ) [equation (4)], meaning that an indirect 'para'-effect through

$$da_{Na}/dT = 0.447 - 0.037 \sigma_m - 0.064 \sigma^- \quad (4)$$

the unsubstituted ring [valence-bond structure (12)] is responsible for 56.1% of the whole substituent effect and a direct 'meta'-effect for the remaining 43.9%.\*

According to the first explanation, as the negative charge density at the carbonyl group decreases (caused by an electron-withdrawing substituent), the equilibrium distance between the carbonyl bond and the sodium ion is lengthened. The sodium ion will then be positioned at a point where the electron spin density gradient along the direction of the z-axis becomes smaller.

It was mentioned in the Introduction that a positive  $da_{Na}/dT$  value for fluoren-9-one ketyls can be explained (if one leaves out

the dynamic equilibrium model) by either of two mechanisms, (a) the 'classical' static vibrational model, where at higher temperatures the cation stays, on average, longer in regions of higher electron spin density<sup>3,7</sup> and (b) a model where at higher temperatures, through lengthening of the average distance between the cation and the solvent oxygen, the electron spin density increases at the cation, whose location relative to the radical-anion is assumed not to change with temperature.<sup>6</sup>

In the first of these cases, the 'classical'<sup>3,7</sup> static vibrational model, it is obvious that if the sodium ion is located somewhere where the gradient of the electron spin density is smaller, the effect of the vibration movements, or a displacement of the equilibrium position on  $a_{Na}$ , will also be relatively small.

In the second case, if we assume again that, through the effect of an electron-withdrawing substituent, the distance between the sodium ion and the carbonyl bond becomes larger than in the unsubstituted fluoren-9-one ketyl, the cation-mediated spin delocalization to the solvent will also be less efficient. Variation with temperature of the distance between the sodium ion and the nearest oxygen atom of a solvent molecule should then also have a smaller effect on the spin delocalization to the solvent and thus a smaller effect on the sodium coupling  $a_{Na}$ .

Whatever is the correct explanation, it seems that it is not necessary to resort to a dynamic equilibrium model for the sodium ketyls of substituted fluoren-9-ones in order to rationalize all reported observations.

It should, however, be mentioned that the effect of hydrogen-bonding solvents, which when mixed with an ethereal solvent bring about a significant increase in  $a_{Na}$ ,<sup>4</sup> was claimed to support a dynamic equilibrium model for fluorenone ketyls. One can, however, predict that a hydrogen bond from the solvent to the carbonyl oxygen will drastically increase the unpaired electron spin density at the carbonyl carbon atom: it is sufficient to consider the valence-bond formula (14) in order to come to this conclusion. If we assume that the position of the sodium ion relative to the radical-anion is still the same as in an ethereal solvent, *i.e.*, according to Lubitz *et al.*<sup>6</sup> nearer to the carbonyl carbon than to the oxygen, the increase in  $a_{Na}$  would be easily explained by the increase of spin delocalization to the sodium ion caused by this increase of electron spin density at the carbonyl carbon.

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