Substituent Effects on the Properties of Stable Aromatic Free Radicals. The Criterion for Non-Hammett Behavior[1]

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Abstract: Substitution in the *para* positions of the aryl groups of the triarylaminium salt and the 1-picryl-2,2-diarylhydrazyl free radicals strongly affects the optical and esr spectra of these substances. In the aminium salt series, either donor or acceptor substituents alter each type of absorption in the same direction. In the hydrazyl series, donor and acceptor substituents shift each type of absorption in opposite directions. These observations can be interpreted in terms of the contributions of structures which place only an unpaired electron, or either an unpaired electron or an unshared electron pair, on the atom to which is attached the aromatic rings which contain the substituents in these molecules. Generalization of these ideas affords a structural basis for predicting the nature of substituent effects in other types of stable free radicals. Those unsubstituted radicals for which one can write both structures $G—C_6H_4—X\cdot$ with an unpaired electron, and $G—C_6H_4—X:$ with an unshared electron pair, on the atom *para* to the site of substitution, belong to class O. Those radicals for which only the first structure can be written for the unsubstituted radical are assigned to class S. Class O (for opposite) radicals exhibit Hammett-like behavior, with donor and acceptor substituents shifting observed properties in opposite directions, but properties of class S (for same) radicals are shifted in the same direction by either donor or acceptor substituents. Known types of stable free radicals are classified on the basis of this structural criterion, and the classifications are shown to be consistent with the available data on these systems.

The Hammett equation correlates the effects of substitution in a benzene ring on reaction rates or equilibria of electron-paired compounds, within limits which have become reasonably clearly defined over the years.[2–4a] The equation has also been applied to the correlation of a number of physical properties with structure.[3–5] Among these are the longest wavelength ultraviolet absorption frequencies of substituted aromatic systems.[4b]

The applicability of the Hammett relationship to the reaction rates and equilibria or other properties of free radicals has not been so clear. This is in part because the difficulties in preparing and studying most classes of free radicals are so great that few investigations have been conducted over a wide enough range of substituent types or of measurable properties to afford a conclusive test of radical behavior. It is also due to the intervention of polar effects which lead to Hammett-type correlations for a variety of reactions which involve transient free radicals.[6] For just one property of one type of stable radical, the data show that the Hammett equation does *not* apply: dissociation of hexaarylethanes to triarylmethyl radicals is increased both by electron-withdrawing and electron-donating substituents. Non-Hammett behavior has been predicted for the unpaired electron distribution in triarylmethyl radicals, but there is little direct evidence to support this prediction.

The problem of substituent effects in stable free radicals can also be stated in terms of equilibria 1–3. Equilibrium 1 is shifted to the right by substitution of a *para* nitro group in each of the aromatic rings.[7] Equilibrium 2 is shifted to the left by the same substitution.[8] Equilibrium 3 is shifted to the left by substitution of *para* nitro groups in the Ar′′ rings, but it is shifted to the right by the same substitution in the Ar′ rings.[9] This multiplicity of substitution effects has been mentioned with various expressions of surprise by Wheland,[10] by Hückel,[11] and by Leffler,[12] among those who have surveyed these results.

$$\mathrm{Ar_3C—CAr_3 \;=\; 2Ar_3C\cdot} \qquad (1)$$

$$\mathrm{Ar_2\ddot{N}—\ddot{N}Ar_2 \;=\; 2Ar_2\ddot{N}\cdot} \qquad (2)$$

$$\mathrm{Ar''_2\ddot{N}—\ddot{N}(Ar')—\ddot{N}(Ar')—\ddot{N}Ar''_2 = 2Ar''_2\ddot{N}—\underset{\cdot\cdot}{\dot{N}}—Ar'} \qquad (3)$$

There is general agreement that the aromatic free radicals are stabilized[13] relative to their dimers by delocalization of the unpaired electron and (for most

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(2) (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII; (b) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

(3) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(4) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963: (a) pp 381–387; (b) pp 258–262.

(5) (a) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961); (b) H. S. Gutowsky, D. W. McColl, B. R. McGarvey, and L. H. Meyer, *J. Am. Chem. Soc.*, **74**, 4809 (1952).

(6) These cases will be considered in the discussion section.

(7) Data on substituent effects in the hexaarylethanes are summarized by M. J. S. Dewar, "Electronic Theory of Organic Chemistry," the Clarendon Press, Oxford, 1949, p 245.

(8) H. Wieland, "Die Hydrazine," F. Enke, Stuttgart, Germany, 1913, pp 71–78.

(9) S. Goldschmidt and J. Bader, *Ann.*, **473**, 137 (1929).

(10) G. W. Wheland, "Advanced Organic Chemistry," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1949, pp 730–734. These remarks are omitted in the third edition, but no general explanation of substitution effects in free radicals is proposed there.

(11) W. Hückel, "Theoretical Principles of Organic Chemistry," Elsevier Publishing Co., New York, N. Y., 1955, pp 195–197.

(12) J. E. Leffler, "The Reactive Intermediates of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, p 67.

(13) "Stability" of free radicals has been variously used to refer to the position of equilibrium between radicals and dimer, to reactivity toward oxygen, water, halogens, or other reagents, and to their tendency to disproportionate. The term "stable" will be used here to designate radicals which can exist in measurable concentration in equilibrium with their dimers. The class of stable free radicals will include species which differ widely in their reactivities toward various reagents or in their tendencies to disproportionate irreversibly.

