The Transmission of Electronic Effects through Carbon, Oxygen, and Sulfur Atoms. Proton Magnetic Resonance Chemical Shifts for Toluenes, Acetophenones, and Thioanisoles[1a,b]

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Received November 1, 1965

Proton magnetic resonance (pmr) shifts are reported for substituted toluenes, acetophenones, and thioanisoles. The Hammett ρ values (in cps/σ) are -12.8, -8.3, and -6.9, respectively. Based on a survey of over 25 families of the type R–C_6H_4T–H, the normal fall-off factor in ρ for the group T = 0, 1, 2, and 3 atoms is *ca.* 2–3/atom in carbon tetrachloride. When T can conjugate with the benzene ring, *e.g.*, T = O, N, and C≡C, the electronic communication between the substituent R and the terminal proton is enhanced: oxygen, preferably positive oxygen, appears to be a far better conductor of electronic effects on proton magnetic shielding than any other group examined thus far. Using ρ as an index of transmission efficiency, we are able to test theories of attenuation of pmr chemical shifts. Finally, having collected available ρ values for oxygen and sulfur, we propose a general scheme in which both the magnitude and the ease of transmission of electronic effects are compared. In nonconjugative situations, it is difficult to make predictions. In a conjugative role as an acceptor or an acceptor–donor of negative charge, sulfur is a better transmitter than oxygen, but, as a conjugative donor, sulfur is worse than oxygen.

Nuclear magnetic resonance (nmr) is a relatively new approach to the old problem of the transmission of electronic effects in chemical systems. Specifically, how are proton chemical shifts ($\Delta\nu$) altered when additional atoms are inserted between the substituent and the reaction "site"? We report here on the proton magnetic resonance (pmr) $\Delta\nu$ of thioanisoles, toluenes, and acetophenones.[1e] In a more general context we then inquire about the electronic communication in R–C_6H_4T–H, in which R = substituent, C_6H_4T = transmitting group, and H = reaction site. Finally, particular attention is given to oxygen and sulfur when they form part of the transmitting group.

As a substituent is moved down a chain from a terminal proton the effect of R on $\Delta\nu$ generally diminishes. Two recent reports give similar patterns for series of the type O_2N–$(CH_2)_n$–H, Cl–$(S)_n$$CH_2$–H, CH_3O–$(SO_3)_n$–CH_2–H, etc.:[2,3] $\Delta\nu$ changes drastically from $n = 1$ to $n = 2$ and then more gradually until it essentially levels off at $n = 5$ or 6. In any one of these series, which have the form R–G–H, one might like to ascribe all of the changes in $\Delta\nu$ to changes in the electronic character of G. If this were possible, this would be a simple way to characterize G. However, $\Delta\nu$ is also subject to magnetic anisotropy effects so that it is difficult to estimate how much of the nmr characterization of G as a transmitting group would carry over to other properties, say to kinetic data for the same series.

In aryl families, R–C_6H_4T–H, the substituent and the terminal proton are sufficiently remote so that one could hope that differential anisotropy effects were negligible or at least constant for a given group T. Then, the transmission of electronic effects through T could be studied in the form of the Hammett equation[4]

$$\Delta\nu = \rho\sigma + \Delta\nu_0 \qquad (1)$$

Provided that σ was an invariant index of the electronic properties of the substituent R,[5] ρ would characterize T as well as the conditions of the pmr measurements. Because a whole range of substituents is involved in eq 1, irregularities due to specific substituents, solvent effects, conformations, etc., tend to be averaged; ρ becomes a good attenuation measure through –C_6H_4T–.[6]

Though the present model is too simple, particularly in the nmr context, it can be useful. The total nuclear magnetic screening constant, S, may be divided into molecular and environmental contributions.[7] For any family, the medium effects are taken as constant. The diamagnetic, paramagnetic, and magnetically anisotropic contributions to S can be termed "systematic" when their effect on R is the same for all families and when their effect on –C_6H_4T– is the same for all substituents. Now, $\Delta\nu_0$ for R = H or $\sigma = 0$ is the fundamental quantity of eq 1. When hydrogen (H) is replaced by R, $\rho\sigma$ becomes an increment to $\Delta\nu_0$. As we have seen, σ and ρ are assumed to be independent. Therefore, to the extent that eq 1 applies, we gain insight into the pmr property and the molecular system. In this paper, we report a set of ρ values which measure the ability of T to relay electronic effects. These ρ values fall into a rough but discernible pattern so that the exceptional and "superconducting" groups T stand out.

Experimental Section[8]

Chemicals.—The thioanisoles, toluenes, and acetophenones were generally commercially available and used without further purification. The absence of spurious signals in the pmr spectrum was taken as indication of adequate purity. *p*-Bromo- (98%), *p*-chloro- (98%), *p*-amino-, and the unsubstituted thioanisole (98%) were gifts of Evans Chemetics, Inc; *p*-methylthioanisole was synthesized Mr. A. Caplan. A good grade of carbon tetrachloride was used as the solvent.

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[1] (a) This work has been supported in part by the National Institutes of Health, U. S. Public Health Service and by the Office of Ordnance Research, U. S. Army. (b) Taken in part from the Ph.D. thesis of S. H. M. (c) National Science Foundation Fellow, 1961–1963. (d) National Science Foundation Senior Research Fellow at University College, London, 1963–1964; to whom inquiries should be addressed.

(1e) NOTE ADDED IN PROOF.—Data on the toluenes and acetophenones may be found in a report by Y. Yukawa, M. Sakai, K. Kabazawa, and Y. Tsuno, *Mem. Inst. Sci. Ind. Res. Osaka Univ.*, **17**, 185 (1960).

[2] W. Hofman, L. Stefaniak, T. Urbánski, and M. Witanowski, *J. Am. Chem. Soc.*, **86**, 554 (1964).

[3] J. R. Van Wazer and D. Grant, *ibid.*, **86**, 1450 (1964).

[4] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953); P. R. Wells, *ibid.*, **63**, 171 (1963).

[5] In this paper we shall use the symbol σ as a substituent constant and not as a shielding contribution to the pmr chemical shift as is often done.

[6] (a) W. K. Kwok, R. A. More O'Ferrall, and S. I. Miller, *Tetrahedron*, **20**, 1913 (1964); (b) J. D. S. Ritter and S. I. Miller, *J. Am. Chem. Soc.*, **86**, 1507 (1964).

[7] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 11; L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, Chapter 4.

