monium ions from the line for primary R groups is probably due to some type of steric effect, but we have no convincing detailed explanation for this deviation or for the smaller deviations by the other points.

Experimental Section

The kinetics of the dedeuteration of isobutyraldehyde-2-*d* were studied by nmr measurements of the type described previously, in which the reactions were stopped by the addition of hydrochloric acid and the reaction mixtures extracted with chloroform.[3-5]

In order to learn whether any significant amount of isobutyraldehyde was present in the form of imine or iminium ion rather than aldehyde or aldehyde hydrate, measurements were made on glycine ethyl ester hydrochloride, the most strongly acidic amine salt used and therefore the one for which the largest fraction of free amine will be present (at a given pH) to transform aldehyde to imine. An acetate buffer was used to give a pH of 5.7, as basic as the most basic of the kinetic reaction solutions. The presence of the glycine ethyl ester hydrochloride in various concentrations up to 0.34 *M* in 0.122 *M* solutions of isobutyraldehyde was found to have no detectable effect on the absorbance at the 2850-A aldehyde maximum (at which the hydrochloride absorbs negligibly). It was therefore concluded that less than 1% of the aldehyde was transformed to the imine or iminium ion (neither of which should absorb significantly at 2850 A) under these conditions.

p*K* **Measurements.**—Potentiometric measurements at 35° were made as described previously[3-5] to determine that pK_a for *p*-nitrobenzylammonium chloride is 8.240 and 8.260 at ionic strengths 0.0029 and 0.0050 *M* and pK_a for cyclopropylammonium chloride is 8.911, 8.914, and 8.944 at ionic strengths 0.034, 0.049, and 0.164 *M*. Values extrapolated to zero ionic strength are 8.21 and 8.90, respectively.

Registry No.—Isobutyraldehyde-2-*d*, 4303-51-9.

Acknowledgment.—We wish to acknowledge our indebtedness to the National Science Foundation for grants that permitted the purchase of the nmr spectrometers used in this investigation.

Electron Spin Resonance Studies of Substituent Effects. II. Diaryl Nitroxides[1]

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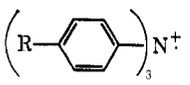
Six *para* and four *meta* symmetrically substituted diaryl nitroxides were formed by photolysis of the corresponding nitroso compounds. The nitrogen hyperfine splitting constants (hfsc's) give a good correlation with σ, but for substituents which withdraw electrons strongly by resonance a better correlation is obtained with σ^-. Substituent effects on hfscs were surveyed for a variety of aromatic radicals. Charged radicals appear to be more sensitive to substituent than uncharged radicals. Almost all results indicate that in radical systems the *p*-F substituent has a slight electron-supplying effect.

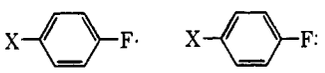
Electron spin resonance spectroscopy offers a convenient method of measuring substituent effects on electron density, for the hyperfine splitting constant (hfsc) of a nucleus is related to unpaired electron densities. Since the Hammett σ constant is interpreted as a measure of the substituent effect on electron density at an atom,[3] it is desirable to learn if the substituent effect on nuclear hfscs in aromatic free radicals relates in any manner to the σ constant. Recently, it was found that methyl hfsc's in *meta*- and *para*-substituted 1-phenyl-1,2-propanesemidiones give a correlation with σ constants derived from the ionization of benzoic acids.[1] Sixteen substituents of the twenty-one studied were found to be "well behaved;" *i.e.*, they give an excellent correlation with σ constants. These were *m*-CN, *m*-CF_3, *m*-Br, *m*-Cl, *p*-Br, *p*-Cl, *m*-OCH_3, *p*-H, *m*-CH_3, *m*-NH_2, *p*-CH_3, *p*-$C(CH_3)_3$, *p*-NH_2, and *m*-O^-. The five "ill-behaved" substituents were *p*-CN, *p*-CF_3, *p*-Ph, *p*-F, and *p*-$N(CH_3)_2$. Here we present results in another system.

