mg of a slightly yellow oil. This was crystallized from ether–hexane to give 387.9 mg (76%), mp 92.0–120.0°. Slow crystallization from ether–hexane gave three crops: 119.4 mg, mp 124.5–126.0°; 78.0 mg, mp 109.2–124.0°; and 115.7 mg, mp 90.4–122.2°. The nmr ($CDCl_3$) and infrared (CS_2) spectra of crops 1 and 3 were identical in all respects, indicating that the wide melting range is due to two crystalline forms of 4-phenyl-5-*p*-chlorophenylcyclohex-2-en-1-one. Extensive recrystallization did not narrow the melting point range; infrared (CS_2): 3.29, 3.38, 3.45, 5.96 (C=O), 7.23, 7.68, 7.91, 8.09, 8.72, 9.15, 9.29, 9.72, 9.85, 11.87, 12.11, 13.20, 13.44, and 14.32 μ; nmr ($CDCl_3$): τ 2.92 multiplet (10 H, 9 aryl, 1 vinyl), 3.75 doublet of doublets (1 H, vinyl, J_{AB} = 10.2 cps, J_{BX} = 2.5 cps), 6.05–7.52, complex multiplet (4 H, benzylic and α-methylene).

Anal. Calcd for $C_{18}H_{15}ClO$: C, 76.45; H, 5.35; Cl, 12.54. Found: C, 76.29; H, 5.55; Cl, 12.81.

3-*p*-Chlorophenyl-4-phenylphenol. The general method of Polaczkowa and Porowska[27] was used. A solution of 422.0 mg (1.50 mmoles) of 4-phenyl-5-*p*-chlorophenylcyclohex-2-en-1-one in 1.50 ml of 97% acetic acid was heated to 75°, and then a solution of 240 mg (1.50 mmoles) of bromine in 1.50 ml of 97% acetic acid was added. The mixture was heated at 102° for 2 hr, allowed to cool, and made basic by addition of saturated sodium bicarbonate solution. The aqueous solution was extracted with chloroform; the organic extracts were washed with water and concentrated *in vacuo* to yield 446.0 mg of an oil. This was crystallized from carbon tetrachloride–hexane to yield successive crops of 219.5 mg, mp 127.2–130.0°; 16.8 mg, mp 127.2–129.2°; and 26.4 mg, mp 120.0–126.0°, giving a total of 262.7 mg (62%). A sample was recrystallized from hexane to mp 129.1–131.1°; infrared ($CHCl_3$): 2.77, 2.98 (broad), 3.31, 6.23, 6.31, 6.41, 6.78, 6.90, 7.01, 7.27, 7.65, 8.54, 9.17, 9.85, 9.92, 11.21, 12.05, and 14.33 μ; (CS_2): 13.05, 13.56, 13.82, and 14.13 μ; nmr ($CDCl_3$): τ 2.92 multiplet (12 H, aryl) and 4.68 broad singlet (1 H, hydroxyl).

Anal. Calcd for $C_{18}H_{13}ClO$: C, 77.00; H, 4.67; Cl, 12.63. Found: C, 77.02; H, 4.67; Cl, 12.56.

3-*p*-Cyanophenyl-4-phenylphenol. A modified procedure based on the method of Newman and Boden was used.[28] A mixture of 246.8 mg (2.75 mmoles) of cuprous cyanide and 196.2 mg (0.70 mmole) of 3-*p*-chlorophenyl-4-phenylphenol in 1.0 ml of N-methyl-2-pyrrolidone was stirred at reflux for 14 hr. The cooled reaction mixture was taken up in sufficient benzene and 30% ammonium hydroxide for solution. A black solid, possibly elemental copper, remained undissolved between the layers and was discarded. The aqueous solution was extracted with benzene, and the combined organic extracts were washed with ammonium hydroxide, then with water, dried, and concentrated *in vacuo* to give 166 mg of a brown solid. This was chromatographed on a 1.6 × 43 cm silica gel column, slurry packed with 15% ether–hexane. The crude product was placed on the column in a minimum of ethyl acetate. The column was eluted with 15% ether–hexane and 100-ml fractions were collected. Fractions 4–15 yielded 118.8 mg (62%) of 3-*p*-cyanophenyl-4-phenylphenol, mp 220.5–224.5°. This was recrystallized from ethyl acetate–hexane and then methanol to mp 222.8–225.4°; infrared (KBr): 2.95, 4.47 (C≡N), 6.25, 6.32, 6.44, 6.66, 6.77, 6.99, 7.12, 7.53, 7.64, 7.88, 8.38, 11.22, 11.91, 12.11, 13.05, 13.45, 13.71, 14.06, and 14.30 μ; nmr (CD_3COCD_3): τ 1.38 singlet (1 H, hydroxyl) and 2.72 complex multiplet (12 H, aryl).

Anal. Calcd for $C_{19}H_{13}NO$: C, 84.11; H, 4.83; N, 5.16. Found: C, 84.35; H, 5.03; N, 5.29.

2-*p*-Cyanophenyl-3-phenylphenol.[23] An authentic sample of this compound[23] had mp 206–209° and spectra as follows; infrared (KBr): 2.94, 4.45, 6.22, 6.32, 6.37, 6.88, 7.14, 7.52, 7.68, 7.85, 7.97, 8.13, 8.49, 8.57, 8.67, 9.02, 9.12, 9.34, 9.77, 9.95, 10.38, 10.47, 11.10, 11.74, 11.96, 12.46, 13.12, 13.29, and 14.21 μ; nmr (CD_3COCD_3): τ 1.65 singlet (1 H, phenolic) and 2.77 complex multiplet (12 H, aryl).

Acknowledgment. We wish to express appreciation for a Predoctoral National Science Foundation Fellowship for J. O. G. and for helpful support from National Science Foundation Grant GP-1966 and from ARO(D).