[8] Detailed information is given in the Ph.D. thesis of S. H. Marcus Illinois Institute of Technology, 1965.

Pmr Measurements.—The spectra of the thioanisoles were taken at Illinois Institute of Technology on a Varian A-60 spectrometer. Operating details have been given previously.[8,9] The chemical shifts, $\Delta\nu$ from tetramethylsilane (TMS) internal standard, are values at infinite dilution obtained by extrapolating the data at three concentrations below 3 *M;* the value at any given concentration was based on three determinations. The maximum spread was <0.3 cps with a mean of 0.1 cps; these data are precise to ±0.2 cps.

The spectra of the toluenes and the acetophenones were taken at University College, London, on a Perkin-Elmer 60-Mc nmr spectrometer. The magnet gap temperature was 33°. The carbon tetrachloride solutions were 0.10 *M* in compound and *ca.* 0.005 *M* in TMS. The root-mean-square uncertainty in $\Delta\nu$ varied 0.2–0.5 cps; we estimate the average uncertainty as ±0.4 cps.

Results and Discussion

The Hammett equation was used to correlate both our data from Table I as well as literature data. The standard *meta* and *para* σ values listed by McDaniel and Brown were used,[10] and the parameters of eq 1 were computed by recommended least-squares methods.[4] For completeness, a few correlations of subfamilies, *e.g.*, *ortho*, *meta*, or *para* substituents with σ (*para*), σ (*meta*), and σ (*para*), respectively, were made; these will be referred to incidentally. [Since a generally reliable set of *ortho* σ values is unavailable, correlations of properties involving *ortho* substituents are often made with σ (*para*).] Table II gives the calculated results.

TABLE I

CHEMICAL SHIFTS FOR THE METHYL PROTONS OF THE TOLUENES, ACETOPHENONES, AND THIOANISOLES IN CARBON TETRACHLORIDE[a]

R	$-\nu_{CH_3}$ (toluenes)	$-\nu_{CH_3}$ (acetophenones)	$-\nu_{SCH_3}$ (thioanisoles)
p-$N(CH_3)_2$			139.8[b]
m-OCH_3			140.4[b,c]
p-NH_2	132.2	145.4	140.5
m-$N(CH_3)_2$			142.8[b]
m-NH_2	134.5		143.2
p-OH	136.0		144.4
p-OCH_3	136.7	148.7	142.7,[d] 142.8[b]
p-SCH_3			144.0[b]
p-CH_3	137.9	150.0	144.4
m-SCH_3			145.8[b]
m-OH	138.2		
3,5-$(SCH_3)_2$			145.8[b]
m-CH_3	139.0		
p-Br	139.4	152.4	146.2, 145.6[d]
p-F	139.7		
p-Cl	140.1	152.5	146.0
m-Br	140.5		
m-Cl	141.0	153.1	
H	141.6	152.6	146.5, 145,[d] 145.2[b]
m-F	142.0		
m-CN	145.6		
p-SH	138.4		
m-SH	138.3		
p-CN	147.1		
m-COOH	148.0		
p-NO_2	150.3	158.3	152.5[d]
m-NO_2	150.6		
p-SO_2Cl	151.7		

[a] Values are from this study, except as noted. Units are in cycles per second. [b] A. Zweig and J. E. Lehnsen, *J. Am. Chem. Soc.*, **87,** 2647 (1965). [c] This value was not used to obtain ρ. [d] D. W. Larsen and A. L. Allred, *J. Am. Chem. Soc.*, **87,** 1216 (1965).

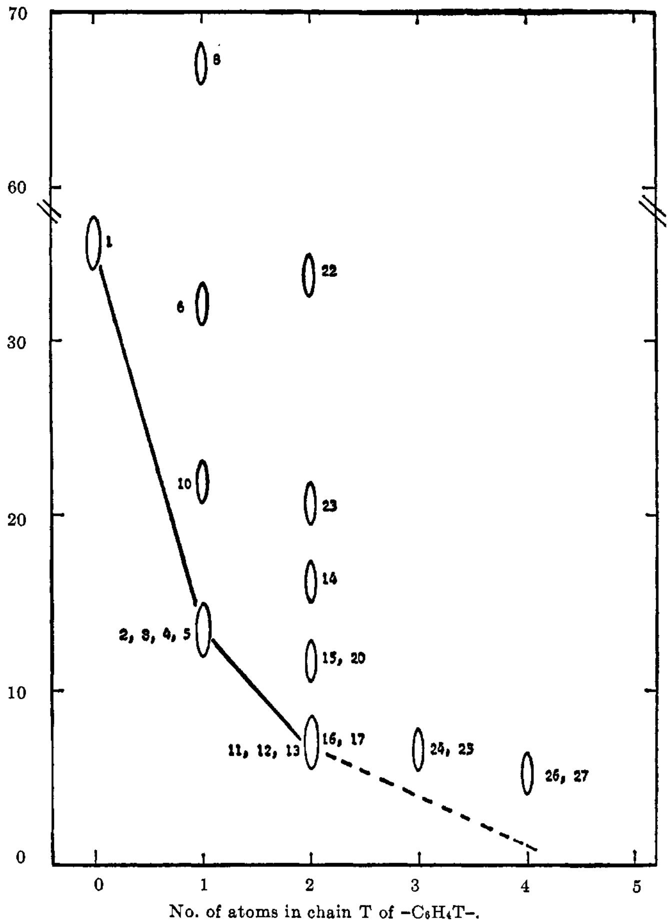

Figure 1.—Hammett ρ values for pmr $\Delta\nu$. Numbers refer to the families of Table II. The dotted line has a slope of *ca.* 2.

Several tests of eq 1 have already been reported, see the citations to Table II. The standard σ values as well as σ^0, σ^+, σ^-, σ_R, and extended versions of 1, *e.g.*

$$\Delta\nu = \rho'\sigma' + \rho''\sigma'' + \Delta\nu_0 \qquad (2)$$

have all been considered in particular cases.[11-13] Some of these alternate σ values are given in the next to the last column of Table II. Depending on the system, the fit to eq 1 has occasionally been "improved" both by including or excluding *meta* substituents.[13] In fact, there is no agreement at the present time as to what scales should be used for rate or equilibrium data and there is even less experience with nmr data. For consistency, we have chosen the original σ values. This fixes the scale of electronic effects and the burden of their transmission devolves on ρ. Subject to the limitations of this model, comparisons of widely different families can now be made.