Of primary concern is the recognition of conditions where the properties of a free radical will follow a Hammett relationship. In radicals of the type I,



I

it is found that both electron-withdrawing and electron-supplying groups decrease the nitrogen hfsc, A^N.[4] The criterion for determining whether an aromatic radical will follow a Hammett relationship has been stated by Walter[4] as follows. For a functional group F with a substituent X, if resonance structures can be drawn with an unpaired electron (II) and an unshared



II III

electron pair (III) on the atom *para* to the site of substitution, then the system will exhibit Hammett behavior.

Even if electron distribution within a system follows a Hammett relationship, however, in radicals this fact must be detected by measuring a nuclear hfsc. For protons α or β to a radical site, the hfsc's are directly proportional to the spin density at the site,[5] but for nuclei which supply orbitals to the π system, the hfsc is also a function of the spin density at the adjoining atoms.[6] For an atom X attached to three other atoms Y_1, Y_2, and Y_3, the hfsc is given by expression IV

$$A^X = Q_X^X \rho_X + \sum_{i=1}^{3} Q_X^{Y_i} \rho_{Y_i}$$

IV

(1) E. T. Strom, *J. Am. Chem. Soc.*, **88**, 2065 (1966), is to be considered part I of the series.

(2) Author to whom inquiries should be sent at the Mobil Oil Corp., Field Research Laboratory, Dallas, Texas 75221.

(3) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp 186–194.

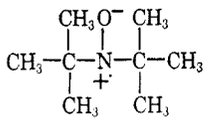
(4) R. I. Walter, *J. Am. Chem. Soc.*, **88**, 1923 (1966).

(5) H. M. McConnell, *J. Chem. Phys.*, **24**, 632 (1956); A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958).

(6) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).

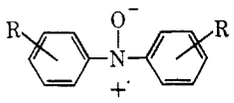
where parameter Q_X^X measures the contribution (in gauss) to the hfsc from the spin density on atom X,[7] parameter Q_X^Y measures the contribution to the hfsc from the spin density on atoms Y, and the ρ values are the spin densities on atoms X and Y. We can expect a linear correlation between A^X and ρ_X only when one of three conditions apply: (1) the spin densities at the adjoining atoms are very small or zero, (2) the parameters Q_X^Y are very small or zero, or (3) the spin densities on the adjoining atoms, ρ_{YI}, fortuitously change by exactly the same percentage as ρ_X.

One functional group where the hfsc might reflect spin density in a linear manner is the nitroxide function. When spin densities in di-*t*-butyl nitroxide (V) were



V

shifted by means of solvent effects, it was found that the ^{13}C hfsc of the methyl carbon was linearly related to the nitrogen hfsc, A^N.[8] Lemaire and Rassat concluded that A^N was solely a function of the nitrogen spin density. Accordingly, we decided to study symmetrically substituted diaryl nitroxides (VI). By Walter's



VI

criterion,[4] these radicals should give a Hammett relationship. While this manuscript was in preparation a study of substituent effects in diaryl nitroxides was published by Neugebauer and Fischer.[9] These studies prove to be complementary and the combination of both sets of data allows more conclusions to be drawn.

Results and Discussion

Symmetrically substituted diaryl nitroxides were prepared by photolysis of the corresponding nitrosobenzene[10] with unfiltered ultraviolet light. The main limitation of this method appears to be that the nitroso compound must exist in solution in the dimeric form to at least a small extent; for the *para*-dimethylamino derivative, existing solely as the monomer,[11a] gives no diaryl nitroxide on irradiation.[11b] Our results and those of Neugebauer and Fischer are given in Table I.

