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Use of Carbon-13 Substituent Chemical Shifts To Scale Non-Hydrogen-Bonding Dipolar Interactions of Protonic Solvents[1a]

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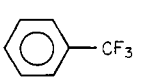
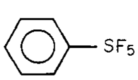
Abstract: The aromatic ^{13}C NMR shifts induced by protonic solvents in very dilute solutions of benzotrifluoride and phenylsulfur pentafluoride provide a novel means of scaling the dipolar character of these bulk solvents with little or no effects from solute–solvent hydrogen bonding. That is, these shifts have been utilized to define π solvatochromic parameters for 17 (OH, NH, and CH) protonic solvents. These results agree with previously obtained values for the strongly self-associated alcohols. However, for other more weakly self-associated solvents, evidence is presented that the method gives more reliable π values and provides the means for scaling hydrogen-bond donor abilities (α values) of relatively strong protonic solvents. The widely varying sensitivities (s) to solvent dipolarity of the para-carbon atom substituent chemical shifts for monosubstituted benzenes are determined by both the substituent-induced polarization of the benzene π electrons and by the substituent π-electron delocalization to or from the ring. This is shown by a unique DSP correlation of the s values.

In an earlier paper[2] an attempt was made to obtain for bulk protonic solvents a measure of the solvent dipolarity[3] parameter, π^*. A necessary requirement is that the UV–visible spectral shifts of the nitro compound solutes[2] which were used as probes be unaffected by the ability of such solvents to act as hydrogen-bond donors. The results obtained for the relatively strong self-associated alcohols, CH_3OH and C_2H_5OH (and water), have been strongly supported by dual solvent parameter correlations, i.e., using the π^* values and α values, which scale solvent hydrogen-bond donor ability.[4] However, π^* values from the UV–visible results are subject to question for the more weakly self-associated alcohols, e.g., t-C_4H_9OH or CF_3CH_2OH (which may engage in type A hydrogen bonding[4] to some measurable extent), as well as for protonic solvents which dimerize or polymerize in such a manner that residual (available) hydrogen-bond donor sites are present, i.e., $HCONH_2$ and $(CH_2OH)_2$.

Since recent evidence[5] indicates that electron-enriched aromatic nitro groups can engage in significant hydrogen-bond acceptor interactions, the above concerns require investigation. The sensitivity to solvent dipolarity of the ^{13}C chemical shifts of the para carbon of certain monosubstituted benzenes makes this kind of spectroscopic probe of a most attractive prospect for reinvestigation of the π^* values for protonic solvents. For this purpose we have selected as probe solutes benzotrifluoride (I) and phenylsulfur pentafluoride (II). This selection is based upon results presented herein as well as the previously obtained F_p–SCS for the corresponding para-substituted fluorobenzenes which indicated that the CF_3 and SF_5 substituents do not have significant hydrogen-bond acceptor ability from protonic solvents even as strong as trifluoroacetic acid.[6a] These highly fluorinated substituents have strongly deactivated lone-pair electrons, resulting from the mutual interactions of the very electronegative fluorines. Further, the strong electron-attracting ability of these substituents deactivates the benzene ring as a hydrogen-bond acceptor from protonic solvents. We are not aware of any other spectroscopic probe which has the potential to avoid effects of solvent hydrogen bonding. The success of the present method can be readily tested by comparing the solvent effects on the appropriate substituent chemical shifts for strong HBD solvents, e.g., CH_3CO_2H, $HCONH_2$, HCO_2H, and CF_3CO_2H, with those for the corresponding methyl derivatives which are non-HBD solvents, i.e., $CH_3CO_2CH_3$, $HCON(CH_3)_2$, HCO_2CH_3, and $CF_3CO_2CH_3$, respectively. If hydrogen bonding is absent, the solvent-induced dipolar shifts should be similar for these pairs of solvents.


I


II

The results of these and other measurements are reported in this paper. A scale of dipolarity parameters, π, for protonic solvents, is given, based upon the available results from all suitable spectroscopic probes. That is, for the aliphatic series protonic solvents investigated here (excluding the polychlorinated solvents $HCCl_3$ and H_2CCl_2) eq 1 is applicable if solvent hydrogen-bonding

$$XYZ = XYZ_0 + s\pi \qquad (1)$$

effects are absent,[2] where XYZ is a solute property in any such solvent having a dipolarity parameter π, XYZ_0 is the corresponding property in the reference solvent cyclohexane, and s is the susceptibility of the solute property to solvent dipolarity. In the case of the more polarizable polychlorinated aliphatic solvents, CCl_4, $HCCl_3$, and H_2CCl_2 the π values obtained from carbon-13 NMR shifts of I and II are less than the π^* values obtained from UV-visible spectral shifts by an amount $d\delta$.[4] In a subsequent paper,[7] the π values for protonic solvents are used to obtain an improved and extended α scale of solvent hydrogen-bond donor strengths.

Experimental

All solvents were purified by published methods.[8] Benzotrifluoride was obtained from Aldrich Chemical Co. and was used as supplied. A

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(1) (a) This work was supported in part by a grant from the Public Health Service. (b) Naval Surface Weapons Center, White Oak Laboratory, Silver Spring, MD 20910.

(2) Kamlet, M. J.; Abboud, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 6027.

(3) The term *dipolarity* is intended as a more specific description that the frequently missed term solvent *polarity*, which has included the effects of specific hydrogen-bonding interactions in varying combinations with the effect of dipolar solute–solvent interactions.

(4) (a) Kamlet, M. J.; Taft, R. W. *J. Chem. Soc., Perkin Trans. 2* **1979**, 349. (b) Taft, R. W.; Kamlet, M. J. *ibid.* **1979**, 1723. (c) Taft, R. W.; Kamlet, M. J. *Org. Magn. Reson.* **1980**, *14*, 485. (d) Kamlet, M. J.; Dickinson, C.; Taft, R. W. *Chem. Phys. Lett.* **1981**, *77*, 69. (e) Kamlet, M. J.; Dickinson, C.; Taft, R. W. *J. Chem. Soc., Perkin Trans 2* **1981**, 353. (f) Taft, R. W.; Pienta, N. J.; Kamlet, M. J.; Arnett, E. M. *J. Org. Chem.* **1981**, *43*, 661. (g) Kamlet, M. J.; Abboud, J. L. M.; Taft, R. W. *Prog. Phys. Org. Chem.* **1981**, *13*, 485.

(5) (a) Fujio, M.; McIver, R. T., Jr.; Taft, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 4017. (b) Taft, K. W.; Kamlet, M. J.; Abboud, J. L. M. *Bull. Chem. Soc. Jpn*, accepted for publication.

(6) (a) Taft, R. W.; Price, E.; Fox, I. R.; Lewis, I. C.; Andersen, K. K.; Davis, G. T. *J. Am. Chem. Soc.* **1963**, *85*, 709. (b) Taft, R. W.; Gurka, D.; Joris, L.; Schleyer, P. v. R.; Rakshys, J. W. *Ibid.* **1969**, *91*, 4801.

(7) Chawla, B.; Fujio, M.; Simanyi, L.; Pollack, S. K.; Lebrilla, C.; Taft, R. W., in preparation.

(8) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Compounds"; Pergamon Press: New York, 1966.

