Diethyl 2-deuteriobenzoylmalonate, bp 128–130° (0.2 mm), was prepared by the ethoxymagnesium malonic ester procedure of Hauser.[26]

Diethyl 2-Deuteriobenzoylmalonate Enol *p*-Bromobenzenesulfonate.—A modification of the procedure of Fleming and Harley-Mason[27] was used. To a stirred suspension of 6 g (0.11 mol) of sodium methoxide in 50 ml of dry tetrahydrofuran was added dropwise a solution of 24 g (0.1 mol) of diethyl 2-deuteriobenzoylmalonate in 35 ml of tetrahydrofuran. After stirring at 25° for 3 hr the mixture was cooled to −78° and a solution of 34 g (0.14 mol) of *p*-bromobenzensulfonyl chloride in 100 ml of tetrahydrofuran was added. The reaction mixture was allowed to warm to room temperature and to stand at room temperature 2 days. The reaction mixture was concentrated and poured into water, and the aqueous layer was extracted with ether. The ether extracts were washed with sodium bicarbonate solution, dried over anhydrous sodium sulfate and evaporated to afford, after one recrystallization from ethanol, 29 g (60% yield) of the enol bromobenzenesulfonate, mp 91–93° (lit.[27] mp 91–91.5°).

2-Deuteriophenylpropiolic Acid.—The procedure of Fleming and Harley-Mason[27] was employed. 2-Deuteriophenylpropiolic acid was isolated in 50% yield. Isotopic analysis was carried out at 9–12 V, nominal, using either the parent ion region of the acid, m/e 144, or (better) the parent ion of phenylacetylene produced from the acid in the heated inlet. In a typical preparation of 2-deuteriobenzyldimethylamine, the phenylpropiolic acid had the composition 1.5% d_0, 1.5% d_2, 97% d_1.

1-Phenylnaphthalene-2,3-dicarboxylic Acid Anhydride.—The procedure of Michael and Bucher[3] as generalized by Baddar, *et al.*,[28] was used. Typically, a solution of 1.26 g of phenylpropiolic acid in 60 ml of acetic anhydride was heated under reflux for 3.5 hr. Evaporation of the solvent *in vacuo* and washing of the precipitate with ether gave a 66% yield of the anhydride, mp 264–265°. Decreasing the concentration of phenylpropiolic acid, and diluting the acetic anhydride with acetic acid decreased the yield under these reflux conditions. When a solution of 100 mg of phenylpropiolic acid (d_1) in a mixture of 4.5 ml of acetic anhydride and 1 ml of acetic acid was refluxed 16 hr, the yield of 1-phenylnaphthalene-2,3-dicarboxylic anhydride was 26%. Substantial amounts of recovered phenylpropiolic acid were detected in those reactions that were incomplete.[29] In experiments using a solvent mixture of acetic anhydride and acetic acid-d_1, the solvent was prepared by addition of the requisite amount of deuterium oxide to acetic anhydride, followed by brief refluxing. Results of the various experiments using labeled and unlabeled phenylpropiolic acid and labeled and unlabeled acetic acid-containing acetic anhydride as solvent are in Table I.

Registry No.—I, 637-44-5.

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(26) (a) H. G. Walker and C. R. Hauser, *J. Amer. Chem.*, **68**, 1386 (1946). (b) *Org. Syn.*, **30**, 70, (1950).

(27) I. Fleming and J. Harley-Mason, *J. Chem. Soc.*, 4771 (1963).

(28) F. G. Baddar and L. S. El-Assal, *ibid.*, 1267 (1948).

(29) The recovered phenylpropiolic acid was of undiluted isotope composition by mass spectrum.

The Transmission of Electronic Effects. Proton Magnetic Resonance Chemical Shifts for Benzyl Halides in Several Solvents[1a]

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Proton magnetic resonance (pmr) shifts are reported for substituted benzyl fluorides, chlorides, and bromides in several solvents. At finite concentrations, molecules of the same or different compounds interact specifically. Thus the apparent association constant for benzyl chloride and *p*-nitrobenzyl chloride in carbon tetrachloride at *ca.* 37° is $K = 0.27\ M^{-1}$. Obviously, comparisons of substituent effects should be made with chemical shifts at infinite dilution (ν^0). Even so, each ν^0 of the benzyl halides still reflects specific interactions with the solvent peculiar to itself. Attempted correlations of ν^0 of the benzyl halides according to Hammett or Yukawa–Tsuno relations are poor. A literature survey of *ca.* 100 Hammett correlations of pmr data indicates that the majority of them have unsatisfactory correlation coefficients, *e.g.*, <0.90–0.95. The ρ values appear to have no pattern. However, the use of a polar solvent with certain families, *e.g.*, DMSO for phenols and amines, gives large ρ values and excellent correlations; presumably enhanced electronic effects typical of chemical reactions dominate possible anisotropy effects on ν^0. In general, ρ's cannot be used in the way that reactivity ρ's are used, namely as indices of transmission efficiency in aryl systems Ar–T–H.

It is generally agreed that proton magnetic resonances (pmr) chemical shifts at any point in a molecule are in some sense related to the rest of the molecule and its environment. By examining this relation, a number of workers have attempted to reduce its complexity. Contributions from π-electron density, resonance, electric field, magnetic field, van der Waals forces, and ring currents have all appeared to be important at least for some systems or some substituents.[2] On this basis, it has sometimes appeared that the factors that affect substituent chemical shifts (SCS) are understood. In our own survey of the transmission of electronic effects from a substituent (R) to a proton in *ca.* 30 aryl systems, *e.g.*, $R{-}C_6H_4T{-}H$, we too seemed to uncover an underlying regularity that appeared to apply to some systems.[3] In this study we examine the transmission of electronic effects in the benzyl halides in some depth and find that such regularities are often more apparent than real.

As a family, the benzyl halides are of considerable interest.[4] Pmr studies of related families are available and comparison with the toluenes, say, is possible. Our work was completed about the time that a paper on both the ^{1}H and ^{19}F nmr spectra of benzyl fluorides appeared.[5] A graphical comparison of the pmr chemical shifts for the ten substituted benzyl fluorides common to Béguin's work and ours, indicated significant discrepancies for seven of the compounds. After coping with this problem, we could approach the initial issue, namely, substituent effects on chemical shifts.

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(1) (a) This work was supported by the National Science Foundation, Grant GP 5740. (b) Postdoctoral fellow, 1966–1967. (c) Author to whom inquiries should be addressed.

(2) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, Oxford, 1965, Chapter 4.

