Heterocyclic Free Radicals. Part VI.[1] Substituent Effects on the Distribution of the Spin Density in 10-Arylphenoxazine and 10-Arylphenothiazine Cation Radicals

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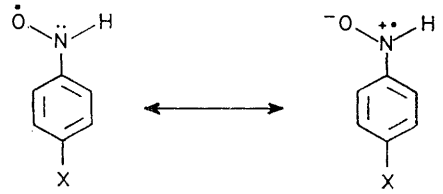
An examination of the e.s.r. spectra of >50 cation radicals derived from 10-arylphenoxazines and 10-arylphenothiazines shows that the spin distribution is influenced essentially inductively by the aryl substituent for substituents other than *p*-alkylamino-groups. The variations in spin distribution are correlated using established substituent constants and it is concluded that the radicals do not deviate significantly from the geometry previously adduced for the cation radicals of 10-phenylphenoxazine and 10-phenylphenothiazine. When the aryl substituents are *p*-alkylamino-groups, the spin distribution and probably also the geometry of the radicals are markedly perturbed from that in the respective 10-phenylazine cation radicals.

JANZEN [2] has reviewed the subject of the correlation of hyperfine splittings (h.f.s.) by substituent constants of the Hammett-type and has emphasised that established σ-values suffice for the correlation of trends in h.f.s. values within a family of radicals provided the substituent does not acquire a large proportion of the unpaired spin. Thus, according to Janzen a *valid* substituent is one which influences spin distribution within a radical by dipolar mechanisms only. For example, in aryl nitroxide radicals the variation in a_N with substitution depends on how the substituents influence the relative weightings of structures (1a and b)



(1a) (1b)

(1c) (1d)

by contributions such as (1c and d) according to whether X is, respectively, electron accepting or donating: the valid substituent is involved essentially with electron-pair displacements within the radical. An *invalid* substituent, which would not be well behaved in a plot using Hammett-type σ-values, is one which grossly perturbs the spin distribution in the radical. For example, a nitro-substituent is invalid in benzonitrile anion radicals. The radical does not correlate with other benzonitrile anion radicals and it is better considered a cyanonitrobenzene anion radical: the nitro 'substituent' has become the major spin bearing structure within the radical.

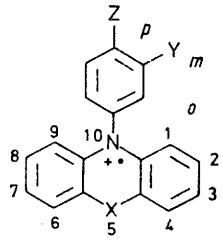
Accepting Janzen's tenet,[2] one may alternatively use hyperfine splitting correlations as a probe for the behaviour of differing kinds of σ-value. The hyperfine splitting of a nucleus within a radical is a direct measure of the unpaired electron density at that nucleus: for a wide variety of π-radicals it is found that the splitting from an 'α' proton (*i.e.* >Ċ–H) is directly proportional to the spin density in the $p^{(\pi)}$ orbital on the adjacent carbon atom (the McConnell relation) and also that a splitting from a nitrogen atom at a position of significant spin density is directly related to $\rho_N(\pi)$.[3] Thus a correlation of hyperfine splittings using particular σ-values may give insight into the adequacy of the σ-values in describing the electron distribution.

We felt there would be value in an investigation of substituent effects in arylphenoxazines and arylphenothiazines for the following reasons. A high twist angle between the planes of the aryl ring and the heterocyclic ring for these [1] and similar radical systems [4-9] has been inferred, and it is of interest to determine how the electron distribution responds to substitution in these cases. Also, Janzen [2] has indicated the paucity of data for cationic radicals by contrast with anionic and neutral radical families. We expected that the high intrinsic stability of oxazine and thiazine cation radicals would assist the investigation since the e.s.r. spectroscopic measurements could be made on species indefinitely stable under ambient conditions and also since a wide range of validity of substituents is expected in stable radical systems.

To avoid confusion between the numbering of the

[1] Part V, D. Clarke, B. C. Gilbert, and P. Hanson, *J.C.S. Perkin II*, 1975, 1078.
[2] E. G. Janzen, *Accounts Chem. Res.*, 1969, **2**, 279.
[3] F. Gerson, 'High Resolution E.S.R. Spectroscopy,' Wiley–Verlag Chemie, 1970, p. 41.
[4] A. Lomax, L. S. Marcoux, and A. J. Bard, *J. Phys. Chem.*, 1972, **76**, 3958.
[5] L. Lunazzi, A. Mangini, G. Placucci, and C. Vincenzi, *J.C.S. Perkin I*, 1972, 2418.
[6] L. O. Wheeler, K. S. V. Santhanam, and A. J. Bard, *J. Phys. Chem.*, 1967, **71**, 2223.
[7] M. D. Sevilla and G. Vincow, *J. Phys. Chem.*, 1968, **72**, 3641.
[8] K. Maruyama, M. Yoshida, and K. Murakami, *Bull. Chem. Soc. Japan*, 1970, **43**, 152.
[9] Y. Yamada, S. Toyoda, and K. Ouchi, *J. Phys. Chem.*, 1974, **78**, 2512.

heterocycle and the aryl ring we denote as *para*-series those radicals where in (2) Z is the substituent and Y is H and as *meta*-series the converse.



(2)

X = O, oxazine family
X = S, thiazine family

RESULTS

(a) *Oxidants.*—The arylphenoxazines and arylphenothiazines have been oxidised to their respective cation radicals using three oxidant–solvent systems: $AlCl_3$–$MeNO_2$, $Tl(OAc)_3$–$MeNO_2$, and H_2SO_4–$MeNO_2$. For the majority of radicals the results were independent of the oxidant. If, in individual cases, resolution of the spectra varied with oxidant, the system $Tl(OAc)_3$–$MeNO_2$ usually gave the best results. For a minority of substrates a more important dependence of the results on the medium was found. All the amino-substituents, NH_2, NHMe, and NMe_2, gave one kind of behaviour with $AlCl_3$–$MeNO_2$ and H_2SO_4–$MeNO_2$ but different behaviour with $Tl(OAc)_3$–$MeNO_2$. We interpret the former behaviour as resulting from conversion of the amino-groups into their respective ammonio-derivatives by protonation in $AlCl_3$–$MeNO_2$ and H_2SO_4–$MeNO_2$, whilst with the thallium(III) oxidant results consistent with unprotonated amino-groups are obtained (see below). We envisage the source of protons in $AlCl_3$–$MeNO_2$ to be HCl arising by hydrolysis of $AlCl_3$ by adventitious water, present at concentrations comparable with that of the organic substrate (*ca.* 10^{-6}M). The substituent NHAc, which we examined in arylphenothiazines, also yields results which vary with the medium. Again this could be due to a protonation of the substituent.

(b) *E.s.r. Spectra.*—Well resolved spectra were obtained from both the *meta*- and *para*-series of arylphenoxazine cation radicals. The overall spectrum width was *ca.* 3 mT and nitrogen hyperfine splittings were readily and accurately measurable; these are presented in Table 1a.

Comparison of spectra from the *meta*-series with the spectrum of the unsubstituted analogue and with spectra of *para*-substituted isomers shows that, as expected,[1] in the *meta*-series a small splitting has been removed by the incorporation of the substituent, *i.e.* the lines have the 'doublet' appearance associated with an odd number of interacting protons having the smallest resolvable splitting. The effect is particularly noticeable on the main nitrogen lines ($M_N = 0, \pm 1$, $\Sigma M_H = 0$) (see Figures 1 and 2). Assignments of proton splittings for selected radicals are made in Table 2; the basis for these assignments is discussed in a later section.

For the arylphenothiazine cation radicals the overall spectrum width was rather less, *ca.* 2.5 mT. By contrast with the oxazines the resolution of the spectra was somewhat variable and, in general, the *para*-series was better resolved than the *meta*-series. However, in each case the nitrogen splitting was quite unambiguous; experimental values of a_N are presented in Table 1b.