Substituent Effects on the Hyperfine Splitting Constants of N,N-Dimethylaniline Cation Radicals[1]

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Abstract: The effects of *meta* and *para* substituents on the hyperfine splitting constants of the CH_3 protons, nitrogen, and the ring protons of N,N-dimethylaniline cation radicals in acetonitrile solution have been determined. The effects of *para* −R substituents are well correlated by σ^+ parameters and those of *para* +R substituents by σ_I parameters, both on a single regression line. The effects of *meta* −R substituents are found to be unique, with enhancement exceeding that expected for even *para* σ^+ parameters. A bisectional analysis of the observed substituent effects to polar effects (σ_I dependence) and π-delocalization effects ($\sigma_R{}^+$ dependence) has been carried out. This analysis indicates for strong −R substituents that the ratio of corresponding *para* to *meta* π-delocalization effects is (uniquely) less than one. Model HMO calculations give spin density distributions in accord with these findings. In further accord with the theoretical calculations, it is concluded that the correlations of the experimental splitting constants with σ values indicate that a close correspondence exists between the effects of substituents on spin and charge density distributions.

The relationship between nuclear hyperfine splitting constants (hfsc) from electron spin resonance (esr) spectrometry and substituent constants provides an approach to the understanding of the relationship of spin density to electron pair density distributions. This conclusion follows from the known relationships between hfsc and spin density[2] and between σ_R values and electron-pair densities.[3]

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[1] This work was supported in part by grants from the National Science Foundation and the U. S. Public Health Service.

[2] (a) H. M. McConnell, *J. Chem. Phys.*, **24**, 632, 746 (1956); (b) H. M. McConnelland H. H. Dearman, *ibid.*, **28**, 51 (1958).

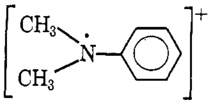
[3] (a) R. W. Taft, F. Prosser, L. Goodman, and G. T. Davis, *ibid.*, **38**, 380 (1963); (b) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 3146 (1963); (c) R. G. Pews, Y. Tsuno, and R. W. Taft, *ibid.*, **89**, 2391 (1967); (d) C. S. Giam and R. W. Taft, *ibid.*, **89**, 2397 (1967).

In several anion-radical systems, hfsc have been found to satisfactorily follow the Hammett $\sigma\rho$ relationship. Maki and Geske[4] correlated the nitrogen couplings of *meta*- and *para*-substituted nitrobenzene anion radicals with corresponding polarographic reduction potentials, $\Delta E_{1/2}$, and with σ values. These correlations were extended by Kolker and Waters.[5] Strom[6] has shown the Hammett equation applies for the CH_3 coupling constants for a series of *meta*- and *para*-substituted 1-phenyl-1,2-propanedione anion radicals. The data of Fraenkel, *et al.*,[7] for the nitrogen couplings of *para*-substituted benzonitrile anion radicals also follow a generally satisfactory correlation with σ values.

The cation radicals of *para*-substituted triphenylamine, in contrast, have been reported recently by Walter to have nitrogen coupling constants which do not follow a linear Hammett relationship.[8]

The purpose of this investigation has been to establish the relationship of coupling constants in a radical cation series with substituent σ values. Further, in terms of the bisection of σ^9 ($\sigma = \sigma_I + \sigma_R$) to determine: (a) if +R and −R substituents have the (usual) effects of opposite directions or the (novel) effects of the same direction (as proposed by Walter[8]); (b) the σ_I and σ_R combination, if any, which best describes the observed substituent effects on coupling constants; and (c) the ratio of R effects for corresponding *meta* and *para* substituents, in order to establish whether this ratio is usual (1:2–5, respectively) or novel (about 1:1) as implied by valence bond structures.[10]

We have selected as the parent cation radical the coplanar ion derived from N,N-dimethylaniline (I) in order to maximize the substituent effects on coupling constants and to obtain couplings at several positions (specifically, CH_3, N, and ring protons). In an attempt to ensure the greatest possible extent of generality of the results, a substantial variety of substituents have been investigated.



I

Experimental Section

Materials. N,N,N′,N′-Tetramethyl-*p*-phenylenediamine was prepared from the hydrochloride (Eastman), by neutralization with aqueous sodium hydroxide, extraction with ether followed by recrystallization from absolute methanol. *p*-N,N-dimethylaminobenzaldehyde (K & K Labs) and *p*-N,N-dimethylbenzoic acid (K & K) were recrystallized from 95% ethanol. *p*-Nitro-N,N-dimethylaniline (Eastman) was recrystallized from water. N,N-Dimethyl-*p*-toluidine (Eastman), N,N-dimethyl-*m*-toluidine (Eastman), N,N-dimethyl-*p*-phenylenediamine (K & K), N,N-dimethyl-*m*-phenylenediamine (K & K), and N,N-dimethylaniline (Fisher) were distilled under reduced pressure and stored under an inert atmosphere until use. 4,4′-Bis(N,N-dimethylamino)benzophenone (Eastman), *p*-bromo-N,N-dimethylaniline (Eastman), *m*-N,N-dimethylaminobenzoic acid (Eastman), and *m*-nitro-N,N-dimethylaniline (Eastman) were used as obtained; *m*- and *p*-fluoro-N,N-dimethylaniline were donated by Mr. Joseph Rakshys of this laboratory, and were used as obtained. N,N-Dimethyl-*m*-anisidine and 3,5-dimethoxy-N,N-dimethylaniline were donated by Dr. Arnold Zweig of American Cyanamid Corporation, and were used as obtained. N,N-Di-methyl-*m*-aminophenol (K & K) was sublimed before use. Acetonitrile (Eastman Spectrograde or Baker Analyzed reagent) was dried by the method of Coetzee, *et al.*[11]

Ethyl-*p*-N,N-dimethylaminobenzoate and **ethyl *m*-N,N-dimethylaminobenzoate** were prepared from the corresponding acids by esterification using EtOH–HCl and refluxing for 8 hr.[12a] The structure and purity of the products were determined by proton nuclear magnetic resonance (pmr) spectroscopy.

Sodium *p*-N,N-dimethylaminobenzoate was prepared by reacting the corresponding acid with 1 equiv of NaOH in hot water and filtering the crystals which separated on cooling.

N,N,N′,N′-Tetramethyl-*m*-phenylenediamine was prepared by methylation of *m*-phenylenediamine (Eastman) using methyl sulfate, similar to the method of Vogel.[12b] The structure of the product was verified from its pmr spectrum.

3,5-Di-*t*-butyl N,N-dimethylaniline was prepared from the corresponding aniline obtained from laboratory stock, by methylation with methyl sulfate.[12b] The purity and structure of the product were ascertained from its pmr spectrum.

