Substituent Effects in Fluoren-9-one Ketyls. Part 2.[1] The Electrolytic Reduction of Fluoren-9-ones studied by Cyclic Voltammetry and Electron Spin Resonance Spectroscopy

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A series of fluorenones bearing substituents in positions 2 or 3 was reduced electrolytically in *NN*-dimethylformamide solution using tetrabutylammonium perchlorate as supporting electrolyte. The resulting species were proved to be the one-electron reduction products, *i.e.* the paramagnetic radical-anions. The half-wave reduction potentials were determined by cyclic voltammetry. Correlation analysis of the reduction potentials *versus* the substituent constants was used to show that the transmission of substituent effects through the unsubstituted ring is important for fluorenones substituted in position 2, but unimportant if the substituent is attached to position 3. The hyperfine structure of e.s.r. spectra of the paramagnetic solutions was interpreted and the coupling constants assigned from the results of semi-empirical spin density calculations. In most cases the effect of substituents on the electron spin distribution was found to be relatively slight.

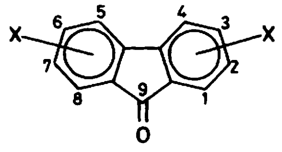
Fluorenone (1; X = Y = H), a non-alternant benzenoid aromatic ketone, has been shown by *X*-ray crystallography to be planar.[2] This molecule, due to its well defined geometry, seemed to us particularly suitable for study of the electronic effects of substituents on radical-anions of aromatic ketones in liquid solution. With benzophenones, complications arising from hindered rotation of the benzene rings render problematic the interpretation of their i.r.-[3,4] and u.v.-spectra,[5] as well as the e.s.r.[6] and ENDOR spectra[7] of their radical-anions in liquid solution. The data are usually not sufficient to determine the preferred average conformations of the radical-anions in solution, which most probably are variable according to the nature and position of the substituent and according to the environment (counter-ion and solvent).

Dehl and Fraenkel[8] and Takeshita and Hirota[9] studied the e.s.r. spectra of the radical-anion of fluorenone in *NN*-dimethylformamide (DMF, the solvent used in this study) with various counter-ions. They interpreted the e.s.r. spectrum as due to four groups of two protons. The largest hyperfine splitting constant (in absolute value) was assigned to positions 3 and 6 (*ca.* 300 μT), and in decreasing order follow positions 1 and 8 (*ca.* 190 μT), positions 4 and 5 (*ca.* 65 μT), and positions 2 and 7 (<3 μT). They found these assignments in reasonable agreement with spin densities calculated by the Hückel–McLachlan[10] method.

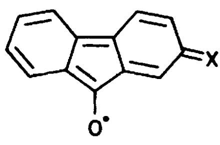
Various authors,[9,11–13] who used fluorenone ketyls in research on ion association in solution, found these assignments consistent with their results, which include ^{13}C and ^{17}O labelling of the carbonyl group and ENDOR spectroscopy. We do not know, however, of any experiments with fluorenone labelled in other positions which might give a more direct confirmation of the assignments.

Ketyls from 1-, 2-, 3-, 4-amino-, and 2,7-diamino-fluorenones have been already studied by e.s.r.[14] as have those from 2,7-difluorofluorenone.[8] There is a more recent study[1] on e.s.r., ENDOR, and TRIPLE resonance of sodium ketyls from 1-, 2-, 3-, 4-fluoro-, and 2,7-difluoro-fluorenone.

Nadjo and Savéant[15] studied the electrolytical reduction of five 2-substituted fluorenones by cyclic voltammetry and e.s.r., without giving an interpretation of the e.s.r. spectra. They did not detect any chemical change (not even carbon–halogen bond cleavage in 2-bromofluorenone) other than the reversible uptake of one electron. They showed the half-wave reduction potentials to correlate with the σ_m Hammett substituent constants. We found this surprising, because it would mean that the stabilizing effect of an electron-attracting substituent in position 2 by resonance structure (2) was negligible.