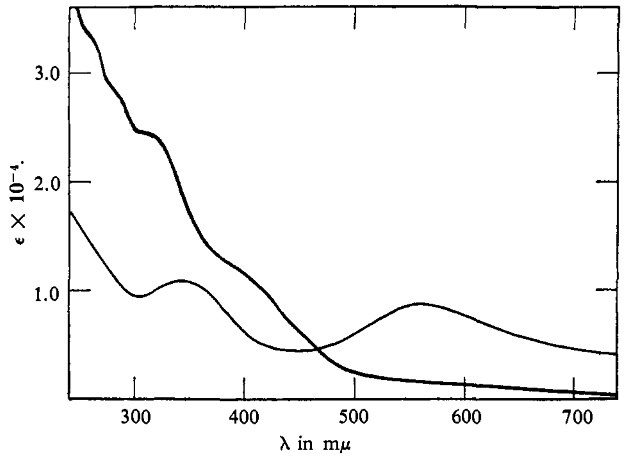
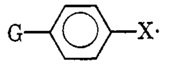


Figure 1.

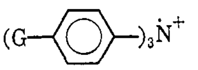
classes of free radicals) by F strain resulting from crowding of the aromatic rings in the dimers.[14] There does not seem to be a generally accepted explanation for the varied effects of substitution in different classes of radicals. It is one purpose of this paper to show that some substituent-sensitive physical properties of two classes of free radicals are affected quite differently by substitution. A second is to test a criterion for predicting the effects of substituents G in those free radicals in which structure I, with the unpaired electron on the central atom —X (which might be B, C, N, O, or S in various types of free radicals) *para* to the substituent, makes an important contribution to the resonance hybrid.



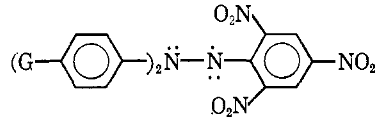
I

Experimental Section

The two classes of free radicals chosen for this study are the substituted triarylaminium salts (II) and the substituted 1-picryl-2,2-diarylhydrazyls (III). All substituents G are in the *para* positions, and all of the two (or three) aromatic rings contain the



II



III

same substituents in a given free radical. The synthesis of most of the triarylamines and aminium salts[15,16] and the 1-picryl-2,2-diarylhydrazines and hydrazyls[17] whose properties are considered here has already been described. Syntheses of the others will be reported elsewhere. Ideally, the data to be compared for these compounds should all be obtained from solutions in a single solvent. This is impossible for these two series of compounds, because of solubility and stability problems.

Visible-ultraviolet spectra were run on a Beckman Model DU spectrophotometer or (in some cases) on a Cary Model 14 spectrophotometer.[18] Data from the two instruments checked well. The solvent used for most radicals was acetonitrile which had been refluxed and distilled from four portions of phosphorus pentoxide, and then fractionated through a Todd column. Samples of the radicals which were available in crystalline form were weighed and diluted to volume immediately before use. Solutions of the aminium salts which contain strong electron-accepting groups ($COOCH_3$, $SO_3^-K^+$, and $COCH_3$) were prepared by oxidation of the amines in reagent grade formic acid solution with lead dioxide. These solutions were not very stable; they were filtered immediately, and stored in liquid nitrogen until used. They cannot, of course, be used to obtain data in the ultraviolet region. Deviations from Beer's law were largest for the most easily reducible radicals, and in the wrong direction to indicate dimerization at higher concentrations. They are believed to be due to reaction of a small amount of the free radical with oxidizable impurities in the solvent.

Electron spin resonance measurements on the hydrazyl radicals in benzene solution have already been reported.[19] Data for the aminium salts were recorded at 9300 *M* using a Varian V-4502 esr system with a 9-in. magnet.[20] The magnetic field was calibrated using a proton probe and frequency counter. Samples were held in the cavity in 0.05 × 0.9 × 2.5 cm quartz cells which were oriented in the plane of maximum magnetic field by rotation to maximize the signal. They were made up as described above at approximately 3×10^{-4} *F* concentration (the exact concentration is uncertain in some cases because of partial decomposition of the samples) in degassed reagent grade formic acid solution. The precision in the determination of the N^{14} hyperfine coupling constants is estimated to be ±0.2 oersted.

The esr spectra of a number of the aminium salts show an anomaly in the apparent intensities of the lines when observed in formic acid solution: the center component of the threefold pattern due to N^{14} splitting is enhanced in intensity relative to the outer components. This effect is greatest for the trianisylaminium radical, and disappears when this spectrum is observed in acetonitrile solution. It probably is due to small variations in line widths in the three components of the spectrum. It appears not to affect the N^{14} hyperfine coupling constants significantly. In most cases, a great deal of proton hyperfine structure also was resolved. The proton coupling constants are rather sensitive to solvent, but the values are not pertinent to the problems considered here, and will be reported elsewhere.

Results

Data on the optical spectra and the esr hyperfine coupling constants for the hydrazyl free radicals are summarized in Table I. The spectra of the hydrazines are also given for the record, but are not germane to the argument. Figure 1 shows typical spectra for 1-picryl-2,2-di-*p*-anisylhydrazine and the corresponding free radical.[21] The features of these spectra are characteristic of all these compounds: the hydrazine spectra tail off into the visible region to give the hydrazines their deep red-brown color, but the curve is sufficiently flat in the region of the long-wavelength free-radical absorption maximum that the position of the latter would not be seriously affected by small amounts of hydrazine present as an impurity. The extinction coefficients for the radical peaks fall in the range 0.75–1.36×10^4.

It has been shown in two cases by N^{15} labeling that the larger hyperfine coupling constant corresponds to the picryl nitrogen.[19] Since the values fall into two nonoverlapping sets, it seems probable that all of the larger constants are associated with this nitrogen, and they are so listed in Table I. The N^{14} isotropic hyperfine splittings are probably only approximately propor-

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[14] For a discussion see G. W. Wheland, "Advanced Organic Chemistry," 3rd ed, John Wiley and Sons, Inc., New York, N. Y., 1959, pp 785–791.

[15] T. N. Baker, W. P. Doherty, W. S. Kelley, W. Newmeyer, J. E. Rogers, R. S. Spalding, and R. I. Walter, *J. Org. Chem.*, **30**, 3714 (1965).

[16] R. I. Walter, *J. Am. Chem. Soc.*, **77**, 5999 (1955).