(3) S. H. Marcus, W. F. Reynolds, and S. I. Miller, *J. Org. Chem.*, **31**, 1872 (1966).

(4) R. R. Fraser, Gurudata, C. Reyes-Zamora, and R. B. Swingle, *Can. J. Chem.*, **46**, 1595 (1968).

(5) C. Béguin, *Bull. Chim. Soc. Fr.*, 4214 (1967).

Experimental Section

Spectra.—Proton nmr spectra were measured by a Varian A 60 spectrometer operating at 60 Mc. The spectra were calibrated by the side-band technique with a Hewlett-Packard 200 CDR wide range oscillator and 5245 L electronic counter. The sample temperature was 37 ± 1°. The sample tubes were 5 mm o.d. Tetramethylsilane (TMS) was used in the solution as an internal standard. Each sample was scanned several times at a rate of 1 Hz/sec. The solvents used were spectrograde or freshly distilled before use.

Initially, shifts ν were obtained at several concentrations in the range 0.4–1.5 mol/l.; but since the dilution plots of ν were usually curved and quite specific for each compound, ν was measured on four or five solutions in the range 0.01–0.2 mol fraction (solute/solvent), accurately prepared by weight and extrapolated to ν^0 at infinite dilution.

It has been reported that the SCS of a benzyl halide was independent of both concentration and the presence of another benzyl halide.[4,5] To investigate these claims, we investigated dilution effects in several straightforward ways; some of the results are given in Figures 1 and 2.

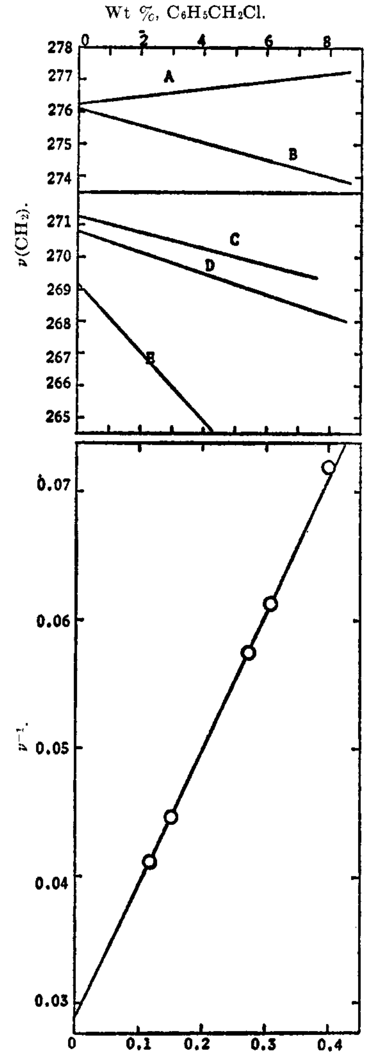

Figure 1.—Solute-solute interactions and chemical shifts of the benzyl chlorides in carbon tetrachloride. Upper box: A, p-$O_2NC_6H_4CH_2Cl$; B, p-$O_2NC_6H_4CH_2Cl$ in the presence of $C_6H_5CH_2Cl$, $(NO_2):(H) = 2:1$; C, $C_6H_5CH_2Cl$ in the presence of p-$O_2NC_6H_4CH_2Cl$, $(NO_2):(H) = 2:1$; D, $C_6H_5CH_2Cl$ in the presence of p-$ClC_6H_4CH_2Cl$, $(H):(Cl) = 4.95:2.55$; E, p-$ClC_6H_4CH_2Cl$ in the presence of $C_6H_5CH_2Cl$, $(H):(Cl) = 4.95:2.55$. The weight ratios in solution are indicated here. Lower box: $\nu(CH_2)$ for *ca.* 0.1 M p-$O_2NC_6H_4CH_2Cl$ in the presence of $C_6H_5CH_2Cl$. A slope of 0.1055 and intercept of 0.0295 lead to an apparent equilibrium constant for association of $K = 0.27\ M^{-1}$.

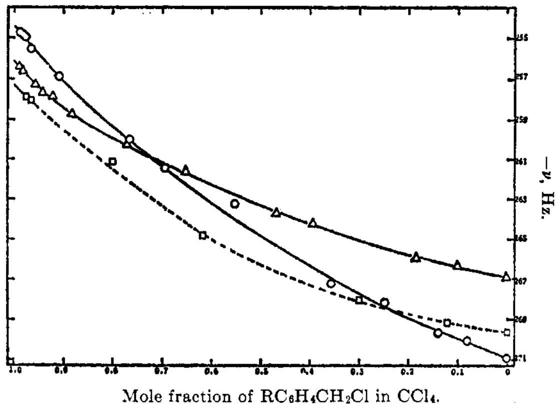

Figure 2.—Dilution plots of the benzyl chlorides, $RC_6H_4CH_2Cl$: ○, R = H; □, R = 4-CH_3; △, R = 4-Cl.

Benzyl Halides.—The origins and properties of the benzyl halides are given in Table I. Several bromides were made from the benzyl alcohols or by bromination of the toluenes. The benzyl fluorides were made more or less according to the following procedure, with variations to suit individual compounds, as needed. p-Methoxybenzyl chloride, p- and m-methyl- and p-fluorobenzylfluorides appeared to be unstable and decomposed, even when kept in sealed tubes.

***m*-Trifluoromethylbenzyl Fluoride.**—In a 300-ml three-necked flask, fitted with a mercury sealed stirrer, reflux condenser, and a dropping funnel, was placed anhydrous potassium fluoride powder (15 g, 0.26 mol), which had been dried at 140° overnight, and freshly distilled N-methyl-2-pyrrolidone (40 ml). The reflux condenser and the dropping funnel were fitted with drying tubes. The mixture was heated to 165° in an oil bath. m-Trifluoromethylbenzyl chloride (22.5 g, 0.116 mol) was added slowly during 1 hr, and the heating and the stirring were continued for 2 hr. After cooling, the reaction mixture was treated with ice water and extracted with ether. The ether solution was washed with water to remove the methylpyrrolidone, dried over Drierite and evaporated. Distillation of the residue gave the following fractions: m-trifluoromethylbenzyl fluoride (8.1 g), bp 66–68° (22 torr); m-trifluoromethylbenzyl chloride (13.3 g), bp 70–71° (11 torr). The yield of fluoride was 96% based on the reacted chloride and 40% based on the starting chloride. The fluoride was purified by redistillation in a Vigreux column: bp 49.0–49.5° (11 torr); $n^{25}D$ 1.4252. *Anal.* Calcd for $C_8H_6F_4$: C, 53.94; H, 3.39. Found: C, 53.63; H, 3.34.

