Extension of the Unified Scale of Solvent Polarities to Acceptor Probes: Concerns about β–π^* Parameters

Russell S. Drago

Department of Chemistry, University of Florida, Gainesville, Florida 32611

Received March 16, 1992

The previously reported unified scale of nonspecific solvation, S', is extended to acceptor probes in this article. Incomplete complexation of the acceptor in weak donor solvents is proposed with 4-nitroaniline. This proposal is supported by data for a series of other substituted nitroanilines. The Kamlet–Taft β–π^* parameters are derived assuming complete complexation of the probe. Averaging in the effects of incomplete complexation into β and π^* limits the utility of these parameters. In those instances where discrepancies exist in S' and π^*, a good correlation of S' and the Dimroth–Reichardt $E_T(30)$ parameters exists.

Introduction

In the first paper in this series,[1] it was shown that a multitude of scales for estimating solvent polarity could be combined into one unified scale. This was accomplished by a least-squares data fit of systems that were devoid of specific donor–acceptor interactions (including π-stacking) and of solute aggregation problems. Solvents with rotational conformers of different polarity were also excluded. In all, over 300 data points were fit to eq 1:

$$\Delta\chi = S'P + W \quad (1)$$

Solvation parameters, S', for 31 solvents as well as probe parameters, P, and probe values, W, for 30 probes are reported. In eq 1, S' is a measure of solvent polarity, P measures the susceptibility of the probe property to nonspecific solvation, and W is the gas-phase value plus any constant change in the property that occurs in the probe when added to a solvent, i.e., a non-zero intercept. Probe spectral shifts (electronic, NMR, and EPR spectra), $\Delta\chi$, can be calculated for over 900 systems by substituting these solvent parameters and the reported[1] probe parameters into eq 1.

The model is impressive, for it correlates a wide variety of physical properties (electronic transitions, NMR chemical shifts, and EPR hyperfine couplings), as well as a wide range of probe dimensions and shapes. The use of the same S' parameters for a wide variety of solute shapes and sizes suggests a dynamic cavity model for solvation. Solvent rearranges to form a cavity for the solute that maximizes the nonspecific solvent–solute interactions at the expense of solvent–solvent and solute–solute interactions. With a spectroscopic correlation only the solvent–solute interactions are relevant if the probe is soluble and dispersed in the solvent. In contrast, solubility and enthalpies of solution depend on both specific and nonspecific solvent–solute, solute–solute, and solvent–solvent interactions.

The E and C model[2] is now widely recognized[3] as a method for calculating enthalpies and spectral shifts for specific donor–acceptor interactions. Enthalpies are correlated with

$$-\Delta H = E_A E_B + C_A C_B + W \quad (2)$$

When applied to physicochemical properties other than enthalpies, the equation takes the form

$$\Delta\chi = E_A^* E_B + C_A^* C_B + W^* \quad (3)$$

where the asterisk can be placed on either the acceptor or donor to indicate which is undergoing the spectral change as the other is varied. When a constant value of E_A^* and C_A^* is found for measurements with several different donors using enthalpy-based parameters, E_B and C_B, in eq 3, the physicochemical measurements of the acceptor are shown to be determined by the same factors that influence bond strength.

The enthalpy data set used to determine the electrostatic and covalent parameters for donor–acceptor bonding is limited to those systems that have minimal, if any,[4] nonspecific solvation contributions. The data set used to determine the P and S parameters is devoid of specific donor–acceptor interactions and treats nonspecific interactions. We are now in a position to test the combination of these models to analyze measurements of specific interactions in polar solvents. Adding eq 1 and 2 produces the equation:

$$\Delta\chi - W = E_A^* E_B + C_A^* C_B + P_A S'_B \quad (4)$$

The asterisks indicate an acceptor probe in a basic solvent. Asterisks on E_B^* and C_B^* and the term $P_B S_A'$ would be employed when a basic probe is studied in acidic solvents. Reported[2] enthalpy-based donor parameters are used in the former system and enthalpy-based acceptor parameters in the latter.

In this paper, we test eq 4 on systems involving specific donor solvent–acceptor probe interactions in polar solvents. We find that the resulting unified solvation parameters and specific interaction parameters are not in agreement with the Kamlet–Taft β–π^* parameters.[5] The β and π^* reactivity parameters[5] are derived by assuming complete complexation of the acceptor probe in the solvent. The derivation also assumes that no specific π–π^* interactions occur between π-probes and π-solvents. The breakdown in these assumptions restricts the utility of these parameters.