The ρ values of Table II provide the necessary information on the transmission of electronic effects. At the outset, it should be clear how far from quantitative

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[9] S. H. Marcus and S. I. Miller, *J. Phys. Chem.*, **68,** 331 (1964).

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

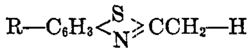
[11] (a) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Japan*, **32,** 960, 965 (1959); (b) Y. Yukawa and H. Yamada, *J. Chem. Soc. Japan, Pure Chem. Sec.*, **85,** 501 (1964).

[12] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Am. Chem. Soc.*, **85,** 709, 3146 (1963).

[13] (a) L. K. Dyall, *Australian J. Chem.*, **17,** 419 (1964). (b) Y. Yonemoto, W. F. Reynolds, H. M. Hutton, and T. Schaeffer, *Can. J. Chem.* **43,** 2668 (1965). (c) Data on the anilines in carbon tetrachloride are given by W. F. Reynolds, Ph.D. Thesis, University of Manitoba, 1963.

TABLE II

GROUP ATTENUATION FACTORS FOR PMR CHEMICAL SHIFTS AS INDICATED BY HAMMETT ρ VALUES

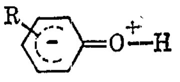
No.	R—C$_6$H$_4$T—H[a]	Atoms[b] in T	$-\rho$,[a] cps/σ	$\Delta\nu_0$[a]	r[c]	S[a]	N[d]	Solvent	Other σ values[e]	Ref
1	R—C$_6$H$_4$—H	0	35.6	0.209[f]	0.836	0.137	20	Neat		17
	4-R—C$_6$H$_4$—H		43	0.199[f]	0.905	0.145	9	Neat		
	3-R—C$_6$H$_4$—H		24.7	0.169[f]	0.658	0.126	11	Neat		
2	R—C$_6$H$_4$CH$_2$—H	1	12.8	138.9	0.884	2.56	22	CCl$_4$		*p*
	4-R—C$_6$H$_4$CH$_2$—H		12.5	139.6	0.926	2.33	12	CCl$_4$		
	3-R—C$_6$H$_4$CH$_2$—H		14.2	138.0	0.811	2.88	11	CCl$_4$		
3	4-R—C$_6$H$_4$(CHCH$_3$)—H	1	12.1	154.1	0.938	2.00	9	CS$_2$		*g*
4	R—C$_6$H$_4$(CR′CH$_2$R″)[h,i]	1	13.1	234.0	0.966	2.18	5	CS$_2$		*g*
5	R—C$_6$H$_4$CO—H	1	14.4	9.85	0.847	0.06	22	CCl$_4$		*j*
	4-R—C$_6$H$_4$CO—H		15.4	9.89	0.963	0.039	9	CCl$_4$		
	3-R—C$_6$H$_4$CO—H		10.6	9.88	0.69	0.051	8	CCl$_4$		
6a	R—C$_6$H$_4$NH—H	1	21					C$_6$H$_{12}$		13b
6			31.9	197.0	0.967	1.6	13	CCl$_4$		13b
7	R—C$_6$H$_4$NH—H	1	54.5	229.9	0.975	3.5	20	CH$_3$CN	σ^-	13a
	4-R—C$_6$H$_4$NH—H		88.7	233.8	0.968	7.0		CH$_3$CN	σ^-	
8	R—2,6-(*t*-C$_4$H$_9$)$_2$C$_6$H$_2$O—H	1	66.9	301.6	0.914	11.1	11	CCl$_4$	σ^-	*k*
9	R—C$_6$H$_4$O—H	1	101.4	0.744[f]	0.973	0.140	22	DMSO	σ^-	15
	4-R—C$_6$H$_4$O—H		108	0.707[f]	0.978	0.163	12	DMSO		15
	3-R—C$_6$H$_4$O—H		85.8	0.775[f]	0.998	0.0176	7	DMSO		15
10	R—C$_6$H$_4$S—H	1	21.8	195.1	0.952	2.62	11	CCl$_4$	σ^-	9
11a	R—C$_6$H$_4$C(=C(CN)$_2$)—H	1	14.6	2.322[n]	0.85		20	CHCl$_3$		*v*
	4-R—C$_6$H$_4$C(=C(CN)$_2$)—H	1	15.5	2.303[n]	0.95		10	CHCl$_3$		*v*
11	R—C$_6$H$_4$CH$_2$CH$_2$—H	2	6.76	71.4	0.967	0.789	9	CCl$_4$		*g*
12	*cis*-R—C$_6$H$_4$(CHR′CHR″)—H[h,l]	2	6.66	172.5	0.985	0.716	5	CS$_2$		*g*
13	*trans*-R—C$_6$H$_4$(CHR′CHR″)—H[h,m]	2	6.45	140.7	0.907	1.86	5	CS$_2$		*g*
14	R—C$_6$H$_4$OCH$_2$—H	2	16.2	6.35[n]	0.891	0.0442	15	CCl$_4$		*o*
	4-R—C$_6$H$_4$OCH$_2$—H		15.7	6.35	0.866	0.048	12	CCl$_4$		*o*
15	4-R—C$_6$H$_4$OCH(CH$_3$)—H	2	11.6	6.12[n]	0.923	0.035	8	CCl$_4$		*o*
	4-R—C$_6$H$_4$OCH(CH$_3$)—H		11.6	6.10	0.973	0.028	5	CCl$_4$		*o*
16	R—C$_6$H$_4$SCH$_2$—H	2	6.88	145.0	0.937	1.10	14	CCl$_4$		*p*
	4-R—C$_6$H$_4$SCH$_2$—H		7.11	145.3	0.949	1.17	10	CCl$_4$		*p*
	3-R—C$_6$H$_4$SCH$_2$—H		4.19	143.8	0.374	2.25	6	CCl$_4$		*p*
17	R—C$_6$H$_4$COCH$_2$—H	2	8.34	151.1	0.975	0.895	8	CCl$_4$		*p*
18	R—C$_6$H$_4$COCH$_2$—H	2	19.9	3.365	0.776	0.112	6	HSO$_3$F		*q*
19	R—C$_6$H$_4$C(CH$_3$)O$^+$—H	2	156.3	13.22[f]	0.983	0.200	6	HSO$_3$F	σ^+	*q*
20	R—C$_6$H$_4$COCH(COCH$_3$)—H	2	11.9	5.92[n]	0.890	0.061	6	CCl$_4$		*r*
21	R—C$_6$H$_4$C(OH)=C(COCH$_3$)—H	2	7.02	3.86[n]	0.864	0.041	6	CCl$_4$		*r*
22	R—C$_6$H$_4$CO(=CHCOCH$_3$)—H	2	33.7	6.17[n]	0.945	0.116	6	CCl$_4$		*r*
23	R—C$_6$H$_4$C≡C—H	2	20.6	7.12[n]	0.975	0.031	18	CCl$_4$	σ_I, σ_R	*s*, 11b
	4-R—C$_6$H$_4$C≡C—H		21.9	7.11	0.984	0.0279	13	CCl$_4$		*s*, 11b
	3-R—C$_6$H$_4$C≡C—H		18.66	7.13[n]	0.985	0.018	6	CCl$_4$		*s*, 11b
24	R—C$_6$H$_4$OCH$_2$CH$_2$—H	3	6.96	8.68[n]	0.938	0.019	8	CCl$_4$		*o*
	4-R—C$_6$H$_4$OCH$_2$CH$_2$—H		6.84	8.67	0.985	0.012	5	CCl$_4$		*o*
25	 $\mathrm{R{-}C_6H_3}{<}\overset{\mathrm{S}}{\underset{\mathrm{N}}{}}{\geqslant}\mathrm{CCH_2{-}H}$	3	6.74	168.8			12	CDCl$_3$		*t*
26	R—C$_6$H$_4$COCH$_2$COCH$_2$—H	4	4.66	7.71[n]	0.899	0.023	6	CCl$_4$		*r*
27	R—C$_6$H$_4$COH=CHCOCH$_2$—H	4	5.63	7.84[n]	0.929	0.022	6	CCl$_4$		*r*
28	1-R—2,6-(CH$_3$)$_2$C$_6$H$_2$—4-H	0	20.8	21.4	0.843	7.58	12	CCl$_4$	σ_R	*u*
	1-R—2,6-(CH$_3$)$_2$C$_6$H$_2$—3-H		16.0	24.2	0.908	2.45	12	CCl$_4$	σ_R	*u*
29	2-R—3-CH$_3$C$_6$H$_3$CH$_2$—H	1	9.9	7.69	0.718	0.091	12	CCl$_4$		*u*
30	2-R—C$_6$H$_4$OCH$_2$—H	2	9.6	6.28[n]	0.782	0.052	10	CCl$_4$		*o*
31	2-R—C$_6$H$_4$C≡C—H	2	4.03	6.83[n]	0.175	0.177	8	CCl$_4$	σ_I, σ_R	*s*