0002-7863/81/1503-6924$01.25/0

Table I. C_p-SCS Values for Monosubstituted Benzenes, C_6H_5X, in Dilute Solutions of Methanol[a] and of Aprotic Solvents[b]

	solvents					
subst, X	c-C_6H_{12} (0.00)[c]	CCl_4 (0.08)[c]	CH_3OH (0.60)[c]	$(CH_3)_2CO$ (0.71)[c]	$HCON(CH_3)_2$ (0.88)[c]	$(CH_3)_2SO$ (1.00)[c]
$N(CH_3)_2$	−11.13	−11.16	−11.06	−11.99	−12.06	−12.21
OCH_3	−7.77	−7.75	−7.90	−7.89	−7.81	−7.85
OC_6H_5	−5.33	−5.26	−5.04	−4.99	−4.98	−4.89
F	−4.52	−4.49	−4.08	−4.03	−3.90[a]	−3.84
Cl	−2.18	−2.08	−1.62	−1.55	−1.38	−1.35
Br	−1.75	−1.62	−1.21	−1.08	−0.99	−0.90
H	0.00	0.00	0.00	0.00	0.00	0.00
$SOCH_3$	1.78	2.07	3.26	2.29	2.32	2.35
CF_3	3.09	3.21	3.83	4.00	4.21	4.25
SF_5	2.82	2.94	3.73	3.94	4.18	4.23
CH_3CO	3.93	4.18	5.04	4.58	4.70	4.83
$CO_2C_2H_5$	3.99	4.12	4.91	4.68	4.78	4.90
CN	3.58	3.80	4.83	4.70	4.96	5.01
NO_2	5.20	5.53	6.50	6.58	6.82	6.95
CHO	5.29	5.51	6.31	6.00	6.15	6.22

[a] From this work. [b] From ref 10. [c] π value for solvent, this paper and ref 2.

1-g sample of phenylsulfur pentafluoride was the generous gift of Professor C. Scharts.[9]

Samples were prepared in 10-mm NMR tubes, at a concentration of either 5%, 3%, or 1% volume/volume (v/v) of solute and 0.5% v/v benzene as an internal reference. For locking purposes (except in the case of $CDCl_3$ as a solvent), a 5-mm coaxial tube containing Me_2SO-d_6 (Aldrich) was used.

Spectra were taken of the 5% v/v solutions of benzotrifluoride on a Bruker WH-90. Spectra in methanol were taken similarly by using 3% v/v solutions. All of the $C_6H_5SF_5$ studies were performed with a Bruker WM-250 and 1% v/v solutions. A number of the experiments with $C_6H_5CF_3$ were repeated on the WM-250 spectrometer with 1% v/v solutions, and the results were found to be essentially identical with the initial values. Spectra recorded on the WH-90 were accumulated with 8K data points and a spectral width of 5000 Hz, yielding a resolution of 0.05 ppm. Spectra accumulated on the WM-250 were taken with 16K data points and a spectral width of 15000 Hz, resulting in a resolution of 0.01 ppm. Shifts were found to be reproducible with different solute and solvent samples to ±0.03 ppm or better.

Discussion

In Table I the C_p-SCS values are given for an extended series of monosubstituted benzenes in dilute methanol solutions. Also given for comparison are the previously obtained[10] C_p-SCS values in dilute cyclohexane, carbon tetrachloride, acetone, *N*,*N*-dimethylformamide (DMF), and dimethyl sulfoxide (Me_2SO) solutions.[11] For nonhydrogen bond acceptor substituents (OC_6H_5, F, Cl, Br, CF_3, SF_5) the C_p-SCS are very well correlated (cf. Table II) by the solvent dipolarity parameter, π, including the results in methanol.

$$\int = \int_0 + s\pi \qquad (1)$$

For moderately weak to strong hydrogen-bond acceptor substituents ($N(CH_3)_2$, $SOCH_3$, $CO_2C_5H_5$, CHO, CN), C_p-SCS values are significantly more positive in methanol than in acetone, although the reverse is expected from a correlation with π values. Omitting the results in methanol for these hydrogen-bond acceptor substituents, C_p-SCS values are equally well correlated by the π values (cf. Table II). The hydrogen-bonding effects of methanol on these C_p-SCS values may be estimated as $\int_{obsd} - (\int_0 + s\pi)$. The hyrogen-bonding effects obtained in this way in general correlate satisfactorily with the available β^4 or $pK_{HB}{}^{6b}$ values of the monosubstituted benzenes or with the $pK_{HB}{}^{6b}$ values for the corresponding methyl derivative (cf. Table III). It is clear that the C_p-SCS values provide a sensitive discrimination between strong hydrogen-bond acceptor and weak or nonhydrogen-bond acceptor substituents in hydrogen-bond donor solvents, e.g., methanol.

As noted previously,[10] the s values obtained (Table II) in the correlations of the solvent dipolarity effects on the C_p-SCS are

Table II. Correlation of Solvent Dipolarity Effects on C_p-SCS Values for Monosubstituted Benzenes

	σ_I[a]	$\sigma_R{}^0$[b]	$\int_0$[c]- (exptl)	$\int_0$[d]- (eq 1)	s[e]- (eq 1)	s[f]- (eq 2)	r[g]- (eq 1)
$N(CH_3)_2$	0.06	−0.55	−11.13	−11.11	−1.12	−0.86	0.997
OCH_3	0.25	−0.42	−7.77	−7.76	−0.10	−0.16	0.777
OC_6H_5	0.38	−0.32	−5.33	−5.31	0.41	0.34	0.991
F	0.50	−0.31	−4.52	−4.53	0.73	0.65	0.998
Cl	0.46	−0.18	−2.18	−2.16	0.85	0.80	0.997
Br	0.44	−0.16	−1.75	−1.74	0.83	0.77	0.997
$SOCH_3$	0.36	0.07	1.78	*h*	*h*	*h*	*h*
CF_3	0.43	0.08	3.09	3.11	1.20	1.16	0.998
SF_5	0.58	0.04	2.82	2.83	1.47	1.46	0.997
CN	0.58	0.08	3.58	3.64	1.44	1.53	0.996
CH_3CO	0.22	0.16	3.93	4.02	0.80	0.78	0.984
$CO_2C_2H_5$	0.17	0.16	3.99	4.02	0.88	0.65	0.998
NO_2	0.65	0.15	5.20	5.30	1.70	1.83	0.995
CHO	0.32	0.22	5.29	5.36	0.88	1.13	0.991

[a] σ_I values from ref 5 except values for OC_6H_5, SF_5, and Br which are from ref 24. [b] $\sigma_R{}^0$ values from ref 10 except values for OC_6H_5, SF_5, and Br which are from ref 24. [c] Observed C_p-SCS in cyclohexane. Reference signal is internal benzene. [d] Calculated C_p-SCS in cyclohexane by least-square fit to eq 1. [e] s value obtained from least-squares fit to eq 1 for C_p-SCS values in all solvents of Table I, except for $N(CH_3)_2$, OCH_3, $SOCH_3$, CN, CH_3CO, $CO_2C_2H_5$, NO_2, and CHO substituents the value in methanol solution is excluded. [f] s value calculated from the dual substituent parameter equation (2). [g] Correlation coefficient for fit to eq 1. [h] Omitted from correlation by eq 1 since DMF and Me_2SO apparently give significant nonprotonic Lewis acid-base interactions with this substituent, cf. ref 10.