Results and Discussion

Since SCS and solvent effects on SCS have been dealt with theoretically by many groups without notable success, we shall remain fairly close to the data. We shall have some concrete things to say about how to and how not to go about correlating pmr data. We have also extended our survey of Hammett-type pmr correlations and have made a value judgement on them.

Solute–Solute and Solute–Solvent Interactions.—Our pmr data for substituted benzyl halides are given in Tables I and II. Infinite dilution chemical shifts (ν^0) were obtained from concentration dependence plots of ν (Figures 1 and 2). The solvents in Table II were chosen to test various hypotheses concerning solvent effects on ν^0; since these tests were inconclusive, they are not elaborated on here.

Since the previously mentioned differences between Béguin's chemical shifts and ours are outside experimental uncertainties, we investigated the idea that his method could involve specific solute–solute interactions. Béguin obtained $\nu_R(CH_2)-\nu_H(CH_2)$ from a single solution of 8% substituted benzyl fluoride and 4% benzyl fluoride; we obtained $\nu_R^0(CH_2)-\nu_R^0(CH_2)$ for such systems by extrapolating shifts referenced to TMS

TABLE I

PREPARATION AND PROPERTIES OF BENZYL HALIDES, $RC_6H_4CH_2X$

R	Mp or bp (torr), °C	$n^{25}D$	Lit. mp or bp (torr), °C	Lit. $n^{20}D$	Ref	$-\nu^0$ (CH_2), Hz
			X = Cl			
H	63–64 (12)	1.5386	69 (15)	1.5390	*a, b, i*	271.5
p-CH_3	89–90 (16)	1.5328	192		*a*	268.4
m-CH_3	91.5–93.5 (20)	1.5329	96 (23)	1.5345	*b, c*	268.2
p-F	75–76 (20)	1.5114	73 (18)	1.5118	*l, i*	270.3
m-F	73–74 (25)	1.5128	70 (36)	1.5131	*l, c*	270.5
p-Cl	105–106 (19)		114–117 (30)		*b, d*	270.1
m-Cl	101–102 (18)	1.5546	44 (0.3)	1.5556[n]	*c, g*	268.7
m-CF_3	70–71 (11)	1.4622				274.8
p-NO_2	71–72		71.8–72.4		*a, d*	276.9
m-NO_2	45–46					278.2
p-OCH_3	92.8–93.0 (2.5)	1.5489	92.5 (1.5)	1.5491	*a*	268.8
m-OCH_3	87.0–87.5 (2)	1.5430	55 (0.3)		*c*	269.8
			X = Br			
H	197–198		84 (13)		*a, i*	264.6
p-Br	129–130 (18)		117–119 (10)		*f*	261.6
m-CN	92–93		92.5–93.5		*g*	266.6
p-*t*-Bu	132.5 (13)		132.5 (14)		*h, i*	263.0
p-Ph	85–86		85		*j*	268.4
			X = F[m]			
H	45–46 (18)	1.4886	50 (27)	1.4980	*f, i*	318.6
p-CH_3	50–50.5 (12)	1.4918	60 (14)	1.4918	*f, i*	313.7[m]
m-CH_3	63.0–63.2 (10.5)	1.4948	48.5 (8.5)	1.4952	*f*	315.6[m]
p-F	45–46 (19)	1.4654	54 (28)	1.4667	*f*	317.0[m]
m-F	38.5 (11)	1.4652	41 (15)	1.4660	*f*	320.0[m]
p-Cl	76.5–78.0 (21)	1.5140	72–73 (16)	1.5149	*f*	318.0
m-Cl	64 (10.5)	1.5148	65 (11)	1.5158	*f*	318.0
p-Br	85–86 (18)		80–81.5 (10)		*f*	316.5[m]
m-CF_3	49.2–49.8 (12)	1.4252			*k*	324.1
p-NO_2	37–38		38.2–38.5		*f*	332.3[m]
m-NO_2	128.0–128.5 (13)	1.5328	91 (3.5)	1.5381	*f*	328.3[m]
p-*t*-Bu	84.8–85.2 (13)	1.4760	90 (12)		*i*	316.0

[a] C. G. S. Swain and W. P. Langsdorf, *J. Amer. Chem. Soc.*, **73,** 2813 (1951). [b] M. S. Kharasch and H. C. Brown, *ibid.*, **61,** 2142 (1939). [c] R. Fuchs and D. M. Carlton, *ibid.*, **85,** 104 (1963). [d] R. Fuchs, *ibid.*, **79,** 6531 (1957). [e] H. Schmidt and P. Karrer, *Helv. Chim. Acta*, **29,** 573 (1946). [f] J. Bernstein, J. S. Roth, and W. T. Miller, Jr., *J. Amer. Chem. Soc.*, **70,** 2310 (1948). [g] J. Von Braun and H. Reich, *Ann.*, **445,** 225 (1925). [h] J. B. Shoesmith and A. Mackie, *J. Chem. Soc.*, 300 (1936). [i] C. W. L. Bevan, *ibid.* 1347 (1960). [j] L. Zervas and I. Dilaris, *J. Amer. Chem. Soc.*, **77,** 5354 (1955). [k] New compound. [l] Pierce Chemical Catalog, F-16, 1967. [m] Values of the HF coupling constants, given as R(J_{HF}), are H (47.71), *p*-CH_3 (48.04), *m*-CH_3 (47.97), *p*-F (47.74), *m*-F (47.86), *p*-Cl (47.80), *m*-Cl (47.52), *p*-Br (48.23), *m*-CF_3 (47.37), *p*-NO_2 (46.92), *m*-NO_2 (47.08). Additional or alternate values of $\nu(CH_2)$ and J_{HF} at finite concentrations are given in ref 5. [n] At 25°.