[a] Except as noted *meta* and *para* substituents were used. All of the ρ values are given in the units cycles per second per Hammett σ unit. To put these on the δ or τ scales divide by ±60. The intercept, $\Delta\nu_0$ and S, the standard deviation, are given in the same units as the original reference to facilitate interpolation in the published data; units different from cycles per second will be noted. [b] This is the chain length of T. [c] The correlation coefficient. [d] Number of compounds. [e] Other σ scales used by previous workers to correlate the same data. [f] $\Delta\nu_0$ and S are for δ (parts per million) units. [g] K. L. Williamson, N. C. Jacobus, and K. T. Soucy, *J. Am. Chem. Soc.*, **86**, 4021 (1964). [h] *p*-Phenylhexachlorobicyclo[2.2.1]-2-heptenes. [i] α carbon. [j] R. E. Klinck and J. B. Stothers, *Can. J. Chem.*, **40**, 1071 (1962). [k] L. A. Cohen and W. M. Jones, *J. Am. Chem. Soc.*, **85**, 3402 (1963). [l] *cis*-β carbon. [m] *trans*-α carbon. [n] $\Delta\nu_0$ and S are for τ (parts per million) units. [o] C. Heathcock, *Can. J. Chem.*, **40**, 1865 (1962). [p] This study. [q] T. Birchall and R. J. Gillespie, *ibid.*, **43**, 1045 (1965) [r] D. Sardella, D. Heinert, and B. L. Shapiro, unpublished results. [s] C. D. Cook and S. S. Danyluk, *Tetrahedron*, **19**, 177 (1963). [t] G. DiModica, E. Barni, and F. Della Monache, *Gazz. Chim. Acta*, **95**, 432 (1965). [u] R. R. Fraser, *Can. J. Chem.*, **38**, 2226 (1960). [v] M. A. Weinberger, R. M. Heggie, and H. L. Holmes, *ibid.*, **43**, 2585 (1965).

we shall have to be; the reader need only scan the column of correlation coefficients to realize that the present correlations are often poorer than many generated in rate and equilibrium applications of eq 1. In fact, those entries whose correlation coefficients are much smaller than 0.9 can be disregarded. Fortunately, the main point we wish to make will stand even if the uncertainty in ρ is *ca.* 25%!

The salient finding is that the minimum attenuation factor per connecting atom is ca. 2-3 in carbon tetrachloride. For T = 0, 1, and 2 atoms in a chain, the "standard" $-\rho$ values in cps/σ are *ca.* 36, 13, and 7; these ρ values define the curve in Figure 1. Surprisingly enough, the fall off of *ca.* 2 is right in the range of 2–3 found for many rate and equilibrium reactions.[4] Although the data are few beyond $T \geq 3$, a leveling off seems to set in, and this is at a value of $\rho \simeq 5$ substantially above 0. Finally, it is of interest that some σ_I values, based on nmr fluorine chemical shifts in the fluorobenzenes, decrease by approximately the same factor when a methylene group is interposed between the substituent and the ring.[12]

Judging by the standard ρ values, we note that some $-C_6H_4T-$ seem to relay electronic effects too efficiently: their points lie above the minimum line of Figure 1. Here, it is significant that T may contain oxygen, nitrogen, the carbon–carbon double bond or the carbon–carbon triple bond, all groups which conjugate readily with the aromatic ring. It has been suggested that resonance structures of the type I and II influence strongly the magnitude of $\Delta\nu$ in these families.[14] Such resonance contributions also appear to magnify the sensitivity of $\Delta\nu$ to remote substituents R. In particular, oxygen is often "superconducting" and not even one or two methylene groups can destroy the exalted communication between R and H! By comparison, sulfur seems to be an ordinary transmitter, except for a relatively small increment in the ρ of the thiophenols.