Table III. Correlation of Calculated Hydrogen-Bonding Effects in Methanol with Corresponding β and pK_{HB} Values

subst, X	β- (C_6H_5X)	pK_{HB}- (C_6H_5X)	pK_{HB}- (CH_3X)	$\int_{obsd} - \int_{calcd}$
OC_6H_5	0.13	<0.02	0.02	0.02
OCH_3	0.22	0.02		−0.08
NO_2	0.39	0.73		0.15
CN	0.41	0.79	0.87	0.33
CO_2Et	0.41	0.88	1.08	0.36
CHO	0.44	0.80		0.42
$COCH_3$	0.49	1.13	1.18	0.54
$N(CH_3)_2$			1.98[b]	0.72
$SOCH_3$	0.73[a]	2.15	2.53	1.06

[a] Estimated from biphenyl sulfoxide and dimethyl sulfoxide values of 0.70 and 0.76, respectively.[4] [b] Value for *n*-$PrN(CH_3)_2$.

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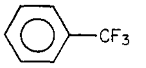
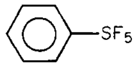
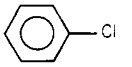
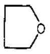
(9) Made available from work of (the late) W. A. Sheppard.

(10) Bromilow, J.; Brownlee, R. T. C.; Lopez, V. O.; Taft, R. W. *J. Org. Chem.* **1979**, *44*, 4766.

(11) These solvents as well as all others considered in this paper are in the select solvent class of aliphatic solvents[4] for which $\pi^* = \pi$, unless otherwise specifically designated, cf. Table V.

Table IV. Carbon-13 Substituent Chemical Shifts in Dilute Solutions ($\leqslant$0.1 M) of Various Solvents[a]

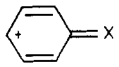
							
solvent	C_p	C_m	C_o	C_p	C_m	C_o	C_p
hexane	3.06	0.28	−2.92				−2.18
cyclohexane	3.09	0.28	−2.94	2.82	0.24	−1.94	−2.19
$(CF_3)_2CHOH$	3.12	0.01	−3.64				−1.97
CF_3CO_2H	3.16	0.13	−3.40	2.97	0.15	−2.38	−2.02
CCl_4	3.21	0.34	−2.96	2.94	0.35	−2.09	−2.08
$(C_2H_5)_3N$	3.35	0.47	−2.94	3.09	0.50	−2.03	−2.02
$CHCl_3$	3.35	0.35	−3.12	3.15	0.41	−2.35	−1.91
CF_3CH_2OH	3.44	0.32	−3.38	3.29	0.32	−2.53	−1.83
CH_2Cl_2	3.59	0.49	−3.05	3.44	0.56	−2.41	−1.83
t-C_4H_9OH	3.59	0.62	−3.18				−1.83
$CF_3CO_2CH_3$	3.62	0.56	−3.18				
1,4-dioxane	3.63	0.57	−3.04				−1.75
n-C_4H_9OH	3.64	0.64	−3.14				
i-C_3H_7OH	3.69	0.70	−3.18				
C_5H_5N	3.71	0.56	−3.29				−1.73
n-C_3H_7OH	3.71	0.68	−3.17				
CH_3CO_2H	3.73	0.65	−3.17	3.65	0.76	−2.25	−1.73
HCO_2H	3.78	0.52	−3.19				
C_2H_5OH	3.78	0.73	−3.12	3.71	0.88	−2.29	−1.67
$CH_3CO_2C_2H_5$	3.80	0.75	−3.18	3.73	0.91	−2.26	−1.62
	3.83	0.75	−3.09	3.71	0.85	−2.24	−1.67
CH_3OH	3.83	0.73	−3.13	3.73	0.82	−2.32	−1.62
$HCO_2C_2H_5$	3.84	0.73	−3.13				
$CH_3CO_2CH_3$	3.86	0.76	−3.10				−1.62
$HCONH_2$	3.86	0.57	−3.45	3.82	0.79	−2.71	−1.59
CH_3NO_2	3.88	0.67	−3.37	3.88	0.82	−2.53	−1.57
CH_3CN	3.94	0.73	−3.29				−1.54
$CH_3COC_2H_5$	3.96	0.86	−3.18				−1.51
$(CH_3)_2CO$	4.00	0.85	−3.18	3.94	1.00	−2.38	−1.55
$(CH_2OH)_2$	4.03	0.82	−3.26				−1.51
$HCON(CH_3)_2$	4.21	0.97	−3.21	4.18	1.21	−2.44	−1.38
$CH_3CON(CH_3)_2$	4.23	1.04	−3.19				−1.35
$(CH_3)_2SO$	4.25	0.95	−3.29	4.23	1.24	−2.59	−1.35

[a] Shifts in ppm relative to internal benzene–positive value downfield.

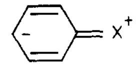
widely varied (from −1.12 to +1.70) and do not correlate with the C_p–SCS values, even in sign. Further, s values do not correlated well with any common single substituent parameter. On the other hand, the dual substituent parameter eq (2) gives an

$$s = 2.45\sigma_I + 1.74\sigma_R^0 - 0.05 \ (n = 14, r = 0.982) \qquad (2)$$

excellent description of the observed dipolar solvent induced shifts, as shown by the agreement in Table II between observed s values and those calculated from eq 2. The first term in eq 2 is the solvent-induced shift (downfield for all of the positive σ_I-values substituents of Table I) which results from the increased substituent electron-withdrawing polarizations of the benzene π electrons as a consequence of increasing substituent–solvent dipole–dipole interaction.[12] The second term is due to the effect of substituent π-electron delocalization at the para carbon (both upfield ($-\sigma_R^0$) or downfield ($+\sigma_R^0$) which is increased by ability of the solvent dipoles to support the charge-separated mesomeric moments.[10,13]



$X = NO_2$, CHO, etc.



$X = N(CH_3)_2$, OCH_3, etc.

The ratio, $\lambda = 1.74/2.48 = 0.70$, indicated that there is greater dependence upon the π-inductive effect for equal values of σ_I and σ_R^0.

Among substituents in the nonhydrogen-bond acceptor class the s values in Table II for CF_3, SF_5, and Cl are the largest. These weak or nonhydrogen bond acceptor substituents are therefore appropriate for the evaluation of π values for protonic solvents. Further evidence for their appropriateness, as well as limitations on the C_p–SCS values for these substituents, comes from the results in other protonic solvents. Table IV gives a summary of ^{13}C substituent chemical shifts at high dilutions in a wide variety of solvents. The shifts are given for the ortho, meta, and para carbon of benzotrifluoride (I) and phenylsulfur pentafluoride (II), but (for reasons indicated below) only for the para carbon of chlorobenzene. Since the CF_3 and SF_5 substituents exert predominant field/inductive effects (cf. σ_I and σ_R^0 values of Table II), the shifts of the ring carbon atoms induced by dipolar aprotic solvents should follow approximately the expectations of the π-inductive effect.[12] Indeed, this is shown by s values from the correlation of the shifts for these solvents according to eq 1: for CF_3, $s_{(p\text{-})} = 1.22$, $s_{(m\text{-})} = 0.68$, $s_{(o\text{-})} = -0.33$; for SF_5, $s_{(p\text{-})} = 1.54$, $s_{(m\text{-})} = 0.98$, $s_{(o\text{-})} = -0.61$.