(1)



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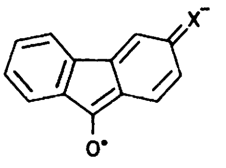

(3)

Other experimental studies of substituent effects in the fluorenone molecule[16,17] report similar results. Parry and Warren[16] have studied the kinetics of the sodium tetrahydridoboranate addition to 2-substituted fluorenones. They concluded, by double regression analysis, that the substituents acted merely as *meta*-substituents, without any partial *para*-character.

For fluorenones substituted in position 3 (*para* in relation to the carbonyl group) Harget *et al.*[17] found, as expected, unambiguous *para*-character.

As Nadjo and Savéant[15] reported only the half-wave reduction potentials for five 2-substituted fluorenones, we found it worthwhile to reinvestigate the field, examining a larger number of 2- and 2,7-, as well as 3- and 3,6-substituted fluorenones.

We did not include 1- and 4-substituted fluorenones in order not to perturb the electronic effects by phenomena caused by possible steric hindrance to planarity or solvation.

By thus enlarging the set of compounds, for which half-wave reduction potentials and interpreted e.s.r. spectra are known, we hoped to get a better view of substituent effects on the radical-anions of fluorenones.

Results and Discussion

Cyclic Voltammetry; the Influence of Substituents on Half-wave Reduction Potentials.—The half-wave reduction potentials relative to a saturated calomel electrode were determined for fluorenone and seventeen substituted fluorenones listed in Table 1, which also contains the relevant σ_m, σ_p,[18] and σ^- [19] substituent constants.

If one uses Hammett's $\sigma = \sigma_m$ for substituents in position 2 (or 7) and $\sigma = \sigma_p$ for substituents in position 3 (or 6) one obtains as best least-mean-squares fit equation (1) which

$$-{}^{1/2}E_R = 0.457\,\sigma - 1.301 \qquad (1)$$

$$\delta\,{}^{1/2}E_R = 0.457\,\sigma + \alpha \qquad (2)$$

can be written as (2) where δ is the Grunwald–Leffler operator,[20] [$\delta\ {}^{1/2}E_R = -{}^{1/2}E_R$ (substituted fluorenone) + ${}^{1/2}E_R$ (fluorenone)] and $\alpha = -0.026$ V, an accidental deviation, which results from not constraining the regression line to pass through the point, which represents $\delta\ {}^{1/2}E_R = 0$, $\sigma = 0$ for unsubstituted fluorenone. The correlation coefficient for this equation is $r = 0.958$, which corresponds to a level of significance larger than 99.9%. The largest deviations in this correlation were the ones for strongly electron-attracting substituents like *e.g.* 3-NO_2 and 2-NO_2.

If one uses σ^- instead of σ_p in those cases, where these values have been determined, there is a slight improvement in the quality of the correlation [equation (3) or (4) with $r = 0.972$].

$$-{}^{1/2}E_R = 0.375\,\sigma - 1.285 \qquad (3)$$

$$\delta\,{}^{1/2}E_R = 0.375\,\sigma - 0.010 \qquad (4)$$

Table 1. Half-wave reduction potentials in DMF of fluorenones

a Unsubstituted, 2-substituted, and 2,7-disubstitued fluorenones

Substituent X	$-{}^{1/2}E_R$/V*	σ_m [18]	σ_p [18]	σ^- [19]
2,7-$(NH_2)_2$	1.495	−0.32	−1.32	
2-NH_2	1.400	−0.16	−0.66	
2-CH_3	1.305	−0.069	−0.170	
H	1.275 [15]	0	0	0
2-OCH_3	1.265 [15]	0.115	−0.268	−0.2
2-F	1.185 [15]	0.337	0.062	−0.02
2-Cl	1.150 [15]	0.373	0.227	
2,7-F_2	1.110	0.674	0.124	−0.04
2,7-Cl_2	1.037	0.746	0.227	
2-NO_2	0.895	0.71	0.78	1.24
2,7-$(NO_2)_2$	0.635	1.42	1.56	2.48