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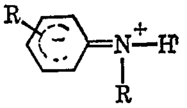
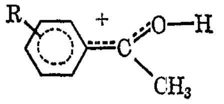
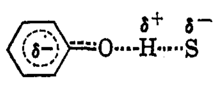


II

The ρ value for protonated acetophenone in fluorosulfuric acid (entry 19, Table II) is extremely high at −156 for T = two atoms. Here, there is the ion III in which pmr $\Delta\nu$ electronic effects are transmitted about twenty times more efficiently than in acetophenone. Though the effect of solvent is impossible to assess, it does appear that, allowing for the fact that T = 2, this is the highest conductivity among available families. Although this effect is probably associated with the positive charge in the connecting atoms, as in I and II, this tentative suggestion will be tested when more charged species are studied.



III



IV

Solvent effect data concerning ρ are few; of these, several seem "out of line" and deserve comment. Compare the entries in Table II for the phenols, $\rho = -66.9$ in carbon tetrachloride and $\rho = -101$ in dimethylsulfoxide; for the anilines, $\rho = -21$ in cyclohexane, $\rho = -31.9$ in carbon tetrachloride, and $\rho = -54.5$ in acetonitrile. According to Ouellette, the enhanced sensitivity to the substituent, a correlation with σ^- values, and the absence of a dilution shift are consistent with a hydrogen-bonded complex between phenol and DMSO, *e.g.*, structure IV.[15] Schaefer, *et al.*, emphasize the tendency for increased hydrogen bonding of anilines in the three solvents;[13b] Dyall points out that additional sensitivity, as reflected in ρ, could arise from strong solvation of the π electrons by a polarizable solvent, *e.g.*, acetonitrile.[13a] All of these factors that increase ρ appear to be reasonable, particularly when their effect on the contributions of structures such as I and II are kept in mind.

Taft, *et al.*, have made detailed solvent studies on fluorine nmr of fluorobenzenes: they dissected the substituent effect into polar (σ_I) and resonance (σ_R) contributions.[12] It still remains to be seen whether the fall off factors, that is the increments in ρ, will be a function of the solvent.

There is a theory, the reaction-field theory, that can be applied here.[16] For a given family in a variety of solvents

$$\rho \propto (\epsilon - 1)/(2\epsilon + n^2) \qquad (3)$$

where ϵ is the dielectric constant of the medium and n is the refractive index of the solute. Tested on the anilines (n^{25}_D 1.584) in cyclohexane (ϵ 2.02), carbon tetrachloride (ϵ 2.24), and acetonitrile (ϵ 37.5), the proportionality required by eq 3 is not found. Admittedly, this test of the reaction field theory is severely limited, but it indicates the utility of pmr ρ values, if not the validity of the theory.

As in structure–reactivity studies,[4] some of the correlations of Table II were poor: there were *meta* and *para* subfamilies, *e.g.*, toluenes and thioanisoles, where the ρ values or the correlation coefficients differed substantially.[13] Here, the Hammett model breaks down and a more elaborate one is required; then there were some obvious "unsystematic" or "specific" effects which could cause difficulties. According to theoretical calculations of the pmr $\Delta\nu$, such effects are to be expected in the benzenes (entry 1).[17] Indeed, the correlation coefficient for this family (entry 1) is low. We would guess, however, that 38 ± 5 was a reasonable estimate for $-\rho$: based on one set of data,[17a] we obtained $-\rho = 35$, and based on another set of data, other workers reported $-\rho = 40$.[17b]

Anisotropy effects can perturb strongly or destroy a predicted electronegativity order of substituents. Thus, double and triple bonds, aromatic rings, substituents with lone pair electrons, and even saturated groups can produce unsystematic changes in $\Delta\nu$.[7] To the many known examples, we add *ortho* families (entries 28–31) in Table II, in which the correlation coefficients are all fairly low. Although such families are not normally included within the scope of the Hammett equation, several reactivity correlations have been found.[18] In fact, the poor pmr correlation for the *ortho*-substituted phenylacetylenes contrasts with the acceptable chemical correlations for such families.[18] Here, each substituent can produce specific effects on the local mag-

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[14] L. H. Meyer, A. Saika, and H. J. Gutowsky, *J. Am. Chem. Soc.*, **75**, 4567 (1953); G. E. Maciel and R. V. James, *ibid.*, **86**, 3893 (1964).

[15] R. J. Ouellette, *Can. J. Chem.*, **43**, 707 (1965).

[16] (a) A. D. Buckingham, *ibid.*, **38**, 300 (1960); J. K. Becconsall and P. Hampson, *Mol. Phys.*, **10**, 21 (1965); J. I. Musher, *J. Chem. Phys.*, **37**, 35 (1962).

[17] (a) T. K. Wu and B. P. Dailey, *J. Chem. Phys.*, **41**, 2796 (1964); (b) H. Spiesecke and W. G. Schneider, *ibid.*, **35**, 731 (1961).

[18] M. Charton, *Can. J. Chem.*, **38**, 2493 (1960); I. Solomon and R. Filler, *J. Am. Chem. Soc.*, **85**, 3492 (1963); D. A. D. Jones and G. G. Smith, *J. Org. Chem.*, **29**, 3531 (1964).

netic environment of the proton and thus lead to poor correlations.

We summarize this section by noting that eq 1 may be useful in storing and predicting $\Delta\nu$ (within limits) and that ρ can be a useful measure of the transmission of electronic effects. It is interesting that pmr electronic effects should fall off systematically with chain length. And where the transmission is exceptional, there is often a structural feature in the family which makes a high ρ value plausible.

Theory of Nmr Substituent Effects.—Inasmuch as the Hammett equation is essentially a phenomenological approach to the transmission of electronic effects, we wish to look briefly at several theoretical approaches to this problem. As pointed out previously, the Hammett ρ value provides a smoothed or averaged index of transmission of electronic effects through $-C_6H_4T-$. Therefore, ρ values could be useful as the "experimental" checks on theory.

Van Wazer and Grant have adapted a theory of substituent anisotropy to obtain substituent effects on pmr $\Delta\nu$ at a proton site.[3] For families such as $R-C_6H_4T-H$, the effect can be approximated by the expression

$$\rho\sigma \simeq [\Delta\chi(1 - 3\cos^2\gamma)_{av}]/3N_0r^3 \qquad (4)$$

where $\Delta\chi/N_0$ is a constant, r and γ are distance and angle parameters between R and the terminal proton.[3] If the atoms in the chain T are the same and if one compares families in coplanar extended conformations, differing by two atoms in chain length, one obtains

$$\rho_i/\rho_{i+2} \simeq (r_{i+2}/r_i)^3 \qquad (5)$$

Using the distances previously recorded for an analogous problem,[6b] we find that the observed attenuations are larger than those predicted by eq 5: the observed fall off factor is *ca.* 4–6 compared with calculated values of 2.5–3 for an increment of two carbon atoms in T. Any discrepancies can be reduced of course by adjusting r to give a steeper dependence; this amounts to reckoning r from a position within RC_6H_4 rather than from R. Incidentally, it seems unlikely that much of the discrepancy could be removed by allowing reasonable variations in the angular dependence.