[17] M. M. Chen, A. F. D'Adamo, and R. I. Walter, *J. Org. Chem.*, **26**, 2721 (1961).

[18] We are indebted to Dr. H. Susi of the Eastern Regional Research Laboratory, U. S. Department of Agriculture, for making this instrument available to us.

[19] M. M. Chen, K. V. Sane, R. I. Walter, and J. S. Weil, *J. Phys. Chem.*, **65**, 713 (1961).

[20] The author is greatly indebted to Professor Melvin Hanna of the University of Colorado for generous permission to use this instrument extensively during the summer of 1963.

[21] Spectra of the hydrazyls in which G is H or CH_3 have already been published: R. H. Poirier, E. J. Kahler, and F. Benington, *J. Org. Chem.*, **17**, 1437 (1952); and R. H. Poirier and F. Benington, *ibid.*, **19**, 1157 (1954).

Table I. Properties of 1-Picryl-2,2-diarylhydrazyl Free Radicals and the Corresponding Hydrazines

Substituent	Longest wavelength absorption maximum in acetonitrile, cm^{-1} × 10^{-4} Hydrazine	Hydrazyl	Esr coupling constants in benzene, oersteds[a] a^{N_1}	a^{N_2}
OCH_3	2.56[b]	1.779	9.3	7.7
CH_3	3.09	1.866	9.8	7.6
H	3.11	1.923	9.9	7.6
$COOCH_3$	3.22	1.976	10.2	7.1
NO_2	2.84	2.058	10.8	6.7
F	3.12	1.923	9.7	8.0
Cl	3.13[b]	1.923	10.0	7.5
Br	3.13[b]	1.923	9.9	7.5
C_6H_5	3.30	1.818	9.5	7.5

[a] Taken from Chen, *et al.*[19] [b] These spectra contained shoulders only, with no well-defined peaks.

tional to the individual spin densities in the hydrazyls, and the proportionality constants are not equal for the two nitrogen atoms. Proportionality is assumed in the discussion of substituent effects which follows. These matters are considered more fully in another paper.[22,23]

The data for the first five substituents listed in Table I (these can be unambiguously identified as either electron donors or acceptors) demonstrate Hammett-type behavior of substituents in the 1-picryl-2,2-diarylhydrazyl free radicals with respect to both optical spectra and unpaired electron distribution. The electron-donating substituents OCH_3 and CH_3 shift the lowest frequency absorption bands to still lower frequencies, decrease the unpaired electron density on N-1, and increase it slightly on N-2 relative to the unsubstituted radical. The electron-accepting substituents $COOCH_3$ and NO_2 affect each of these properties in the opposite direction. The behavior of the phenyl group approximates that of a moderately strong electron donor such as OCH_3. Halogen substitution produces a regular decrease in the sum of the nitrogen hyperfine coupling constants through the series F, Cl, Br, but in all cases the absorption maximum of the radical is not affected.

The longest wavelength absorption maxima and N^{14} hyperfine coupling constants for the triarylaminium salt free radicals are given in Table II, together with the absorption maxima of the amines. (Again, the latter are for the record only, and are not pertinent to the argument except insofar as they provide spectra of a series of identically substituted electron-paired compounds[25] for comparison with the radicals.) The spectra of trianisylamine and the trianisylaminium ion (Figure 2) are reasonably typical of these compounds. The amine absorption is always negligible in the region of the visible absorption maximum of the aminium ion. Extinction coefficients for the visible absorption maxima of the free radicals are in the range 1.3-3.4 × 10^4. For this class of radicals, the hyperfine splitting produced by the central nitrogen atom should be very nearly proportional to the unpaired electron density on that atom.[22]

The data in Table II show that the donor substituents NH_2, OCH_3, and CH_3, and the acceptor substituents

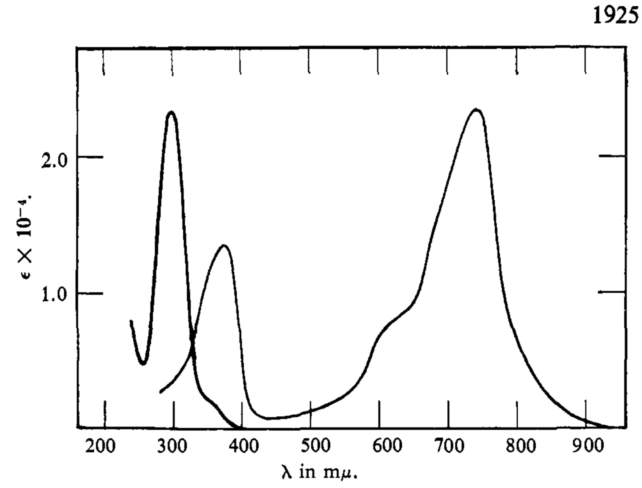

Figure 2.

$SO_3^-K^+$, $COOCH_3$, and $COCH_3$ all shift the optical absorption peak in the visible region to lower frequencies, and all decrease the hyperfine coupling constant for the central nitrogen atom. Clearly, the effects of substitution in the aminium salts are not Hammett type. Increased delocalization of the unpaired electron is accompanied by a shift in the absorption maximum to lower frequencies in these compounds. If it be assumed that both greater delocalization of the electron and stabilization of the ground state result from a substitution, then the excited electronic state involved in the optical transition must be stabilized by the substituent to a greater extent than the ground state, to account for the red shift observed.

