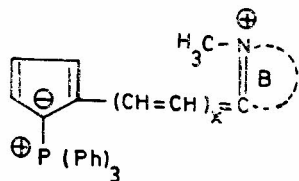


TABLE 3 — ABSORPTION SPECTRA OF *unsym*-PHOSPHOCYANINES

Nature of nucleus B	$x = 1^*$		$x = 2^\dagger$	
	$\lambda_{\max, \text{nm}}$	$-\beta \times 10^{12} \text{erg}$	$\lambda_{\max, \text{nm}}$ Calc.	$\lambda_{\max, \text{nm}}$ Obs.
Thiazoline-2	458	7.03	546	560
Benzoxazole	470	6.85	560	570
α -Naphthoxazole	495	6.5	591	590
β -Naphthoxazole	495	6.5	591	590
Quinoline-2	515	6.25	614	635
Quinoline-4	530	6.62	672	670

* $n = 9$; $\Delta M = 0.6256$.

† $n = 11$; $\Delta M = 0.5220$.

$\Delta M = 0.5176$.

$\Delta M = 0.4464$.

data, we had to resort to a mechanical method of calculation instead of graphical method. The results are presented in Tables 2 and 3. The resonance integral β is calculated for one member of the series and these values are utilized for the prediction of the absorption maxima of the next higher homologue of the series. The calculations of spectral frequencies by the HMO method yield excellent results.

In both HMO and FEMO models (i) the geometry of the ground and the excited states have been assumed to be the same, (ii) a Frank-Condon transition has been assumed, (iii) the alternation of single and double bonds have been neglected, and (iv) no account has been taken for the electronic interactions and spin splitting.

It is quite well known that these absorption bands arise out of singlet-singlet transitions. Although the available data are too limited to permit any generalization, nevertheless, they are suggestive. The observed correlations seem to imply that there is either a high degree of proportionality between the effects of configuration interaction, singlet-triplet splitting and the overall transition energy^{2b} or these factors are relatively unimportant in these dyes as suggested by Dewar¹.

The presence of phosphorus appears to have very little effect on the spectra of the dyes derived from cyclopentadienyltriphenylphosphorane. The second order perturbation to the incorporation of oxygen (merophosphinines) or nitrogen (*unsym*-phosphocyanines) is of a very small magnitude. The details of the nature of second order interaction of such dyes will be reported later.

Another interesting feature of the present investigation is the close analogy between the results predicted by the FEMO model and the simple LCAO model. Such results are, however, not new and have been reported earlier by Ruedenberg and Scherr⁵⁻⁷. Their investigations have established certain simi-

larities between the FEMO and LCAO models, particularly with respect to the accuracy of the quantitative prediction of spectra.

More detailed study of the absorption spectra of these dyes, particularly with respect to the effect of solvent polarity and the state of polarization both in the ground and excited states, are under investigation.

The dyes were prepared by the method reported in the literature⁸. The absorption spectra were recorded in an Unicam SP-600 spectrophotometer.

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Spin Densities & Charge Densities in Some Fluoro-substituted Naphthalene Radical Anions

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A simple additivity model has been used quite successfully to predict unrestricted Hartree-Fock spin densities and charge densities in a series of fluoro-substituted naphthalene radical anions.

IN continuation of the earlier work¹⁻³ from our laboratory in this note we report the results of additivity model calculations of the UHF spin densities and charge densities for a series of fluoro-substituted naphthalene radical anions.