b 3-Substituted and 3,6-disubstituted fluorenones

Substituent X	$-{}^{1/2}E_R$/V*	σ_m [18]	σ_p [18]	σ^- [19]
3-NH_2	1.510	−0.16	−0.66	
3-OCH_3	1.365	0.115	−0.268	−0.2
3-CH_3	1.325	−0.069	−0.170	
H	1.275 [15]	0	0	0
3-F	1.265	0.337	0.062	−0.2
3-Cl	1.205	0.373	0.227	
3-NO_2	0.710	0.71	0.78	1.24
3,6-$(NO_2)_2$	0.485	1.42	1.56	2.48

* Relative to the saturated calomel electrode.

More meaningful least-mean-squares fits are obtained, however, if one uses a diparametric approach similar to the ones mentioned above,[16,17] which were tried without success on the reduction kinetics of substituted fluorenones by sodium tetrahydridoboranate.

In this diparametric regression analysis we assumed *a priori* that any substituent effect is transmitted in part directly *via* the substituted ring and in another part indirectly *via* the unsubstututed ring. The subscripts d and i indicate if the constants refer to the direct or indirect effect respectively. The relationship is hence assumed to take the form (5), ρ_d and ρ_i being reaction

$$\delta\,{}^{1/2}E_R = \rho_d\sigma_d + \rho_i\sigma_i + \alpha \qquad (5)$$

constants and α has an analogous meaning to that in equation (2).

Table 2 lists the results obtained from both monoparametric and diparametric regression analyses.

For 2- and 2,7-substituted fluorenones we took $\sigma_d = \sigma_m$ and $\sigma_i = \sigma^-$ (σ^- meaning σ_p when there were no especially determined σ^- values tabulated). According to Table 2 the linear relationship obtained for 2- and 2,7-fluorenones is (6).

$$\delta\,{}^{1/2}E_R = 0.232\,\sigma_m + 0.128\,\sigma^- - 0.012 \qquad (6)$$

This means that the direct (*meta-*) and the indirect ('*para-*') effect represent approximately the same percentage, 48.6% and 51.4% respectively (after correcting for the variances of the independent variables σ_m and σ^-), which proves that, after all, structures of type (**2**) have to be considered as relevant in studying the effect of substituents in position 2. It is interesting

Table 2. Results of mono- and di-parametric regression analysis of differential half-wave potentials as a function of substituent constants σ_m for non-conjugated substitution and σ^- (or σ_p when σ^- not available) for conjugated substitution

Position of substitution		2 or 2,7	3 or 3,6	2 or 3 2,7 or 3,6
Monoparametric correlation	ρ/V[a]	0.458	0.344	0.375
	$\varepsilon(\rho)$/V[b]	0.037	0.023	0.023
	r[c]	0.973 05	0.986 40	0.971 78
	$\varepsilon(\delta\,{}^{1/2}E_R)$/mV[b]	58.5	62.7	70.7
	α/mV[d]	+44	−9	−10
Diparametric correlation	ρ_d/V[e]	0.232	0.399	0.292
	$\varepsilon(\rho_d)$/V[b]	0.029 04	0.109	0.023
	ρ_i/V[f]	0.128	−0.111	0.099
	$\varepsilon(\rho_i)$/V[b]	0.014 9	0.212	0.021
	r[c]	0.997 48	0.987 12	0.989 07
	$\varepsilon(\delta\,{}^{1/2}E_R)$/mV[b]	19.1	66.9	45.7
	α/mV[d]	−12	−25	+5
	$\overline{\rho_d}$(%)[g]	48.6	87.5	70.7
	$\overline{\rho_i}$(%)[h]	51.4	12.5	29.3