TABLE II

SUBSTITUENT CHEMICAL SHIFTS ($-\nu$) AT INFINITE DILUTION, IN HERTZ FROM TETRAMETHYLSILANE, OF BENZYL CHLORIDES $RC_6H_4CH_2Cl$ IN SEVERAL SOLVENTS AT 37°

		R							
Solvents	Registry no.	H[a]	*p*-CH_3	*m*-CH_3	*p*-Cl	*m*-Cl	*p*-NO_2	*m*-NO_2	*m*-CF_3
C_6H_{12}	100-44-7	265.0	262.8	262.4	262.6	262.4		271.0	267.3
CCl_4	104-82-5	271.5	268.4	268.2	270.1	268.7	276.9	278.2	268.7
Et_2O	620-19-9	273.2			273.0				
Dioxane	104-83-6	277.0			276.3				
$(CH_3)_2CO$	620-20-2	281.3			282.8				
CH_3CN	100-14-1	279.4	277.2		278.4	280.1	284.8	285.8	
C_6H_6	619-23-8	245.2	245.2	247.4	233.3	230.5	229.0	227.5	
n-Hexane	705-29-3	265.5	263.2	263.6	263.5				

[a] Additional data for $C_6H_5CH_2Cl$: $CHCl_3$ (275.4), CH_2Cl_2 (276.7), $(CH_3)_3CCl$ (271.8), *n*-C_4H_9Cl (272.3), $CHBr_3$ (278.3), CH_2Br_2 (276.6), $(BrCH_2)_2$ (276.2), $(CH_3OCH_2)_2$ (278.0), $(n\text{-}C_4H_9)_2O$ (269.5), THF (276.7), CH_3OH (276.6), $(HOCH_2)_2$ (280.0), DMF (287.0).

to infinite dilution. Since the dilution shifts of Figure 1 do not vary in a standard way for different pairs of compounds, it is clear that nonsystematic discrepancies arise in the data from the two approaches. We believe that the complicating factor of specific solute–solute interactions has been minimized in our data.

Recent work has shown that many solvent effects on pmr data can be regarded as arising from complex formation of solvent and solute.[6] We hesitate to

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[6] (a) I. D. Kuntz, Jr., and M. D. Johnston, Jr., *J. Amer. Chem. Soc.*, **89,** 6008 (1967); (b) R. C. Fort, Jr., and T. R. Lindstrom, *Tetrahedron*, **23,** 3227 (1967).

characterize all of the solute–solute interactions of the benzyl chlorides in this way, because of the lack of a consistent pattern in our dilution plots of Figure 1. The slopes of differing magnitude and occasionally of opposite sign are particularly difficult to explain. One possible association reaction, p-$O_2NC_6H_4CH_2Cl$ + $C_6H_5CH_2Cl \rightleftharpoons (p\text{-}O_2NC_6H_4CH_2Cl)\cdots(C_6H_5CH_2Cl)$, was investigated. A standard double reciprocal plot[6a] was used to obtain an apparent $K = 0.27\ M^{-1}$ at 37° in carbon tetrachloride (Figure 1). We call this an "apparent" association, because we have not assessed the well known, but poorly characterized, "aromatic" effects on ν.

At the beginning of our research, we were inclined to obtain accurate ν values at some common concentration, *e.g.*, 5%. Certainly, this was less tedious than collecting data for dilution plots. We discovered, however, that the form of the dilution plot for any benzyl halide in carbon tetrachloride was not readily predictable from the behavior of others in the family. This is shown in the fact that the plots cross, and worse, do not have the same slope at infinite dilution (Figure 2). Whereas Figure 1 illustrates the mutual effect of two solutes, Figure 2 indicates the specific effects of like molecules on one another.

We were also concerned about the possibility that differential solvent factors might be contained in ν^0. Several groups have found solute–solute correlations which may bear on this point. Thus, Marcus and Miller found that the infinite dilution shifts of benzenethiol and n-butanethiol or chloroform and 1-alkynes in a variety of solvents are linearly related.[7] The interpretation is that these solutes must evoke a parallel response from diverse solvents, whether specific interactions be large or small. This idea was tested here. (To conserve space, these plots have been deleted.)

$$\nu^0(\text{solute 1}) = A\nu^0(\text{solute 2}) + B \tag{1}$$

Although more points would have been desirable, it appears that the ν^0 values of benzyl chloride and p-chlorobenzyl chloride *may be,* while those of benzyl chloride and m-nitrobenzyl chloride *are not,* linearly related. *We must conclude that ν^0 of each benzyl chloride probably reflects specific solvent–solute interactions different from those of other benzyl chlorides.*

Pmr Data and Linear Free Energy Relations.—The effect of structure may be examined by means of the Hammett equation[3] (eq 2). Briefly, the model for

$$\nu = \rho\sigma + \nu_0 \tag{2}$$

aryl families R–C_6H_4T–H is based on the notion that the substitutent and the terminal proton are sufficiently remote so that differential effects, *e.g.*, anisotropy, were negligible or at least constant for the transmitting group, C_6H_4T. Provided that the substituent constant σ were an invariant index of the electronic properties of R, ρ would characterize T as well as the reaction conditions. Because ρ derives from a family of compounds, one hopes that specific irregularities of solvent, conformation, etc., tend to be smoothed and averaged.[3] Unfortunately, this model is largely based on untenable assumptions, as we shall see.

Our data on benzyl halides may be treated in various ways, but we need only display a few of them. For example, we have used standard Hammett σ values to test eq 2 for the benzyl fluorides in carbon tetrachloride and benzyl chlorides in cyclohexane. The correlations are poor and eq 2 is *not* obeyed. Béguin had already shown that a plot of ν of the benzyl fluorides against σ^+ deviates grossly from linearity.[5] It is interesting, however, that the correlation of ^{19}F ν values with σ is eminently satisfactory.[5]

Incidentally, using our data and Béguin's, we have attempted to correlate the coupling constants (J_{HF}) of the benzyl fluorides with the Hammett σ. Here too the data scatter. In any case, we are not aware of any theoretical connection between J and substituent constants, although a few examples have been published.[8]

Several workers have attempted to improve deficient Hammett correlations by using more parameters. Of these, the Yukawa-Tsuno equation has been tested most recently, but chiefly for reactivity data.[9] Adapted

$$\nu = \rho(\sigma^0 + r\Delta\bar{\sigma}_R^+ + r'\Delta\bar{\sigma}_R^-) + \text{constant} \tag{3}$$

to nmr data, it takes the form[10,11] of eq 3. The substituent constants σ^0 are based on phenylacetic acid and ester reactivities, and $\Delta\bar{\sigma}_R^+ = (\sigma^+ - \sigma^0)$ and $\Delta\bar{\sigma}_R^- = (\sigma^- - \sigma^0)$, in which σ^+ and σ^- are the usual resonance substitutent constants.[9] Because $\Delta\bar{\sigma}_R^\pm = 0$ for *meta* substituents, we would normally expect these to define a Hammett line. Since eq 3 separates inductive and resonance effects in a way which is related to, but not identical with, Taft's approach, we shall not consider the latter.[12,13]