***m*- and *p*-N,N-dimethylaminoacetanilide** were prepared by acetylation of the corresponding N,N-dimethylphenylenediamines.[12c] Product compositions were verified from the pmr and infrared spectra.

Sodium perchlorate (Fisher) was obtained as the monohydrate, and was dried *in vacuo* at 100° for 24 hr, then was recrystallized from absolute alcohol and redried at 120° for another 24 hr in a vacuum oven.[13]

Procedure. Samples were prepared at about 5×10^{-4} *M* in the aniline, and 0.1 *M* in sodium perchlorate. The sample cell for esr work was a modified flat cell similar to the Varian Electrolytic Cell Accessory. The cell and the solutions were purged for 5–10 min with purified argon to remove oxygen, and after filling the cell, the solutions were purged another 2 min before electrolysis was begun. The argon purge was continued during the electrolysis.

Cation radicals of the anilines were generated *in situ* using a platinum gauze anode and a platinum coil cathode, with a saturated calomel electrode as the reference electrode. The studies were carried out using a Varian V-4500 esr spectrometer with 100-Kc field modulation. Field calibrations were made using a Harvey-Wells precision gaussmeter, and are reproducible to ±0.02 gauss. All samples were electrolyzed at potentials 0.1 to 0.3 v more positive than the potentials at which the first signs of an esr signal appeared.[14]

Ring proton coupling assignments were made on the basis of simple Hückel molecular orbital (HMO) calculations, and by analogy to other compounds.[15]

Results

The nuclear hfsc of *para*-substituted N,N-dimethylaniline cation radicals (DMA^+) are summarized in Table I. The linewidths of all the *para* compounds were 0.15 gauss or less.

N,N,N′,N′-Tetramethyl-*p*-phenylenediamine cation radical (Wurster's blue) was previously studied by Weissman[16] and by Carrington.[17] In acetonitrile, we were unable to resolve the nitrogen couplings, but by chemical oxidation in $CHCl_3$–EtOH (80:20), we ob-

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

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

[6] E. T. Strom, *J. Am. Chem. Soc.*, **88**, 2065 (1966).

[7] P. H. Rieger, I. Bernal, K. Reinmuth, and G. K. Fraenkel, *ibid.*, **85**, 683 (1963).

[8] R. I. Walter, *ibid.*, **88**, 1923 (1966).

[9] (a) R. W. Taft, *ibid.*, **79**, 1045 (1957); (b) R. W. Taft and I. C. Lewis, *ibid.*, **81**, 5343 (1959).

[10] R. W. Taft, I. R. Fox, and I. C. Lewis, *ibid.*, **83**, 3349 (1961).

[11] J. F. Coetzee, G. Cunningham, D. McGuire, and G. Padmanabhan, *Anal. Chem.*, **34**, 1139 (1962).

[12] A. I. Vogel, "Textbook on Practical Organic Chemistry," 3rd ed, John Wiley and Sons, Inc., New York, N. Y., 1962: (a) p 1000; (b) p 572; (c) p 577.

[13] This is similar to the method of I. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, **79**, 870, 1852, 6110 (1957).

[14] Typically, these potentials were nearly identical with the polarographic oxidation potentials for N,N-dimethylanilines reported by (a) I. R. Fox, R. W. Taft, and J. M. Schempf, Technical Report to the Office of Naval Research, The Pennsylvania State University, June 1959; (b) A. Zweig, J. E. Lancaster, M. T. Neglia, and W. H. Jura, *J. Am. Chem. Soc.*, **86**, 4130 (1964).

[15] P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2811 (1962).

[16] S. I. Weissman, *ibid.*, **22**, 1135 (1954).

[17] J. R. Bolton, A. Carrington, and J. dos Santos-Viega, *Mol. Phys.*, **5**, 615 (1962).

Table I. Coupling Constants of *para*-Substituted N,N-Dimethylaniline Cation Radicals[a]

Substituent	a_{CH_3}	a_N	$a_H{}^o$	$a_H{}^m$	a_X	$\sigma_R{}^{+\,d}$	σ_I	Ref
$N(CH_3)_2$[b]	6.83	7.01	1.97	1.97	...	−1.97	0.10	This work
	6.76	6.99	1.97	1.97	...			Carrington[17]
NH_2	7.75	7.62	2.65	1.46	5.16(H) 4.73(N)	−1.67	0.10	This work
OCH_3	10.40	10.00	4.25	1.82	1.85(H)	−1.03	0.25	Adams[18]
$NHCOCH_3$	10.70	10.24	4.10	2.02	...	−0.84	0.24	This work
CH_3	12.22	11.17	5.21	1.36	9.97(H)	−0.26	−0.05	This work
	12.20	11.06	5.30	1.35	10.00(H)			Adams[18]
F	12.95	11.68	5.24	1.38	20.80(F)	−0.59	0.52	This work
CHO	14.00	12.10	5.90	1.96	...	0.11	0.31	This work
$CO_2C_2H_5$	14.16	12.14	5.83	1.78	0.36(H)[c]	0.24	0.21	This work
CO_2H	14.42	12.52	6.00	1.96	...	0.11	0.34	This work
NO_2	14.83	12.80	5.86	1.87	3.91(N)	0.18	0.60	This work
$C_6H_4N(CH_3)_2$	4.74	4.86	1.63	0.79	...	...	...	Fritsch and Adams[23] also this work
$COC_6H_4N(CH_3)_2$	13.37	11.58	5.57	1.88	...	...	...	This work

[a] Coupling constants in CH_3CN, 0.1 *M* $NaClO_4$ added, 23°. In gauss, ±0.05 gauss. [b] Coupling constants in $CHCl_3$–EtOH (80:20), 23°. In gauss, ±0.03 gauss. [c] Methylene proton splitting. [d] Values of $\sigma_R{}^+ = \sigma^+ - \sigma_I$.

served the fine splittings of the lines which are attributable to the nitrogen nuclei. A complete analysis of the spectrum gave nearly identical couplings with those reported by Carrington.[17] Our values of the various hfsc are reported in Table I, along with those of Carrington for comparison.

N,N-Dimethyl-*p*-phenylenediamine cation radical was also investigated by Weissman,[16] but the spectrum was poorly resolved. We have obtained a well-resolved spectrum which shows some line broadening due to the nearly overlapping lines of the amine protons and nitrogens. The values listed give the best fit to the spectrum, but assignment of the ring proton couplings is arbitrary, being based solely on analogy with the other compounds in the series (*i.e.*, $a_H{}^o > a_H{}^m$).