[a] Monoparametric regression coefficient, 'reaction constant' in volts [using σ_m for 2- and 2,7-substitution and σ^- (σ_p) for 3- and 3,6-substitution]. [b] Standard deviation of magnitude in parentheses. [c] Correlation coefficient. [d] Value calculated for $\delta\,{}^{1/2}E_R$ from correlation for $\sigma = 0$, instead of its experimental value of $\delta\,{}^{1/2}E_R = 0$. [e] Regression coefficient defined in equation (5) (reaction constant) characterizing 'direct' substituent effect [using δ_m for 2-substitution and σ^- (σ_p) for 3-substitution]. [f] Regression coefficient defined in equation (5) characterizing 'indirect' substituent effects [using σ^- (σ_p) for 2-substitution and σ_m for 3-substitution]. [g] $\overline{\rho_d} = 100\,\rho'_d/(\rho'_i + \rho'_d)$ where $\rho'_d = |\rho_d|\sum_{j=1}^{n}(\sigma_{dj} - \overline{\sigma_d})^2/\sum_{j=1}^{n}({}^{1/2}E_{Rj} - {}^{1/2}\overline{E}_R)^2$ and $\rho'_i = |\rho_i|\sum_{j=1}^{n}(\sigma_{ij} - \overline{\sigma_i})^2/\sum_{j=1}^{n}({}^{1/2}E_{Rj} - {}^{1/2}\overline{E}_R)^2$. [h] $\overline{\rho_i} = 100\,\rho'_i/(\rho'_i + \rho'_d)$.

to compare the results of this regression analysis with the ones obtained by Parry and Warren[16] for the reduction of fluorenones by tetrahydridoboranate: There the '*para*-'effect, through the unsubstituted ring, is negligible.

This can be easily understood if one considers that the resonance effect of a substituent X in the fluorenone ground-state, as well as in the hydride-transfer transition state, is less important compared with the resonance effect [*e.g.* structure (**2**)] in the radical-anion and in the transition state of the electron-transfer reaction.

For 3- and 3,6-substituted fluorenones the correlation is (7).

$$\delta^{1/2}E_R = 0.399\,\sigma^- - 0.11\,\sigma_m - 0.025 \qquad (7)$$

Here the negative value of ρ_i has no possible physical interpretation. As the standard error, by which it is affected, is twice as large, it is more sensible to discard the second term and to write equation (8) resulting from the monoparametric regression analysis for the 3-substituted fluorenones.

$$\delta^{1/2}E_R = 0.344\,\sigma^- - 0.009 \qquad (8)$$

This result reflects the exclusive *para*-character of the substituent effect in position 3, by analogy with the results of Harget *et al.*[17] on the reduction of 3-substituted fluorenones by tetrahydridoboranate, although their results reflect the loss of conjugation in the transition state, which ours do not, as expected. This means that the unsubstituted ring is not much involved and resonance structures like (**3**) play a relevant role.

E.s.r.—The e.s.r. spectra of the radical-anions, generated by reducing electrolytically the substituted fluorenones in a 0.1M solution of tetrabutylammonium perchlorate in DMF at room temperature, were compared with computer simulations[21] until no further improvement could be obtained by adjusting the values of the coupling constants (*e.g.* Figure). The moduli of the coupling constants listed in Tables 3 and 5 were obtained from these computer simulations. The signs and assignments of the aromatic ^1H coupling constants (Table 3) are however not only based on a mere comparison with the calculated values of Table 4. Although these signs and assignments are ultimately only tentative, various other factors were taken into consideration, to lend them a significantly higher degree of reliability; this will be discussed below in more detail.

The calculated aromatic ^1H coupling constants of Table 4 arise from the results of Hückel–McLachlan molecular orbital calculations of spin densities,[10] using the parameters recommended by Takeshita and Hirota[9] for fluorenone and McLachlan's parameter $\lambda = 1.2$. In the parametrization of substituents the inductive model was used for methyl and methoxy groups ($\delta_C = -0.15$ and -0.32, respectively[22]) and the heteroatom model for other substituents. Values from the literature were used for the Coulomb (δ) and exchange (γ) integral corrections (in units of β): $\delta_F = 2.5$, $\gamma_{C\text{-}F} = 0.62$,[23] $\delta_C = 2.0$, $\gamma_{C\text{-}C} = 0.4$,[24] $\delta_N = 2.2$, $\delta_O = 1.4$, $\gamma_{C\text{-}N} = 1.2$, $\gamma_{N\text{-}O} = 1.67$.[25]