Wittstruck and Trachtenberg have tried another approach.[14] They assume that the chemical shift in RC_6H_4T–H is made up additively from the shift in some parent $[\delta_0(H)]$ plus changes ascribed to the substituents R interacting through inductive (**I**), resonance (**R**), field (**F**), and magnetic field (**M**) effects over the chain C_6H_4 and T connecting R and H. The last terms $\Delta\delta^{\mathbf{F}}$ and $\Delta\delta^{\mathbf{M}}$ can be approximated by the

$$\delta_R(H) = \delta_0(H) + \sum(\Delta\delta^{\mathbf{I}} + \Delta\delta^{\mathbf{R}} + \Delta\delta^{\mathbf{F}} + \Delta\delta^{\mathbf{M}}) \tag{4}$$

equations of Buckingham and McConnell; these of course have an explicit dependence on molecular geometry.[2,14] The fact that SCS of one β proton of a family of styrenes was linearly related to the SCS of the other with unit slope was a strong indication that the last two terms of eq 4 cannot be significant, because of the spatial difference in the β protons. At the same time, the expectation that resonance and inductive effects might be identical at the β carbon was confirmed. Although the symbolism is different, the analysis of Wittstruck and Trachtenberg now resembles that used by Taft, *et al.*,[12,13] or Yukawa and Tsuno for substituent effects,[9] or that used by Marcus, *et al.*, for attenuation of electronic effects.[3] *If* one is to use a multiparameter treatment, one might just as well use eq 3.

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(7) S. H. Marcus and S. I. Miller, *J. Phys. Chem.*, **73,** 453 (1969).

(8) Gurudata, J. B. Stothers, and J. D. Talman, *Can. J. Chem.*, **45,** 731 (1967).

(9) Y. Yukawa, Y. Tsuno, and M. Sawada, *Bull. Chem. Soc. Jap.*, **39,** 2274 (1966); Y. Yukawa and Y. Tsuno, *Mem. Inst. Sci. Ind. Res. Osaka Univ.*, **23,** 71 (1966).

(10) Y. Yukawa, Y. Tsuno, and H. Yamada, *ibid.*, **23,** 79 (1966).

(11) Y. Yukawa and H. Yamada, *Nippon Kagaku Zasshi*, **85,** 501 (1964).

(12) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2,** 323 (1964).

(13) P. Wells, S. Ehrenson, and R. W. Taft, *ibid.*, **6,** 147 (1968).

(14) T. A. Wittstruck and E. N. Trachtenberg, *J. Amer. Chem. Soc.*, **89,** 3803, 3810 (1967).

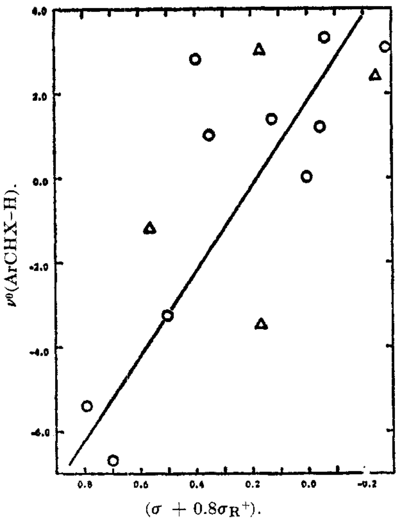

Figure 3.—Attempted correlation of the type $\Delta\nu^0 = \rho(\sigma + 0.8\Delta\sigma_R^+)$. Data taken in carbon tetrachloride: ○, X = Cl; △, X = Br.

Our attempts to correlate the benzyl halide data with versions of eq 3 were not very promising (see Figure 3). The scatter in the *meta* substituents and the gross departure for ν^0(H) and ν^0(phenyl) from the other points are simply not reconcilable with the basic assumptions behind the relation.

Yukawa, *et al.*, have used eq 3 for the phenylacetylenes,[11] and the 1,1-diphenylethylenes.[10] To obtain a satisfactory fit for the diphenylenes, Buckingham and McConnell corrections for anisotropy and field effects were applied.[10] It is not clear why these families should require different treatment. Moreover, Wittstruck and Trachtenberg indicated that the Buckingham and McConnell corrections are probably insignificant for similar families.[14]

We then sought a more limited relation. Granting that there might be specific interactions, we selected pairs of related families in which cancellation of these effects could reaonably be expected, when ν^0 values were compared (Figures 4 and 5). Some of the pairs are benzyl chlorides (bromides) *vs.* benzyl fluorides; benzyl chlorides *vs.* toluenes;[3] 1,1-diphenylethylenes[10] *vs.* styrenes.[8] Again, the scatter is often more impressive than the fit. It is not merely a question that *certain* substituents *sometimes* deviate. Depending on the families, errant points may belong to *m*- or *p*-nitro, hydrogen, halogen, alkyl, etc., substituents. Clearly, many, if not all, ν^0 values reflect specific interactions which preclude precise parallel behavior of a given substituent in different systems.

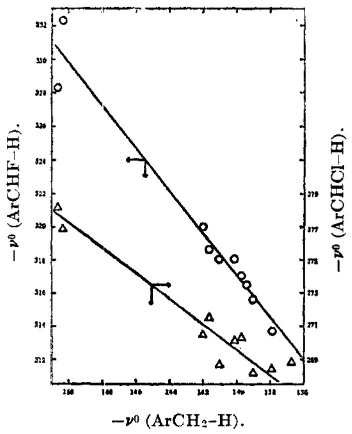

Figure 4.—Chemical shift correlations of related families in carbon tetrachloride. Toluene data is from ref 3.

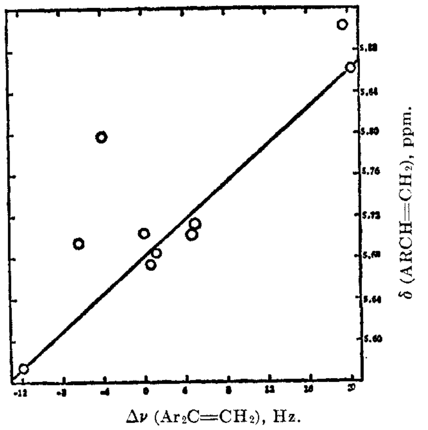

Figure 5.—Chemical shift correlation for β protons, *cis* to aryl. Pmr data from refs 8 and 10.