Table II. Properties of Triarylaminium Salt Free Radicals and the Corresponding Amines

Substituent	Longest wavelength absorption maximum in acetonitrile, cm^{-1} × 10^{-4} Amine	Aminium ion	Nitrogen esr coupling constant in formic acid, oersteds
NH_2	3.26	1.195	6.9
OCH_3	3.38	1.400	8.9
CH_3	3.36	1.497	9.5[a]
H	3.36	1.524[b]	*c*
$SO_3^-K^+$	...	1.456[d]	9.4
$COOCH_3$	2.88	1.447[d]	9.2
$COCH_3$	2.76	1.408[d]	8.7
F	3.97	1.577	9.7[a]
Cl	3.29	1.458	9.0
Br	3.27	1.408	...
C_6H_5	2.94	1.209	8.4

[a] There is no threefold hyperfine splitting due to N^{14} visible in these spectra at large sweep modulations. Complete analysis of the hyperfine patterns gives the values listed. [b] This figure is taken from the absorption maximum reported by Lewis and Lipkin[24] for the photooxidation product of triphenylamine in EPA glass at 90°K. Because of the change in solvent, this value is estimated to be about 200 cm^{-1} low for acetonitrile solution (by analogy with the tritolylaminium ion also reported by Lewis and Lipkin). [c] We have been unable to oxidize solutions of triphenylamine to the radical for esr study. The blue color which appears in acid solutions of triphenylamine in the presence of an oxidizing agent is evidently due to an initial free radical (purplish blue color) which quickly decomposes to give a gray-blue solution which is diamagnetic. [d] Value in formic acid solution; the estimated correction for acetonitrile as solvent is +50 cm^{-1}.

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(22) R. I. Walter, *J. Am. Chem. Soc.*, **88**, 1930 (1966).

(23) Evidence for the failure of proportionality of coupling constants to spin densities in the hydrazyls is given by N. W. Lord and S. M. Blinder, *J. Chem. Phys.*, **34**, 1708 (1961).

(24) G. N. Lewis and D. Lipkin, *J. Am. Chem. Soc.*, **64**, 2801 (1942).

(25) L. Doub and J. M. Vandenbelt, *ibid.*, **69**, 2714 (1947).

Ambiguities remain in the interpretation of the effects of the other substituents studied in the aminium salt series. The large changes produced by phenyl substitution in this case afford no basis for classification of this substituent as a donor or acceptor in this type of radical. The substantial effects of halogen substitution on the aminium salt spectra contrast with the absence of any shifts in the absorptions of the halogen-substituted hydrazyls. These data on the aminium salts are the first clear experimental evidence that the substituent effects observed previously only in the dimerization equilibria of the triarylmethyl radicals can apply more generally to other properties and to other types of stable free radicals.

Discussion

The effects of substitution on the unpaired electron distributions and optical spectra of the hydrazyl and aminium salt free radicals exactly parallel those reported (but not fully realized, for lack of sufficient variety of substituents) in a study of substituent effects on the esr line widths of polycrystalline samples of some of the same radicals.[26,27] In that paper, the effects of substitution in these two classes of compounds were discussed at length on the basis of an extension of ideas applied by Branch and Calvin[28] to an earlier treatment of the substituent effects reported for the diarylnitrogen and the triarylmethyl free radicals. (A possible difficulty in their application of the argument to the diarylnitrogen radicals will be discussed subsequently in this paper.) Substituent effects on the esr spectra of the hydrazyl radical series have been interpreted separately.[19] In both papers, the data were interpreted qualitatively in terms of the effects of various valence-bond structures on π-electron distribution.

A Structural Criterion for Substituent Effects. The theory applied to these earlier discussions is summarized and generalized here, with slight modifications. It is assumed that the substituents affect free-radical properties by changing the distribution of the unpaired electron in the π system. The atom X in formula I is taken to be nitrogen, as it is in the compounds listed in Tables I and II, but this is not necessary to the argument.

A. An unpaired electron on a site *para* to a substituent on a benzene ring, structure I, can be delocalized to both donor and acceptor substituents.

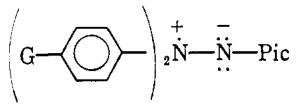
B. An unshared electron pair on a site *para* to a substituent cannot be delocalized by interaction with a donor group, but can be delocalized to an acceptor group.

C. Interaction of an electron pair with an acceptor group will occur at the expense of delocalization of an unpaired spin, when both are possible. The delocalizations are competitive in the sense that increased weight of structures in which an unshared electron pair is delocalized to the substituent (as that substituent becomes a better pair acceptor) requires that the relative weight of structures with the unpaired electron in the substituent must be smaller.

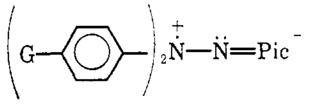
D. Changes in the distribution of the unpaired electron will affect directly the hyperfine splitting of the esr spectra by nuclei with nonzero nuclear magnetic moments such as N^{14}. Presumably they also affect optical transitions which are due to excitation of the unpaired electron, or of a paired electron from a lower level to the hole which remains in the half-filled MO. (A general parallel has been established between the magnitude of the shift of the absorption band in diamagnetic aromatic compounds and the additional possibilities for electron pair delocalization involving the attached substituent group.[25]) In addition, the changes in unpaired electron distribution should determine the positions of free-radical–dimer equilibria (when these occur) by altering the relative stabilities of these two species: the dimer is favored by a high density of the unpaired electron at the atom at which the dimer bond forms.

For the aminium salts, no reasonable structure can be written which places an unshared electron pair on the central nitrogen atom (unless this unshared pair has been transferred from a substituent). Consequently, delocalization of an unshared pair to acceptor groups is impossible, both donor and acceptor substituents delocalize the unpaired electron, and both affect properties in the same direction.