However, it is immediately apparent from the results in Table IV that the C–SCS values for the strong hydrogen bond donor solvents, e.g., CF_3CH_2OH, $(CF_3)_2CHOH$, and CF_3CO_2H, do not provide reasonable measures of the dipolarity of these solvents. For example, the C_p–SCS value for benzotrifluoride in $(CF_3)_2CHOH$ is essentially identical with that in cyclohexane, and the C_m– and C_o–SCS are even smaller in the former solvent than the latter. In fact, trends of this kind are reflected in all of the C–SCS

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(12) (a) Anderson, G. L.; Parish, R. C.; Stock, L. M. *J. Am. Chem. Soc.* **1971**, *93*, 6984. (b) Reynolds, W. F.; Peat, I. R.; Freedman, M. H.; Lyerla, J. R. *Can. J. chem.* **1973**, *51*, 1857. (c) Dayal, S. K.; Taft, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 5595. (d) Reynolds, W. F.; Hamer, G. K. *Ibid.* **1978**, *98*, 7296. (e) Brownlee, R. T. C.; Butt, G.; Chan, M. P.; Topsom, R. D. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1486. (f) Hehre, W. J.; Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1976**, *12*, 159. (g) Ewing, D. F.; Sotheeswaran, S.; Toyne, K. J. *Tetrahedron Lett.* **1977**, 2041. (h) Adcock, W.; Khor, T. C. *J. Am. Chem. Soc.* **1978**, *100*, 7799.

(13) (a) Gutbezahl, B.; Grunwald, E. *J. Am. Chem. soc.* **1953**, *75*, 559. (b) Smith, J. W. *J. Chem. Soc.* **1953**, 109.

Table V. C^{13} Shifts of the Para Relative to the Meta Carbon of Benzotrifluoride and Phenylsulfur Pentafluoride in Selected Hydrogen-Bond Donor and Aprotic Solvents

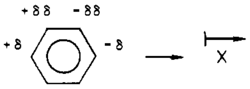
	$\int_{\text{m-CF}_3}^{\text{p-CF}_3}$	$\int_{\text{m-SF}_5}^{\text{p-SF}_5}$	$\int_{\text{o-CF}_3}^{\text{p-CF}_3}$	$\int_{\text{o-SF}_5}^{\text{p-SF}_5}$
CF_3CO_2H	3.03	2.82	6.56	5.35
$CF_3CO_2CH_3$	3.03		6.80	
CH_3CO_2H	3.08	2.89	6.90	5.90
$CH_3CO_2CH_3$	3.10		6.96	
$CH_3CO_2C_2H_5$	3.05	2.82	6.98	5.99
HCO_2H	3.26		6.97	
$HCO_2C_2H_5$	3.11		6.97	
$HCONH_5$	3.29	3.03	7.31	6.53
$HCON(CH_3)_2$	3.24	2.97	7.42	6.62
CF_3CH_2OH	3.12	2.97	6.80	5.82
CH_3CH_2OH	3.05	2.83	6.90	6.00
$(CF_3)_2CHOH$	3.11		6.76	
$(CH_3)_2CHOH$	2.99		6.87	

values for the weakly self-associated protonic solvents. The problem must arise at least in part from the fact that the internal benzene standard is itself giving rise to shifts resulting from its hydrogen-bond acceptor ability.[14]

On the other hand, if the ring positions of I and II are sufficiently deactivated as hydrogen-bond acceptor sites by the substituent electron-withdrawing effect, the shifts of one carbon position relative to another may provide the desired probe of solvent dipolarity. The shifts of the para relative to the meta carbons of I and II (but not chlorobenzene) are indeed shown by the data in Table V to meet the requirements expected. It may be noted in this connection that the use of a reference signal within the solute molecule was used successfully in previous F NMR studies of solvent effects.[15]

In Table V the shifts of the para relative to the meta carbon (given as $\int_m^p = C_p\text{–SCS} - C_m\text{–SCS}$) of I and II are compared in trifluoracetic acid, formic acid, acetic acid, and formamide solvents with the corresponding shifts in the methyl or ethyl esters of the carboxylic acids or the *N*,*N*-dimethylformamide solvents. Also compared are $\int_m^p$ values for ethanol, 2-propanol, trifluoroethanol, and hexafluoro-2-propanol. Table V shows that $\int_m^p$ values are indeed similar (or equal) for the protonic solvent as for the corresponding methyl or ethyl derivatives or for the fluorinated compared to the unfluorinated alcohols. These results for I and II are in marked contrast to those *for hydrogen-bond acceptor solutes*, e.g., pyridine[7] or the strong hydrogen-bond acceptor substituents of Table I, *which give* $\int_m^p$ *values that are downfield shifted by 0.6 ppm (or greater) in the protonic solvents compared to those of their alkyl derivative solvents.*

Also recorded in Table V are the shifts ($\int_o^p = C_p\text{–SCS} - C_o\text{–SCS}$) of the para relative to the ortho carbon for I and II, which are larger, of course, than corresponding $\int_m^p$ values. The $\int_m^p$ values in the strong hydrogen-bond donor solvents tend to be generally slightly larger than the values for the corresponding weak or nonhydrogen-bond donor solvent with which they are compared in Table V. This results seems reasonable in terms of solvent dipolarity, since, if anything, the protonic solvents would be expected to be somewhat more dipolar. On the other hand, the $\int_o^p$ values are in each case smaller (not larger) for the strong hydrogen-bond donor solvent than the corresponding weak or nonhydrogen-bond donor solvent with which it is compared in Table V. The explanation seems to be nicely consistent with substituent-induced polarization of the benzene π electrons[12] ($\sigma_I\rho_I$ terms of eq 2).



The para carbon and to a lesser extent the meta carbons are deshielded but the ortho carbons are shielded,[12] making the latter potentially a stronger hydrogen bond acceptor position. Evidently, in the very strong hydrogen-bond donor solvents this potential is realized. The result is that the ortho carbon is somewhat downfield shifted (but less so than unsubstituted benzene carbon), thus reducing the $\int_o^p$ value in these solvents. However, in the strong self-associated weaker hydrogen-bond donor solvents (e.g., CH_3OH, C_2H_5OH), this potential is not realized, and the $\int_o^p$ value provides a reasonably good measure of the dipolarity of such solvents.

In Table VI are given the individual π_i values calculated for the protonic solvents (and CCl_4) from each of the following ^{13}C solvent-induced shifts: $\int_{\text{m-CF}_3}^{\text{p-CF}_3}$, $\int_{\text{m-SF}_5}^{\text{p-SF}_5}$, $\int_{\text{o-CF}_3}^{\text{p-CF}_3}$, $\int_{\text{o-SF}_5}^{\text{p-SF}_5}$, $\int_H^{\text{p-CF}_3}$, $\int_H^{\text{p-SF}_5}$, and $\int_H^{\text{p-Cl}}$ (where $\int_H^p$ is the indicated C_p–SCS value of Table III). The calculation is made according to eq 1 as

$$\pi_i = \int_i - \int_0 / s_i$$

where $\int_0$ and s_i values are based upon the fits for nonhydrogen-bond donor solvents to eq 1. Also given in Table VI are the π_i^* values obtained in the same manner from the solvent-induced shifts in the π–π^* transitions for the four nitro compound solutes used in the original attempt to obtain the dipolarity parameters for protonic solvents.[2]