A plot of A^N *vs.* σ is shown in Figure 1. The splitting constants plotted are those measured by us plus values taken from ref 9 for substituents we did not study. It

TABLE I
NITROGEN HFSC IN DIARYL NITROXIDES

Substituent	A^N (this work)[a]	A^N (ref 9)[b]	σ[c]
p-NO_2	...	8.38 ± 0.01	0.778 (σ^- 1.27)
p-COOMe	8.82 ± 0.03	...	0.315[d] (σ^- 0.636)
p-COOEt	...	8.89 ± 0.01	0.45 (σ^- 0.678)
m-NO_2	9.10 ± 0.06	...	0.710
m-F	9.27 ± 0.04	...	0.337
m-Cl	9.34 ± 0.03	...	0.373
p-Br	9.35 ± 0.04	9.30 ± 0.05	0.232
p-Cl	9.39 ± 0.04	...	0.227
m-COOMe	9.42 ± 0.05	...	(0.37)[e]
p-H	9.70 ± 0.05	9.66 ± 0.01	0.000
p-F	9.80 ± 0.03	9.76 ± 0.01	0.062
p-CH_3	9.81 ± 0.05	9.79 ± 0.01	−0.171
p-OCH_3	...	10.07 ± 0.01	−0.268

[a] Measured in benzene at 25°. [b] Formed by oxidation of the corresponding diarylamine in xylene. [c] The σ values are taken from D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958), except where noted, while the σ^- values are taken from H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953). [d] Taken from Jaffé's compilation. [e] Not given in the above compilations. Assumed equal to σ for *m*-COOEt as given in the compilation of McDaniel and Brown.

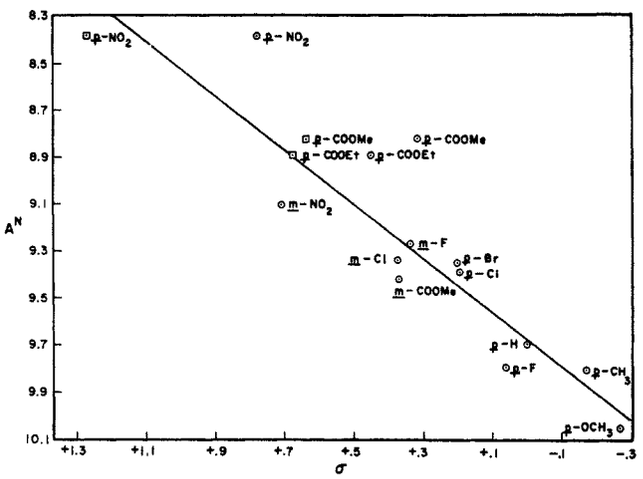


Figure 1. Plot of A^N *vs.* σ and σ^- (data taken from this work and ref 9): ⊙, σ points; ⊡, σ^- points.

has been demonstrated by Janzen[12] that hfsc's within a series correlate better for −R groups with σ^- than σ; thus the σ^- points are also shown on the graph. The correlation coefficient between A^N and σ is 0.882. The value using σ^- constants for *p*-NO_2, *p*-COOEt, and *p*-COOMe is 0.971. The correlation cofficient for the seven substituents found to be "well behaved" in the earlier study and A^N is 0.978. The corresponding least-squares line is shown in Figure 1. We conclude, therefore, that σ^- values do improve the correlation. This is opposite to the conclusion reached earlier;[9] however, less data were available at that time.

A considerable amount of data have in recent years been obtained on the variation of hfsc within a functional group in substituted benzenoid radical systems. Most of the measurements involved a nitrogen hfsc and most studies dealt solely with *para* substituents. Plots similar to Figure 1 could be used to determine how well the hfsc's correlate with σ, but the slope of the least-squares line will have units of gauss and will be useless

(7) The parameter Q_X^X can be broken down into parameters measuring the contributions from spin polarization of the various X–Y σ bonds as well as polarization of the 1s electrons on atom X.

(8) H. Lemaire and A. Rassat, *J. Chim. Phys.*, **61**, 1580 (1964).