(c) *Correlations.*—Previous workers [2,10] interested in the correlation of hyperfine splittings by σ-constants have usually plotted a_X against σ. If, however, one wishes to make comparisons between families of radicals then variations in hyperfine splitting relative to the unsubstituted parent species should be plotted (*cf.* the use of log k/k_0, rather than log k, against σ for the correlation of reactivities). Consequently, we use $\Delta a_X = (a_X - a_X^0)$ where a_X is the hyperfine splitting of interest in a substituted radical and a_X^0 is the corresponding splitting in the unsubstituted radical. Since a hyperfine splitting corresponds to an energy difference between magnetic states, arising from interaction between electronic and nuclear magnetic moments in the applied field, it is not necessary to plot a

TABLE 1

a. Nitrogen hyperfine splittings for the cation radicals derived from 10-arylphenoxazines

	meta-Series		*para*-Series	
Substituent	a_N/mT	Δa_N [a]/μT	a_N/mT	Δa_N [a]/μT
H	0.855 [b]	0	0.855 [b]	0
Me	0.860	5	0.861	6
OMe	0.850	−5	0.854	−1
CO_2Et	0.840	−15	0.843	−12
Cl	0.841	−14	0.842	−13
F	0.840	−15	0.840	−15
CF_3	0.837	−18	0.839	−16
NO_2	0.828	−23	0.832	−27
NH_3^+	0.830	−25	0.833	−22
NH_2Me^+	0.829	−26	0.833	−22
$NHMe_2^+$	0.826	−29	0.829	−26
NH_2	0.864	9	0.864	9
NHMe	0.866	11	0.858	3
NMe_2	0.867	12	0.806 [c]	−49
$NHCO_2Et$	0.852	−3	0.853	−2

b. Nitrogen hyperfine splittings for the cation radicals derived from 10-arylphenothiazines

	meta-Series		*para*-Series	
Substituent	a_N/mT	Δa_N [a]/μT	a_N/mT	Δa_N [a]/μT
H	0.695 [b]	0	0.695 [b]	0
Me	0.699	4	0.700	5
OMe	0.690	−5	0.691	−4
SMe	0.687	−8	0.688	−7
COMe			0.682	−13
CO_2Et	0.679	−16	0.680	−15
Cl	0.676	−19	0.678	−17
F	0.673	−22	0.676	−19
CF_3	0.671	−24	0.675	−20
CN	0.667	−28	0.670	−25
SO_2Me			0.668	−27
NO_2	0.662	−33	0.665	−30
NH_3^+	0.665	−30	0.667	−28
NH_2Me^+	0.663	−32	0.665	−30
$NHMe_2^+$	0.661	−34	0.663	−32
NH_2	0.703	8	0.702	7
NHMe	0.705	10		
NMe_2	0.707	12	0.770; 0.515 [c]	
NHAc (1) [d]	0.690	−5	0.693	−2
NHAc (2) [e]	0.675	−20	0.679	−16
$NHCO_2Et$	0.692	−3	0.693	−2

[a] $\Delta a_N = (a_N - a_N^0)$. [b] *i.e.* a_N^0. [c] Invalid substituent, see text. [d] Non-protonating oxidant used. [e] Protonating oxidant used.

[10] B. M. Latta and R. W. Taft, *J. Amer. Chem. Soc.*, 1967, **89**, 5172.

logarithmic function of the splitting.[11] It should be noted, however, that the slopes of Δa_x against σ plots, like those obtained from other spectroscopic σ-correlations [12] and unlike those from reactivities (log k/k_0) are not dimensionless but have the dimensions of the spectroscopic variable.

No simple set of σ-values of the Hammett-type served to correlate adequately all the Δa_N values obtained for the two families of cation radical. The *meta*-substituted arylthiazines and -oxazines were well correlated by σ_m, but by comparison σ_p failed for the corresponding *para*-values (see Table 3). This remains true when, as in Table 3, the data for the substituents NHMe and NMe_2 are neglected as invalid [see (d) below]. Latta and Taft [10] have found that σ^- served to correlate the effects of electron-donating substituents on hyperfine splittings in *NN*-dimethylanilinium radicals. This failed, too, in the cases of the arylphenoxazine and -phenothiazine series. The single σ value which gave overall the best correlation of both *meta*- and *para*-substituents in both families was σ_I (see Table 3). The σ_I values used in determining the least squares lines

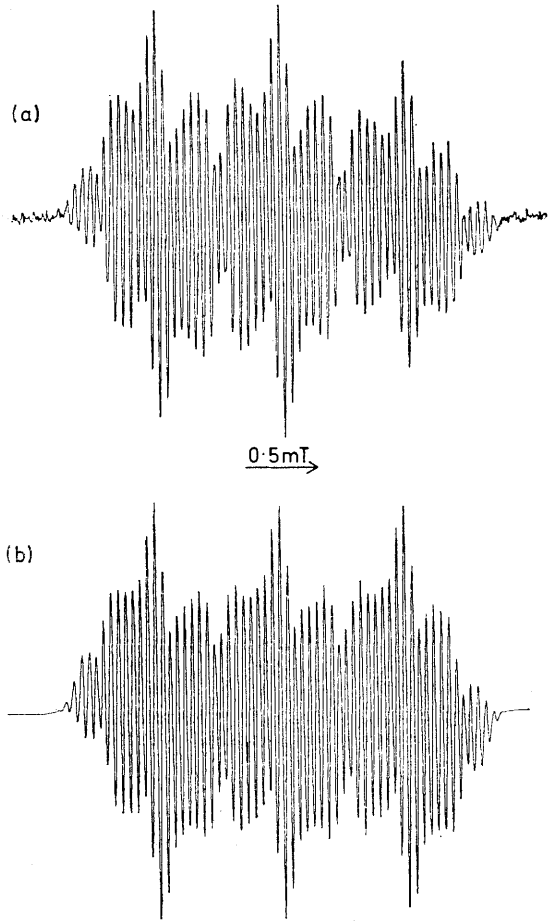


FIGURE 1(a) E.s.r. spectrum of the cation radical from 10-(4-methoxyphenyl)phenoxazine; (b) simulated spectrum

of Table 3, and in Figure 3, are taken from Taft's [13] most recent compendium of statistically optimised values. We have certain substituents, *e.g.* the ammonio-groups and $NHCO_2Et$, for which Taft quotes no σ_I values; our experimental results for these substituents are consequently not used in the statistical analysis summarised in Table 3.

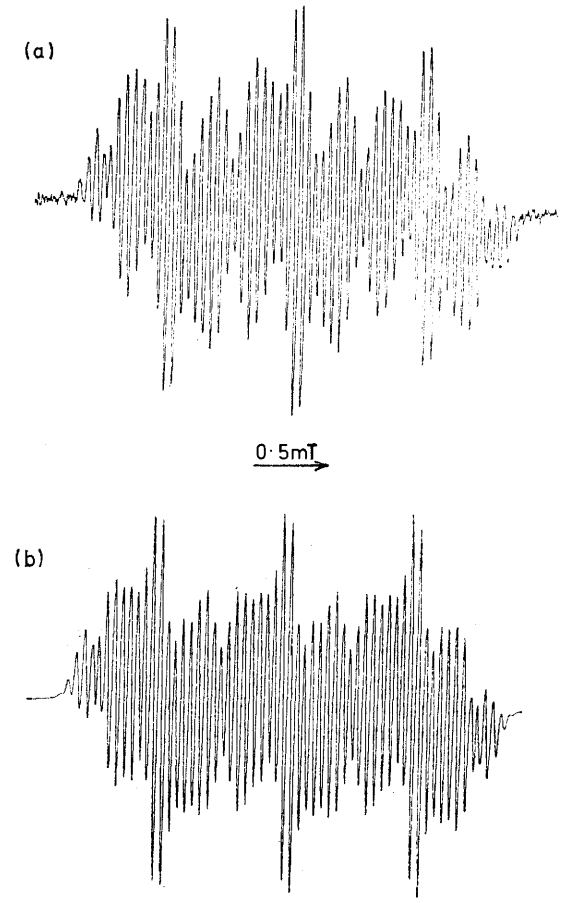


FIGURE 2(a) E.s.r. spectrum of the cation radical from 10-(3-methoxyphenyl)phenoxazine; (b) simulated spectrum

However, if Charton's [14] σ_I values for the ammonio-groups and for $NHCO_2Et$ are used their experimental Δa_N values are adequately correlated with the other data (see Figure 3). Also, we have ensured that each regression line is found using an adequate 'basis set' of substituents; *i.e.* following Taft *et al.*[13] we have used substituents covering the full range of electronic character and in numbers as large as practicable to optimise the statistical treatments.