The moduli of the spin densities calculated in this way were correlated by a regression analysis *versus* the experimental

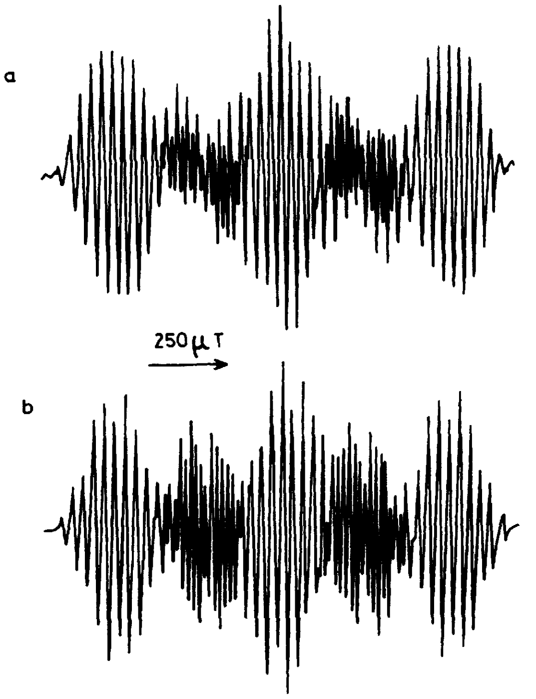

Figure. a, E.s.r. spectrum of the radical-anion of 3-methoxyfluoren-9-one (1; X = 3-OCH$_3$, Y = H). b, Computer simulation of the same spectrum

Table 3. Experimental aromatic proton splitting constants (µT) of substituted fluorenone ketyl solutions prepared by electrolysis in DMF with 0.1M-tetrabutylammonium perchlorate.

	Position							
Substituent(s)	1	2	3	4	5	6	7	8
None	−191.9	<0.8	−311.0	+64.5	+64.5	−311.0	<0.8	−191.9
2,7-Difluoro	−239.0		−304.3	+69.0	+69.0	−304.3		−239.0
2,7-Dichloro	−202.7		−315.8	+68.2	+68.2	−315.8		−202.7
2,7-Dinitro	−275.4		−25.8	−51.7	−51.7	−25.8		−275.4
3,6-Dinitro	−107.0	+24.0		−81.0	−81.0		+24.0	−107.0
2-Fluoro	−251.0		−319.0	+70.3	+74.1	−321.3	−26.2	−221.9
2-Chloro	−203.0		−275.0	+64.0	+67.0	−338.5	−13.0	−192.5
2-Methoxy	−229.9		−283.4	+66.8	+69.5	−317.2	+18.2	−210.2
2-Methyl	−211.4		−298.6	+65.8	+68.0	−313.0	−9.5	−207.0
2-Nitro	+94.7		+79.4	−111.0	−140.5	+16.9	−492.0	+16.9
3-Fluoro	−181.7	−14.4		+57.0	+59.0	−306.0	−14.0	−181.7
3-Chloro	−182.0	<8		+57.5	+73.5	−288.0	<8	−187.2
3-Methoxy	−171.8	+41.0		+40.5	+63.6	−316.8	−2.2	−181.8
3-Methyl	−192.5	+13.0		+64.2	+64.2	−305.0	−13.0	−192.5
3-Nitro	−30.5	−214.1		−121.1	−119.1	+28.4	−240.5	+6.0

Table 4. Calculated aromatic proton hyperfine splittings (in µT) and linear least-mean-squares parameters for substituted fluorene ketyls