N,N-Dimethyl-*p*-anisidine cation radical was investigated by Adams and co-workers,[18] and the values listed in Table I are from this source.

p-N,N-Dimethylaminoacetanilide cation radical has a spectrum which exhibits a marked alternating line-width effect. This may be due to restricted rotation of the acetylamino group.[19] There are nine major groups of lines which arise from the methyl proton and nitrogen couplings.

N,N-Dimethyl-*p*-toluidine cation radical is an unstable species, but by employing the *in situ* technique to generate the radical, sufficient concentration was obtained to permit observation of a well-resolved spectrum with slightly broadened lines. The couplings are very similar to those reported by Adams[18] for this species.

p-Fluoro-N,N-dimethylaniline cation radical shows a very large coupling with a single nucleus having a spin of 0.5, which is apparently due to the fluorine atom. The magnitude of the splitting appears consistent with the coupling reported for a *p*-fluorine in the nitrobenzene anion radical series.[4,20] Recent investigations of fluorine-substituted ion radicals have shown that fluorine hfsc are normally larger than the hfsc for protons in a comparable environment.[21]

4,4′-Bis(N,N-dimethylamino)benzophenone cation radical has an esr spectrum which shows the coupling of six equivalent protons, one nitrogen nucleus, and two sets of two equivalent protons. This is consistent with the assumption that the two rings are not equivalent, and, moreover, that the carbonyl is either rotating freely or is locked out of the plane of the ring, since the *meta* protons would not otherwise appear equivalent.[19]

p-N,N-Dimethylaminobenzaldehyde, *p*-N,N-dimethylaminobenzoic acid, and ethyl *p*-N,N-dimethylaminobenzoate cation radicals all have nearly identical spectra, except for very small differences in the nitrogen and methyl proton hfsc. In addition, the ester shows a splitting of each line into a partially resolved triplet, presumably because of a very small coupling of the unpaired electron with the methylene protons of the ethyl group. No coupling for the aldehyde or carboxylic protons was observed in the other cases, however.

p-Nitro-N,N-dimethylaniline cation radical showed the largest methyl proton and nitrogen hfsc of all the compounds studied. The spectrum of this species was similar to that of the carbonyl-containing compounds, but it showed an additional nitrogen coupling of about the same magnitude as the ring proton hfsc.

Three compounds, N,N-dimethylaniline, *p*-bromo-N,N-dimethylaniline, and sodium *p*-N,N-dimethylaminobenzoate, all gave identical spectra when oxidized, which were the same as that reported by Galus and Adams[22] for N,N′-tetramethylbenzidine cation radical. (The correct interpretation of the spectrum was later reported by Fritsch and Adams.[23]) Apparently, all three couple at the *para* position to form the benzidine product.[24]

The nuclear hfsc for *meta*-substituted N,N-dimethylaniline cation radicals are summarized in Table II.

N,N,N′,N′-Tetramethyl-*m*-phenylenediamine cation radical and 3,5-dimethoxy-N,N-dimethylaniline cation radical have spectra which are of poor quality, due partly to the large number of lines expected (780 and 882, respectively), and partly to the short lifetimes of the radical species. Under very carefully controlled oxida-

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(18) E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy, and R. N. Adams, *J. Am. Chem. Soc.*, **88**, 3498 (1966).

(19) D. H. Geske, *Progr. Phys. Org. Chem.*, **4**, 164 (1966).

(20) M. Kaplan, J. R. Bolton, and G. K. Fraenkel, *J. Chem. Phys.*, **42**, 955 (1965).

(21) A. Carrington, A. Hudson, and R. C. Longuet-Higgins, *Mol. Phys.*, **9**, 377 (1965).

(22) Z. Galus and R. N. Adams, *J. Chem. Phys.*, **36**, 2814 (1962).

(23) J. M. Fritsch and R. N. Adams, *ibid.*, **43**, 1887 (1965).

(24) T. Mizoguchi and R. N. Adams, *J. Am. Chem. Soc.*, **84**, 2058 (1962).

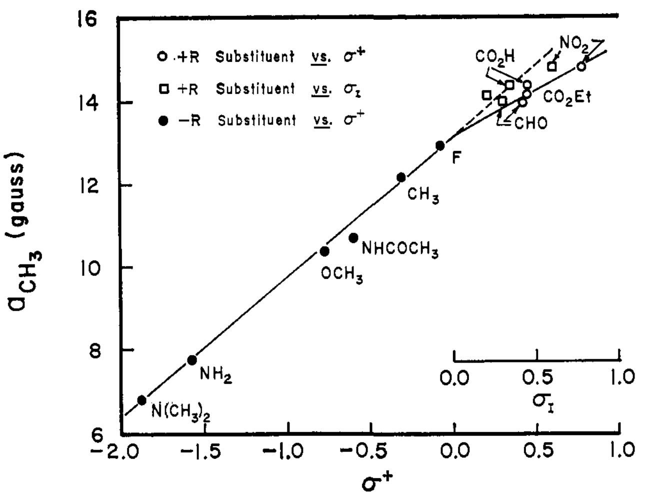

Figure 1. Relationship between a_{CH_3} and σ^+ (or σ_I): ordinate, a_{CH_3}, gauss; abscissa, σ^+.

tion, weak but fairly well-resolved spectra were obtained, but absolute certainty with regard to the coupling constant values is not possible. The values listed in Table II give the best fit to the observed spectra.

Table II. Coupling Constants of *meta*-Substituted N,N-Dimethylaniline Cation Radicals[a]

Substituent	a_{CH_3}	a_N	a_2	a_4	a_5	a_6	a_X
$N(CH_3)_2$[b]	5.2	5.2	2.5	7.1	1.0	7.1	...
NH_2[c]	7.25	7.25	2.39	5.39	0.85	5.39	4.83 (H,N)
3,5-Di-OCH_3[b]	5.4	5.4	6.0	6.0	...	6.0	...
OH[b,d]	7.5	7.5	...	...	...	...	...
3,5-Di-*t*-C_4H_{10}	12.44	11.24	5.35	8.18	...	5.35	...
CO_2H	14.75	14.66	1.74	7.46	...	5.20	...
$CO_2C_2H_5$	10.97	10.54	1.92	5.66	...	4.89	0.98 (H)[e]
NO_2[c]	14.82	12.78	1.80	6.27	...	5.93	0.74 (N)

[a] Coupling constants in CH_3CN, 0.1 *M* $NaClO_4$ added, 23°. In gauss, ±0.10 gauss, except as noted. [b] Error of measurement, ±0.50 gauss (estimated). [c] Error of measurement, ±0.5 gauss (estimated). [d] No ring proton coupling constants determined for this compound. [e] Methylene proton coupling constant.