Another theory, which emphasizes the substituent electric field, has been given by Buckingham.[16] In the context of our work

$$\rho\sigma \propto AE_i\cos\Theta_i + BE_i^2 \qquad (6)$$

where A and B are constants, Θ is the angle between the electric field vector and the direction of the bond to the proton, and E is the electric or "reaction" field of the molecular dipole.[16] At the relatively large distances, r, of the substituent to the reaction site, the second term of eq 6 can be ignored. Again, it is convenient to make the comparison

$$\rho_i/\rho_{i+2} \simeq (E_i\cos\Theta_i)/(E_{i+2}\cos\Theta_{i+2}) \qquad (7)$$

for families in coplanar extended conformations differing by two atoms in the chain length. Excluding the substituted benzenes ($T = 0$), increments of two atoms in the chain length tend to make $\Theta_i \simeq \Theta_{i+2}$. If this is allowed, then eq 7 reduces to eq 5, because $E \propto r^{-3}$.[16] In general, however, $\Theta_i \gtrless \Theta_{i+2}$. In fact, the same comments that were made about eq 5 apply here. Finally, it is of interest that for the specific case of benzenes *vs.* *p*-toluenes, in which both Θ values can be estimated, the calculated fall-off factor is about right (*ca.* 3) according to eq 7, but the predicted shifts are too low.

Wu and Dailey have demonstrated that pmr $\Delta\nu$ of aryl protons in substituted benzenes can be correlated with HMO π-electron density variations induced by substituents.[17a] Similar treatments were cited for other π systems, *e.g.*, the pmr $\Delta\nu$ of the methyl group of polymethoxybenzenes.[17a] It is difficult, however, to see how this HMO theory should be adapted to many of the families of Table II in which the proton is two or more atoms distant from the aromatic nucleus.

To summarize, we note that three theoretical approaches are inadequate to account for pmr substituent effects. It may be possible to adjust the calculations—here we are rephrasing Wu and Dailey[17]—of HMO electron densities, anisotropy and electric field effects simultaneously to account for observed $\Delta\nu$, but the significance of such an agreement is questionable. What is clear, however, is that the experimental ρ values can be used to test and/or calibrate theory.

Electronic Effects in Oxygen and Sulfur Compounds.—Discussions on the participation of 3d orbitals in the bonding of second row elements, *e.g.*, Si, P, and S continue to be lively.[19–24] Because ρ values for several properties are now available, we are able to take a fresh look at the relative abilities of divalent oxygen and sulfur to transmit electronic effects. Table III gives the correlation data; those for nitrogen provide an independent reference set. Again, we stress that, because the ρ values are based on a whole family, we are likely to have a more reliable transmission index than if we compared two compounds. Secondly, one should remember that ρ does not measure the absolute magnitude of the measured property but relative changes produced by substituents.

Excluding the pmr data, the ρ values of Table III indicate that the transmission efficiency of electronic effects through oxygen and sulfur are rather similar, with perhaps a marginal advantage for oxygen, but those values could reflect conjugative and nonconjugative modes of transmission. Therefore, one ought to separate these modes first. Entries 1, 5, and 6 of Table III, which probably involve inductive relay of electronic effects, indicate that oxygen and sulfur are about equally efficient transmitters.[24] Of the remaining entries of Table III, only in 9 and 10 is oxygen favored decisively over sulfur. As we have indicated earlier, this increased efficiency reflects a *conjugative donating superiority* in oxygen. These observations on trans-

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(19) G. Cilento, *Chem. Rev.*, **60**, 147 (1960).

(20) "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, Inc., New York, N. Y., 1961: (a) Chapter 7 by R. C. Passerini, (b) Chapter 11 by A. J. Parker, (c) Chapter 23 by J. F. Arens, are particularly relevant.

(21) C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press, Inc., New York, N. Y., 1962, Chapter 2.

(22) "Advances in Molecular Spectroscopy. Proceedings of the IVth International Meeting on Molecular Spectroscopy," Vol. 2, A. Mangini, Ed., Pergamon Press Inc., New York, N. Y., 1962: (a) A. Modena, p 483, (b) R. Passerini, A. Arcoria, and N. Marziano, p 492, are relevant.

(23) J. F. Arens, *Boll. Sci. Fac. Chim. Ind. Bologna*, **21**, 1 (1963).

(24) D. J. Pasto, D. McMillan, and T. Murphy, *J. Org. Chem.*, **30**, 2688 (1965). On the basis of ρ values of 0.30 and 0.23 for the pK values of phenylmercapto- and phenoxyacetic acid families, these workers suggest that sulfur transmits inductive effects more efficiently than does oxygen. According to the data available to us (Table III), both ρ values are close to 0.3. In any case, it is risky to rely too heavily on small differences in ρ when the ρ values are themselves small.[6]

Table III

The Efficiency of Transmission of Electronic Effects as Indicated by Correlations of Reactivity and Spectroscopic Data[a]

No.	System	Conditions, °C	Property	$\rho(X = O)$	$\rho(X = S)$	$\rho(X = N)$
1	$RXH \rightleftharpoons RX^- + H^+$	H_2O, 25	$-pK$[b]	3.9[c,d]	3.4[d]	3.1[d,e]
2	$RR'PX(OH) \rightleftharpoons RR'PXO^- + H^+$	80% ethanol	$-pK$[f]	1.2[f]	1.3[f]	
3	$RR'PX(XH) \rightleftharpoons RR'PX_2^- + H^+$	80% ethanol	$-pK$[f]	1.2[f]	0[f]	
4	$RC_6H_4XH \rightleftharpoons RX^- + H^+$	49% ethanol, 25	$-pK$	2.5[g]	2.2[g]	3.4[g,h]
5	$RC_6H_4XCH_2COOH \rightleftharpoons RC_6H_4XCH_2COO^- + H^+$	H_2O, 25	$-pK$	0.3[i]	0.3[j]	0.3[k]
6	$RC_6H_4XCOCH_2CH_2C_6H_5 + OH^- \rightleftharpoons RC_6H_4XH + C_6H_5CH_2CH_2COO^-$	70% acetone, 0	Log k	1.46[l]	1.46[l]	
7	$5\text{-}RC_4H_2X\text{-}2\text{-}COOH \rightleftharpoons 5\text{-}RC_4H_2X\text{-}2\text{-}COO^- + H^+$	H_2O, 25	$-pK$	1.4[m]	1.1[m]	
8	$5\text{-}RC_4H_2X\text{-}2\text{-}COOC_2H_5 + OH^- \rightleftharpoons 5\text{-}RC_4H_2X\text{-}2\text{-}COO^- + C_2H_5OH$	88% ethanol, 25	Log k	3[m]	2.6[m]	
9	RC_6H_4XH (pmr, cps)	CCl_4	$\nu(XH)$	−67[n]	−22[n]	−32[n]
10	$RC_6H_4XCH_3$ (pmr, cps)	CCl_4	$\nu(CH_3)$	−16[n]	−7[n]	