Inspection of plots of Δa_N against σ_I for both the *meta*- and *para*-series of substituents in each family of radicals indicates that the points appropriate to substituents of $+M$ electronic character lie away from a line arbitrarily drawn through the origin, the co-ordinate appropriate to the unsubstituted radical, and points appropriate to substituents of electron-withdrawing character, in the sense that their Δa_N are more positive than 'expected', *e.g.* Figure 3.

Although not a σ constant, Dewar and Grisdale's [15] field parameter F/r_{ij} serves to correlate both *meta*- and *para*-

[11] K. W. Bowers, in 'Radical Ions,' eds. E. T. Kaiser and L. Kevan, Interscience, New York, 1968, p. 211.
[12] J. Shorter, 'Correlation Analysis in Organic Chemistry,' Clarendon, Oxford, 1973, ch. 4.
[13] S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Progr. Phys. Org. Chem.*, 1973, **10**, 1.
[14] M. Charton, *J. Org. Chem.*, 1963, **29**, 122.
[15] M. J. S. Dewar and P. J. Grisdale, *J. Amer. Chem. Soc.*, 1962, **84**, 3548.

TABLE 2

Complete assignments of hyperfine splittings in selected 10-arylphenoxazine and 10-arylphenothiazine cation radicals

	a(N)	a(1-H)	a(2-H)	a(3-H)	a(4-H)	a(*o*)	a(*m*)	a(X)
10-(X-Phenyl)phenoxazine								
X = H	(+)0.855	(−)0.142	(−)0.056	(−)0.303	(+)0.063	(−)0.050	(+)0.050	(−)0.018
X = 4-MeO	(+)0.854	(−)0.144	(−)0.054	(−)0.302	(+)0.054	(−)0.054	(+)0.054	
X = 3-MeO	(+)0.850	(−)0.143	(−)0.054	(−)0.302	(+)0.054	(−)0.054	(+)0.054	
X = 4-CF_3	(+)0.839	(−)0.130	(−)0.130	(−)0.297	(+)0.052	(−)0.052	(+)0.052	(±)0.014
X = 4-NO_2	(+)0.832	(−)0.123	(−)0.123	(−)0.296	(−)0.050	(−)0.050	(+)0.050	
10-(X-Phenyl)phenothiazine								
X = H	(+)0.695	(−)0.090	(−)0.090	(−)0.215	(+)0.022	(−)0.033	(+)0.022	(−)0.012
X = 4-Cl	(+)0.678	(−)0.084	(−)0.120	(−)0.208		(−)0.035	(+)0.019	
X = 4-NO_2	(+)0.665	(−)0.073	(−)0.130	(−)0.202	(±)0.016	(−)0.033	(+)0.016	

Experimental spectra were satisfactorily simulated using the coupling constants given in this Table.

TABLE 3

Statistical results for correlations by single parameter expressions: $\Delta a_N = \rho x + c$

Family	Series	n [a]	x	$-\rho/\mu T$	c	s [b]	r [c]
Oxazines	*meta*	9	σ_m	43.449	1.617	1.394	0.995
	meta	9	σ_I	55.001	9.373	5.346	0.929
	para	8	σ_p	21.983	−5.487	4.979	0.915
	para	8	σ^+	14.233	−9.086	5.767	0.883
	para	8	σ_I	47.890	8.098	4.396	0.934
	meta + *para*	16	F/r_{ij}	43.726	1.664	1.789	0.988
Thiazines	*meta*	11	σ_m	50.372	0.134	2.300	0.990
	meta	11	σ_I	65.512	9.384	4.901	0.952
	para	12	σ_p	24.027	−8.022	5.185	0.909
	para	12	σ^+	15.269	−12.767	6.097	0.872
	para	12	σ_I	55.106	6.359	3.700	0.955
	meta + *para*	22	F/r_{ij}	50.312	0.007	2.103	0.986

[a] No. of data sets. [b] Standard deviation of the estimate. [c] Correlation coefficient.

substituents on the same regression line; it also removes the dichotomy between $+M$ and other substituent types. From the definition of F it is tantamount to using σ_m values with an appropriate factor for substituents in both *meta*- and *para*-positions (see Table 3 and Figure 4 for the correlation of *p* and *m*-arylphenothiazine Δa_N using F/r_{ij}).

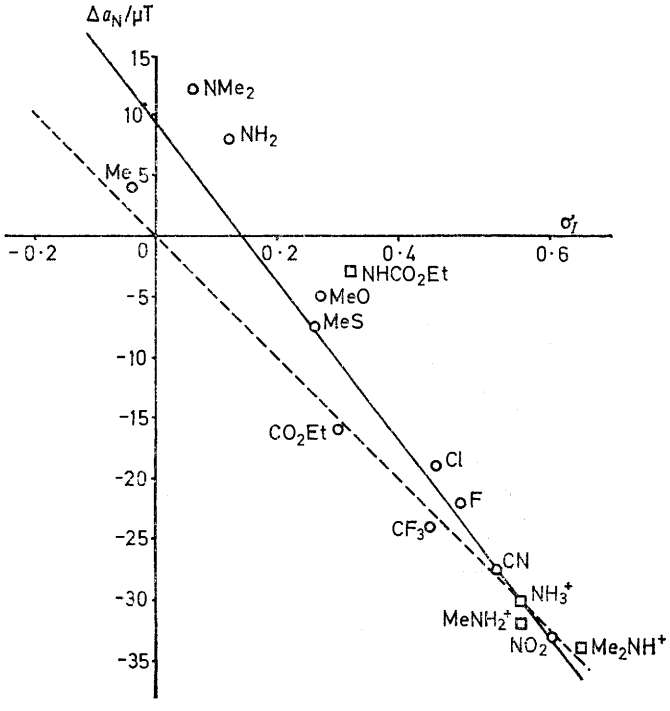


FIGURE 3 Variation of Δa_N with σ_I for the series of cation radicals from 10-(3-X-phenyl)phenothiazines: (——) least squares line; (– – – –) arbitrary line through origin; Taft's σ_I values ○; Charton's σ_I values □

We have also subjected the data to statistical analysis in terms of a dual parameter expression of the form: $\Delta a_N = \rho_I\sigma_I + \rho_R\sigma_R$, using each of Taft's ranks of σ_R, *i.e.* σ_R(BA), σ_R^0, σ_R^- and σ_R^+, with σ_I. The results are presented in Table 4. In order that correlations within a series remain strictly comparable, *i.e.* involve the same number of degrees of freedom, we have excluded data obtained on the thiazines for SMe, for no constant σ_R^+ value exists for this substituent. (The value of σ_R^+ for SMe which these results imply is 0.357, outside the range of literature values [13]). We have also excluded data for NHAc on account of the previously mentioned medium-dependence of a_N and variability of σ_R values.[13] The dual parameter treatment gives an improved precision of correlation: contrast Figures 3 and 5 which correlate the same data (except for SMe, excluded from the dual parameter treatment as stated above).