N,N-Dimethyl-*m*-phenylenediamine cation radical has a spectrum of better quality than the preceding two compounds, and is characterized by a pattern which can be unequivocally assigned to six equivalent methyl protons. Two of the ring proton couplings are so nearly the same that within the error of measurement they could not be distinguished.

3,5-Di-*t*-butyl-N,N-dimethylaniline cation radical gives a spectrum which is of as good quality as the *para*-substituted compounds. It is characterized by a large methyl proton splitting and a large coupling due to a single proton (the *para* proton).

m-N,N-Dimethylaminobenzoic acid cation radical also gives a spectrum of good quality and shows three nonequivalent proton couplings which arise from the ring protons. These are assigned to positions on the basis of the HMO calculations ($\rho_{C_4} > \rho_{C_6} > \rho_{C_2} >> \rho_{C_5} \cong 0$).

Ethyl *m*-N,N-dimethylaminobenzoate cation radical shows a much smaller methyl proton hfsc than would be anticipated from its similarity to the corresponding acid. There is no apparent reason for this discrepancy on a structural basis.

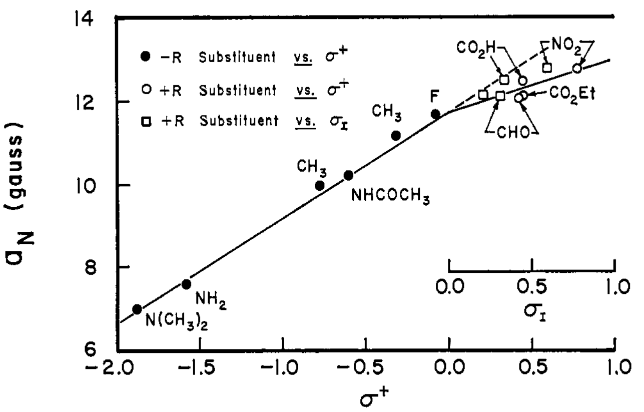

Figure 2. Relationship between a_N and σ^+ (or σ_I): ordinate, a_N, gauss; abscissa, σ^+.

m-Nitro-N,N-dimethylaniline cation radical has a methyl proton coupling constant nearly identical with the corresponding *para* compound, and very nearly the same as the *m*-benzoic acid cation radical. Only three nonequivalent ring proton couplings were resolved, although the breadth of the lines suggests that a fourth coupling not greater than 0.15 gauss is present in the spectrum.

m-N,N-Dimethylaminophenol cation radical did not have a well-resolved spectrum, but showed only seven broad lines, presumably due to the methyl protons and nitrogen. The separation between the lines is given as the methyl and nitrogen hfsc in Table II.

As occurred for certain of the *para*-substituted compounds, some of the *meta* compounds also coupled to give apparent benzidine-type products. These were the cation radicals from N,N-dimethyl-*m*-anisidine, N,N-dimethyl-*m*-toluidine, *m*-N,N-dimethylaminoacetanilide, and *m*-fluoro-N,N-dimethylaniline. The methyl hfsc of the dimers are listed in Table III.

Table III. Coupling Constants of Some Dimerized *meta*-Substituted N,N-Dimethylaniline Cation Radicals[a]

Subst	a_{CH_3}	Subst	a_{CH_3}
OCH_3	5.2	$NHCOCH_3$	4.82
CH_3	6.58	F	4.97

[a] Coupling constants in CH_3CN, 0.1 *M* $NaClO_4$ added, 25°. In gauss, ±0.10 gauss, except OCH_3, ±0.50 gauss.

Discussion

σ Correlations of Hyperfine Splitting Constants. The data from Table I were plotted against the available variety of σ parameters.[25] Generally satisfactory correlations were obtained only with $\sigma_{(p)}$ and $\sigma_{(p)}{}^+$. In accord with the structural analogy between the N,N-dimethylaniline cation radical and the *t*-cumyl cation,[26] the more precise relationship was found with the $\sigma_{(p)}{}^+$ values. Figures 1–3 show plots of the coupling constants *vs.* $\sigma_{(p)}{}^+$ values for the *para*-substituted DMA+ from Table I.

The conjugatively electron-accepting (+R) substituents describe a separate, more shallow regression line

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(25) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 334 (1964).

(26) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **79**, 1913 (1957).

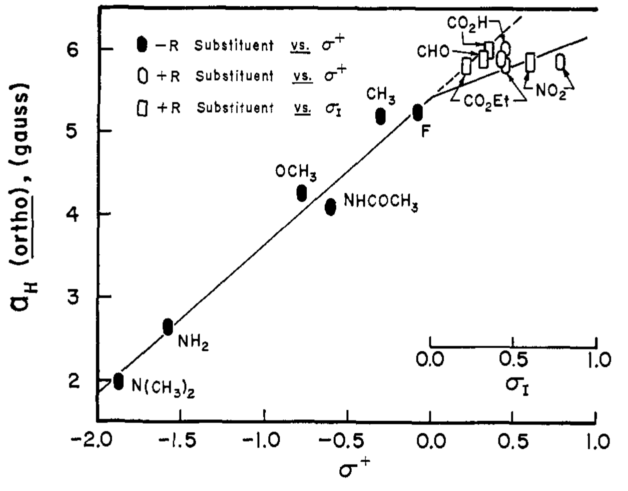

Figure 3. Relationship between a_H(*ortho*) and σ^+ [or σ_I]: ordinate, a_H, gauss; abscissa, σ^+.

than that for the electron-donating (−R) substituents (*cf.* Figures 1–3). However, in spite of the dual regression lines, it is clear that +R and −R substituents have the (normal) effects on the coupling constants of opposite directions (+R increases, −R decreases; *cf.* Table I). The present results therefore are not in accord with the hypothesis of Walter[8] that both +R and −R substituents should decrease the nitrogen coupling constant.[27]

In view of the bisection of σ values[9] (*e.g.*, $\sigma^+ = \sigma_R^+ + \sigma_I$), it appeared plausible that π delocalization effects (σ_R^+) might essentially be limited to −R substituents. That is, the coupling constants might be sensitive only to polar effects (σ_I) for +R substituents. Such a relationship has been demonstrated by Vaughan[28] for the effects of +R substituents in the ionization of 4-substituted pyridinium ions.