Results and Discussion

Interpretation of the Solvent Dependence of 4-Nitrophenol and 4-Nitroaniline. The relevant equation

(1) Drago, R. S. *J. Chem. Soc. Perkin*, in press.
(2) (a) Drago, R. S. *Coord. Chem. Rev.* **1980**, *33*, 251. (b) Drago, R. S.; Ferris, D. C.; Wong, N. *J. Am. Chem. Soc.* **1990**, *112*, 8953 and references cited therein. (c) Drago, R. S. *Struct. Bonding (Berlin)* **1973**, *15*, 73.
(3) The E and C model is described in most textbooks on Inorganic Chemistry.
(4) (a) Drago, R. S.; Ferris, D. C.; Wong, N. *J. Am. Chem. Soc.* **1990**, *112*, 8953. (b) Drago, R. S.; Wong, N. M.; Ferris, D. C. *J. Am. Chem. Soc.* **1991**, *113*, 1970.
(5) (a) Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 377. (b) Minesinger, R. R.; Jones, M. E.; Taft, R. W.; Kamlet, M. J. *J. Org. Chem.*, **1977**, *42*, 1929. (c) Kamlet, M. J.; Jones, M. E.; Taft, R. W.; Abboud, J.-L. M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 342. (d) Kamlet, M. J.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877. (e) Kamlet, M. J.; Abboud, J.-L. M.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 6027.

0022-3263/92/1957-6547$03.00/0

Table I. Fit of Solvent Changes in the Electronic Transition (kK) of 4-Nitrophenol and 4-Nitroaniline to eq 4

solvent	ν_{exptl}[4]	ν_{calc}	solvent	ν_{exptl}[4]	ν_{calc}
4-$NO_2C_6H_5OH$ (E_A* = −0.269; C_A* = −0.246; P = −1.08; W = 35.22)					
$(CH_2)_4O$	32.47	32.41	$CH_3C(O)C_2H_5$	32.57	32.59
$HC(O)N(CH_3)_2$	31.35	31.30	$(C_2H_5)_2O$	33.11	33.02
$CH_3C(O)N(CH_3)_2$	31.30	31.37	$(n\text{-}C_4H_9)_2O$	33.17	33.19
$(CH_3)_2SO$	31.06	30.96	$(C_2H_5O)_3PO$	31.70	31.86
$O(CH_2CH_2)_2O$	32.89	32.79	C_5H_5N	31.44	31.53
4-$NO_2C_6H_4NH_2$ (E_A* = −0.801; C_A* = −0.143; P = −1.06; W = 31.06)					
$(CH_2)_4O$	27.59	27.64	$O(CH_2CH_2)_2O$	28.25	(27.80)
$HC(O)N(CH_3)_2$	26.18	26.16	$CH_3C(O)OC_2H_5$	27.93	(27.71)
$CH_3C(O)N(CH_3)_2$	26.21	26.15	$(C_2H_5)_2O$	28.65	(28.10)
$(CH_3)_2SO$	25.71	25.74	$(n\text{-}C_4H_9)_2O$	29.03	(28.21)
$(C_2H_5O)_3PO$	26.49	26.62	$(CH_3)_2CO$	27.32	(26.86)
$(C_2H_5)_3N$	28.77	28.76	C_5H_5N	26.42	(26.83)

for treating spectral shifts of probes that are capable of hydrogen bonding to donor solvents is eq 4. Since E_B, C_B, and S_B' are known, the individual data sets for an acceptor probe are solved for four unknowns E_A*, C_A*, P_A, and W. The results of fitting the 4-nitrophenol and 4-nitroaniline acceptor probes to eq 4 are shown in Table I.

The available experimental data for 4-nitrophenol are fit very well. The W value of 35.22 leads to a calculated value of 35.06 for cyclohexane (S' = 0.15) compared to an experimental value of 34.97. Except for pyridine, where specific π–π charge-transfer interactions complicate the picture, an equally good fit of the data to eq 4 results for the parameters C_A* = 0.06, E_A* = 0.46, and P = 1.01. This indicates a very shallow minimum in the data set leading to large errors in the breakup of the specific interaction into E_A* and C_A* components.[6] As a result, the parameters for this probe (E_A*, C_A*, β, or π) should only be used to predict shifts for donors whose C_B/E_B ratio falls in the range of 0.4–1.5. Interpretations involving covalent–electrostatic contributions to the specific interaction are without meaning.