In the hydrazyl free-radical series, an unshared electron pair is on the atom *para* to the substituents in structure III. Structure IV places the unpaired electron on this atom; it is stabilized by donation of an unshared electron pair on the picryl nitrogen to the picryl group, V. Consequently, either an unpaired electron or an electron pair can be available on X (in this case, nitrogen atom number two) for interaction with the substituents G. When these are donor groups, only interaction with the unpaired electron is possible, structures IV and V are more important, and the unpaired electron density on the picryl nitrogen is reduced. As G become better acceptors, the interaction with the electron pair will be increasingly important (assumption C), and the unpaired electron will tend to be localized on the picryl nitrogen (structure III). Substituent effects in these compounds thus differ for donor and acceptor groups. This argument also accounts for the observed effects of change in the Ar′ rings on equilibrium 3. Goldschmidt and co-workers[29] reported that this equilibrium is shifted to the right by Ar′ groups in the order C_6H_5 < COC_6H_5 < picryl. This is also the order of increasing ability of these groups to accept an



IV



V

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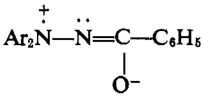
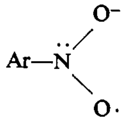
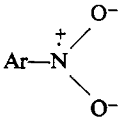
(26) R. I. Walter, R. S. Codrington, A. F. D'Adamo, Jr., and H. C. Torrey, *J. Chem. Phys.*, **25**, 319 (1956).

(27) Data on the esr spectra of polycrystalline samples are potentially unreliable because the effects of molecular structure on crystal structure (rather than on electron distribution) have never been shown not to determine the line widths observed. The regularities reported in this reference have been questioned on this basis by R. G. Bennett and A. Henglein, *J. Chem. Phys.*, **30**, 1117 (1959). The latter authors found a different order for the esr line widths of polycrystalline samples of monosubstituted diarylpicrylhydrazyls. However, our studies of better crystallized samples of the disubstituted hydrazyl radicals indicate that the general order of the substitution effects reported earlier is reproducible for well-crystallized samples. In addition, the fact that substitution affects the optical spectra and solution esr hyperfine coupling constants in the same way as the polycrystalline esr line widths lends support to the theory proposed earlier for the latter.

(28) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, pp 327–328.

(29) See ref 9 and earlier papers in the series by Goldschmidt.

Table III. Classification of Substitution Effects in Stable Aromatic Free Radicals

	Radical type		Properties studied[a]	Substit types[b]	Ref no.
			A. Class S Radicals		
a	$Ar_3\dot{N}^+$		Esr, opt	D, A	This paper
b	$Ar_3\dot{C}$		Dim	D, A	7
c	$Ar_3\dot{B}^-$		None		36
d	$Ar_2\ddot{N}-\overset{+}{\dot{N}}Ar_2$		None		37
			B. Class O Radicals		
e	$Ar_2\ddot{N}-\underset{\cdot\cdot}{\dot{N}}-Pic$	$Ar_2\overset{+}{\dot{N}}-\ddot{N}=Pic:^-$	Esr, opt	D, A	This paper
f	$Ar_2\ddot{N}-\underset{\cdot\cdot}{\dot{N}}-COC_6H_5$	 $Ar_2\overset{+}{\dot{N}}-\ddot{N}=C(O^-)-C_6H_5$	Opt, dim	D, A[c]	29,32,38
g			Esr	D, A	39
h	$Ar_2\ddot{N}-\underset{\cdot\cdot}{\dot{O}}:$	$Ar_2\overset{+}{\dot{N}}-\underset{\cdot\cdot}{\ddot{O}}:^-$	Esr, opt	D	40
i	$Ar_2\overset{-}{\ddot{C}}-\underset{\cdot\cdot}{\ddot{O}}:$	$Ar_2\dot{C}-\underset{\cdot\cdot}{\ddot{O}}:^-$	None		
			C. Possibly class O		
j	$Ar_2\dot{N}:$, $Ar-\underset{\cdot\cdot}{\dot{N}}-H$		Esr, opt, dim	D	8, 41
k	$Ar-\underset{\cdot\cdot}{\dot{O}}:$		Esr, opt	D	42

[a] Abbreviations: opt for optical spectra, dim for dimerization. [b] D for donor groups, A for acceptors. [c] Very few examples of either type of substituent have been studied quantitatively.

electron pair, to stabilize structures like V, and thus to stabilize the unpaired electron on nitrogen two. By assumption D, this delocalization of the electron from the picryl nitrogen, which is the site of dimerization, should increase the stability of radicals relative to dimer in the same order. Group Ar′ thus functions to transfer the unpaired electron to N-2; this function of Ar′ was pointed out years ago by Ingold,[30] and appears to be confirmed by the dipole moment data of Turkevich, Oesper, and Smyth.[31] The N-N bond has been formulated as a three-electron bond, which also implies a high probability that the unpaired electron can reside on either nitrogen.[32]

This theory of substituent effects requires that electron pair delocalization contribute more importantly to the resonance hybrid than unpaired electron delocalization, when the presence of an electron-acceptor substituent makes both possible. This seems reasonable in view of the known effects of acceptor substituents on rates of aromatic substitution. The rates of electrophilic nitration of nitrobenzene and benzene differ by a factor greater than 10^6, while the rates of free-radical arylation of these compounds differ by a factor of 4.[33] (Part of this rate difference must result from the polar withdrawal of electrons by the nitro group; this will aid attack by an electrophilic reagent, but have little effect on homolytic attack.)

Additional support for the competitive effect postulated is provided by rate studies which indicate that polar structures dominate radical processes whenever they are possible. Walling and co-workers[34] made the first such suggestion to account for alternation and rate effects in the radical-initiated growth of copolymer chains in which one reactant is a *para*-substituted styrene. Leffler[35] showed that the free-radical decomposition of symmetrically substituted dibenzoyl peroxides becomes a polar process in 4-nitro-4′-methoxydibenzoyl peroxide. The interpretations of these results in terms of postulated polar contributions to the transition states are confirmed nicely by the data in Table I on the properties of the nonreacting hydrazyl free radicals.