Accordingly, in Figures 1–3, the coupling constants for +R *para*-substituted DMA⁺ are also plotted *vs.* σ_I values. With the use of σ^+ values for −R substituents and σ_I values for +R substituents, satisfactory linear relationships with a single regression line are found in each plot. The following equations describe the correlation relationships (in gauss). The last term

$$a_{CH_3} = 13.13 + 3.41\sigma_I + 3.41\sigma_R^+ \qquad (1)$$

$$a_N = 11.75 + 2.62\sigma_I + 2.62\sigma_R^+ \qquad (2)$$

$$-a_H{}^o = 5.44 + 1.80\sigma_I + 1.80\sigma_R^+ \qquad (3)$$

applies only for −R substituents.

The values of σ^+ for *p*-OCH₃, *p*-F, and *p*-NHCOCH₃ are taken from Brown and Okamoto.[26] The σ^+ value (−1.87) for *p*-N(CH₃)₂ is from Deno and Evans[29] based upon Ar₂CHOH ionization. The σ^+ value (−1.57) for *p*-NH₂ was obtained from polarographic oxidation potential data for *meta*- and *para*-substituted anilines.[30]

Investigations of anion radicals[4,6] have shown that coupling constants for *meta*- and *para*-substituted compounds lie on the same regression line when $\sigma_{(m)}$ values are used for the former. That is, in terms of bisection of the observed substituent effects to I and R effects, the *para* to *meta* ratio is normal at approximately 2–3:1. We do not find, however, a similar result applicable to the coupling constants for *meta*-substituted DMA⁺. Values of $\sigma_{(m)}$ are inadequate to describe the *meta*-substituent effects recorded in Table II according to eq 1–3. Even $\sigma_{(p)}{}^+$ values are not sufficiently enhanced (negative) to give correct magnitudes for the *meta* results.

In Table IV are listed the *para* to *meta* ratios, $\alpha_p/\alpha_m \equiv$ *pmr*, of the methyl and nitrogen coupling constants for corresponding *para* and *meta* substituents. It is apparent that *pmr* tends to lie near unity for all substituents. R values for the π delocalization effects of *meta* and *para* substituents are obtained in accord with earlrie treatments[9] by the following modification of eq 1.

$$R_{CH_3} = a_{CH_3} - 13.13 - 3.41\sigma_I \qquad (1')$$

Table IV also lists values for R and the *para* to *meta* R ratios obtained through the use of eq 1′. In line with the above discussion, R values for substituents of the +R type tend toward zero, and R_p/R_m values for substituents of the −R type are found to be unique, *i.e.*, less than unity. The uniqueness of this result is appreciated in view of the fact that in no previous σ-type correlation of either physical or chemical properties of *meta* and *para* substituents has it been found that R_p/R_m has an absolute value less than approximately 2.

Table IV. Comparison of Resonance Effects in *meta*- and *para*-Substituted N,N-Dimethylaniline Cation Radicals

Subst	*pmr*[a]	R_p[b]	R_m[b]	R_p/R_m	$\sigma_{(m)}{}^{+\prime}$ [c]
N(CH₃)₂	1.31	−6.64	−8.27	0.80	−2.33
NH₂	1.06	−5.72	−6.22	0.92	−1.72
OCH₃[d]	1.13	−3.58	−4.29	0.83	−1.01
CH₃[e]	0.98	−0.74	−0.71	1.04	−0.25
CO₂C₂H₅	1.29	0.31	−2.88	...	...
CO₂H	0.98	0.13	0.46	...	...
NO₂	1.00	−0.35	−0.36	...	...

[a] *pmr* = a_{CH_3}(*para*)/a_{CH_3}(*meta*). [b] R_p and R_m are defined by eq 1′. [c] $\sigma_{(m)}{}^{+\prime} = R_m/3.41 + \sigma_I$. [d] R_m is calculated from the value of a_{CH_3} for 3,5-dimethoxy-N,N-dimethylaniline and corrected by a statistical factor of 2. [e] R_m is calculated from the value of a_{CH_3} for 3,5-di-*t*-butyl-N,N-dimethylaniline and corrected by a statistical factor of 2.

The unique features of the present results are illustrated in Figure 4 in which the π delocalization effect values, R_{CH_3}, from Table IV are plotted for both *meta* and *para* substituents *vs.* σ_R^+ values ($\sigma_R^+ \equiv \sigma^+ - \sigma_I$). Within the precision of this analysis, the R_{CH_3} values for +R substituents are shown to be negligibly small. On

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(27) In this regard, the results for nitrogen coupling in the triphenylamine cation radicals in acetonitrile solution also appear not to be in accord with the hypothesis of Walter. Professor Walter has kindly provided samples of the tris-*p*-CH₃CO and tris-*p*-CO₂CH₃ substituted triphenylamines from which the following a_N values were obtained (under similar conditions to those employed here for DMA⁺): 9.93 and 10.06 gauss, respectively. Adams and co-workers[18] have obtained for the tris-*p*-Cl, CH₃-, and OCH₃-substituted TPA⁺ ions the following a_N values in acetonitrile solution: 9.52, 9.45, and 8.97 gauss, respectively. These figures show a linear relationship between correspondingly substituted DMA⁺ and TPA⁺ ions, indicating that +R *para* substituents increase a_N in both series. The results of Walter were obtained in formic acid solution. Further, Professor Walter has pointed out to us his use of spectra taken under high modulation which does introduce some uncertainty in the a_N values reported.[27a]

(27a) However, attention is called to a_N = 10.16 obtained for unsubstituted TPA⁺ in SO₂ by H. van Willigen (*J. Am. Chem. Soc.*, **89**, 2229 (1967)).

(28) A. Fischer, W. J. Galloway, and J. Vaughan, *J. Chem. Soc.*, 3591 (1964).