Transmission of Electronic Effects and Pmr Data.—The Hammett relation is not simply intended for concise data storage or display, although this might be considered as a minimum requirement.[9,12,15] The line parameters have, or at least they should have, meaning. Now, ρ values have been used to assess the efficiency of transmission of electronic effects. Whether the comparison is made with a standard, as eq 7, in which the

$$\rho_{C_6H_4T}/\rho_{C_6H_4} = \epsilon \qquad (7)$$

fall-off factor ϵ is obtained, or in some other way, the magnitude of ρ might be expected to vary systematically.[15]

A number of the reported Hammett correlations of pmr data have been collected.[3] We extend this compilation here to probe further the question of the meaning of ρ. Table III follows a standard format.[3] The numbers identifying the families follow those of Table II, ref 3. Equation 2 and the McDaniel-Brown σ values were used, only when we processed the data. Previously, we noted that perhaps two-thirds of the pmr correlations coefficients (r) of eq 2 were less than 0.95. Judging from our data in the benzyl halides and plots of literature data, this pattern seems general. In fact, most workers do not give r.

For the present, we disregard low correlation coefficients and plot ρ *vs.* chain length T in Figure 6. Data from strongly polar solvents *e.g.*, acetone, DMSO, etc. were not included. From an earlier version of this figure, it was concluded that the "standard" $-\rho$ values of 36, 13, 7 could be discerned for T = 0, 1, or 2 atoms in the side chain to benzene.[3] These ρ values also seemed to show the conventional fall-off of 2–3 per atom in T. Exceptionally high ρ values were considered to be superconducting and seemed to be related to the structure of T. Figure 6 now makes it clear that "standard" values of ρ cannot be assigned.

The most numerous entries in Table III are for T = 1 and 2 and these also show the largest spread in ρ. Clearly, *there is no clustering in* ρ *around one value for*

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[15] W. K. Kwok, R. A. More O'Ferrall, and S. I. Miller, *Tetrahedron,* **20,** 1913 (1964), and related papers.

TABLE III

GROUP ATTENUATION FACTORS FOR PMR SHIFTS AS INDICATED BY HAMMETT ρ VALUES[a]

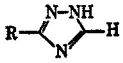
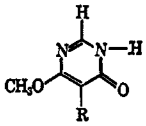
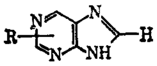
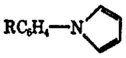
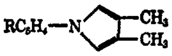
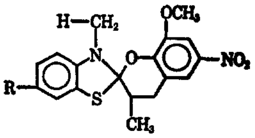
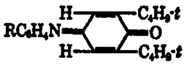
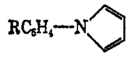
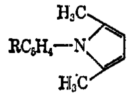
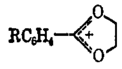
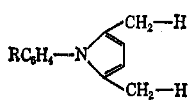
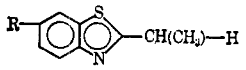
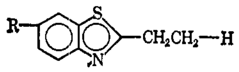
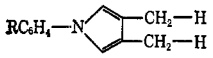
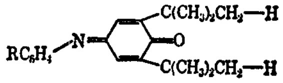
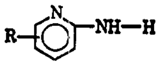
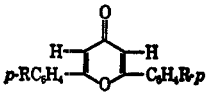
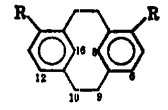
Code no.	RC_6H_4T-H		Atoms in T	−ρ/σ, Hz	No. of R	Solvent	Ref
32			0	64	14	$(CD_3)_2CO$	*b*
33	5-R-2-(*trans*-$C_6H_5CH{=}CH$-)C_6H_3-H		0	18.6	5	$CDCl_3$	*c*
34		1-H	0	76	5	DMSO	*d*
35		2-H	0	23.2	5	DMSO	*d*
36	$RC_6H_4C(=CH_2)$—H		1	16	8	$(CD_3)_2CO$	*e*
37	$RC_6H_4CH(CH_2COOH)$—H		1	8.2	5	$(CD_3)_2CO$	*e*
38	$RC_6H_4CH(CH_3)$—H		1	14	6	$(CD_3)_2CO$	*e*
39	*trans*-$RC_6H_4C(=CHCOOH)$—H		1	8.6	11	$(CD_3)_2CO$	*e*
40	*cis*-$RC_6H_4C(=CHCOOH)$—H		1	20.4	9	$(CD_3)_2CO$	*e*
41	*trans*-4-$RC_6H_4C(=CHC_6H_5)$—H		1	*Ca.* 2.5	17	$CDCl_3$	*c*
42	$RC_6H_4CH_2$—H		1	12	8	$CDCl_3$	*f*
43	$RC_6H_4CH(OH)$—H		1	12.6	6	$CDCl_3$	*f*
44	$RC_6H_4CH(OCH_3)$—H		1	9	6	$CDCl_3$	*f*
45	RC_6H_4CH(2-dihydropyranyl)-H		1	9	8	$CDCl_3$	*f*
46	$RC_6H_4CH(SCH_3)$—H		1	6	4	$CDCl_3$	*f*
47	$RC_6H_4CH(SC_6H_5)$—H		1	4.8	5	$CDCl_3$	*f*
48	$RC_6H_4CH(SOCH_3)$—H		1	7.8	5	$CDCl_3$	*f*
49	$RC_6H_4CH(SOC_6H_5)$—H		1	12	5	$CDCl_3$	*f*
50	$RC_6H_4(SO_2CH_3)$—H		1	9.6	5	$CDCl_3$	*f*
51	$RC_6H_4(SO_2C_6H_5)$—H		1	9.6	5	$CDCl_3$	*f*
52	RC_6H_4CHCl—H		1	6.6	5	$CDCl_3$	*f*
53	RC_6H_4CHBr—H		1	1.2	5	$CDCl_3$	*f*
54	4-R-2,6-(*t*-$C_4H_9)_2C_6H_2O$-H		1	45.6	6	CCl_4	*g*
55	RC_6H_4O-H		1	109.8	18	HMPA	*h*
56	RC_6H_4O-H		1	92 (79)	20 (16)	DMSO	*i*, *v*
57	$RC_6H_4CH_2CH_2$-H		2	4.6	6	$(CD_3)_2CO$	*e*
58	$RC_6H_4CH_2CH(COOH)$-H		2	8.2	5	$(CD_3)_2CO$	*e*
59	$(RC_6H_4)_2C{=}CH$-H		2	15	16	CCl_4	*j*
60	*cis*-$RC_6H_4CH{=}CH$-H		2	24	8	$(CD_3)_2CO$	*e*
61	*trans*-$RC_6H_4CH{=}CH$-H		2	23.6	8	$(CD_3)_2CO$	*e*
62	*trans*-$RC_6H_4CH{=}C(COOH)$-H		2	20.6	11	$(CD_3)_2CO$	*e*
63	*trans*-$RC_6H_4CH{=}C(COOH)$-H		2	16.2	6	CF_3COOH	*k*
64	*trans*-$RC_6H_4CH{=}C(COOH)$-H		2	20	10	DMSO	*k*
65	*cis*-$RC_6H_4CH{=}C(COOH)$-H		2	23.6	9	$(CD_3)_2CO$	*e*
66	*trans*-$RC_6H_4CH{=}C(C_6H_5)$-H		2	16.6	17	$CDCl_3$	*c*
67	*cis*-$RC_6H_4CH{=}C(C_6H_5)$-H		2	17.6	7	$CDCl_3$	*l*
68	$RC_6H_4C(O)O$-H		2	88	13	pyridine	*m*
69	$RC_6H_4CH_2O$-H		2	24	7	DMSO	*n*
70	$RC_6H_4CH(CH_3)O$-H		2	27	5	DMSO	*n*
71	$RC_6H_4C(CH_3)_2O$-H		2	30.6	4	DMSO	*n*
72	$RC_6H_4C(CH_3)$(*i*-C_3H_7)O-H		2	37.8	3	DMSO	*n*
73	$RC_6H_4C(CH_3)(C_6H_5)O$-H		2	40.8	6	DMSO	*n*
74	R-2-$CH_3C_6H_3C(CH_3)_2O$-H		2	40.2	4	DMSO	*n*
75	4-R-2-$NO_2C_6H_3S(O)CH(CH_3)$-H		2	7.2	5	$CDCl_3$	*o*
76	4-$RC_6H_4N(CH_3)CH_2$-H		2	10.1	15	$CHCl_3$	*p*
77			2	20.5	17	DMSO	*q*
78		α-H	2	14	7	CCl_4	*r*
79		α-H	2	14	8	CCl_4	*r*
80			2	8.3	10	$CDCl_3$	*s*
81		*syn*-H	3	15	13	CCl_4	*t*
82		*anti*-H	3	1.1		CCl_4	*t*
83	4-R-2-$NO_2C_6H_3S(O)CH_2CH_2$-H			4.8	5	$CDCl_3$	*o*