For a fluorine substituent at position-1 of the naphthalene radical anion, the changes in the spin densities at 1, 2, 3, 4, 5, 6, 7 and 8 positions are represented by a, b, c, d, e, f, g and h respectively. Similarly, for a fluorine substituent at position-2 of the naphthalene radical anion, the changes in the spin densities at 1, 2, 3, 4, 5, 6, 7 and 8 positions are designated a', b', c', d', e', f', g' and h' respectively. Expressions resulting from an additivity model for the spin densities in 1-fluoro- and 2-fluoro-naphthalene radical anions are given in Table 1

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TABLE 1 — CALCULATED UHF SPIN DENSITIES IN NAPHTHALENE, 1-FLUORO- AND 2-FLUORONAPHTHALENE RADICAL ANIONS^(a)

Position	Expression for ρ_i	ρ_i		Calc parameter values
		I	II	
NAPHTHALENE				
1	α	0.2145		$\alpha = 0.2145$
2	β	0.0486		$\beta = 0.0486$
1-FLUORONAPHTHALENE				
1(F)	$a+\alpha$	0.2146		$a = 0.0001$
2	$b+\beta$	0.0365		$b = -0.0121$
3	$c+\beta$	0.0500		$c = 0.0014$
4	$d+\alpha$	0.1918		$d = -0.0227$
5	$e+\alpha$	0.2198		$e = 0.0053$
6	$f+\beta$	0.0547		$f = 0.0061$
7	$g+\beta$	0.0460		$g = -0.0026$
8	$h+\alpha$	0.2319		$h = 0.0174$
2-FLUORONAPHTHALENE				
1	$a'+\alpha$	0.1986		$a' = -0.0159$
2(F)	$b'+\beta$	0.0410		$b' = -0.0076$
3	$c'+\beta$	0.0620		$c' = 0.0134$
4	$d'+\alpha$	0.2246		$d' = 0.0101$
5	$e'+\alpha$	0.2233		$e' = 0.0088$
6	$f'+\beta$	0.0389		$f' = -0.0097$
7	$g'+\beta$	0.0578		$g' = 0.0092$
8	$h'+\alpha$	0.2050		$h' = -0.0095$

(a) ρ_i values were obtained from standard UHF calculations using the parameters given in refs. 1 and 2.

TABLE 2 — PREDICTED UHF SPIN DENSITIES (ρ_i) IN FLUORO-SUBSTITUTED NAPHTHALENE ANIONS^(a)

Position	Expression for ρ_i	ρ_i (b)		Error
		I	II	
1,2-DIFLUORONAPHTHALENE				
1(F)	$a+a'+\alpha$	0.199	0.201	0.002
2(F)	$b+b'+\beta$	0.029	0.030	0.001
3	$c+c'+\beta$	0.063	0.063	0.000
4	$d+d'+\alpha$	0.202	0.202	0.000
5	$e+e'+\alpha$	0.229	0.228	-0.001
6	$f+f'+\beta$	0.045	0.045	0.000
7	$g+g'+\beta$	0.055	0.055	0.000
8	$h+h'+\alpha$	0.222	0.222	0.000
2,6-DIFLUORONAPHTHALENE				
1	$a'+e'+\alpha$	0.207	0.207	0.000
2(F)	$b'+f'+\beta$	0.031	0.032	0.001
3	$c'+g'+\beta$	0.071	0.071	0.000
4	$d'+h'+\alpha$	0.215	0.215	0.000
1,2,3,4-TETRAFLUORONAPHTHALENE				
1(F)	$a+d+a'+d'+\alpha$	0.186	0.187	-0.001
2(F)	$b+c+b'+c'+\beta$	0.044	0.043	-0.001
5	$e+h+e'+h'+\alpha$	0.237	0.237	-0.000
6	$f+g+f'+g'+\beta$	0.052	0.052	0.000
1,3,4,5,7,8-HEXAFLUORONAPHTHALENE				
1(F)	$a+d+e+h+d'+h'+\alpha$	0.215	0.213	-0.002
2	$b+c+f+g+c'+g'+\beta$	0.064	0.067	0.003
3(F)	$b+c+f+g+b'+f'+\beta$	0.024	0.022	-0.002
4(F)	$a+d+e+h+a'+e'+\alpha$	0.208	0.209	0.001

TABLE 2 — PREDICTED UHF SPIN DENSITIES (ρ_i) IN FLUORO-SUBSTITUTED, NAPHTHALENE ANIONS^(a) — contd

Position	Expression for ρ_i	ρ_i		Error
		I	II	
1,2,3,4,5,6,7,8-OCTAFLUORONAPHTHALENE				
1(F)	$a+d+e+h+a'+d'+e'+h'+\alpha$	0.208	0.210	0.002
2(F)	$b+c+f+g+b'+c'+f'+g'+\beta$	0.047	0.046	-0.001

(a) Calculations were carried out for all fluorinated naphthalene radical anions. To save space, we have listed the results for only a few representative systems. Results for rest of the systems can be made available on request.