(29) N. C. Deno and W. L. Evans, *J. Am. Chem. Soc.*, **79**, 5804 (1957).

(30) Data from ref 14a.

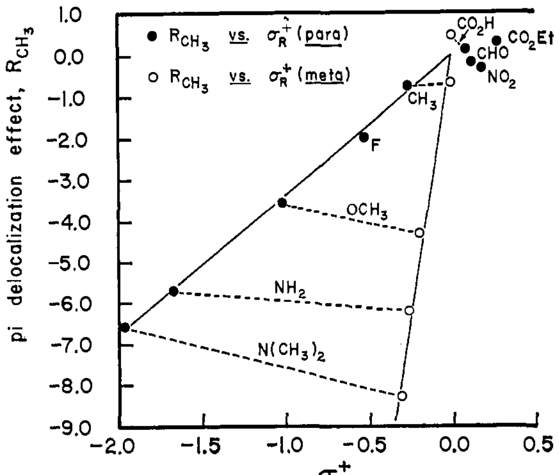

Figure 4. Plot of π-delocalization effect, R_{CH_3}, *vs.* $\sigma_R^+\cdot$: ordinate, R_{CH_3}, gauss; abscissa, $\sigma_R^+ \equiv \sigma^+ - \sigma_I$.

the other hand, the π delocalization effects for $-R$ substituents are relatively large, and well correlated by σ_R^+ values. The unique enhancement of the $-R$ *meta*-substituent π delocalization effects on the coupling constants of DMA^+ are illustrated by the much steeper regression line for *meta* than *para* $-R$ substituents. This result is also expressed in Table IV in terms of unique $\sigma_{(m)}^{+\cdot}$ values obtained from the observed effects of *meta* $-R$ substituents.

Theoretical Interpretations. This investigation was prompted by the conclusion based upon valence bond structures[10] that the delocalization effects of $-R$ substutuents from the *meta* position of cation radicals of the DMA^+ type, compared to normal σ_m effects, should be uniquely enhanced. In Figure 5, structures a–d and e–h suggest that the effects of corresponding *m*- and *p*-X substituents on the nitrogen spin density should be nearly equivalent (as observed, *cf.* discussion above), and that *meta* $-R$ substituents tend to cause substantial spin delocalization into the ring, particularly at the C_2, C_4, and C_6 positions (Figure 5a–d). This prediction of the valence bond structures is supported by the observation of large proton hfsc from the aromatic protons of *meta* $-R$-substituted DMA^+ (*cf.* Table II). Valence bond structures for *meta* $+R$-substituted benzonitrile anion radicals predict similar behavior. Fraenkel, *et al.*,[7] have reported an interpretation of the spectrum for isophthalonitrile anion radical which is in agreement with the valence bond predictions, but the authors have expressed uncertainty about the actual species which was observed.

In order to further investigate the theoretical implications of the correlations of the coupling constants with σ values, hypothetical models for *meta*- and *para*-substituted DMA^+ have been considered which can be treated by the HMO theory. Melchior and Maki[31] found that a suitable approximation of the spin density distribution in *p*-phenylenediamine cation radical was obtained usng $a_N = a_C + 0.85\beta_{CC}$ and $\beta_{CN} = \beta_{CC}$. We have chosen to make similar calculations for $XC_6H_4N(CH_3)_2^+$ using $a_N = a_C + 0.50\beta_{CC}$, $a_X = a_C + h_X\beta_{CC}$ and $\beta_{CN} = \beta_{CX} = \beta_{CC}$. where X is a "united atom" substituent with $h_X = 0.5$, 1.0, 1.5, 2.0, and 2.5.

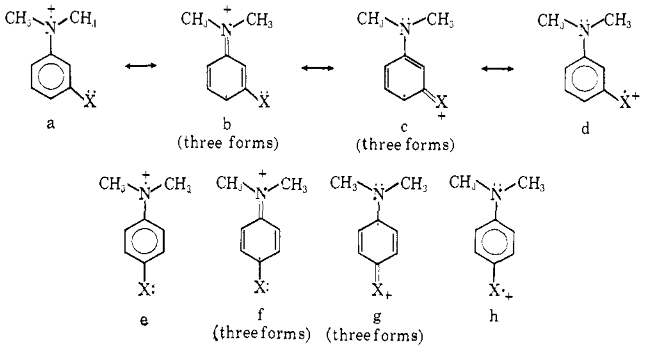

Figure 5. Valence bond structures of *meta*- and *para*-substituted N,N-dimethylaniline cation radicals.

In this manner, calculations were obtained for two series each of five *meta* and five *para* hypothetical substituted DMA^+. The results for $h_X = 0.5$, as shown in Table V, actually do give a good approximation of the spin distribution for both *m*- and *p*-$(CH_3)_2NC_6H_4N(CH_3)_2\cdot^+$ cation radicals.

Table V. Comparison of HMO Calculations and Experimental Results for N,N,N′,N′-Tetramethyl-*m*-phenylenediamine and N,N,N′,N′-Tetramethyl-*p*-phenylenediamine Cation Radicals

meta				para			
Position	ρ_i	a_i (calcd),[a] gauss	$\lvert a_i\rvert$ (obsd), gauss	Position	ρ_i	a_i (calcd),[a] gauss	$\lvert a_i\rvert$ (obsd), gauss
N	0.2278	5.7	5.2	N	0.2857	7.14	6.83
1,3	0.0151	...	...	1,4	0.0714	...	...
2	0.0000	0.0	2.5	2,3,5,6	0.0714	−2.00	1.97
4,6	0.2571	−7.2	7.1				
5	0.0000	0.0	1.0				

[a] Values used were $Q_H^{NCH_3} = 25.0$ gauss, $Q_H^{C-H} = -28.0$ gauss, in accord with the suggestion of A. McLachlan (*Mol. Phys.*, **1**, 233, (1958)).

The HMO calculations are of particular interest with respect to the effects of *meta* and *para* substituents on the spin and charge densities at the nitrogen atom. Corresponding effects on the total π electronic energy of the highest filled molecular orbital (hfmo) were also obtained. These results are summarized in Table VI.