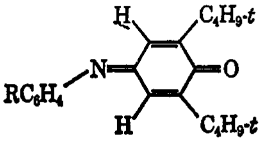
TABLE III (*Continued*)

Code no.	RC_6H_4T-H		Atoms in T	$-\rho/\sigma$, Hz	No. of R	Solvent	Ref
84		β-H	3	6	7	CCl_4	*r*
85		β-H	3	8	8	CCl_4	*r*
86			3	14.1	14	FSO_3H	*u*
87			3	3.3	8	CCl_4	*r*
88			3	11	11	$CDCl_3$	*s*
89			4	7.9	11	$CDCl_3$	*s*
90			4	1.9	8	CCl_4	*r*
91		*syn*-H	6	~2.2	12	CCl_4	*t*
92		*anti*-H	6	~2.4	12	CCl_4	*t*
56a	RC_6H_4NH-H		1	79.27	15	DMSO	*v*
56b			1	76.87	5	DMSO	*v*
56c			1	81.1	4	DMSO	*v*
67a			2	5.0	5	$CDCl_3$	*w*
35a		(8,16) H	~0	17.6	4	CCl_4	*x*
35b		(6,12) H	0	36.0	4	CCl_4	*x*
35c		(9,10 equatorial) H	1	9.7	5	CCl_4	*x*

[a] The general format of this table follows that of Table II, ref 3. Thirty one ρ values are listed there. [b] W. Freiberg and C.-F. Kröger, *Tetrahedron Lett.*, 2109 (1967). [c] H. Güsten and M. Salzwedel, *Tetrahedron*, **23**, 173 (1967). [d] G. M. Kheifets, N. V. Khromov-Borisov, A. I. Koltsov, and M. V. Volkenstein, *Tetrahedron*, **23**, 1197 (1967). [e] Reference 14. [f] Reference 4. [g] V. F. Bystrov, V. V. Ershov, and V. P. Lezina, *Opt. Spectrosc.*, **17**, 290 (1964). [h] Reference 23. [i] Reference 22. [j] Reference 10. [k] A. R. Katritzky and F. J. Swinbourne, *J. Chem. Soc.*, 6707 (1965). [l] H. Güsten and M. Salzwedel, *Tetrahedron*, **23**, 187 (1967). [m] Y. Kondo, K. Kondo, T. Takemoto, and T. Ikenoue, *Chem. Pharm. Bull. Jap.*, **12**, 514 (1964). [n] Reference 16. [o] C. Brown and D. R. Hogg, *Chem. Commun.*, 150 (1965). [p] I. D. Rae and L. K. Dyall, *Aust. J. Chem.*, **19**, 835 (1966). [q] W. C. Coburn, Jr., M. C. Thorpe, J. A. Montgomery, and K. Hewson, *J. Org. Chem.*, **30**, 1110 (1966). [r] R. A. Jones, T. M. Spotswood and P. Cheuychit, *Tetrahedron*, **23**, 4469 (1967). [s] R. Gugliemetti, E.-J. Vincent, and J. Metzger, *Bull. Soc. Chim. Fr.*, 4195 (1967). [t] Reference 17. [u] D. A. Tomalia and H. Hart, *Tetrahedron Lett.*, 3389 (1966). [v] Reference 20. [w] H. C. Smitherman and L. N. Ferguson, *Tetrahedron*, **24**, 923 (1968). [x] S. Akabori, T. Sato, and K. Hata, *J. Org. Chem.*, **33**, 3277 (1968).

each T in a given solvent, which would be expected for regular or systematic transmission of electronic effects.[15] All in all, the ρ values seem to make no traditional sense.

Limited "explanations" for limited sets of ρ values have appeared. Two groups have provided rationalizations based on the probable conformation of the benzylic proton with respect to the aromatic ring: in one case the ring diminishes[4] and in the other it enhances transmission[16] (see 42–53 and 69–74 in Table III). We have found an analogous and striking example in the data of Reiker and Kessler for[17]



Here ρ(*syn*):ρ(*anti*) ≃ 15:1 for the quinoid protons (entries 81 and 82, Table III), a clear case of enhanced transmission to a proton near the face of an aryl system. The magnitude of this effect, which seems to be dependent on molecular geometry and on the proximate aryl group, is too large for a substituent anisotropy or electric field.[3]

The solvent can also have an enormous effect on ρ. Consider data for the anilines and phenols given in

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(16) R. J. Ouellette, D. L. Marks, and D. Miller, *J. Amer. Chem. Soc.*, **89**, 913 (1967).