(9) F. A. Neugebauer and P. H. H. Fischer, *Z. Naturforsch.*, **21b**, 1036 (1966).

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(11) (a) K. Nakamoto and R. E. Rundle, *J. Am. Chem. Soc.*, **78**, 1113 (1956). (b) For evidence indicating monomeric origin of the nitroxide, however, see Th. A. J. W. Wajer, A. Mackor, Th. J. de Boer, and J. D. W. van Voorst, *Tetrahedron*, **23**, 4021 (1967).

(12) E. G. Janzen, private communication.

TABLE II
CORRELATIONS OF AROMATIC RADICAL SYSTEMS

System	Solvent	Ref	All points: r	All points: No. of points	All points: Slope	"Well-behaved" points: r	"Well-behaved" points: No. of points	"Well-behaved" points: Slope
$PhC(O^-)=CCH_3$ (O·)	80% DMSO–20% t-BuOH	1	−0.9720	21	−0.3343	−0.9945	16	−0.3433
$PhN(O^-)H$ (+)	$PhCH_3$	16	−0.9497[a] −0.9551[b]	8	−0.0901[a] 0.1225[b]	−0.7978[a] −0.8168[b]	7	−0.0705[a] −0.0930[b]
$PhN(O^-)t$-bu (+)	$(CH_2OH)_2$	17	−0.7513	20	−0.0836	−0.7779	6	−0.0659
$PhN(O^-)C(CH_3)_2C(=CH_2)CH_3$ (+)	PhH	18	−0.9048	7	−0.0924	−0.9837	5	−0.1162
$PhN(O^-)Ph$ (+)	PhH and xylene	This work and ref 9	−0.9708	13	−0.1115	−0.9783	7	−0.1160
$PhNO_2\cdot^-$	Aqueous acetone	19	−0.8597	22	−0.1424	−0.9444	7	−0.1683
$PhNO_2\cdot^-$	Alcohol	20	−0.9314	21	−0.2614	−0.9143	10	−0.1661
$PhNO_2\cdot^-$	CH_3CN	21	−0.9797	13	−0.3427	−0.9799	6	−0.2761
p-$PhPhNO_2\cdot^-$	CH_3CN	22	−0.9730	8	−0.1710	−0.9612	5	−0.1921

[a] Results for hydrogen hfsc's. [b] Results for nitrogen hfsc's.

for measuring the sensitivity of the hfsc to substituent.[13–15] When the ratio of $A^X_{m \text{ or } p \text{ substuent}}$ to $A^X_{p\text{-H}}$ is plotted against σ, however, the slope of the least-squares line will be dimensionless and will correspond to a Hammett ρ value.

We have undertaken a survey of some of the data in the literature to see how well the hfsc correlates with σ and how sensitive the hfsc is to the substituent. The choice of σ constant for a substituent was made in the following manner. If a σ^- constant for a −R substituent was available from Jaffé's review,[16] this was used. For other substituents σ values were taken from the compilation of McDaniel and Brown (M and B).[17] If no σ value was found in M and B, then a value was used from Jaffé's compendium. For nitrobenzene anion radicals, the p-nitro point was not used. Calculations of the correlation coefficient (r) for A^X *vs.* σ and the slope of the least-squares line for a plot of $A^X_{p \text{ or } m \text{ substuent}}/A^X_{p\text{-H}}$ *vs.* σ were performed both for all points and for those points previously demonstrated to be "well behaved" in 1-phenyl-1,2-propane semidiones.[1] The correlation for "well-behaved" points is attempted for a fairer comparison of the diverse systems surveyed; however, this is not a completely satisfying measure for the study of ref 1 encompassed very few −R groups. The results are shown in Table II.[18–22] By Walter's criterion all systems surveyed should exhibit Hammett behavior.