The data fit of all the solvents for 4-nitroaniline is poor. Solving a full data set for four unknowns can give a fair fit with unreasonable parameters when unusual chemistry is involved. Accordingly, this data set is solved by fixing W at the value found in cyclohexane plus 0.15 (i.e., estimating P = 1). A poor fit still results. Running several fits, varying W by ±0.5 (or more if improvement is observed) in 0.1 increments, does not improve matters. The pattern observed in the deviation of experimental and calculated values suggests that aniline derivatives are such poor acceptors that they are not fully complexed when dissolved in poor donor solvents. Incomplete complexation would lead to a predicted shift that is larger than that observed experimentally. Diethyl ether and di-*n*-butyl ether miss in the same direction. Though these donors are comparable in strength to THF, the unfavorable entropy term associated with the ethyl and butyl groups' loss of rotational freedom upon adduct formation makes a positive contribution to ΔG (i.e., ΔS is more negative) for these systems. This leads to a small K and incomplete complexation. Accordingly, the poor donors[8] (E_B below 1.8 with C_B below 1.4) as well as the ethers were omitted. The omitted systems are indicated by parentheses on the data in Table I. An excellent fit of the remaining systems results which is optimal[9] with a value of W equal to 31.06. The W value of 31.06 leads to a calculated value of 30.90 for cyclohexane compared to an experimental value of 31.01. Specific interactions do not exist in cyclohexane, and agreement of the calculated and experimental values suggests the probe is not extensively associated at the concentrations employed. It is also important to note that the C/E ratio of the omitted donors fall inside the range of the remaining donors employed in the fit. It is often possible to fit poorly behaved systems by restricting the C/E ratio of the bases involved.

It is not sufficient that the data can be fit well by assuming an incomplete complexation model to eliminate donors.[10] The values of ν that are calculated for the omitted donor solvents using the parameters from the restricted data fit must show deviations consistent with the explanation offered to exclude them. In this system all of the weak coordinating solvents give rise to smaller experimental shifts then calculated. Furthermore, if we attribute the deviation, Δ, to incomplete complexation, the fraction of 4-nitroaniline not complexed, % free, can be estimated with eq 5. This formula leads to 15%, 33%,

$$\% \text{ free} = \Delta/(E_A{}^*E_B + C_A{}^*C_B) \qquad (5)$$

29%, 27%, and 47% free acceptor in the solvents ethyl acetate, diethyl ether, acetone, dioxane and di-*n*-butyl ether, respectively. At 1×10^{-4} probe concentration in pure

(6) This data set has also been analyzed[7] by subtracting the frequency of the transition for 4-nitroanisole from that of 4-nitrophenol in the same solvent to correct the phenol for nonspecific solvation. The resulting $\Delta\nu$ is then corrected for the frequency difference of 4-nitrophenol and 4-nitroanisole in an inert solvent to give the specific acid base contribution to the phenol shift. These values of the acid–base contribution to $\Delta\nu$ can be fit[7] with E_A* = −0.559; C_A* = −0.090, and W = 0.78 where W corresponds to the frequency difference of the 4-nitrophenol and 4-nitroanisole transitions in hexane. The standard deviation of the fit of all the donors in Table I is 0.06 kK compared to a standard deviation of 0.08 for the $\Delta\nu$ fit. The donor–acceptor contribution to the frequency shift of the 4-nitrophenol–$CH_3CON(CH_3)_2$ adduct, for example, is calculated to be 0.67 in the $\Delta\nu$ fit and 0.95 from eq 4. This suggests that 4-nitroanisole slightly underestimates the nonspecific solvation of 4-nitrophenol. The C_A* and E_A* values from the two data fits are not in good agreement. The C_B/E_B ratios of the donors that were employed in this study do not vary enough to accurately define E_A* and C_A*. This accounts for the difference in the C_A* and E_A* values from the $\Delta\nu$ fit and those from eq 4.

(7) Drago, R. S.; Vogel, G. C. *J. Am. Chem. Soc.* **1992**, *114*, 0000.

(8) The E and C parameters measure the enthalpy contribution to ΔG. They provide an estimate of donor strength which in a related series and in the absence of unusual entropy effects parallels ΔG. An unusual entropy effect is proposed for diethyl and di-*n*-butyl ether leading to a $-\Delta S$ contribution.

(9) The criterion for optimal involves selecting the fit with the W value that produces the smallest total standard deviation in calculated and experimental frequencies with all the stronger coordinating solvents fitting to 0.1 kK (experimental error) or better. When any one of the solvents excluded is added into the optimal data set (Table I) the fit becomes poorer and one of the better coordinating solvents does not fit to within the 0.1 kK error limit.