Table VI. Results of HMO Calculations for *meta*- and *para*-Substituted N,N-Dimethylaniline Cation Radicals

h_X	ρ_N[a]	q_N[b]	χ_{hfmo}[c]	E_π[d]
		meta Compounds		
0.50	0.2278	0.4942	0.2424	$9\alpha + 10.85\beta$
1.00	0.4858	0.7543	0.2711	$9\alpha + 11.72\beta$
1.50	0.5035	0.7719	0.2738	$9\alpha + 12.64\beta$
2.00	0.5088	0.7777	0.2747	$9\alpha + 13.58\beta$
2.50	0.5113	0.7805	0.2752	$9\alpha + 14.54\beta$
		para Compounds		
0.50	0.2857	0.5127	0.0000	$9\alpha + 11.03\beta$
1.00	0.3807	0.6172	0.1051	$9\alpha + 11.83\beta$
1.50	0.4336	0.6763	0.1591	$9\alpha + 12.71\beta$
2.00	0.4610	0.7082	0.1890	$9\alpha + 13.63\beta$
2.50	0.4763	0.7268	0.2073	$9\alpha + 14.58\beta$
		Unsubstituted		
	0.5181	0.7872	0.2767[e]	$7\alpha + 9.27\beta$[f]

[a] Unpaired electron density at nitrogen. [b] $q_N = 2.0000 -$ total electron density at nitrogen = excess positive charge density. [c] Coefficient of β, $E(\psi[\text{hfmo}]) = \alpha + \chi\beta$. [d] Total energy π, $E_\pi = \Sigma_i n_i E(\psi_i)$. [e] χ^0_{hfmo}. [f] E^0_π.

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(31) M. T. Melchior and A. H. Maki, *J. Chem. Phys.*, **34**, 471 (1961).

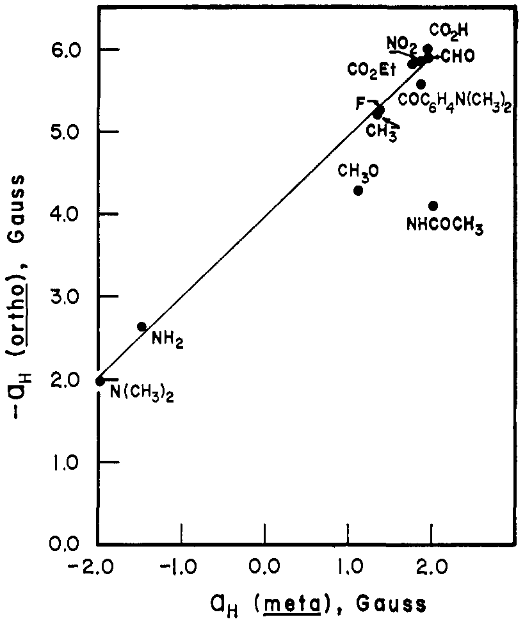

Figure 6. Relationship between ring proton coupling constants: ordinate, $-a_H(ortho)$, gauss; abscissa, $a_H(meta)$, gauss.

The calculated values of nitrogen spin and charge density, ρ_N and q_N, respectively, are directly related to each other for both the *meta* and *para* series, although slightly different slopes and intercepts are indicated for the two series.

$$q_N = 1.122\rho_N + 0.192 \qquad (para \text{ series}) \quad (4)$$

$$q_N = 1.044\rho_N + 0.246 \qquad (meta \text{ series}) \quad (5)$$

$$q(ortho) = 1.077\rho_{C_2,C_6} + 0.107 \qquad (para \text{ series}) \quad (6)$$

There is a slight curvature indicated in these relationships, but the correlations from the linear approximations are satisfactory: $r = 0.996$ for the *para* series, and $r = 0.999$ for the *meta*.

A direct proportionality between σ_R values and π charge density has been shown to exist in aromatic systems.[3] Consequently, if the HMO calculations are reliable regarding the close correspondence of substituent effects on the spin densities and the charge densities, the correlation with σ_R^+ of the π delocalization effect on the coupling constants (Figure 4) is justified.

When the substituent is a strong electron-pair donor, as indicated in Table VI by a value of h_X appropriate in magnitude to that for $N(CH_3)_2$ ($h_X \cong 0.50$), the spin density at nitrogen is actually smaller for the *meta* compound than its *para* isomer. As the value of h_X increases, the value of ρ_N increases more gradually for the *para* than for the *meta* compounds. When $h_X \geq 1.0$, $\rho_N(m) > \rho_N(p)$. The HMO calculations thus anticipate that strong $-R$ *meta* substituents ($h_X \leq 0.7$), *e.g.*, $N(CH_3)_2$ and NH_2, will cause a greater decrease in the nitrogen atom spin density than will the corresponding *para* substituent. The HMO model calculations are therefore in striking accord with the novel R_p/R_m ratio found in this study for DMA^+ (*cf.* Table VI).

It is worthy of note that the energies of hfmo's of Table VI indicate larger substituent stabilization effects from the *para* than the *meta* position. That is, in contrast to the effects on spin density ($R_p/R_m < 1$) the effects on energy are indicated as less novel ($R_p/R_m \cong 3$ as compared with $R_p/R_m \cong 10$ for *t*-cumyl chloride solvolysis,[9] for example). Zweig and co-workers have shown that the HMO calculations of energies of the hfmo's do correlate satisfactorily the relative polarographic oxidation potentials of *meta*- and *para*-substituted N,N-dimethylanilines.[14b]

Ring Proton Coupling Constants. Maki and Geske[4] suggested that there is a relationship between the *ortho*- and *meta*-proton couplings in *para*-substituted nitrobenzene anion radicals. They assumed that the spin density at the *meta* positions is negative for all compounds except the symmetrically disubstituted compound. With this assumption, they found that a plot of a_H*ortho vs.* a_H*meta* yielded a satisfactory linear relationship with a negative slope. By similar reasoning, it appears that the spin densities at the *meta* positions in the *para*-substituted DMA^+ are negative in all but the two *p*-phenylenediamine cation radicals. Figure 6 shows the relationship between the two coupling constants in this series obtained with this assumption. One of the compounds in the series, *p*-$NHCOCH_3$, does not fit the regression line formed by the other compounds. The reason for this deviation is not clear, but may be related to the alternating line-width phenomenon noted earlier for this substituent. Notwithstanding the deviation of this point, it is evident that there is a generally good inverse linear relationship between the two ring proton coupling constants for the majority of the compounds.

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