It is difficult to make comparisons among the correlations for all points since some studies encompassed more "ill-behaved" points than others. Detailed comparisons should not even be made among the correlations of "well-behaved" points, for, in general, only five to seven points were available. This means that deviation of a single point can affect r and the slope markedly. For example, the poor correlation of phenyl-t-butyl nitroxides for "well-behaved" points stems mainly from an anomalous value for the p-NH_2 substituent. Occasionally the correlation for "well-behaved" points is worse than the correlation for all points. This demonstrates that a point is not necessarily "ill behaved" just because it has not been shown to be "well behaved." Nevertheless, some general trends can be discerned. It appears that charged radical systems are more sensitive to substituent than the neutral systems. The sensitivity of the nitrobenzene radical anions is 1.5–2.5 that of the nitroxides. Among the nitrobenzene radicals, both the correlation with σ and the sensitivity of A^N to substituent are best for the results in the dipolar aprotic solvent acetonitrile. It would appear that hydrogen bonding of functional groups militates against maximum interaction of substituent. Furthermore, a comparison of slopes for nitrobenzene and p-nitrobiphenyl anion radicals in acetonitrile shows that the extra phenyl group attenuates the effect of the substituent, a very reasonable result.

We also note that the results in nonprotonic solvents for "well-behaved" points indicate that most radical systems studied correlate rather well with σ. We infer that for many systems, condition 3 (*vide supra*) applies.

Our survey evinces that electron spin resonance studies of stable radicals offer an excellent method of ordering the electron-supplying or electron-withdrawing ability of substituents. While these results will in many cases parallel the predictions of σ constants,

(13) In the previous study,[1] "Hammett ρ" values were calculated for 1-phenyl-1,2-propanesemidiones, phenyl-t-butyl nitroxides,[14] and nitrobenzene anion radicals[15] for plots of A^X *vs.* σ. Inadvertently the axes were reversed in making the calculations so the reciprocals of the slopes rather than the slopes were published. Such slopes in any event will not reflect the sensitivity of the system to substituent for the above reasons.

(14) H. Lemaire, Y. Marechal, R. Ramasseul, and A. Rassat, *Bull. Soc. Chim. France*, 372 (1965). The value given for p-CHO may be in error. See A. Calder and A. R. Forrester, *Chem. Commun.*, 682 (1967).

(15) P. L. Kolker and W. A. Waters, *J. Chem. Soc.*, 1136 (1964).

(16) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1963).

(17) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

(18) Th. A. J. W. Wajer, A. Mackor, Th. J. de Boer, and J. D. W. van Voorst, *Tetrahedron Letters*, 1941 (1967).

(19) A. B. Sullivan, *J. Org. Chem.*, **31**, 2811 (1966).

(20) P. B. Ayscough, F. P. Sargent, and A. Wilson, *ibid.*, 5418 (1963).

(21) A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1862 (1961).

(22) L. S. Degtyarev, L. N. Ganyuk, A. M. Golubenkova, and A. I. Brodskii, *Dokl. Akad. Nauk SSSR*, **157**, 1406 (1964).

some differences have already been noted.[1] The esr results, based on an eigenvector property of a single species, may actually be a more trustworthy measure of the electronic effect of a substituent than a σ constant based on differences between two species. To illustrate, in all but one of the systems of Table II, the *p*-F substituent is found to be slightly electron supplying. The σ constant classifies this substituent as slightly electron withdrawing. Recently, Birchall and Jolly[23] concluded from ionization constants of substituted anilines in anhydrous ammonia that *p*-F was electron supplying and the σ value should be -0.05 in systems where direct resonance effects are possible rather than 0.006. We intend to study substituent effects in other systems, paying particular attention to the "ill-behaved" substituents.