	Position										
Substituents(s)	1	2	3	4	5	6	7	8	Q^{H}_{CH}[a]	r[b]	S (%)[c]
H[d]	−192	−15	−307	+76	+76	−307	−15	−192	−2.981	0.9979	>99.9
2,7-Difluoro[e]	−224		−288	+73	+73	−288		−224	−2.896	0.9954	>99.0
2,7-Dichloro[f]	−216		−306	+71	+71	−306		−216	−2.987	0.9982	>99.0
2,7-Dinitro[g]	−166		−163	−24	−24	−163		−166	−6.698	0.5931	
3,6-Dinitro[g]	−102	+25		−87	−87		+25	−102	−0.661	0.9965	>99.0
2-Fluoro[e]	−243		−311	+64	+73	−339	−21	−218	−3.111	0.9986	>99.9
2-Chloro[f]	−208		−296	+67	+71	−310	−18	−197	−2.919	0.9958	>99.9
2-Methoxy[h]	−258		−254	+66	+84	−318	−4	−203	−2.927	0.9931	>99.9
2-Methyl[i]	−227		−285	+65	+74	−316	−15	−202	−2.936	0.9984	>99.9
2-Nitro[g]	+89		+87	−162	−164	+40	−462	+36	−2.141	0.9899	>99.9
3-Fluoro[e]	−182	+2		+54	+74	−300	−18	−184	−2.837	0.9981	>99.9
3-Chloro[f]	−191			+62	+72	−279		−191	−2.704	0.9990	>99.9
3-Methoxy[h]	−176	+35		+32	+87	−309	−14	−181	−2.888	0.9966	>99.9
3-Methyl[i]	−187	+7		+56	+78	−309	−17	−188	−2.916	0.9985	>99.9
3-Nitro[g]	−7	−201		−156	−117	+19	−231	+1	−1.114	0.9838	>99.9

[a] Q^{H}_{CH} is McConnell's constant, in µT, determined by the least-mean-squares method for each case. [b] r is the correlation coefficient. [c] S is the significance of the correlation by Fischer's test. [d] Hückel–McLachlan MO parameters used were, in units of β_{C-C}:[8] $\delta_9 = 0.1$; $\delta_{14} = 1.15$; $\gamma_{9.10} = \gamma_{9.13} = 1.3$; $\gamma_{11,12} = 0.8$; $\gamma_{9.14} = 1.6$. [e] $\gamma_{CF} = 0.62$; $\delta_F = 2.5$.[23] [f] $\gamma_{C-Cl} = 0.4$; $\delta_{Cl} = 2.0$.[24] [g] $\delta_N = 2.2$; $\delta_O = 1.4$; $\gamma_{C-N} = 1.2$; $\gamma_{N-O} = 1.67$.[25] [h] $\delta_{C(C-OCH_3)} = -0.32$.[22] [i] $\delta_{C(C-CH_3)} = -0.15$.[22]

Table 5. Experimental splitting constants (µT) assigned to substituents

Substituent	Position	Splitting (µT)
F	2	−119.3
	2,7	−112.7
	3	+612.5
Cl	2	<4
	2,7	<4
	3	<4
OCH_3	2	⩽1.5
	3	+2.2
CH_3	2	+19.5
	3	+305.0
NO_2	2	−366
	2,7	−31.0
	3	<3
	3,6	<2

values without signs of the ^1H coupling constants of Table 3 for each radical-anion. The various regression coefficients Q^{H}_{CH} were adopted as the best possible McConnell constants[26] and are also listed in Table 4, together with the correlation coefficients and the level of significance, which give an idea of the reliability of the various assignments.

By making these tentative assignments, one automatically attributes signs to the couplings. By determining the same signs experimentally, the assignments become even more reliable. This seemed to us, however, only necessary for positions of very low spin density, where some uncertainty about the signs of the proton couplings remains if one relies exclusively on spin density calculations. This is the case for protons in positions 2 and 7 where $|a_H| < 30$ µT. In these cases we could extrapolate from TRIPLE resonance experiments for sodium ketyls of the same fluorenones in THF, which yield the signs of these coupling constants.[20,27] The extrapolation was carried out according to the procedure outlined by Lubitz,[11] which is based on the difference in gas-phase electron affinity of the cations Na^+ and $(C_4H_9)_4N^+$, assuming the sensitivity of the splittings to electron affinity as 5 µT eV^{-1}. Therefore, a splitting constant for position 2 (or 7) is expected to be 16 µT more negative in the electrolytically generated species than in the sodium ion pair.