(b) ρ_i values under I were obtained using an additivity model (see text). Those given under II were obtained from standard UHF calculations using parameters given in refs. 1 and 2.

TABLE 3 — CALCULATED UHF CHARGE DENSITIES ON THE RING CARBON ATOMS OF NAPHTHALENE, 1-FLUORO- AND 2-FLUORONAPHTHALENE RADICAL ANIONS^(a)

Position	Expression for q_i (res)	q_i (res)	Calc. parameter values
1	σ	-0.1961	$\sigma = -0.1961$
2	γ	-0.0876	$\gamma = -0.0876$
1-FLUORONAPHTHALENE			
1(F)	$A+\sigma$	-0.1609	$A = 0.0352$
2	$B+\gamma$	-0.1154	$B = -0.0278$
3	$C+\gamma$	-0.0771	$C = 0.0105$
4	$D+\sigma$	-0.2023	$D = -0.0062$
5	$E+\sigma$	-0.2073	$E = -0.0112$
6	$F+\gamma$	-0.0853	$F = 0.0023$
7	$G+\gamma$	-0.0905	$G = -0.0029$
8	$H+\sigma$	-0.2032	$H = -0.0071$
2-FLUORONAPHTHALENE			
1	$A'+\sigma$	-0.2218	$A' = -0.0257$
2(F)	$B'+\gamma$	-0.0504	$B' = 0.0372$
3	$C'+\gamma$	-0.1236	$C' = -0.0360$
4	$D'+\sigma$	-0.1862	$D' = 0.0099$
5	$E'+\sigma$	-0.1946	$E' = 0.0015$
6	$F'+\gamma$	-0.0871	$F' = 0.0005$
7	$G'+\gamma$	-0.0905	$G' = -0.0029$
8	$H'+\sigma$	-0.1985	$H' = -0.0024$

(a) q_i (res) = $(1 - q_i)$ where q_i is the π -electron density on carbon atom i obtained from standard UHF calculations using the parameters given in refs. 1 and 2.

along with the calculated UHF spin density values for the same. The parameters $a, b, c, d, e, f, g, h, a', b', c', d', e', f', g'$ and h' have been calculated using the data given in Table 1 and are also listed in Table 1. Expressions for spin densities derived from the additivity model are given in Table 2 for some fluorinated systems. Using these expressions and the parameters in Table 1, spin densities for various positions have been computed and are given in Table 2. Spin density values predicted by the additivity model seem to be in excellent agreement with those obtained directly from standard UHF calculations.

Additivity model was also used along the lines described above for predicting UHF charge densities

TABLE 4 — PREDICTED UHF CHARGE DENSITIES IN FLUORO-SUBSTITUTED NAPHTHALENE RADICAL ANIONS^(a)