Experimental Section

The nitrosobenzenes were a gift of Dr. Travis Stevens (Redstone Arsenal). Solutions 0.1 *M* in the nitrosobenzene were deoxygenated in the degassing apparatus previously described.[24] The solvent was reagent grade benzene. Prior to irradiation many of the solutions contained small concentrations of radical which appeared to be the monophenyl nitroxide. Trace amounts of phenylhydroxyamine impurity could give rise to this radical *via* reaction VII. This reaction has been shown to occur in solution.[25] On irradiation these trace radicals were swamped by the characteristic diaryl nitroxide triplet.

$$\mathrm{PhNHOH} + \mathrm{PhNO} \rightleftharpoons 2\mathrm{PhNHO}\cdot \qquad \text{VII}$$

The ultraviolet source was a Bausch and Lomb SP 200-w. super pressure Hg lamp. Spectra were measured with a Varian V-4500 epr spectrometer equipped with a 9-in. magnet. Sweep rates were calibrated by the spectrum of *p*-benzosemiquinone in aqueous ethanol.[26] Spectra were solved by standard means.

Registry No.—VI (R = *p*-NO_2), 3313-75-5; VI (R = *p*-COOMe), 14210-54-9; VI (R = *p*-CO_2Et), 14210-55-0; VI (R = *m*-NO_2), 14210-56-1; VI (R = *m*-F), 14210-57-2; VI (R = *m*-Cl), 14210-58-3; VI (R = *p*-Br), 14210-59-4; VI (R = *p*-Cl), 14210-60-7; VI (R = *m*-CO_2Me), 14320-17-3; VI (R = *p*-H), 712-51-6; VI (R = *p*-F), 14210-62-9; VI (R = *p*-CH_3), 720-45-6; VI (R = *p*-OCH_3), 2643-00-7.

Acknowledgments.—We are grateful to Dr. Travis Stevens for his generous gift of the starting materials and to Dr. Brinkley Snowden, Jr., for writing a program to calculate correlation coefficients and least-squares slopes. We thank Dr. Edward G. Janzen for his helpful discussions and permission to cite his unpublished work.

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Electron Impact Induced Methyl Migration in Dimethylamino Heteroaromatic Systems[1a,b]

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The syntheses of 2-dimethylamino-5-nitropyrimidine (Ia), 2-di(trideuteriomethyl)amino-5-nitropyrimidine (Ib), and 2-dimethylamino-5-benzenesulfonamidopyrimidine (III) are reported. The mass spectra of Ia, Ib, III, and 6-dimethylaminopurine (II) are analyzed. Intense peaks M − 29 found in the spectra of Ia and II are shown to be due to loss of CH_3N from the molecular ion. This fragmentation is presumably accompanied by methyl migration from the *exo*- to the *endo*-cyclic nitrogen.

Considerable attention has been paid to electron impact induced rearrangements involving groups other than hydrogen after the first cases of such fragmentation processes had been reported.[2] Recently, many cases have been reported in which alkyl or aryl groups migrated under electron impact from a carbon atom to another carbon[3] or to a nitrogen[4] atom in the molecular ion or from a heteroatom to a carbon atom[5] or from one heteroatom to another.[6] We wish to report a new case in which, under electron impact, a methyl group was found to migrate from a nitrogen atom probably to another nitrogen atom in the molecular ion.

In a mass spectral investigation of some substituted purines, an intense (%Σ_{40} 9.5) M − 29 peak was found in the mass spectrum of 6-dimethylaminopurine (II) (Figure 1). A similar M − 29 peak was also intense (%Σ_{40} 6.6) in the mass spectrum of 2-dimethylamino-5-nitropyrimidine (Ia) (Figure 2). The corresponding metastable peaks were detected in both cases (see

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(2) (a) P. Funke, K. G. Das, and A. K. Bose, *J. Am. Chem. Soc.*, **86**, 2527 (1964); (b) A. Mandelbaum and M. Cais, *Tetrahedron Letters*, 3847 (1964); (c) F. Komitsky, J. E. Gurst, and C. Djerassi, *J. Am. Chem. Soc.*, **87**, 1398 (1965).

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