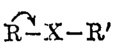
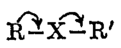
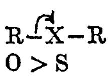
[a] ρ values from the Hammett equation, except as indicated. [b] Taft ρ^*. [c] P. Ballinger and F. Long, *J. Am. Chem. Soc.*, **82,** 795 (1960). [d] M. M. Kreevoy, E. T. Harper, R. E. Duvall, H. S. Wilgus, III, and L. T. Ditsch, *ibid.*, **82,** 4899 (1960). [e] H. K. Hall, *ibid.*, **79,** 5441 (1957). [f] Kabachnik "ρ". M. I. Kabachnik, T. A. Mastrukova, A. E. Shipov, and T. A. Melentyeva, *Tetrahedron* **9,** 10 (1960). [g] H. H. Jaffé, *Chem. Rev.*, **53,** 191 (1953). [h] 30% ethanol. The acid is $RC_6H_4NH_3^+$. [i] N. V. Hayes and G. E. K. Branch, *J. Am. Chem. Soc.*, **65,** 1555 (1943). [j] O. Behaghel, *J. Prakt. Chem.*, **114,** 287 (1926); O. Behaghel and M. Rollmann [*Ber.*, **62,** 2693 (1929)] gave $\rho \simeq 0.4$. Reference 24 gave ρ 0.300. [k] A. Bryson, N. R. Davies, and E. P. Serjeant, *J. Am. Chem. Soc.*, **85,** 1933 (1963). [l] J. Gosselck, *Angew. Chem.*, **18,** 831 (1963). [m] Furan or thiophene system: E. Imoto and Y. Otsuji, *Bull. Osaka Prefecture*, **6,** 115 (1958). [n] See Table II.

mission will now be incorporated into a more comprehensive set of generalizations about oxygen and sulfur.

In Table IV, we present a scheme or system for comparing electronic effects involving oxygen and sulfur. The twelve comparisons in the table were made largely on the basis of published data and discussions. If the factors in a given problem can be defined, then Table IV often suggests the choice one must make.

Table IV

A Comparison of the Magnitude and the Ease of Transmission of Electronic Effects in Oxygen and Sulfur

	Acceptor	Acceptor–donor	Donor
Nonconjugative	$R\rightarrow X-R'$	$R\rightarrow X\rightarrow R'$	$R-X\rightarrow R'$
Magnitude	O > or < S	O ? S	O < or > S
Transmission	$O \simeq S$	$O \simeq S$	$O \simeq S$
Conjugative			
Magnitude	S > O	S > O	O > S
Transmission	S > O	S > O	O > S

The separation according to acceptor and donor abilities has been made by several groups.[21,22a] The horizontal grouping, "nonconjugative," is not to be taken simply as "inductive," for there are aspects of nonconjugative behavior which differ from pure induction. As nucleophiles, oxygen and sulfur compounds are solvent sensitive[25] and also may show varying participation of intrinsic base strength and reducing power or base strength and polarizability, etc.[26,27] In fact, Bunnett has catalogued 17 factors that could influence nucleophilicity.[28] Such factors are simply lumped together here. It is for this reason that there are alternatives in our scheme (Table IV); these indicate that observations of both oxygen superior and inferior to sulfur in a given category have been made.

We have pointed out the problems in assigning an order to the *magnitude* of nonconjugative effects. Judging by their basicity (pK values), we would rate O > S in the acceptor category and O < S in the donor category, but, judging by their usual carbon basicity (as nucleophiles), we would have to reverse these orders.[20b,26,28] As for the acceptor–donor category, the order would depend on the nature of R and R′, *e.g.*, alkyl or chlorine, as well as on all of the other factors mentioned.

The order of *nonconjugative transmission* efficiency has been discussed above with Table III and needs no elaboration; the available data indicate that sulfur and oxygen are about equal here. Because ρ values are few in number, the orders given can only be tentative.

It is probably impossible to find systems with pure *conjugation* effects. However, oxygen cannot easily utilize d orbitals so that sulfur must be favored in situations where orbital expansion is necessary, *i.e.*, in acceptor and acceptor–donor situations.[19–23]

On the other hand, oxygen is the better donor when conjugation is called for. This seems to be true whether one compares the magnitudes of corresponding *para* σ values, or σ_R values (OH *vs.* SH or OCH_3 *vs.* SCH_3),[4,21] or the amount of shielding indicated in the pmr $\Delta\nu$ of acetylenic ethers and thioethers.[29] With regard to donor conjugative transmission, the pertinent ρ values of Table II establish the order O > S. The following comparison is also instructive. The ionization potentials of *n*-butyl alcohol and *n*-butyl mercaptan are 10.04 and 9.14 ev, respectively; these values are consistent with the nonconjugative-magnitude donor category. The ionization potentials of phenol and thiophenol are 8.52 and 8.33 ev, respectively.[30] Subtracting the aliphatic from the aromatic values, we obtain a conjugative contribution of 1.5 ev in phenol and 0.8 ev

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(25) A. J. Parker, *Quart. Rev.* (London), **16,** 163 (1962).

(26) A. J. Parker, *Acta Chem. Scand.*, **16,** 855 (1962).

(27) J. O. Edwards, *J. Am. Chem. Soc.*, **76,** 1540 (1954); **78,** 1819 (1956); R. S. Drago and B. B. Wayland, *ibid.*, **81,** 3571 (1955).

(28) J. F. Bunnett, *Am. Rev. Phys. Chem.*, **14,** (1963).