These ideas can be generalized to give a theory that permits the prediction of substituent effects on the properties of stable free radicals which meet the structural criterion illustrated in formula I. Class S (for *same* effects of donor and acceptor substituents) radicals are those for which only an unpaired electron can be placed on atom X in formula I. Both donor and acceptor substituents will affect its properties in the same direction. Class O (for *opposite* effects of donor and acceptor substituents) radicals are those for which structures can be drawn with either an electron pair or an unpaired electron on atom X. Donor and acceptor substituents will affect its properties in opposite direc-

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(30) C. K. Ingold, *Trans. Faraday Soc.*, **30**, 52 (1934).

(31) J. Turkevich, P. F. Oesper, and C. P. Smyth, *J. Am. Chem. Soc.*, **64**, 1179 (1942).

(32) (a) W. K. Wilmarth and N. Schwartz, *ibid.*, **77**, 4543 (1955); (b) *ibid.*, **77**, 4551 (1955).

(33) D. R. Augood, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 2094 (1952).

(34) C. Walling, E. R. Briggs, K. B. Wolfstirn, and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 1537 (1948).

(35) J. E. Leffler, *ibid.*, **72**, 67 (1950).

(36) J. E. Leffler, E. Dolan, and T. Tanigaki, *ibid.*, **87**, 927 (1965).

(37) E. Weitz and H. W. Schwechten, *Ber.*, **60**, 1203 (1927).

(38) A. F. D'Adamo, Jr., Ph.D. Thesis, Rutgers University, Sept 1954.

(39) A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852 (1961).

(40) P. H. H. Fischer and F. A. Neugebauer, *Z. Naturforsch.*, **19a** 1514 (1964), and references given there. Data from different laboratories cannot easily be compared because of the variety of solvents used.

(41) F. A. Neugebauer and P. H. H. Fischer, *Chem. Ber.*, **98**, 844 (1965).

(42) (a) E. S. Land and G. Porter, *Trans. Faraday Soc.*, **59**, 2016, 2027 (1963); (b) A. Rieker, K. Scheffler, and E. Müller, *Ann.*, **670**, 23 (1963), and preceding papers.

tions. *The properties in question will be all those that are affected by the electron distribution in the π system:* esr hyperfine coupling constants, optical spectra, and reaction rates and equilibria controlled by the radical nature of the reactants, when these involve the site attached to the benzene ring *para* to the substituents or its neighbor in the hydrazyls. In all cases the effect of substitution is measured by comparison of the property in question with that of the unsubstituted free radical. Only *para* substitution is considered, so steric effects should be constant within any series of free radicals which differ only in the nature of the substituents present. When this structural criterion is applied to the known types of stable aromatic free radicals, the classification given in Table III results.

The available evidence in support of these assignments is given in the references listed in Table III. In sum, the assignments of free radicals of types a and b to class S, and of e, f, and g to class O, are consistent with a substantial amount of available data. Assignments of types c, d, h, and i must be regarded as predictions consistent with the inadequate available data, but subject to future experimental verification. No data on these free radicals contradict these assignments.

Support for the assignment of the triarylmethyl radicals to class S is available, but its significance seems not to have been recognized. Fragmentary spectroscopic data on these compounds can be read from absorption curves published by Lewis, Lipkin, and Magel,[43] and are listed in Table IV. They are consistent with the evidence from dimerization data that these radicals belong to class S.

Table IV. Longest Wavelength Absorption Maxima for Trisubstituted Triarylmethyl Free Radicals[a]

para substituent	Maximum, cm^{-1} $\times 10^{-4}$
*t*Bu	1.919
H	1.953
NO_2	1.527

[a] From Lewis, Lipkin, and Magel.[43]

All of the type O free radicals grouped in section B of Table III have three covalent bonds to the central atom. This atom presumably approaches sp^2 hybridization, and only one 2p AO is available for competitive occupancy by the unpaired electron or the unshared electron pair. The situation is less clear for the class O radicals grouped in section C. Each of these has one or more unshared electron pairs which should occupy hybrid orbitals on the central atom. To the extent that these AO's have 2s character, they should be lower energy than the 2p AO which forms part of the aromatic π system; consequently, the latter should be occupied by only the single electron. This assignment of the electron pair would make it incapable of direct interaction with the aromatic ring and the substituents attached to the *para* position on it. π–σ configuration interaction would still be possible, and there are theoretical grounds for expecting that this interaction might be abnormally large for a nitrogen atom.[44]

If the energy difference between hybrid and 2p AO is large and configuration interaction negligible, only the unpaired electron would be delocalized, and these radicals would belong to class S. However, if the delocalization of an unshared electron pair into the aromatic rings and the substituents should stabilize this system appreciably, this effect might make up for the energy required to promote a second electron to this orbital. Thus these two types of free radicals might belong to either class S or class O, with the former more probable, or the assignment might even vary with the property observed. (Branch and Calvin[28] used the diarylnitrogen free radicals as their only example for a class O radical in their treatment of substitution effects. They neglected the problem that the unpaired electron and the unshared pair occupy orthogonal AO's, to a first approximation, in these compounds.)

The theory of Branch and Calvin, which has been generalized here as a means for predicting substituent effects in stable free radicals, is one of a number of nonquantum mechanical theories which have been offered to explain these effects. The early proposal by Ingold[30] is so phrased that it is difficult to use for predictive purposes.

Lewis and Lipkin[45] proposed that the effects of substitution on the relative stabilities of free radicals and their dimers resulted from changes in the polarity of bonds to the atom of the radical at which dimerization occurs. Swain, Stockmayer, and Clarke[46] restated this proposal in terms of the electronic effects of substituents on the charge density at the atom at which the dimer bond forms, and the repulsion of these charges in the dimer. These ideas explain the effects of substituents on the dimerization equilibria of free radicals, but seem inadequate to explain the parallel effects of substituents on unpaired electron density or on optical spectra. To do so, it is necessary to consider the effects of the substituents on the π-electron system.

Simple molecular orbital calculations have been carried out to determine the effects of substitution on unpaired electron densities and on the energies of the lowest energy spectroscopic transitions in the 1-picryl-2,2-diarylhydrazyls and in the triarylmethyls.[22] The results are in agreement with the major trends in the experimental data in Tables I and II, despite the uncertainties involved in assigning coulomb and exchange integrals for the many heteroatoms in these compounds.