In Figure 6 are plotted for both families of radical, a_N(*para*) *versus* a_N(*meta*) values. Precise parallel correlations are obtained which accommodate substituents for which optimised σ_I and σ_R data are not quoted in Taft's review, *i.e.* the various ammonio-groups and $NHCO_2Et$ or for which variability has been noted, *e.g.* SMe and NHAc. The slope of the lines, 0.925 mT, indicates marginally the greater substituent effect from the *meta*-position.

(d) *Invalid Substituents.*—As indicated above, all the amino-groups, NH_2, NHMe, and NMe_2, in both *para*- and *meta*-positions display valid substituent behaviour [2] as ammonio-groups when the appropriate arylphenoxazines and arylphenothiazines are oxidised in protonating media. With the non-acidic oxidant, $Tl(OAc)_3$–$MeNO_2$, differing behaviour is found: the *para*-primary amino-group and

all types of *meta*-amino-substituent exhibit valid behaviour as the unprotonated amino-functions, as demonstrated by their data points falling on the various plots presented

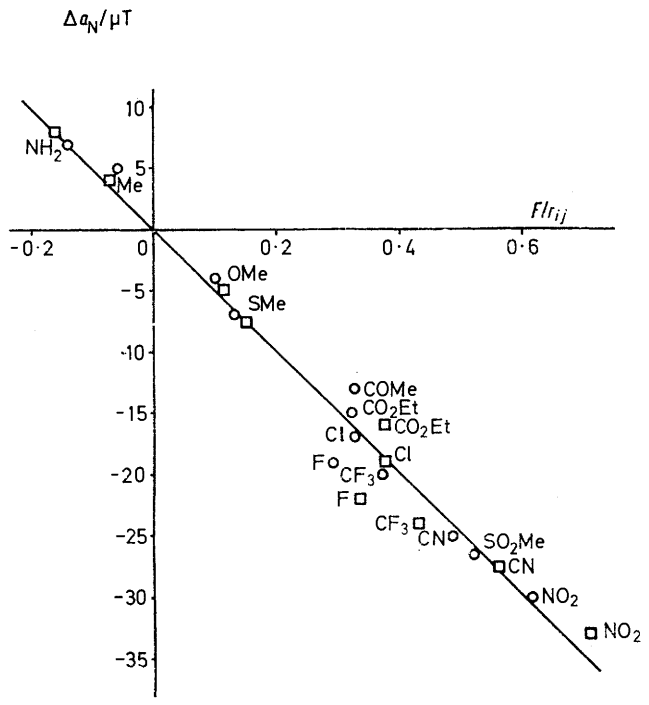
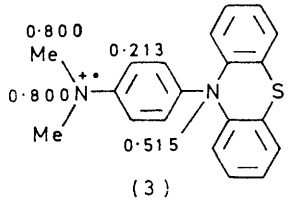


FIGURE 4 Variation of Δa_N with F/r_{ij} for the family of cation radicals from 10-arylphenothiazines: ○, *para*-series; □, *meta*-series

earlier. However, *p*-NHMe and *p*-NMe_2 in both families of radical behave anomalously as judged by comparison with the other substituents (*cf.* Δa_N values in Tables 1a and b).

(i) 10-(4-*Dimethylaminophenyl*)*phenothiazine*. When this material is oxidised by Tl^{III} in $MeNO_2$ an intense blue solution results which contains a free radical whose *g* value is 2.0030; the overall width of the e.s.r. spectrum is *ca.* 7 mT. By contrast, arylphenothiazines with valid substituents give rise to radicals whose solutions are orange-pink in colour, whose *g* values are close to 2.005 0, and whose overall spectrum width is *ca.* 2.5 mT. This is consistent with the radical no longer being phenothiazine-centred but being analogous to a Würster's Blue cation radical.[16] We have simulated the low resolution spectrum of the species using the hyperfine splittings indicated in (3) (in mT) which compare closely with those reported by Latta and Taft [10] for the 4-amino-*NN*-dimethylanilinium radical (4).



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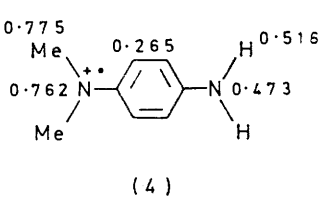


(4)

The assignment of a Würster's Blue structure to the radical implies a geometry with greater overlap of the aryl π-system with the *p*-orbital on the heterocyclic nitrogen than that accepted previously [1] for 10-phenylphenothiazine cation radical for which a dihedral angle of *ca.* 70° was deduced between the plane of the phenyl ring and that assumed for the heterocycle. To test whether the unique behaviour of the radical from 10-(4-dimethylaminophenyl)-phenothiazine was consistent with a more nearly coplanar

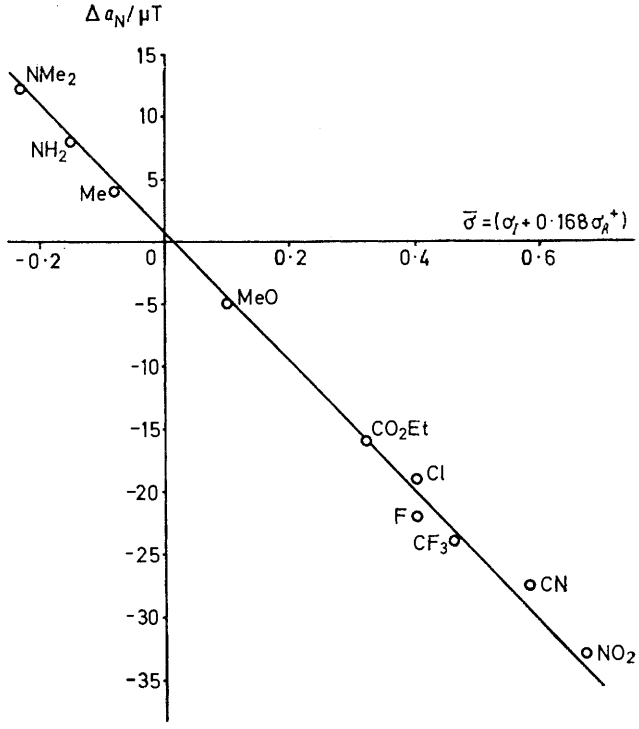


FIGURE 5 Variation of Δa_N with $(\sigma_I + 0.168\sigma_R^+)$ for the series of cation radicals from 10-(3-X-phenyl)phenothiazines

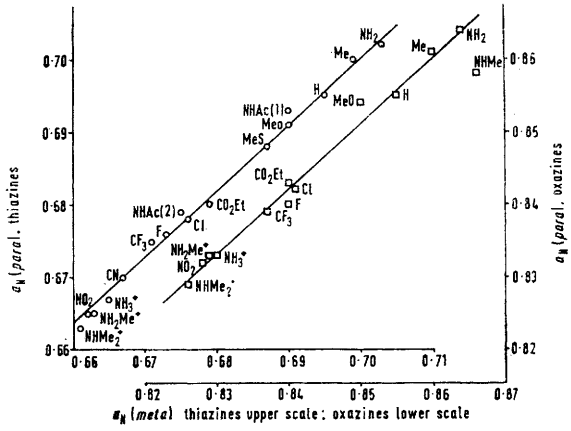


FIGURE 6 Plots of a_N(*para*) against a_N(*meta*) for the families of cation radicals from 10-arylphenothiazines ○, and from 10-arylphenoxazines □

geometry at the heterocyclic nitrogen we synthesised 10-(2-methyl-4-dimethylaminophenyl)phenothiazine in the hope that the 2-methyl substituent in the aryl ring would sterically impede the rotation required of the ring whilst, at the same time, having but a minimal electronic influence

[16] J. R. Bolton, A. Carrington, and J. dos Santos-Veiga, *Mol. Phys.*, 1962, **5**, 615.

on the spin distribution in the derived radical. Although the proton hyperfine splitting of the new radical is not well resolved it is clear from its overall spectrum width (*ca.* 2.5 mT), its three-line envelope and single nitrogen hyperfine splitting (0.705 mT), and its *g* value (2.0052) that it is a phenothiazine-centred radical and not a Würster's Blue analogue. Its colour is consistent with this also. Furthermore, there is a close similarity between a_N values for the available 10-(2-methyl-4-X-phenyl)phenothiazine cation radicals (*i.e.* X = NO_2, a_N 0.665; X = NH_2, a_N 0.704; and X = NMe_2, a_N 0.705 mT) and those for the same substituents X in the valid *meta*-arylphenothiazine series of Table 1b. This implies that NMe_2 is a valid substituent in the *ortho*-methylated series.