The specific π_i values of Table VI are based upon the following data sets and correlation parameters. π_1^*, $\pi \rightarrow \pi^*$ transition, *p*-nitroanisole,[2] $\nu_0 = 3.412\ \mu m^{-1}$, $s_1 = 2.35$, $r = 0.990$, $n = 52$; π_2^*, $\pi \rightarrow \pi^*$ transition, *N*,*N*-dimethyl-*m*-nitroaniline, $\nu_0 = 2.552\ \mu m^{-1}$, $s_2 = 2.21$, $r = 0.991$, $n = 64$; π_3^*, $\pi \rightarrow \pi^*$ transition, *p*-ethylnitrobenzene,[2] $\nu_0 = 3.760\ \mu m^{-1}$, $s_3 = 2.10$, $r = 0.996$, $n = 17$; π_4^*, $\pi \rightarrow \pi^*$ transiti, *p*-methoxy-β-nitrostyrene, $\nu_0 = 29.99\ \mu m^{-1}$, $s_4 = 2.30$, $r = 0.984$, $n = 59$; π_5, ^{13}C $\int_{\text{m-SF}_5}^{\text{p-SF}_5}$ shift, $\int_0 = 2.57$ ppm, $s_5 = 0.50$, $r = 0.913$, $n = 10$; π_6, ^{13}C $\int_{\text{m-CF}_3}^{\text{p-CF}_3}$ shift, $\int_0 = 2.80$ ppm, $s_6 = 0.48$, $r = 0.988$, $n = 21$; π_7, ^{13}C $\int_{\text{o-SF}_5}^{\text{p-SF}_5}$ shift, $\int_6 = 4.82$ ppm, $s_7 = 2.05$, $r = 0.996$, $n = 10$; π_8 ^{13}C $\int_{\text{o-CF}_3}^{\text{p-CF}_3}$ shift, $\int_0 = 6.09$ ppm, $s_8 = 1.51$, $r = 0.996$, $n = 18$; π_9, ^{13}C $\int_H^{\text{p-SF}_5}$ shift, $\int_0 = 2.85$ ppm, $s_9 = 1.54$, $r = 0.993$, $n = 8$ (Me_2SO excl); π_{10}, ^{13}C $\int_H^{\text{p-CF}_3}$ shift, $\int_0 = 3.11$ ppm, $s_{10} = 1.22$, $r = 0.993$, $n = 21$; π_{11}, ^{13}C $\int_H^{\text{p-Cl}}$ shift, $\int_0 = -2.16$ ppm, $s_{11} = 0.88$, $r = 0.990$, $n = 20$.

In view of the evidence already discussed relative to Table V, the preferred π values for protonic solvents (to avoid their H-bonding effects) are the π_5 and π_6 values of Table VI. Other π_i values which are appreciably larger than the π_5 or π_6 values for a given solvent may be rejected on the ground that the solute involved undergoes detectable hydrogen-bond acceptor (or induced dipole—cf. subsequent discussion) interactions with this solvent. Likewise, π_i values obtained which are appreciably smaller than the π_5 or π_6 values may be rejected on the ground that the internal C NMR shift standard (benzene or the ortho carbon of the solute) undergoes detectable hydrogen-bond acceptor interactions with the solvent. However, the basis for rejection of π_i values which are near to the average of π_5 and π_6 values is not clear-cut because of the significantly lower s values for π_5 and π_6. The experimental uncertainty of ±0.03 ppm in shifts translates to uncertainties in π_5 and π_6 values of ±0.06. The average difference between the in common π_5 and π_6 values of Table VI is in fact ±0.06. On the other hand, the s values of 1.2–2.0 for π_7–π_{10} translate to distinctly smaller statistical uncertainties in π_i values. However, this consideration is marred by the greater probability of hydrogen-bonding (and other) effects for these shifts. In Table VI π_i values which have been rejected on the above grounds are designated by parentheses. We acknowledge for the above reasons that it is difficult to defend some of the specifically rejected values but believe that our basis is consistent and rational in terms of both solute and solvent structures as well as in terms of uncertainty considerations. Values of π for protonic solvents which are based upon π_5 and π_6 values alone are given in brackets in Table VI to emphasize the greater uncertainties of these π values and the need for additional tests of them.

For methanol and ethanol all 11 individual π_i vaues are in excellent accord, giving mean values with average deviation of

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(14) (a) Wayland, B. B.; Drago, R. S. *J. Am. Chem. Soc.* **1964**, *86*, 5240. (b) Kamlet, M. J.; Jones, M. E.; Abboud, J. L.; Taft, R. W. *J. Chem. Soc., Perkin Trans. 2* **1979**, 342.

(15) Uschold, R. W.; Taft, R. W. *Org. Magn. Reson.* **1969**, *1*, 375.

Table VI. Solvent Dipolarity Parameters, π, for Protonic Solvents[a]

solvent	no.[4g]	$\pi_1{}^*$	$\pi_2{}^*$	$\pi_3{}^*$	$\pi_4{}^*$	$\pi_5{}^*$	$\pi_6{}^*$	$\pi_7{}^*$	$\pi_8{}^*$	$\pi_9{}^*$	$\pi_{10}{}^*$	$\pi_{11}{}^*$	π_{av}	av dev	n
CCl_4	6	0.24	0.30	0.26	0.29	0.04	0.13	0.10	0.05	0.06	0.06	0.09	0.08 (0.27)[b]	±0.02	7
$HCCl_3$	30	0.70	0.77	0.84	0.76	0.34	0.42	(0.33)	(0.25)	(0.19)	(0.18)	(0.28)	[0.38]	±0.04	2
$t\text{-}C_4H_9OH$	101	(0.50)	(0.48)	(0.56)	(0.58)		0.40		0.45		0.38	0.38	0.40	±0.02	4
$i\text{-}C_3H_7OH$	102	0.50	0.48	0.46	0.56		0.40		0.52		0.46		0.48	±0.04	7
$n\text{-}C_4H_9OH$	103	0.52	0.48	0.50	0.51		0.42		0.46		0.43		0.47	±0.03	7
CF_3CO_2H	203					0.51	0.48	(0.26)	(0.31)	(0.08)	(0.04)	(0.22)	[0.50]	±0.02	2
$n\text{-}C_3H_7OH$	112	0.57	0.54	0.46	0.56		0.48		0.52		0.48		0.52	±0.03	7
C_2H_5OH	104	0.52	0.55	0.52	0.55	0.52	0.52	0.58	0.54	0.56	0.54	0.56	0.54	±0.02	11
CH_3OH	105	0.57	0.62	0.56	0.59	0.69	0.63	0.60	0.59	0.57	0.58	0.60	0.60	±0.03	11
H_2CCl_2	21	0.80	0.84	0.84	0.81	0.62	0.62	(0.50)	(0.36)	(0.36)	(0.39)	(0.38)	[0.62] (0.82)[b]	±0.00	2
CH_3CO_2H	201	0.63	0.67	0.68	(0.51)	0.65	0.58	(0.53)	(0.54)	(0.52)	(0.50)	(0.49)	0.64	±0.03	5
$(CF_3)_2CHOH$	114						0.65		(0.44)		(0.01)	(0.22)	[0.65]		1
$(CH_3)_2CO$	18		0.67	0.70[c]		0.75	0.73	0.73	0.72	0.71	0.73	0.69	0.71	±0.02	9
CF_3CH_2OH	113	(1.01)	(1.06)	(1.11)	(0.89)	0.79	0.67	(0.49)	(0.48)	(0.29)	(0.27)	(0.38)	[0.73]	±0.06	2
CH_3CN	50	0.70	0.72	0.71	0.65		0.85		0.76		(0.68)	(0.70)	0.75	±0.05	5
CH_3NO_2	32		0.86			0.99	0.85	0.78	0.77	(0.67)	(0.63)	(0.67)	0.85	±0.06	5
$(CH_2OH)_2$	107	0.92	0.93	0.93	0.95		0.85		(0.80)		(0.75)	(0.74)	0.92	±0.02	5
HCO_2H	205						0.96		0.58		(0.54)		0.96		1
$HCONH_2$	204	(1.05)	(1.14)	(1.20)	(1.10)	0.92	1.02	(0.83)	0.81	(0.63)	(0.61)	(0.65)	[0.97]	±0.05	2
H_2O	111	1.09	1.05	1.23	0.98								1.09	±0.07	4