Position	Expression for q_i (res)	$q^{(b)}$ (res)		Error
		I	II	
1,2-DIFLUORONAPHTHALENE				
1(F)	A+A'+ σ	-0.187	-0.186	0.001
2(F)	B+B'+ γ	-0.078	-0.078	0.000
3	C+C'+ γ	-0.113	-0.113	0.000
4	D+D'+ σ	-0.192	-0.193	-0.001
5	E+E'+ σ	-0.206	-0.206	0.000
6	F+F'+ γ	-0.085	-0.084	0.001
7	G+G'+ γ	-0.093	-0.094	-0.001
8	H+H'+ σ	-0.206	-0.205	0.001
2,6-DIFLUORONAPHTHALENE				
1	A'+E'+ σ	-0.220	-0.220	0.000
2(F)	B'+F'+ γ	-0.050	-0.050	0.000
3	C'+G'+ γ	-0.127	-0.126	0.001
4	D'+H'+ σ	-0.189	-0.188	0.001
1,2,3,4-TETRAFLUORONAPHTHALENE				
1(F)	A+D+A'+ D'+ σ	-0.183	-0.182	0.001
2(F)	B+C+B'+ C'+ γ	-0.104	-0.102	0.002
5	E+H+E'+ H'+ σ	-0.215	-0.216	-0.001
6	F+G+F'+ G'+ γ	-0.091	-0.090	0.001
1,3,4,5,7,8-HEXAFLUORONAPHTHALENE				
1(F)	A+D+E+H+ D'+H'+ σ	-0.178	-0.176	0.002
2	B+C+F+G+ C'+G'+ γ	-0.144	-0.147	-0.003
3(F)	B+C+F+G+ B'+F'+ γ	-0.068	-0.065	0.003
4(F)	A+D+E+H+ A'+E'+ σ	-0.210	-0.209	0.001
1,2,3,4,5,6,7,8-OCTAFLUORONAPHTHALENE				
1(F)	A+D+E+H+ A'+D'+E'+ H'+ σ	-0.202	-0.202	0.000
2(F)	B+C+F+G+ B'+C'+F'+ F'+G'+ γ	-0.107	-0.105	0.002

(a) See footnote (a) under Table 2.

(b) q_i (res) = $(1 - q_i)$ where q_i is the π -electron density on the carbon atom i . q_i (res) values given under I were obtained using an additivity model (see text). Those given under II were obtained from standard UHF calculations using the parameters given in references 1 and 2.

for a series of fluoro-substituted naphthalene radical anions. The parameters A, B, C, D, E, F, G, H, A', B', C', D', E', F', G' and H' are given in Table 3. These parameters were used to predict the charge densities for all the fluorinated systems studied here. These charge densities were found to be in good agreement with those obtained by direct use of the UHF method. Results of above calculations for a few representative systems are given in Table 4 along with those obtained from UHF calculations.

The present study indicates that a simple additivity model is quite adequate for predicting UHF spin densities and charge densities in a series of fluoro-substituted naphthalene radical anions.

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Gamma-radiation Induced Decomposition in Formates

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Chemical damage induced in crystalline calcium, barium and lead formates by ⁶⁰Co γ -rays has been investigated. Chemical damage, measured as formaldehyde produced, increases with an increase in dose and builds upto a steady state. In the case of lead formate the chemical damage increases with dose at the beginning and reaches a maximum at 50.4 Mrad and then decreases.

IN an earlier publication¹, we reported the result of our work on the chemical damage induced in crystalline lead formate by ⁶⁰Co γ -rays. In the present note the analysis of chemical damage produced by γ -irradiation in crystalline formates of barium, calcium and lead, is presented.

Calcium formate was of AR grade. Barium and lead formates, synthesized² using analytical grade chemicals, were dried to constant weight at 110° and the composition confirmed by analysis. Samples were preserved over phosphorus pentoxide in a vacuum desiccator. Salts were irradiated at room temperature in evacuated pyrex glass ampoules with ⁶⁰Co γ -rays to various doses upto 125 Mrad at a dose rate 0.3 Mrad/hr for lead formate and 0.28 Mrad/hr for calcium and barium formates. The damage product, formaldehyde, was estimated spectrophotometrically³.

Irradiation induced light yellow colour in calcium and barium formates and grey colour in lead formate; the colour intensity increased with dose. The chemical damage measured as formaldehyde produced by various irradiation doses are presented in Table 1.

It is observed that the chemical damage induced by ⁶⁰Co γ -irradiation increases with dose and builds up a steady state. It is of interest to note that in the case of lead formate the concentration of formaldehyde increased with dose at the beginning and reached maximum at 50.4 Mrad and then decreased. It may be due to radiation annealing or radiolytic decomposition of formaldehyde. Qualitative analysis of the irradiated material shows that the other damage products are oxides and carbonates. In the case of lead formate trace

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