One contradiction arises, however, for the 2-methoxyfluorenone ketyl, in that $|a_{H_1}| < |a_{H_3}|$ is assumed, though the corresponding calculated spin densities are in inverse order. We believe that this assumption is nevertheless necessary because of the temperature behaviour of the constants in the sodium ion pair.[27]

It is obvious that when the coupling constants of two protons in a radical-anion differ very little (*e.g.* protons 4 and 5 in several 2-substituted fluorenones or protons 2 and 4 in 3-methoxyfluorenone) the reliability of the distinction between these two positions is very low, but it is also acceptable to say, in such a case, that the physical significance of deciding between the two possibilities is equally negligible.

The coupling constants due to nuclei in substituents are less accessible to theoretical predictions.

The fluorine (^{19}F) splitting constants (Table 5) were identified and their signs were determined by comparison with the data known for the corresponding sodium ketyls.[1] No chlorine (^{33}Cl, ^{35}Cl) splittings could be detected, though in neutral radicals these have been determined to be about one-fifth of the magnitude of the corresponding proton splittings (in the unsubstituted compound).[28] This is probably not true for radical-anions, where one expects electron-attracting substituents to play a more important role in delocalizing charge than in delocalizing unpaired spin.

Variable-temperature e.s.r. (in the range 250—350 K) on the methoxy- and nitro-fluorenone radical-anions did not show any asymmetric line-broadening and did not yield, therefore, any information about the rate of conformational isomerization within this temperature range. The comparison with the radical cation of 1,4-dimethoxybenzene,[29] where e.s.r. reveals the existence of a *cis*- and a *trans*-isomer interconverting too slowly to give place to asymmetric line-broadening in e.s.r. ($\tau > 10^{-8}$ s), suggests that in the radical-anions of methoxy-substituted fluorenones the rotation is slower than 10^{-8} s. The question why one apparently detects only one conformational isomer has to be left open at present.

Influence of Substituents on Spin Distribution in Fluorenone Radical-anions.—The presence of methyl, methoxy, chloro, or fluoro substituents does not affect the nodal properties of the semi-occupied molecular orbital, and the splitting constants are only slightly different from those which were determined for the fluorenone ketyl. On the other hand, the inclusion of a nitro substituent changes the spin distribution extensively and the semi-occupied molecular orbital has nodal properties which correlate with the highest occupied molecular orbital of fluorenone. This should of course be expected since the nitro group contributes only two electrons to the π-system but simultaneously provides two extra low-energy molecular orbitals, which are essentially localized upon the nitro group and respectively bonding and antibonding between the two oxygen atoms. Reasonable correlation between calculated spin densities and proton hyperfine splittings for both 2- and 3-nitrofluorenone lends credibility to the assignments based in Hückel–McLachlan calculations.

The assignments which Table 3 implies for the dinitrofluorenone radical anions are however less reliable, the Hückel–McLachlan calculations predicting, in these cases, that the ninth and tenth molecular orbitals (which have different nodal properties) differ by less than 0.04 β units of energy.

As to the spin transfer to substituents, the ^{19}F splitting constants bear no simple relation to the corresponding proton splitting constants in the unsubstituted compound. This fact has been recently commented upon[30] and it has been shown that for the 3-fluorofluorenone ketyl, the pronounced asymmetric broadening of the e.s.r. spectrum means that $a_F > 0$,[1] pointing to the predominance of an overlap mechanism.

Nitrogen splittings in nitrofluorenone radical anions have rather surprisingly small values if compared with radicals from other nitroaromatic species.[31] The correlation between experimental and calculated proton hyperfine splitting is fair in the cases of mononitrofluorenones (though Q^{H}_{CH} values are rather small), but not very good for dinitrofluorenones, for which selective deuteriation might prove the only method of accurate assignment.