[a] Values in parentheses have been excluded—cf. text. [b] π^* value for $\pi \rightarrow \pi^*$ transition. [c] Value from solvent-induced frequency shift of *p*-nitro-*N*,*N*-dimethylaniline.

±0.03 or less. Similar results are obtained for the available π_i values for the other unsubstituted aliphatic alcohols, except $t\text{-}C_4H_9OH$. The latter alcohol is the least strongly self-associated alcohol[16] so that solute–solvent hydrogen bonding is best able to compete with solvent self-association for this alcohol. This appears to be the reason why $\pi_1{}^*$–$\pi_4{}^*$ values define a mean value of 0.53 ± 0.04, whereas π_6, π_8, π_{10}, and π_{11} give a lower mean value of 0.40 ± 0.02. The latter is the preferred values since weak hydrogen bonding to the nitro compound solutes evidently occurs for this weakly self-associated alcohol.

The relatively strong tendency for dimerization of acetic acid is well-known. The strength of the dimer apparently accounts for the good agreement obtained between the nitro–π^* indicator results (i.e., $\pi_1{}^*$, $\pi_2{}^*$, $\pi_3{}^*$) and the carbon-13 π_5 and π_6 values (giving a mean value of 0.64 ± 0.03). The inherent hydrogen-donor ability of acetic acid is indicated, nevertheless, to be sufficiently high that weak hydrogen-bond donor effects are involved with benzene and the ortho carbons of $C_6H_5CF_3$ and $C_6H_5SF_5$ (π_7–π_{11} values are less than the above mean as is also the $\pi_4{}^*$ value for *p*-methoxy-β-nitrostyrene). Similar results may apply for formic acid, but no $\pi_1{}^*$–$\pi_4{}^*$ values are available for this solvent.

Formamide and ethylene glycol are representative of solvents which are also strongly self-associated. However, their dimers or high polymers have residual acid hydrogens which are not tied up in the self-association. Accordingly, solute–solvent association can occur with these solvents without appreciable interference with their self-association. The consequences of this consideration are as might now be anticipated from the results already discussed, namely $\pi_1{}^*$–$\pi_4{}^*$ values are larger than π_5 and π_6 (the favored values) and π_7–π_{11} are significantly smaller. For ethylene glycol, the apparent effects of hydrogen bonding on $\pi_1{}^*$–$\pi_4{}^*$ values are small, however, so that these values and the π_6 value define a satisfactory measure of dipolarity of this solvent (π = 0.92 ± 0.02). For formamide, only the π_5 and π_6 values appear to us to satisfactorily define its dipolarity (π = 0.97 ± 0.05).

The stronger hydrogen-bond donor more weakly self-associated[17] fluorinated solvents, trifluoroacetic acid, trifluoroethanol, and hexafluor-2-propanol, show the same pattern of solute hydrogen-bond acceptor effects (but substantially larger ones) on the π_i values. The $\pi_1{}^*$–$\pi_4{}^*$ values (where available) are much too large and the π_7–π_{11} are much too small (particularly π_7 and π_{10} values). The somewhat larger π_{11} than π_9 or π_{10} values for these solvents (and for $HCCl_3$) are also understandable as a hydrogen-bonding effect. The chloro substituent which is involved in the π_{11} series is a π donor and its $-\sigma_R{}^0$ effect (eq 2) will tend to increase the basicity of the para carbon. A hydrogen-bond effect on the carbon-13 shift for this carbon is therefore likely, especially in these strong hydrogen-bond donor solvents. However, the effect will be less than for benzene because of the unfavorable σ_I effect of Cl (eq 2), so the hydrogen-bonding effect does not cancel completely but only partially in the $\int_H{}^{p\text{-}Cl}$ shift (with the consequence that $\pi_{11} > \pi_9, \pi_{10}$). For these strong hydrogen-bond donor solvents (as for $HCONH_2$) only π_5 and π_6 values satisfactorily define the dipolarity.

In earlier papers[4,18] evidence has been presented that polychlorinated aliphatic and aromatic solvents have a higher polarizability effect (favoring especially the $\pi \rightarrow \pi^*$ transitions) than do most aliphatic solvents. The consequence of this effect is that the π^* value for carbon tetrachloride is approximately 0.20 unit greater than the π value calculated by eq 1 from ^{19}F and ^{13}C NMR shifts. As shown in Table VI for $CCl_4 \pi^* = 0.29$ and $\pi = \pi^* - d\delta = 0.08$. A similar differential is found for the H_2CCl_2 solvent, $\pi^* = 0.82$ and $\pi = \pi^* - d\delta = 0.62$, the latter value being based upon π_5 and π_6 values only (to eliminated the effects of benzene and other hydrogen-bond acceptor interactions with the this weakly self-associated solvent).

Chloroform is shown by the results in Table VI to have enhanced $\pi_1{}^*$–$\pi_4{}^*$ values due to both its polarizability and its hydrogen-bond donor effects on the nitro compound indicators (apparent $\pi^* = 0.77$, $\pi^* - d\delta = 0.57 > \pi = 0.38 \pm 0.04$). That is, the polarizability corrected $\pi_1{}^*$–$\pi_4{}^*$ values are significantly greater than π = 0.38 ± 0.04 obtained from π_5 and π_6 values. Also π_7–π_{11} values are significantly smaller than 0.38—the same pattern of π_i values as is observed for the other weakly associated strong hydrogen-bond donor solvents, e.g., CF_3CO_2H and CF_3CH_2OH.

Nitromethane, acetonitrile, and acetone solvents typically give small hydrogen-bond donor effects with strong acceptor solutes (the effect for acetone is quite small).[4,7] The mean of $\pi_2{}^*$, π_5, π_6, π_7, and π_8 values (0.85 ± 0.06) gives a satisfactory π value for nitromethene. The smaller π_9, π_{10}, and π_{11} values for this solvent are consistent with an effect of a hydrogen bonding to benzene. All nine of the available π_i values for acetone are in

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(16) Kamlet, M. J.; Kayser, E. G.; Jones, M. E.; Abboud, J. L.; Eastes, J. W.; Taft, R. W. *J. Phys. Chem.* **1978**, *82*, 2477.

(17) (a) Kivinen, A.; Murto, J.; Korppi-Tommola, J.; Kuopio, R. *Acta Chem. Scand.* **1972**, *26*, 904. (b) Rochester, C. H.; Symonds, J. R. *J. Chem. Soc., Faraday Trans.* **1973**, *69*, 1267.