(10) The data fit of these systems has tacitly assumed that all of the different adducts formed by hydrogen bonding of the acceptor probe to different donors (solvents) have the same P value in treating the nonspecific solvation by PS'. A breakdown in this approximation would lead to a different interpretation of the deviations in the fit of the experimental and calculated frequencies when the total data set is employed. The donors in the restricted fit, that give good results, cover a range of shapes and donor strengths. Consequently, this explanation of the deviations is considered less likely than incomplete complexation.

Table II. Electronic Spectral Changes for Acceptor Probes in Donor Solvents (kK)

solvent	ν_{exptl}	ν_{calc}	solvent	ν_{exptl}	ν_{calc}
N-Methyl-4-nitroaniline (E_A* = −0.42; C_A* = −0.31; P = 1.03; W = 29.60)					
$(CH_2)_4O$	26.60	26.50	$CH_3C(O)OC_2H_5$	26.81	(26.77)
$HC(O)N(CH_3)_2$	25.45	25.43	$(C_2H_5)_2O$	27.66	(27.10)
$CH_3C(O)N(CH_3)_2$	25.45	25.47	$(n\text{-}C_4H_9)_2O$	27.82	(27.24)
$(CH_3)_2SO$	25.06	25.06	$(C_2H_5O)_3PO$	25.87	25.93
$(CH_3)_2CO$	26.28	(25.95)	C_5H_5N	25.48	25.54
$O(CH_2CH_2)_2O$	26.92	26.89			
N-Ethyl-4-nitroaniline (E_A* = −0.44; C_A* = −0.31; P = −1.01; W = 29.50)					
$(CH_2)_4O$	26.46	26.38	$CH_3C(O)OC_2H_5$	26.77	(26.65)
$HC(O)N(CH_3)_2$	25.35	25.31	$(C_2H_5)_2O$	27.55	(26.97)
$CH_3C(O)N(CH_3)_2$	25.35	25.35	$(n\text{-}C_4H_9)_2O$	27.78	(27.10)
$(CH_3)_2SO$	24.91	24.94	$(C_2H_5O)_3PO$	25.77	25.80
$(CH_3)_2CO$	26.18	25.83	C_5H_5N	25.38	25.42
$O(CH_2CH_2)_2O$	26.77	26.77			
3-Nitroaniline (E_A* = −0.84; C_A* = −0.17; P = −0.56; W = 29.07)					
$(CH_2)_4O$	26.42	26.37	$CH_3C(O)OC_2H_5$	26.81	(26.53)
$HC(O)N(CH_3)_2$	25.54	25.45	$(C_2H_5)_2O$	27.14	(26.60)
$CH_3C(O)N(CH_3)_2$	25.32	25.38	$(n\text{-}C_4H_9)_2O$	27.36	(26.62)
$(CH_3)_2SO$	25.06	25.12	$(C_2H_5O)_3PO$	25.54	25.52
$(CH_3)_2CO$	26.49	(26.01)	C_5H_5N	25.83	(25.76)
$(C_2H_5)_3N$	26.74	26.75	CH_3CN	26.92	(25.83)
$O(CH_2CH_2)_2O$	26.99	(26.45)			
N-Ethyl-3-nitroaniline (E_A* = −0.50; C_A* = −0.10; P = −0.61; W = 27.21)					
$(CH_2)_4O$	25.19	25.14	$CH_3C(O)OC_2H_5$	25.45	(25.20)
$HC(O)N(CH_3)_2$	24.33	24.28	$(C_2H_5)_2O$	25.97	(25.41)
$CH_3C(O)N(CH_3)_2$	24.24	24.27	$(n\text{-}C_4H_9)_2O$	26.14	(25.47)
$(CH_3)_2SO$	23.98	24.03	$(C_2H_5O)_3PO$	24.48	24.47
$(CH_3)_2CO$	25.06	(24.70)	C_5H_5N	24.39	(24.55)
$(C_2H_5)_3N$	25.74	25.75	CH_3CN	25.16	(24.41)
$O(CH_2CH_2)_2O$	25.51	(25.24)			
3,5-Dinitroaniline (E_A* = −0.80; C_A* = −0.10; P = −0.42; W = 27.52)					
$(CH_2)_4O$	25.25	25.27	$CH_3C(O)OC_2H_5$	25.64	(25.36)
$HC(O)N(CH_3)_2$	24.54	24.46	$(C_2H_5)_2O$	25.84	(25.40)
$CH_3C(O)N(CH_3)_2$	24.27	24.38	$(n\text{-}C_4H_9)_2O$	25.77	(25.40)
$(CH_3)_2SO$	24.18	24.18	$(C_2H_5O)_3PO$	24.48	24.44
$(CH_3)_2CO$	25.28	(24.95)	C_5H_5N	24.69	(24.81)
$(C_2H_5)_3N$	25.70	25.69	CH_3CN	25.74	(24.82)
$O(CH_2CH_2)_2O$	25.67	(25.27)			