(ii) 10-(4-*Dimethylaminophenyl*)*phenoxazine*. Rather remarkably, this substance on oxidation with Tl^{III} in $MeNO_2$ does not give an anilinium radical like its thiazine counterpart. The measured *g* value (2.0032) is characteristic of an oxazine-centred radical (*cf.* *g* 2.0033 for 10-phenylphenoxazine); the spectrum width is *ca.* 3 mT and the colour, mauve, is typical of an arylphenoxazine radical. However, it is clear that its measured nitrogen hyperfine splitting (see Table 1a) is out of sequence with other valid arylphenoxazines. The experimental e.s.r. spectrum is extremely complex and has defied analysis, but from the number of lines observed it seems certain that splittings are obtained from the NMe_2 substituent although we cannot assign values.

(iii) 10-(4-*Methylaminophenyl*)-*phenoxazine and* -*phenothiazine*. Treatment of 10-(4-methylaminophenyl)phenoxazine with Tl^{III} in $MeNO_2$ gives an ill resolved spectrum with a broad three-line envelope and overall width of *ca.* 3 mT. This changes over *ca.* 0.5 h at concentrations typical of the e.s.r. measurements, its resolution improving, until finally a spectrum of overall width *ca.* 6 mT is obtained. At low resolution, this is interpretable in terms of two equivalent nitrogens and six equivalent protons, all with a splitting of *ca.* 0.60 mT. The change from the narrower to the broader spectrum is accelerated if a trace of water is added to the solution. In the case of the corresponding phenothiazine the broader form of spectrum with a similar splitting pattern is obtained immediately. The radical products obtained ultimately from both oxazine and thiazine have identical *g* values (2.0030).

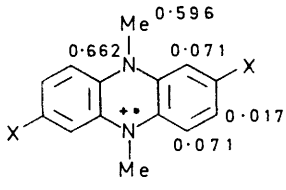
We assign 5,10-dihydrophenazine structures (5) to the final product in each instance. The experimental spectra have been simulated using the splittings (mT) indicated for X = 10-phenoxazinyl; the values found [17] for the parent 5,10-dimethyl-5,10-dihydrophenazine cation radical are shown, (6), for comparison. We exclude the alternative symmetrical dimeric structure, the hydrazine (7), on the grounds that the nitrogen hyperfine splittings for tetra-arylhydrazine cation radicals (*ca.* 0.7 mT [18]) and for the tetra-alkyl analogues (*ca.* 1.30 mT [19]) are both greater than observed in our case.

TABLE 4

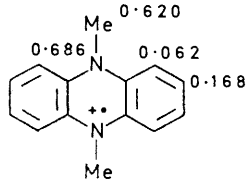
Statistical results for correlations by dual parameter expressions $\Delta a_N = \sigma_I\rho_I + \sigma_R\rho_R$

Family	Series	n [a]	σ_R	$-\rho_I/\mu T$	$-\rho_R/\mu T$	s [b]	r_I [c]	r_R [d]	R [e]	f [f]	$\lambda = \rho_R/\rho_I$
Oxazines	*meta*	9	σ_R(BA)	43.132	13.694	2.088	0.929	0.765	0.991	0.141	0.3175
	meta	9	σ_R^0	44.473	18.624	2.692	0.929	0.731	0.985	0.182	0.4188
	meta	9	σ_R^-	47.018	11.583	3.792	0.929	0.655	0.970	0.256	0.2463
	meta	9	σ_R^+	40.406	8.013	1.558	0.929	0.821	0.995	0.105	0.1983
	para	8	σ_R(BA)	41.067	11.147	1.809	0.934	0.656	0.991	0.135	0.2714
	para	8	σ_R^0	41.792	14.608	2.407	0.934	0.624	0.984	0.179	0.3495
	para	8	σ_R^-	42.124	8.863	3.175	0.934	0.386	0.972	0.236	0.2104
	para	8	σ_R^+	39.110	7.069	1.207	0.934	0.725	0.996	0.090	0.1807
Thiazines	*meta*	10	σ_R(BA)	52.624	13.737	2.062	0.952	0.559	0.993	0.106	0.2610
	meta	10	σ_R^0	51.397	16.255	3.494	0.952	0.808	0.981	0.180	0.3163
	meta	10	σ_R^-	57.483	10.249	4.079	0.952	0.511	0.974	0.210	0.1783
	meta	10	σ_R^+	49.713	8.348	1.138	0.952	0.822	0.998	0.059	0.1679
	para	11	σ_R(BA)	47.443	11.156	1.226	0.954	0.668	0.996	0.066	0.2351
	para	11	σ_R^0	48.034	14.459	1.732	0.954	0.647	0.992	0.094	0.3010
	para	11	σ_R^-	48.487	8.730	2.288	0.954	0.633	0.986	0.124	0.1800
	para	11	σ_R^+	45.891	7.097	0.613	0.954	0.719	0.999	0.033	0.1546

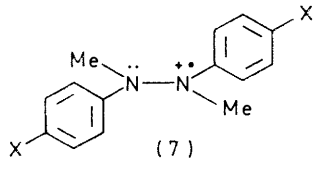
[a] No. of data sets. [b] Standard deviation of the estimate. [c] Correlation coefficient of Δa_N on σ_I. [d] Correlation coefficient of Δa_N on σ_R. [e] Multiple correlation coefficient. [f] See text and ref. 13.



(5)



(6)



(7)

X = phenoxazin-10-yl
or phenothiazin-10-yl

The resolution of the spectrum of the initial arylphenoxazine radical cation is marred presumably by the early presence of (5; X = phenoxazin-10-yl) in the solution. To avoid this we adopted the following procedure: 10-(4-methylaminophenyl)phenoxazine was oxidised by Tl^{III} in $MeNO_2$ acidified with H_2SO_4. The product was thus the stable ammonio-substituted radical. Once all the oxidant was consumed, 1,8-bisdimethylaminonaphthalene (' proton

[17] R. F. Nelson, D. W. Leedy, E. T. Seo, and R. N. Adams, *Z. Analyt. Chem.*, 1967, **224**, 184.

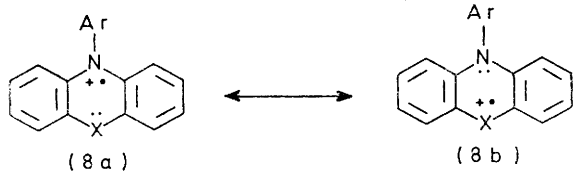
[18] M. R. Das, A. V. Patankar, and B. Venkataraman, *Proc. Indian Acad. Sci.*, 1960, **53***A*, 273.

[19] S. F. Nelsen, G. R. Weisman, P. J. Hintz, D. Olp, and M. R. Fahey, *J. Amer. Chem. Soc.*, 1974, **96**, 2916.

sponge '),[20] was added to reduce acidity and to deprotonate the ammonio-substituent. The supernatant solution from the resultant precipitate contained a slowly decaying radical which displayed a three line spectral envelope. Two hyperfine splittings were measurable: a_N 0.858 and a proton splitting, a_H 0.05 mT. This value for the nitrogen hyperfine splitting may indicate the onset of substituent invalidity for the *p*-NHMe group (see Figure 6 for the displacement from the valid substituent line). The unusual conditions for the generation of the radical, however, indicate that the result should perhaps be viewed with circumspection.