(18) cf. Taft, R. W.; Abboud, J. L. M.; Kamlet, M. J. *J. Am. Chem. Soc.* **1981**, *103*, 1080.

Table VII. Correlation of π Values with Molecular Dipole Moments

solvent	μ, D	π	π(calcd)
$n\text{-}C_6H_{14}$	0.0	−0.08	0.00
$c\text{-}C_6H_{12}$	0.0	0.00	0.00
CCl_4	0.0	0.08[a]	0.00
$(C_2H_5)_3N$	0.7	0.14	0.16
$(C_2H_5)_2O$	1.2	0.27	0.28
$HCCl_3$	1.0	0.38[a]	0.24
$t\text{-}C_4H_9OH$	1.7	0.40	0.41
CF_3CO_2H	2.3	0.50	0.55
$CH_3CO_2C_2H_5$	1.8	0.55	0.43
$(CH_3)_2CO$	2.9	0.71	0.69
CH_3NO_2	3.5	0.85	0.84
$HCON(CH_3)_2$	3.8	0.88	0.91
$(CH_3)_2SO$	3.9	1.00	0.94

[a] This π value is based upon the ^{13}C NMR shifts for which $d\delta = -0.20$. The applicability of this value is limited to spectroscopic probes which have similar $d\delta$ terms.

excellent agreement ($\pi = 0.71 \pm 0.02$), indicating that the solutes involved give negligible hydrogen-bonding interactions with acetone.

Acetonitrile results require some further observations. The $\pi_1{}^*-\pi_4{}^*$ values give $\pi_{av}{}^* = 0.70 \pm 0.02$, whereas $\pi_6 = 0.85$ (no π_5 value available) and π_{10} and π_{11} values are significantly less than π_6. The latter result reflects the expected effect of weak hydrogen bonding of acetonitrile to benzene. However, the smaller π^* than π_6 value requires an alternate explanation. It appears that this could arise from polarizability effects rather than dipolar contributions to π^* values. The solvent polarizability effects have been correlated with the refractive index of the solvent.[18] For aliphatic solvents, there tends to be a nearly constant refractive index. However, for acetonitrile ($\pi^* = 0.70$) and dimethyl sulfoxide ($\pi^* \equiv 1.00$), the refractive index difference is significant, larger than for most pairs of aliphatic solvents. Consequently, with the relatively high dependence of the $\pi \rightarrow \pi^*$ transitions on solvent polarizability ($d = 0$) compared to the relatively low dependence of C–SCS values, there may be a detectable difference in the π^* or π values between acetonitrile and dimethyl sulfoxide due to polarizability rather than dipolar effects. We suggest tentatively this explanation for the above results. Awaiting further analysis, we have taken the mean of $\pi_1{}^*$, $\pi_2{}^*$, $\pi_3{}^*$, π_6, and π_8 values (0.75 ± 0.05) as the currently best available π value for acetonitrile.

A test of the validity of the π values ($=\pi_{av}$) of Table VI for protonic solvents may be made in terms of consistency with the correlation of the π values for the select nonhydrogen-bond donor solvents with their molecular dipole moments.[19] This correlation is given by eq 3. The agreement of observed and calculated (by

$$\pi = (0.24)\mu \text{ D} \tag{3}$$

eq 3) values of π for typical nonhydrogen-bond donor solvents is illustrated in Table VII. The π values obtained in this study for CCl_4, $HCCl_3$, $t\text{-}C_4H_9OH$, CF_3CO_2H, and CH_3NO_2 follow eq 3 to the same level of agreement. Accordingly these solvents have been included in Table VII. These solvents evidently do not form extensively dimers or polymers which are more dipolar than the monomeric solvent molecule. Thus, CCl_4 and $HCCl_3$ have entropies of vaporization (20.5 and 21.0 cal/deg, respectively)[20] which are normal for nonassociated liquids. Both $t\text{-}C_4H_9OH$ and CF_3CO_2H have entropies of vaporization (22.1 and 24.0 cal/deg, respectively),[20] which are somewhat lower than those for the highly associated alcohols (25–27 cal/deg).[20] The difference in solvent-induced shifts of 4-nitroaniline and *N,N*-diethyl-4-nitroaniline in binary mixtures of dimethyl sulfoxide with alcohols show $t\text{-}C_4H_9OH$ to be the least strongly associated alcohol.[16]

Table VIII. Protonic Solvents Which Give Significantly Larger π Values Than Those Calculated from the Molecular Dipole Moment (Eq 3)

solvent	μ, D	π	π(calcd)
$i\text{-}C_3H_7OH$	1.7	0.48	0.41
$n\text{-}C_3H_7OH$	1.7	0.52	0.41
C_2H_5OH	1.7	0.54	0.41
CH_3OH	1.7	0.60	0.41
$HCONH_2$	3.3	0.97	0.78
CH_3CO_2H	1.7	0.64	0.41
CH_2Cl_2	1.6	0.62[a]	0.38
$(CH_2OH)_2$	2.3	0.92	0.55
HCO_2H	1.5	0.96	0.36
H_2O	1.7	1.09	0.41

[a] This π value is based upon the ^{13}C NMR shifts for which $d\delta = -0.20$. The applicability of this value is limited to spectroscopic probes which have similar $d\delta$ terms.

Table IX. Estimated Effects of Benzene Hydrogen-Bond Acceptor Interactions

solvent	$f_{c\text{-}C_6H_{12}}^{C_6H_6}$,[a] ppm	$\Delta f_H^{p\text{-}CF_3}$,[b] ppm	$\Delta f_H^{p\text{-}SF_5}$,[c] ppm
CCl_4	101.20	0.00	0.03
$(CH_3)_4CO$	101.62	0.02	0.00
CH_3OH	101.32	−0.01	−0.04
$CDCl_3$	101.38	0.22	0.29
CH_3NO_2		0.27	0.28
CH_3CO_2H		0.16	0.19
CF_3CO_2H	101.65	0.56	0.65
$HCONH_2$	101.97	0.43	0.52
CF_3CH_2OH	101.71	0.56	0.68
$(CF_3)_2CHOH$	102.30	0.78	

[a] Both at 1% v/v in solvent indicated. Positive value denotes that benzene is downfield shifted. [b] $\Delta f_H^{p\text{-}CF_3} = 3.11 + (1.22)\pi - f_{H(obsd)}^{p\text{-}CF_3}$. [c] $\Delta f_H^{p\text{-}SF_5} = 2.85 + (1.54)\pi - f_{H(obsd)}^{p\text{-}SF_5}$.

On the other hand, the π values calculated by eq 3 for the protonic solvents CH_2Cl_2, i-PrOH, $n\text{-}C_3H_7OH$, C_2H_5OH, CH_3OH, $(CH_2OH)_2$, CF_3CH_2OH, $(CF_3)_2CHOH$, H_2O, CH_3CO_2H, HCO_2H, and $HCONH_2$ are all substantially smaller than the values obtained in Table VI. This is the result expected for the appreciable formation in the bulk solvents of aggregates (dimers or trimers) of higher dipole moments than those of the corresponding monomeric forms of these protonic solvents. For example, Jorgensen[21] has found at the STO-3G level of appropriation the following calculated dipole moments for H_2O: monomer, 1.7 D; dimer, 2.9 F; trimer, 5.0 D. Mecke[22] found that the dipole moment of CH_3OH in binary mixtures with CCl_4 at 20 °C increases from the monomeric values of 1.7 D at high dilutions to a limiting value of 2.9 D. The latter value was attributed to the formation of more dipolar aggregates. The value of 2.9 D in eq 3 gives a calculated π value of 0.70 compared to the experimental value of 0.60 for CH_3OH. Table VIII lists values for μ, π, and π_{calcd} (from eq 3) for this more usual class of protonic solvent.