Experimental

Electrochemical and Spectroscopic Methods.—*NN*-Dimethylformamide (DMF) Uvasol$^{(R)}$ grade was supplied by Merck and stored over molecular sieves. Tetrabutylammonium perchlorate p.a. grade was supplied by Fluka.

Cyclic voltammetry was performed on a Princeton Applied Research potentiostat–galvanostat model 173, with current follower model 176 and universal programmer model 175. As cathode a stationary mercury drop was used. E.s.r. spectra were run on Bruker ER 200tt and ER 200D spectrometers.

The samples for e.s.r. were obtained by applying an increasing direct current voltage to dilute (*ca.* 5×10^{-4}M), oxygen- and moisture-free solutions in DMF, containing 0.1M-tetrabutylammonium perchlorate, until a persistent colour developed near the cathode. Electrolyses were performed in the cavity of the spectrometer when the radical solution was not sufficiently stable. When the radical solutions were stable enough, the electrolysis was performed outside the cavity and capillary samples were taken and sealed.

The e.s.r. spectra were analysed and simulated[21] on a computer until the match with the experimental spectrum could not be further improved.

Synthesis and Purification of Fluoren-9-ones.—All 18 fluoren-9-ones used were recrystallized to constant m.p. or sublimed under vacuum. The m.p.s were measured by thermal microscopy with a Mettler FP52 hot stage and temperature controller. They were found to be in agreement with the published values. Elemental analyses gave satisfactory values.

Fluoren-9-one, Merck or Fluka reagent grade, was recrystallized from ethanol. 2-Nitrofluoren-9-one was prepared[32] by oxidation of 2-nitrofluorene[32] and sublimed under vacuum. 3-Nitrofluoren-9-one was synthesized[33,34] from 2-aminofluoren-9-one and sublimed under vacuum. 2,7-Dinitrofluoren-9-one was prepared[35] by nitration of fluoren-9-one and recrystallized in isopropyl alcohol. 3,6-Dinitrofluoren-9-one was synthesized from 2,7-diaminofluoren-9-one analogously to the above mentioned method[33,36] to obtain 3-nitrofluoren-9-one from 2-aminofluoren-9-one. 2- and 3-aminofluoren-9-one were obtained by reduction of 2-nitrofluoren-9-one[32,33,37] and 3-nitrofluoren-9-one,[38] respectively. 2,7-Diaminofluoren-9-one was obtained by reduction of 2,7-dinitrofluoren-9-one.[36] 2-Methoxy-,[39] 2-fluoro-, 3-fluoro-,[40] 2,7-difluoro-, 2-chloro-, 3-chloro-, and 2,7-dichloro-fluoren-9-one were obtained from the respective amines *via* their diazonium salts. A method described for 3-fluorofluoren-9-one[40] was adapted to prepare 2-fluoro- and 2,7-difluoro-fluoren-9-one, a method described for 1-chlorofluoren-9-one[41] was adapted to synthesize 2- and 3-chlorofluoren-9-one. For 2,7-dichlorofluoren-9-one a more common procedure[42] for Sandmeyer reactions was adapted, the product being extracted from the reaction mixture three times with benzene and the extract evaporated to dryness in a rotary evaporator. For all three chlorofluoren-9-ones mentioned it was necessary to purify the crude product by column chromatography over neutral alumina with 1:1 benzene–light petroleum as eluant, followed by recrystallization in ethanol. 2-Methylfluoren-9-one was prepared from 2-methylfluorene[43] by oxidation with selenium dioxide.[44] 3-Methylfluoren-9-one was prepared by Ullmann reaction[45] from 2-amino-4′-methylbenzophenone.[46–48] 3-Methoxyfluoren-9-one was also prepared by an Ullmann reaction[46] from 2-amino-4′-methoxybenzophenone.[46] Both 3-methyl- and 3-methoxy-fluoren-9-one had also to be further purified by column chromatography as above. The solvent used for recrystallization of 3-methylfluoren-9-one was hexane.

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