DISCUSSION

(a) *Correlations* of Δa_N *by* σ_I.—The work of Stock and co-workers [21] has clearly vindicated the premise of Kirkwood and Westheimer [22] that the ' inductive effects ' of substituent groups are due essentially to the electrostatic fields exerted at a site of interest by polar or dipolar substituents. Furthermore, it has shown that Taft's inductive parameter σ_I is a precise measure of such effects. The statistical analyses we have presented of variation in Δa_N values with substituent in the arylphenoxazine and arylphenothiazine families imply that 85—90% of the variance in Δa_N is correlated by σ_I. In simplest terms, we can say that the primary residence of spin density in these radicals, the nitrogen atom, is also a cationic centre and as such is destabilised relative to the unsubstituted parent radical by the electrostatic fields set up at nitrogen by dipolar and polar, overall electron-withdrawing substituents. As a consequence, the spin distribution in the radicals varies with substitution in a manner which reduces the positive charge and spin density at nitrogen (and hence the experimental observable, a_N) as the electron-withdrawing effect of the substituent increases in magnitude. In phenoxazine and phenothiazine radicals generally, the Group VI heteroatom is the second most important site of unpaired spin density.[23,24] Our suggestion is that the influence of increasingly electron-withdrawing substituents in the aryl ring is to redistribute spin and charge from nitrogen onto the Group VI heteroatom; in valence bond terms it is to increase the weighting of structure (8b) relative to (8a).



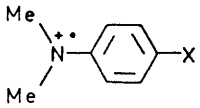
(8a) (8b)

X = O or S

Various observations are in accord with this suggestion. First, in the thiazines there is a small but measurable increase in the *g* value of the radicals as the $-I$ effect of the aryl substituent increases. Thus for 10-(3-dimethylaminophenyl)phenothiazine cation radical g = 2.0051 and 10-(4-nitrophenyl)phenothiazine g = 2.0053, which fact is consistent with increased spin density on the heavier atom.[23]

Secondly, inspection of Table 3 shows that whatever explanatory variable is chosen for correlating Δa_N, the slope ρ is always greater in magnitude for thiazines than for oxazines. This is consistent with a greater weighting for (8b) relative to (8a) when X is the less electronegative group six element.

A third indication that powerfully $-I$ substituents lead to a redistribution of spin in the heterocyclic portion is that the variation in a_N with σ_I in the present radicals is of opposite sign to that found by Latta and Taft [10] for *NN*-dimethylanilinium radicals, (9). In (9), a substituent X which repels positive charge must localise the charge, and hence necessarily unpaired spin, on nitrogen whilst in our radicals the unsaturated heterocyclic



(9)

system replaces the methyl groups in (9) and charge and spin are repelled further, resulting in the observed diminution of a_N with increasing $-I$ effect of the substituent.

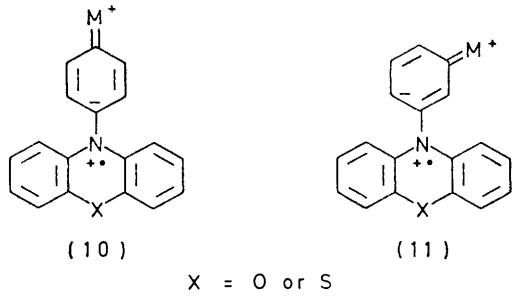
Finally, the heterocyclic proton hyperfine splittings are in accord with the spin redistribution described (Table 2). For the oxazines, where resolution is better, it is apparent that as the aryl substituent becomes progressively more electron withdrawing and a_N decreases, the two largest proton hyperfine splittings also decrease. We assign these to *a*(1-H) and *a*(3-H), the latter being the greater, on the basis of earlier calculation and the fact that these are formally ' *ortho* ' and ' *para* ', respectively, within the heterocycle, to nitrogen. The trends within the remaining heterocyclic proton hyperfine splittings are best discerned by considering as extremes the radicals from 10-phenyl- and 10-(4-nitrophenyl)-phenoxazine. Substitution of the nitro-group results in the two splittings of (−)0.056 and (+)0.063 mT being replaced by splittings of (−)0.123 and (+)0.050 mT. Of the latter, we assign the value of larger magnitude to the proton at C-2 on the grounds that this position, being ' *para* ' within the heterocycle to oxygen, will acquire increasing positive spin density as that on oxygen increases. Since the C-2 position was one of positive spin density in the radical from 10-phenylphenoxazine [1] the coupling constant increases in magnitude on introduction of the nitro-substituent. Increasing spin density on oxygen also places increased positive spin density

[20] R. W. Alder, P. S. Bowman, W. R. S. Steele, and D. R. Winterman, *Chem. Comm.*, 1968, 723.
[21] H. D. Holtz and L. M. Stock, *J. Amer. Chem. Soc.*, 1964, **86**, 5188; F. W. Baker, R. C. Parish, and L. M. Stock, *ibid.*, 1967, **89**, 5677.
[22] J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.* 1938, **6**, 506; 513.
[23] M. F. Chiu, B. C. Gilbert, and P. Hanson, *J. Chem. Soc.* (*B*), 1970, 1700.
[24] P. D. Sullivan and J. R. Bolton, *J. Magnetic Resonance*, 1969, **1**, 356.

on C-4, being formally '*ortho*' within the heterocycle to oxygen. However, since this position in the 10-phenylphenoxazine radical is one of negative spin density,[1] redistribution of spin density onto oxygen results in the decrease in the measured a(4-H) hyperfine splitting. The aryl-ring protons hyperfine splittings are not measurably different between the radical from 10-phenylphenoxazine and its nitrated analogue.

Consider now the arylphenothiazine cation radicals. We had noted earlier [1] an ambiguity in assignment for the 10-phenylphenothiazine cation radical. If the splittings for the latter are assigned (see Table 2) a(1-H) = (−)0.090; a(3-H) = (−)0.215 mT, as previously [1], but a(2-H) = (−)0.090 and a(4-H) = (+)0.022 mT, we see the distribution of splittings resembles that found for the 10-(4-nitrophenyl)phenoxazine cation radical *i.e.* $|a(4\text{-H})| < |a(1\text{-H})| = |a(2\text{-H})| < |a(3\text{-H})|$. This parallelism of spin distributions is understandable in terms of the influence of the nitro-substituent in the oxazine being to redistribute spin density onto the Group VI heteroatom in similar proportion to that found in the unsubstituted 10-phenylphenothiazine cation radical, a concept in harmony with the relative electronegativities of oxygen and sulphur.

(b) *Correlation of* Δa_N *by Dewar and Grisdale's* [15] *Field Parameter,* F/r_{ij}.—We noted earlier that substituents of $+M$ electronic character deviated, in Δa_N against σ_I plots, from a line arbitrarily drawn through the origin and the data points of electron-attracting substituents. Ritchie and Sager [25] had noted similar deviation in plots of σ_I *versus* Dewar and Grisdale's F. When we plot Δa_N against F/r_{ij}, the deviations are compensatory and a precise correlation is found (see Table 3). It is now clear that Dewar's [15] original approximation in evaluating F values [*i.e.* that substituent effects from the benzene *meta*-position are due to the substituents' electrostatic fields alone, whence $F = \sigma_m\sqrt{3}$] was an oversimplification: the F values of $+M$ substituents are 'contaminated' mesomerically by resonance interaction between the $+M$ substituent and the aromatic system. Dewar's [26] later work attempts to separate completely the field effect from mesomeric influences. For present purposes the important point is that the mesomeric contamination present in F gives a parameter which correlates Δa_N better than σ_I, and further it indicates the nature of the electronic interaction which permits it to do so. In valence bond terms, structures of type (10) and (11) serve to influence the relative weighting of (8a and b) so that the nitrogen splitting is enhanced for $+M$ substituents (see Figure 3). The finding that the *para*-series of radical is correlated on the same regression as the *meta*-series without need for involvement of Dewar and Grisdale's [15] mesomeric parameter M is good evidence that there is little conjugation through the N–aryl bond: the result is consistent with our earlier suggestion of a high twist angle between the planes of the aryl and heterocyclic ring systems.[1]