The assumption that the rejected (too small) π_9 and π_{10} values are due to hydrogen-bond acceptor effects for benzene may be checked approximately by measurement of the solvent-induced carbon-13 shifts between benzene and cyclohexane (a nonhydrogen-bond acceptor solute) at high dilutions. Earlier investigators[23] had reported that this shift is essentially solvent independent (101.17 ± 0.07 ppm), based upon the solvents CCl_4, $CDCl_3$, CH_3CO, CH_3OH, CH_3CO_2H, and CF_3CO_2H. These results, which were obtained at relatively high solute concentrations

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(19) Abboud, J. L. M.; Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 8325.

(20) Weissberger, A.; Proskauer, E. S.; Riddick, J. A.; Toops, E. E., Jr. "Organic Solvents; Physical Properties and Methods of Purification"; Interscience: New York, 1955. Stull, D. R.; Westrum, E. F., Jr.; Sinhe, G. C. "The Chemical Thermodynamics of Organic Compounds"; Wiley: New York, 1969.

(21) Jorgensen, W. L., private communication.

(22) Mecke, R.; Reuter, A. *Z. Naturforsch., A* **1949**, *4A*, 368.

(23) Nelson, G. L.; Levy, G. C.; Cargioli, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 3089.

(24) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1.

(both 10% v/v), are apparently inconsistent with other evidence that benzene acts as a hydrogen-bond acceptor.[14]

We have therefore measured this shift with both C_6H_6 and c-C_6H_{12} at 1% v/v in a representative series of solvents. The results are recorded in Table IX and show that the benzene signal is downfield shifted relative to that for c-C_6H_{12} in the hydrogen-bond donor solvents $(CF_3)_2CHOH$, CF_3CH_2OH, CF_3CO_2H, and $HCONH_2$ compared to the weak or nonhydrogen-bond donor solvents CCl_4, CH_3OH, $(CH_3)_2CO$, and $CDCl_3$.

The effects of hydrogen-bond donor solvents on the benzene shift may be estimated probably somewhat more reliably from the C_p–SCS values for I and II by taking the difference between the shift calculated by eq 1 and that observed (Table IV). These estimates are also recorded in Table IX. The closer similarity to the structural environment of the benzene carbon with the para carbons of I and II than with the carbon of c-C_6H_{12} probably makes these latter estimates the best measure of the benzene hydrogen-bond acceptor effects.

Electron-Transfer-Induced Reactions. Termination Steps and Efficiency of the Chain Process in $S_{RN}1$ Aromatic Substitutions

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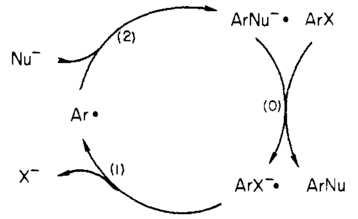
Abstract: An important part of the mechanistic sequence of $S_{RN}1$ aromatic substitution reactions $ArX + Nu^- \rightarrow ArNu + X^-$ is a chain process, the propagation of which involves three intermediate radicals: $ArX^{-}\cdot$, $Ar\cdot$ and $ArNu^{-}\cdot$. A quantitative kinetic model describing the propagation of the chain process is presented and discussed in terms of the time required for reaching a given conversion of the starting ArX. The influence of electron transfer from $ArX^{-}\cdot$ and $ArNu^{-}\cdot$ to $Ar\cdot$ as main termination steps deactivating the chain process in solvents of low H atom donating ability (liquid NH_3) is then investigated. This is a built-in problem in $S_{RN}1$ reactions: the propagation cycle produces the elements of its own destruction. The outcome of this competition is shown to essentially depend upon three parameters, featuring each one of the three steps of the propagation cycle: the rate constant for decomposition of $ArX^{-}\cdot$ into $Ar\cdot$, the rate constant for the addition of the nucleophile on $Ar\cdot$, and the difference of the standard potentials of the $ArX/ArX^{-}\cdot$ and $ArNu/ArNu^{-}\cdot$ redox couples. From previous rate and potential data, a number of systems appear to involve rather unefficient chain processes even though a rather good substitution yield can be obtained. A remarkable exception is the reaction of $(EtO)_2PO^-$ and 4-chlorobenzonitrile where a 100% conversion is obtained in about 10 min by introducing less than 0.01 electron per molecule of the substrate into the solution. It is shown that the main previous observations of homogeneous $S_{RN}1$ processes, particularly the influence of the nature of the leaving group X on reaction times and product distribution, can be interpreted in the framework of the same model which regards electron transfer to $Ar\cdot$, and in some cases to $ArNu^{-}\cdot$, as the essential cause for the deactivation of the chain process. In organic solvents, a significant additional termination step is the abstraction of hydrogen atoms from the solvent by the intermediate aryl radical $Ar\cdot$. A kinetic model is presented for the case where H atom abstraction is the main termination step and used to discuss the experimental results obtained with the reaction of the cyanide ion and 4-bromobenzophenone in acetonitrile.

One remarkable feature of $S_{RN}1$ aromatic substitution reactions[2,3]

$$ArX + Nu^- \rightarrow ArNu + X^-$$

is the involvement of a *chain process* that allows the reaction to propagate according to Scheme I.

Scheme I



The *initiation* devices devised so far were essentially of three types: injection of solvated electrons into the solution by addition of alkali metals in liquid ammonia,[2] injection of electrons by means of an electrode set at a suitable potential,[3] and photochemical stimulation.[2,4] In the first two cases the initiation steps involve the formation of the anion radical of the substrate, $ArX^{-}\cdot$, which then enters the propagation cycle. The exact nature of the photoinitiation process giving rise to one of the three species $ArX^{-}\cdot$, $Ar\cdot$, or $ArNu^{-}\cdot$ functioning in the propagation cycle still remains open to question. The initiation mechanism of $S_{RN}1$ reactions occurring in the dark without purposely added electron-donating initiators[5] is even more obscure.

So far, a reasonably complete characterization of the kinetics of $S_{RN}1$ processes was reached only in the case of electrochemical control of the reaction.[3] This provided a rigorous demonstration of the mechanism of $S_{RN}1$ reactions and led to the determination of the rate constants of the key steps for a number of experimental systems.[3,6-10,12] It is noteworthy that the mechanism of elec-

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(2) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.

(3) Savéant, J. M. *Acc. Chem. Res.* **1980**, *13*, 323.

(4) Hoz, S.; Bunnett, J. F. *J. Am. Chem. Soc.* **1977**, *99*, 4690.

(5) Scamehorn, R. G.; Bunnett, J. F. *J. Org. Chem.* **1977**, *42*, 1449.

(6) Amatore, C.; Savéant, J. M.; Thiébault, A. *J. Electroanal. Chem.* **1979**, *103*, 303.

0002-7863/81/1503-6930$01.25/0