Quantitative Hammett Correlations. The theory of substituent effects proposed here has obvious implications for the application of the Hammett equation to free-radical systems. Past efforts to obtain rate ratio–σ correlations for free radicals have involved the implicit assumption that the effectiveness of any substituent in contributing to resonance through an unpaired-electron structure will be proportional to its ability to contribute through electron-paired structures. There has been no evidence that this is the case, other than the somewhat mixed success of the correlations.

A treatment of substituent effects in free radicals by a perturbation method based upon molecular orbital theory has been published by Dewar.[47] The results

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(43) G. N. Lewis, D. Lipkin, and T. T. Magel, *J. Am. Chem. Soc.*, **66**, 1579 (1944).

(44) Private communication from Professor Martin Karplus.

(45) G. N. Lewis and D. Lipkin, *J. Am. Chem. Soc.*, **63**, 3232 (1941).

(46) C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *ibid.*, **72**, 5426 (1950).

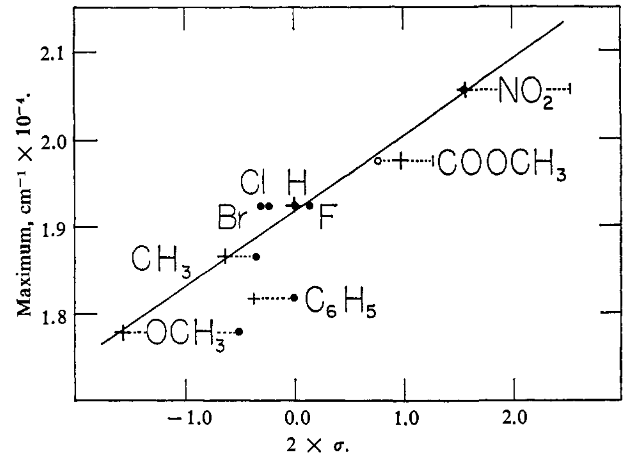

Figure 3.

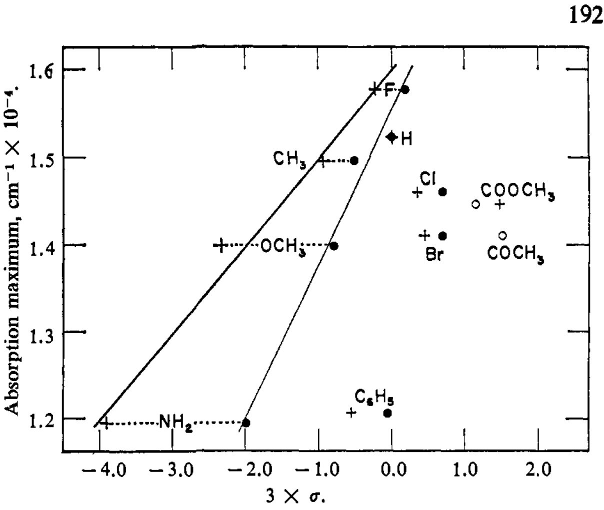

Figure 4.

which will be useful here are theorems 62 and 63. They predict that the effectiveness of a given donor substituent should be about half as great in stabilizing a radical as in stabilizing a cation. In class O radicals, the effect of an electron-acceptor substituent is due principally to interaction with an unshared pair of electrons on the central atom, and the effectiveness of the substituent should be that given by its usual σ constant. Thus the effects of substitution in class O radicals should be proportional to $\sigma/2$ for substituents with $\sigma < 0$, and proportional to σ for substituents with $\sigma > 0$, within the probably not very great precision of the molecular orbital treatment.

These and other possibilities are tested by the points plotted in Figure 3, where the σ values are taken from McDaniel and Brown's table.[2b] No line can be drawn through the entire range of substituent types if one uses the black points for the usual σ values in the range $\sigma < 0$. Clearly the fit would be still poorer if $2 \times \sigma/2$ were used in this region. Since interaction of the substituents with the central atom X is possible only when an unpaired electron is on that atom, and since delocalization of the unpaired electron also involves delocalization of a positive charge, σ^+ values[48] might be more appropriate for these cases. With them, a good least-squares fit is obtained for the substituents OCH_3, CH_3, $COOCH_3$, NO_2, and H. The correlation coefficient for these five points (the larger plus signs) is 0.993. The halogens and the phenyl group[49] do not fit the correlation. This failure to correlate the halogen-substituted compounds may be related to the important inductive effects which these substituents display in polar reactions. These should be much less significant in free-radical systems, and this would imply that different σ values should be used in these cases. The correlation of the acceptor substituents is best when minimum σ values which correspond to the σ^n of van Bekkum, Verkade, and Wepster[50] are used. The correlation seems satisfactory, particularly in view of the fact that the electronically excited state involved in the spectroscopic transition differs from the transition state involved in the chemical reactions for which the σ constants were evaluated. There is no necessity that one set of constants should reflect the effects of substitution on both upper states, although a number of absorption maxima–substituent constant correlations have been described.[4b,26]

The Hammett correlation should break down completely for free radicals which belong to class S, since the effect of substitution should be proportional to $\sigma/2$ for $\sigma < 0$, and proportional to $-\sigma$ for $\sigma > 0$ (by Dewar's theorem 62). The plot for the triarylaminium radical spectra is given in Figure 4. The absence of a correlation effective through the entire range of σ values is evident. Correlation of the points for donor substituents only is successful when the σ^+ constants are used, and almost as good when σ values are used. The halogens and phenyl group again fail to fit any correlation based upon the other substituents. The electron-accepting groups studied do not represent a very wide range of positive σ values, and the scatter is severe. (We have been unable to oxidize tris(*p*-nitrophenyl)amine to the aminium ion.) This may be an indication of the difference in effectiveness of these groups in contributing to electron pair *vs.* unpaired electron delocalization.