(17) A. Reiker and H. Kessler, *Tetrahedron*, **23**, 3723 (1967).

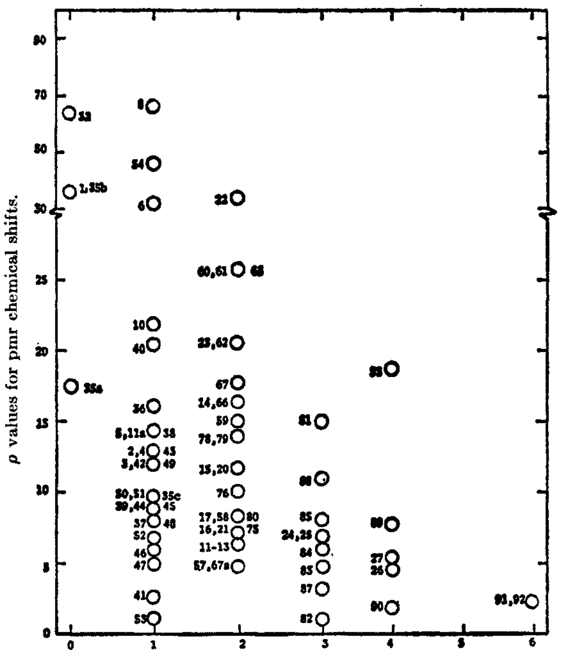

Figure 6.—Transmission of substituent effects and Hammett ρ values. The pmr data are given in Table IV or ref 3. ρ values for highly polar solvents are not included here.

Table IV.[18–23] The enhanced ρ values, *e.g.*, in DMSO, have been ascribed to hydrogen bonding[18,20,22] as well as to the interaction of the polarizable medium with the conjugated system.[19] We have also seen that even in an "inert" solvent, ν^0 may reflect differential solvent effects within a given family, *e.g.*, the benzyl halides. Since such solvent effects on ν are not really well understood, their effect on ρ cannot very well be treated.

Aside from theory, there may yet be a useful application of a *large* solvent effect on SCS and on ρ. The Hammett correlations of anilines in acetonitrile[19] or anilines, phenols, aminopyridines, and aminopyrimidines in DMSO[20] have relatively high (for their chain length *T*) and similar $\rho \simeq -78$, as well as high ($r > 0.95$) correlation coefficients. In DMSO, for example, the proton site may look like $\mathrm{ArT{-}H^{\delta+} \cdots {}^{\delta-}OS(CH_3)_2}$. This "chemical" interaction has rendered the proton more sensitive to substituent effects that are scaled to reactivity (σ). If SCS may be ascribed to both magnetic anisotropy as well as chemical effects, then these solvents seem to "bring out" or enhance the latter so that it dominates. (There is an analogy here with ^{19}F nmr in which the magnetic anisotropy effects on SCS are considered to be unimportant.) Therefore, it would seem interesting to investigate correlations in "active" solvents, particularly when the fit to eq 2 for families in relatively inert solvents, such as carbon tetrachloride, is poor.

We return to the important issue, namely, that pmr correlations are usually poor relative to reactivity correlations. Although an equation such as eq 3 may often improve the correlation, this is by no means certain (Figure 3).[10] Even what we regard as minimum correlations, that is between SCS of related families, *e.g.*, Figures 4 and 5, do not stand up well. These deal purely with SCS and involve no reactivity criteria of substituent effects, as in eq 2. The particular aryl familes we chose for comparison, *e.g.*, toluenes *vs.* benzyl halides or styrenes *vs.* 1,1-diphenylethylenes, provide an important test of both theoretical and phenomenological approaches to SCS. Any possible adjustments by most theoretical approaches to SCS or by theories of the solvent effect on SCS should be unnecessary here, because of the similar disposition of the protons being compared. If theory cannot cope with the systems of Figures 4 and 5 they should be less than adequate for more complex correlations.

At the present time, we must conclude that pmr correlations of the Hammett type are of little value. Certainly, if they are to be attempted, it is desirable to have infinite dilution data on a fair number (>10) of representative compounds.[24] As for correlations in Table III, the majority of them do not satisfy the basic requirement of being precise, *e.g.*, correlation coefficient $r > 0.95$.[3] More important, the theoretical significance of the acceptable correlations is usually obscure. MO calculations, for example, which lead to charge density *vs.* ν correlations[20] tell us nothing about ρ and presumably reflect the "chemical" as opposed to the magnetic factors on SCS. A large number of effects on, or contributions to, SCS have been noted, *e.g.*, conformation, solvent, anisotropy, charge density, ring current, etc. To attempt to identify and isolate these appears to be most urgent.

Table IV

Solvent	$-\rho(\mathrm{ArNH_2})/\sigma$, Hz	Solvent	$-\rho(\mathrm{ArOH})/\sigma$, Hz
C_6H_{12}	21[a]	CCl_4	67[d]
CCl_4	32[a]	DMSO	79, 92, 101[c,e]
CH_3CN	55[b]	HMPA	110[f]
DMSO	79[c]		

[a] Reference 18. [b] Reference 19. [c] Reference 20. [d] Reference 21. [e] Reference 22. [f] Reference 23.

Registry No.—*m*-Trifluoromethylbenzyl fluoride, 19519-94-9.

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(18) Y. Yonemoto, W. F. Reynolds, H. M. Hutton, and T. Schaeffer, *Can. J. Chem.*, **43**, 2668 (1965); W. F. Reynolds, Ph.D. Thesis, University of Manitoba, 1963.

(19) L. K. Dyall, *Aust. J. Chem.*, **17**, 419 (1964).

(20) B. M. Lynch, B. C. Macdonald, and J. G. K. Webb, *Tetrahedron*, **24**, 3595 (1968).

(21) This ρ value is for the 2,6-di-*i*-butylphenols. If anything, the value for phenols without *ortho* substituents should be lower.[16] L. A. Cohen and W. M. Jones, *J. Amer. Chem.*, **85**, 3403 (1963).

(22) R. J. Ouellette, *Can. J. Chem.*, **43**, 707 (1965); J. G. Traynham and G. A. Knesel, *J. Org. Chem.*, **31**, 3350 (1966).

(23) M. W. Dietrich, J. S. Nash, and R. E. Keller, *Anal. Chem.*, **38**, 1479 (1966).

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