(29) W. A. Drenth and A. Loewenstein, *Rec. Trav. Chim.*, **18,** 635 (1962).

(30) A. Terenin and F. Vilessov, "Advances in Photochemistry," Vol. 2, W. A. Noyes, G. S. Hammond, and J. N. Pitts, Jr., Ed., Interscience Publishers, Inc., New York, N. Y., pp. 385–421; R. W. Kiser, "Additions and Corrections to Tables of Ionization Potentials," TID-6142, Department of Chemistry, Kansas State University, Manhattan, Kan., 1962.

in thiophenol. This manipulation of figures provides a plausible rationale for the conjugative-magnitude donor category but it should be clear that other experimental observations may be more difficult to dissect.

The alternatives set out in Table IV are sometimes difficult to sort out: in any given system the balance of nonconjugative and conjugative effects may be changing; the measured property may be dependent on medium, on both reactant and product, or ground state and excited state, etc. In other cases, misunderstandings have arisen because the type of results found in one situation, donor conjugative transmission, were not found or perhaps contradicted in another situation, acceptor conjugative transmission. The ultraviolet spectral transitions of certain oxygen and sulfur compounds have been discussed and fall in our conjugative donor category;[20c,22b,31] aspects of the reactivity toward nucleophiles of ethynyl ethers and thioethers have been clearly elucidated and clearly fall into the conjugative acceptor category:[20c,23] it is no contradiction to propose sulfur d-orbital participation in the latter case and not in the former.

Acknowledgment.—We wish to thank Mr. A. Caplan for preparing one of the thioanisoles and Mr. D. Sardella for providing his unpublished data on the benzoylacetones.

[31] L. Goodman and R. W. Taft, *J. Am. Chem. Soc.*, **87**, 4385 (1965). Ultraviolet spectral evidence in this paper places sulfur in the conjugative acceptor–donor category.

Proton Magnetic Resonance Studies of Pyrazoles

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Received December 10, 1965

4-Proton chemical shift data for 54 pyrazoles are correlated in the empirical equation $\delta_4 = \delta_4(\mathrm{s}) + \alpha_1 + \alpha_3 + \alpha_5$, where $\delta_4(\mathrm{s})$ is a constant for each solvent, and α_1, α_3, and α_5 are empirical constants that represent the effect of replacing a methyl substituent by another group at positions 1, 3, and 5 of the pyrazole nucleus. The equation can be used for isomer identification and for the study of tautomers. The α constants of the equation are correlated with Hammett σ constants. It was observed in the nmr spectra that a phenyl group attached to a pyrazole ring appears as a multiplet resonance unless a substituent is α to it. Under the latter condition the phenyl resonance is a singlet. Chemical shift data are used to distinguish relative coplanarity of the phenyl and pyrazole rings. Ring proton coupling constants of pyrazoles are discussed.

Proton magnetic resonance data for substituted pyrazoles are of utility in the assignment of isomers and tautomers, and yield parameters of theoretical interest. Williams[1] found that the spin–spin coupling constants of the annular protons in 1-acylpyrazoles fell into narrow ranges and made structural assignments on that basis. For 1-alkyl-3- or -5-methylpyrazole pairs synthesized unequivocally, Habraken and Moore[2] found a paramagnetic displacement of the C-3(5) ring proton peak and a diamagnetic shift of the methyl peak on going from the 3-methyl to the 5-methyl isomer. Finar and Mooney[3] have noted that the 3-, 4-, and 5-protons of pyrazoles can generally be distinguished by the region of their chemical shifts and shift behavior in trifluoroacetic acid. Other nmr publications on substituted pyrazole have appeared.[4]

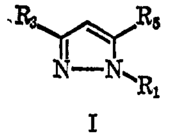
This paper presents additional nmr data for 54 pyrazoles all unsubstituted at the 4-position. An additive relationship, involving empirical constants, for calculating the chemical shift of the 4-proton in substituted pyrazoles has been found. This expression appears to be unambiguous for isomer identification of 1-substituted compounds and would seem to indicate which tautomer predominates in 1-H pyrazoles. The constants correlate with electron densities.[5-7] Chemical shift data of the phenyl series reflect coplanarity or noncoplanarity of the aromatic ring[8] and would seem to be of value in the study of induced currents and aromaticities in the pyrazole ring.

Experimental Section

The nmr spectra were measured at 60 Mc with either a Varian A-60 or a Varian HA-60 spectrometer, or both. The audiofrequency side-banding technique was used on the HA-60 to obtain accurate frequency values for chemical shifts and coupling constants. Shifts are reported in δ values (parts per million) downfield from internal tetramethylsilane. Solution concentrations were 0.5–2.5 *M* (*ca.* 5% w/v) in deuteriochloroform.

Results and Discussion

General.—The chemical shifts of 1,3,5-tribsustituted pyrazoles I and 1-H 3,5-disubstituted pyrazoles have been measured. They are tabulated in Tables I and II, respectively.



I

We have observed an additive relationship among the chemical shifts of the 4-proton in 1,3,5-trisubstituted pyrazoles. It takes the form

$$\delta_4 = \delta_4(\mathrm{s}) + \alpha_1 + \alpha_3 + \alpha_5 \qquad (1)$$

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[1] J. K. Williams, *J. Org. Chem.*, **29**, 1377 (1964).

[2] C. L. Habraken and J. A. Moore, *ibid.*, **30**, 1892 (1965); *cf.*, also, J. A. Moore and C. L. Habraken, *J. Am. Chem. Soc.*, **86**, 1456 (1964).

[3] I. L. Finar and E. F. Mooney, *Spectrochim. Acta*, **20**, 1269 (1964).

[4] (a) M. Cola and A. Perotti, *Gazz. Chim. Ital.*, **94**, 1268 (1964); (b) V. Papesch and R. M. Dodson, *J. Org. Chem.*, **30**, 199 (1965); (c) T. Yamauchi and J. A. Moore, *ibid.*, **31**, 42 (1966); (d) J. D. Albright and L. Goldman, *ibid.*, **31**, 273 (1966).

[5] C. G. Hall, A. Hardisson, and L. M. Jackman, *Tetrahedron*, **19**, Suppl. **2**, 101 (1963).

[6] T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

[7] B. P. Dailey, *J. Chem. Phys.*, **41**, 2304 (1964).

[8] B. M. Lynch and Y. Y. Hung, *Can. J. Chem.*, **42**, 1605 (1964).