(10) (11)

X = O or S

(c) *Correlations of* Δa_N *by Dual Parameter Expressions.*—The observation of hyperfine splittings from nuclei in the aryl moiety of the arylphenoxazine and arylphenothiazine cation radicals requires that the aryl ring and the heterocycle do not have completely decoupled π-systems. Application of elementary trigonometry to a model of the radicals which has C–N = C–C = 1.395 Å,[27,28] C–H = 1.084 Å,[27] and a van der Waals separation of 2.4 Å,[29] of *o*-aryl and heterocyclic 1- and 9-hydrogens, both ring systems being assumed planar, leads to a predicted dihedral angle of 66°. Similar twist angles have been suggested for these [1] and structurally related systems.[4-9] Our dual parameter analysis gives further experimental evidence that a dihedral angle of this size is essentially correct. Inspection of Table 4 shows that σ_R^+ is statistically the best partner for σ_I in correlating Δa_N. In all series, for σ_R^+ the standard deviation of the estimate s is a minimum; the correlation coefficient, r_R, of Δa_N on σ_R is a maximum; the multiple correlation coefficient R is maximised and the f-parameter, Taft's [13] suggested criterion of precision of correlation, falls on or below his critical value of 0.1 in each case. Intuitively also, σ_R^+ is the resonance parameter expected best to accommodate the results: the radicals possess unit cationic charge which may be delocalised on to the substituent. It is noteworthy that this is true for cation radicals even when the substituent is in the *meta*-position, and also that coplanarity of aryl and heterocyclic moieties is not required for the substituent to exercise its stabilising influence from either position. Structures (12) and (13) are the relevant canonical forms; it can be seen that the substituent acquires the cationic charge in each case but that no double bond character is assigned to the N–aryl linkage, which may consequently be twisted. The only constraint is that the degree of twist should be such as to give finite probability for transmission of spin from nitrogen into the aryl ring, *i.e.* $\theta < 90°$.

The coefficients ρ_R and ρ_I are the susceptibilities of

[25] C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 1964, **2**, 323.

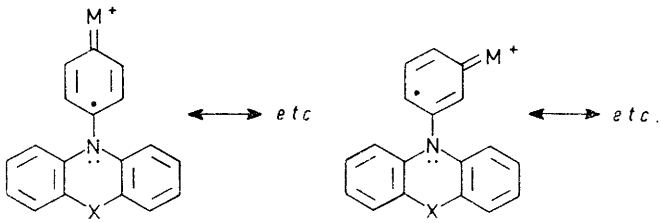
[26] M. J. S. Dewar, R. Golden, and J. M. Harris, *J. Amer. Chem. Soc.*, 1971, **93**, 4187.

[27] 'Tables of Interatomic Distances and Configuration in Molecules and Ions,' Chem. Soc. Special Publication 11, London, 1958.

[28] M. Mohammed and B. R. Sundheim, *Theor. Chim. Acta*, 1968, **10**, 222.

[29] 'Handbook of Chemistry and Physics,' ed. R. C. Weast, Chemical Rubber Co., Cleveland, 1971—72, 52nd edn., Table D146.

Δa_N separately to the mesomeric and inductive (field) effects of the substituents, and their ratio, $\lambda = \rho_R/\rho_I$, is an indication of their relative importance. For a reactivity or property correlated by Brown's [30] σ^+, $\lambda = 1$. The introduction of a twist angle into the bond between a site of interest and a substituted benzene ring should



(12) (13)

X = O or S

not, to a first approximation, influence the inductive field effects transmitted from the substituent to the site. However, mesomeric effects involving N-*p* and aryl-π overlap will be reduced as the twist angle increases, the angular dependence of the transmission of mesomeric effects varying as $\cos^2\theta$.[31] The ratio λ, therefore, in our case, reflects the degree of twist: $\lambda = \lambda_0\cos^2\theta$. When $\theta = 0$, $\lambda = 1$ whence $\lambda_0 = 1$ and $\lambda = \cos^2\theta$. The λ values generated using all the σ_R values give rise to θ values in the range 50—67°. The resonance parameter which gives the best statistical fit of the results, σ_R^+, yields an average value of $\theta = 64°$ for the two series of oxazine radical and $\theta = 66°$ for the two thiazine series. This difference and the fact that the *meta*-series give θ values *ca.* 1° less than the *para*-series are not regarded as significant.

All our results are thus consistent with the valid arylphenoxazine and arylphenothiazine cation radicals behaving as heterocycle-centred radicals in which both the aryl and heterocyclic portions are planar and in which a preferred angle of *ca.* 65° is subtended between the planes. The magnitude of this angle is the minimum that the species can accommodate without serious intramolecular steric crowding occurring between the *o*-hydrogens of the aryl ring and the 1- and 9-hydrogens of the heterocycle.

Planarity of the heterocycle is an assumption [1,23] but for the valid substituents there is no experimental reason for assuming otherwise. Even if it transpires that in the radicals the heterocycles are not planar we would suggest that nevertheless the heterocycle's geometry is fixed in each family throughout the range of valid substitution. There is no indication of gradual geometry change over the range of valid substitution. On the contrary, the linearity of the plots of Figure 6 implies constancy of relative substituent effects from *meta*- and *para*-positions. Any geometric variation, for example associated with the more powerfully mesomeric groups ($+M$ or $-M$) causing the radicals to tolerate a smaller dihedral angle in order to maximise overlap between the non-bonding orbital on the heterocyclic nitrogen and the aryl π-system, would confer curvature on the Figure 6 plots, for such overlap would be associated with *para*-quinonoid canonical structures implying the greater substituent effect from the *para*-position.

(d) *Invalid Substituents.*—A trend is apparent in the behaviour of the invalid substituents which suggests degrees of invalidity. For example, in both oxazine and thiazine families the *p*-dimethylamino-substituent is invalid; however, the radical is heterocycle-centred in the oxazine but substituent-centred in the thiazine. For *p*-NHMe we may have observed the heterocycle-centred radical in the case of the oxazine, but the formation of the 5,10-dihydrophenazine system, particularly in the presence of base (water), implies that it may react as, or give rise to, a substituent-centred radical. Our failure to observe a heterocycle-centred radical with the *p*-NHMe substituent in the thiazine family may imply the non-existence of this species, which would be consistent with the difference in behaviour of NMe_2 between the two families. We suggest that these trends in the behaviour of invalidly substituted systems can be explained by differing degrees of change from the geometry deduced for the radicals with valid substituents. The Würster's Blue type of behaviour of the radical from 10-(4-dimethylaminophenyl)phenothiazine clearly necessitates efficient overlap of the non-bonding orbital of the heterocyclic nitrogen with the aryl π-system. To achieve this a wholly planar structure is not feasible, for this would require an approach of the *o*-aryl hydrogens to the heterocyclic 1- and 9-hydrogens of *ca.* 0.5 Å. Now if the radical is substituent-centred, the phenothiazine system might be expected to approximate the shape it normally exhibits in the unoxidised form *i.e.* folded with a dihedral angle <180° between the planes of the lateral

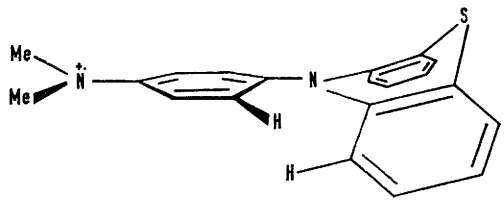


FIGURE 7 Proposed preferred conformation of the cation radical from 10-(4-dimethylaminophenyl)phenothiazine

carbocyclic rings.[32] Crystal structures determined on several nitrogen-substituted phenothiazines show that even in the folded heterocycle (dihedral angle, *ca.* 140°) the nitrogen remains essentially trigonal, the $\hat{CNC}$ angles being consistently closer to 120° than to the tetrahedral angle.[33] A molecular model shows that a geometry may be possible in which the aryl ring and a trigonal phenothiazine nitrogen are co-planar but where the pheno-