Plots of esr hyperfine coupling constants against the substituent constants show more scatter for both types of free radicals, presumably because of the lower precision of the data. Otherwise, the results are about the same as in the case of the optical spectra.

We turn now to the implications of these dual effects of substitution on the properties of nonreacting stable free radicals for the application of the Hammett equation to rate constants for reactions which involve transient radicals. Two types of substituent effects might be expected when radical properties dominate the transition state, which would correspond to the substituent effects in stable class S and class O radicals. A large proportion of the free-radical reactions which have been studied involve some type of substituted benzyl radicals as intermediates. It is generally recognized that substituent effects in simple radicals of this type should belong to class S, in agreement with the structural criterion proposed here. However, there seems to be no reaction in which this type of substitution effect

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(47) Reference 7, pp 243–248, and M. J. S. Dewar, *J. Am. Chem. Soc.*, 74, 3353 (1952).

(48) H. C. Brown and Y. Okamoto, *ibid.*, 80, 4979 (1958).

(49) Dr. Anton Rieker (private communication from the University, Tubingen), has also found that the properties of hindered phenoxy radicals in which the *para* substituent is the phenyl group do not fit the correlations which are observed with other substituents in free radicals of this class.

(50) H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. Trav. Chim.*, 78, 815 (1959).

on rate has actually been recognized. In fact, Hammett-type correlations are now so generally expected in reactions which involve free radicals that Jaffé's review of these reactions[3] tabulated correlations of rate ratios with σ without mentioning that the dimerization of triarylmethyl radicals cannot be correlated in this manner. Evidently the proposal by Walling, Mayo, and coworkers[34] that transition states in radical reactions are stabilized substantially by polar effects which involve electron pair delocalization applies quite generally,[51,52] and the rates are correlated better by σ^+ than by σ.[53] The structures of the transition states in these reactions are such that delocalization of an unshared electron pair becomes possible (although it would not be possible in the isolated radicals), and this determines substitution behavior in the same manner as in the hydrazyls. It may turn out that only dimerization reactions, in which polar effects cannot be large, will display class S effects of substitution on rates or equilibria.

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(51) G. A. Russell and R. C. Williamson, Jr., *J. Am. Chem. Soc.*, **86**, 2357 (1964).

(52) P. D. Bartlett and G. Rüchardt, *ibid.*, **82**, 1760 (1960).

(53) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 1744 (1963).

Substituent Effects on the Properties of Stable Aromatic Free Radicals. An LCAO–MO Treatment[1]

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Abstract: Simple LCAO–MO calculations have been carried out for the 1-picryl-2,2-diphenylhydrazyl and triphenylmethyl free radicals, and for their derivatives which contain two or three nitro or methoxy groups. Details of the unpaired electron distribution in the hydrazyl radicals are more closely reproduced when the parameters used are evaluated systematically. The coulomb integrals are determined from orbital electronegativities for atoms in the correct valence states, corrected for the number of electrons contributed to the π system and for formal charge. Exchange integrals are determined from bond lengths, with the assumption that a bond with a given overlap integral has the same exchange integral as a carbon–carbon bond with the same overlap. The calculations also include a study of the effect of rotation of an aromatic ring on its interaction with two orthogonal 2p atomic orbitals on an adjacent atom which is assumed to be sp hybridized. The results of these calculations reproduce the trends in optical spectra and unpaired electron densities (these must be assumed to be systematically related to the observed nitrogen hyperfine coupling constants) which led to the empirical division of free radicals into two classes, based upon effects of substitution on these properties. The parameters which give the optimum fit of properties of the three hydrazyl radicals are used to predict effects of other types of substitution in this free-radical system. The results show that MO calculations with input parameters whose values lie in a reasonable range can give a wide range of unpaired electron densities on the hydrazine nitrogen atoms, and thus cannot be used to establish the relative values of these densities.

This paper presents the results of a theoretical study of the effects of substitution on the optical and esr spectra of two types of stable aromatic free radicals. Experimentally, substitution effects in the 1-picryl-2,2-diarylhydrazyl and the triarylaminium salt free radicals have been shown to fall into two different patterns.[2] In the former, electron-donor and electron-acceptor substituents in the *para* positions of the two aromatic rings shift both the nitrogen esr hyperfine coupling constants and the positions of the longest wavelength absorption bands in opposite directions. Free radicals which display this behavior have been labeled class O. In the triarylaminium salts, both types of substituents shift each of these properties in the same direction. Free radicals of this type have been labeled class S. A structural criterion has been proposed for the assignment of other types of aromatic free radicals to the two classes represented by these two series of compounds,[2] and the triarylmethyl radicals fit the assignment to class S on the basis both of their structures and somewhat meager data on their experimental behavior. The additional complications which arise in treating the ionic charge on the aminium salts led to the choice of the triarylmethyl free radicals as representatives of class S in carrying out these computations.

No systematic theoretical treatment of substitution effects in these free radicals has been carried out, although calculations have been reported on the unsubstituted compounds. The results of both simple MO and VB computations for triphenylmethyl have been summarized by Karplus and Fraenkel.[3] Comparison with the experimental data shows that there is not a great deal to choose between the quantitative results of the two methods, except in the respect that the VB

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(1) Most of this work was carried out at Columbia University and the University of Minnesota while the author held a National Science Foundation Science Faculty Fellowship in 1960–1961. It is a pleasure to acknowledge the help of Professor Martin Karplus, whose constant interest and generous contributions of advice and background information made it possible to carry out this study. The author is also indebted to the IBM Watson Scientific Laboratory, the Control Data Corporation, and the NASA Institute for Space Studies for donations of computer time.

(2) R. I. Walter, *J. Am. Chem. Soc.*, **88**, 1923 (1966).

(3) (a) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961); (b) see Table VII of ref 3a.