[30] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.
[31] B. M. Wepster, *Progr. Stereochem.*, 1958, **2**, 99.
[32] D. Feil, M. H. Linck, and J. J. H. McDowell, *Nature*, 1965, **207**, 285.
[33] M. C. Malmstrom and A. W. Cordes, *J. Heterocyclic Chem.*, 1972, **9**, 325.

thiazine system is folded (Figure 7). The model, with the same dimensions as that earlier considered for valid radicals, indicates that a fold angle of 140° in the phenothiazine would give rise to a dihedral angle of *ca.* 25° between the planes of the aryl ring and each lateral carbocycle of the phenothiazine. This would necessitate closer than van der Waals approach of the *o*-aryl and phenothiazine 1- and 9-hydrogens. However, the model probably underestimates the C–N bond lengths in a folded phenothiazine,[33] and the real molecule may further distort by out-of-plane bending of the interacting hydrogens.[34] The energetics of similar 'skew-helix' species have been discussed by Hoffmann *et al.*[35] It seems clear from the magnitudes of the measured nitrogen hyperfine splittings, however, and by comparison of them with those in (4),[10] that there is no significant *bending* at the heterocyclic nitrogen (*i.e.* distortion from trigonal towards tetrahedral), for a_N would increase rapidly with the proportion of *s* character in the orbital of the unpaired electron.[36]

The suggestion of steric crowding in the radical from 10-(4-dimethylaminophenyl)phenothiazine is clearly consistent with the observation of valid behaviour of *p*-NMe_2 when an *o*-methyl group is introduced into the molecule. The behaviour of the radical from 10-(4-dimethylaminophenyl)phenoxazine is also understandable if it be accepted that the phenoxazine heterocycle is less able to fold than phenothiazine. No crystal structure of a phenoxazine seems to have been undertaken but the weight of evidence is that phenoxazine is planar in the solid phase;[37-39] dielectric relaxation measurements indicate that when oxygen replaces sulphur in folded molecules such as phenothiazine the resultant molecule is more nearly planar.[40] Since folding of the heterocycle reduces overlap of the non-bonding orbital on nitrogen with the π-systems of the lateral carbocycles a smaller degree of fold in the oxazine could result in the lower energy condition being for the radical to remain heterocycle-centred. However, the non-correlation of the measured Δa_N with those of validly substituted arylphenoxazines implies that a change has occurred which we suggest is one of relative geometry.

EXPERIMENTAL

(a) *E.s.r.*—All e.s.r. spectra were obtained on a Varian E3 spectrometer at ambient temperature. Hyperfine splittings were measured to within 0.005 mT by comparison with the spectrum of a solution of *p*-benzosemiquinone in aqueous ethanol [a(H) 0.2368 ± 0.0001 mT [41]] and g values were measured by comparison with an aqueous solution of Fremy's salt (g 2.0055).[42]

Solutions of cation radicals on which measurements were made were prepared using dry nitromethane (distilled from CaH_2) and were deoxygenated with a stream of nitrogen before and during mixing.

The computer simulation of spectra used a FORTRAN IV programme in which Lorentzian line-shape was assumed.[23] The multiple regression programme used in the dual parameter statistical analysis was written by Dr. M. Green. All computation was executed on an ICL 4130 computer.

(b) *Syntheses.*—The necessary arylphenoxazines and arylphenothiazines have been prepared by three main routes: (A) Ullmann arylation of the parent heterocycles with an appropriate aryl iodide; [1] (B) nucleophilic displacement of activated halogen from a suitable *para*-substituted aryl halide by the conjugate base of the parent heterocycles; [43] and (C) further elaboration of a product of routes (A) or (B).

(A) *Ullmann arylations.* Routinely, phenoxazine and phenothiazine were arylated by refluxing overnight with the appropriate aryl iodide, in nitrobenzene protected by nitrogen, in the presence of K_2CO_3 and copper bronze. However, it was found necessary to shorten the reaction time (to *ca.* 6 h) when the substituent in the aryl iodide was electron withdrawing. Aryl iodides were preferable to bromides; all were known compounds and were either commercially available or were readily synthesised by Sandmeyer reaction on an accessible aniline or by trans-halogenation from the bromide *via* Grignard reaction. Yields from Ullmann reaction were variable in the range of 20—80%. The crude product was obtained after distillation of the nitrobenzene solvent.

(B) *Nucleophilic arylation.* The conjugate bases of phenoxazine and phenothiazine were generated by treating the heterocycles, under nitrogen, with a small excess of NaH in dry dimethyl sulphoxide. After evolution of hydrogen was complete, the aryl chloride (for *p*-NO_2) or fluoride (for *p*-CN or *p*-SO_2Me) was added and the temperature maintained for 1.5 h at 60—70°. Next the reaction mixture was poured into water, neutralised with dilute HCl and the crude product collected by filtration.

The crude products from routes (A) and (B) were purified by chromatography on alumina, eluting with light petroleum–diethyl ether or benzene–chloroform of a polarity suitable to the substance of interest.

(C) *Elaborations of other materials.* Aryl-phenoxazines and -phenothiazines with primary amino-substituents were prepared by reduction of the appropriate nitroaryl precursor using hydrazine hydrate and 5% Pd on C in 90% ethanol.[44] To synthesise their acetyl and carbamate derivatives, these amines were treated either with acetyl chloride or with ethyl chloroformate in pyridine. Substances with the substituent NHMe were obtained by a reduction of the above carbamates using lithium aluminium hydride [45] in refluxing

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TABLE 5

M.p.s (°C) for 10-arylphenoxazines and 10-arylphenothiazines

Aryl substituent	Phenoxazine family *meta*-Series	Phenoxazine family *para*-Series	Phenothiazine family *meta*-Series	Phenothiazine family *para*-Series
H	138—139 (lit.,[47a] 138—139)		94—95 (lit.,[47b] 94—95)	
OMe	161—162	172—173	132—133	172—173
SMe			93—96	153—154
Me	123—124	126—127	129—130	152—154 (lit., [47c] 135—136)
F	138—139	120—121	64—66	104—105
Cl	95—96	183—184	106—107	121—122
COMe				178—179
CO_2Et	92—93	142—143	107—109	82—84
CF_3	105—106	196—197	58—59	126—127
CN			122—123	157—158
SO_2Me				204—205
NO_2	149—150	200—201	69—71	156—157 (lit.,[47d] 156—157)
NMe_2	234—235	240—242	140—142	208—210
NHMe	152—154	173—175	126—128	182—183
NH_2	206—208	221—222	155—157	180—181 (lit.,[48] 179—181)
NHAc			128—131	232—233 (lit.,[48] 219—220)
$NHCO_2Et$	200—204	148—149	160—162	220—222

tetrahydrofuran. Aryl-phenoxazines and -phenothiazines with the substituent NMe_2 were obtained by methylation of the primary amines with Me_2SO_4 in refluxing benzene in the presence of K_2CO_3. After removal of the solvent, the required products were obtained as the first eluting amines on chromatography with silica eluting with benzene–cyclohexane (1 : 1).

10-(3-Cyanophenyl)phenothiazine was prepared from 10-(3-chlorophenyl)phenothiazine by refluxing with CuCN in quinoline for 36 h.[46]

Most materials were recrystallised from ethanol, although particular substances required admixture of either chloroform or water. The fluorophenylphenothiazines were crystallised (at −70°) from hexane. Satisfactory analyses were obtained for all new substances. M.p. data are presented in Table 5.

We thank the S.R.C. for a research studentship (to D. C.).

[5/1165 *Received*, 16*th June*, 1975]

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