solvent, 25% free acceptor, would correspond to an equilibrium formation constant of about 0.3. This is a reasonable estimate of the equilibrium constant for these donors coordinating to 4-nitroaniline. Equilibrium constants of 0.3, 0.5, and 0.6 at 20 °C are reported[11] for *p*-bromoaniline reacting with di-*n*-butyl ether, tetrahydropyran, and dioxane. Since errors of ±0.5 are usual for such low values of K, assigning a K of <0.3, for weak donor adducts of 4-nitroaniline, is supported by these studies.

The donor strength ($-\Delta H$) of the solvents is given by the E_B and C_B parameters. The extent of complexation, i.e., the % free acceptor, is determined by ΔG. Weak donors will not have a large enough enthalpy to lead to an appreciable $-\Delta G$. However, donors of moderate strength can have unfavorable entropy contributions that reduce K. Both entropy and enthalpy effects determine the extent of complexation.

The E_A* and C_A* values reported in Table II for 4-nitroaniline are in fair agreement[12] with those obtained from a $\Delta\nu$ fit employing *N,N*-diethyl-4-nitroaniline as a model compound to correct for nonspecific interaction (E_A* = −1.02 and C_A* = −0.185). The data point for $(C_2H_5)_3N$ helps to define the C_A*/E* ratio better for this system than for 4-nitrophenol. It is significant to note that even in the $\Delta\nu$ fit, di-*n*-butyl ether, diethyl ether, and dioxane were omitted because they missed badly, again in the direction of incomplete complexation.

The donor–acceptor contribution to the shift is greater for 4-nitroaniline than for 4-nitrophenol even though the former is behaving as a weaker acceptor leading to incomplete complexation. In comparing different probes, probe electronic properties govern the response of the probe to the donor–acceptor interaction. Consequently, the shift for a given acceptor as the donor is varied may be related to donor strength, but the response of the different probes (i.e., the E_A* and C_A* values) toward a given base may not reflect acceptor strength. For a given strength ($-\Delta H$) of donor–acceptor interaction, the electronic transition of 4-nitroaniline is changed more on adduct formation than that of 4-nitrophenol.

Extension of eq 4 to Other Acceptor Probes. One of the main advantages of the E and C analysis is the ability to detect unusual trends in reactivity and spectroscopy.[2] Clearly, the ability of the E and C model to correlate the enthalpies and OH frequency shifts of a wide variety of phenols and pyrroles suggests unusual behavior for 4-nitroaniline. When an unusual effect is indicated, independent confirmation is sought by further experimentation.[2a] Incomplete complexation of a solute in a solvent is difficult to ascertain experimentally. One test

(11) Lauranson, J.; Pineau, P. *J. Chim. Phys.* **1968**, *65*, 1937.

(12) Slightly larger contributions to the shift from the donor–acceptor interaction are calculated in the $\Delta\nu$ fit than in the fit reported here. As is the case for 4-nitroanisole, this suggests that *N,N*-diethyl-4-nitroaniline slightly underestimates the nonspecific solvation contribution.

of the incomplete complexation proposal for the 4-nitroaniline shifts involves examining other substituted nitroanilines[5b,c] to determine if the explanation can be consistently applied. The results are given in Table II. The first two systems listed involve substituting an amine proton of 4-nitroaniline by a methyl or ethyl group. The two systems produce identical results within experimental error. The cyclohexane frequencies are calculated to be 29.44 and 29.35 kK, respectively, compared to experimental values of 29.37 and 29.15. These two acceptor probes are not fully coordinated in acetone (28%), di-*n*-butyl ether (50% free), diethyl ether (45% free), and ethyl acetate (12% free). In contrast to 4-nitroaniline, these two solutes are well behaved in acetone and dioxane. These results suggest that the acceptor strengths of the *N*-methyl and *N*-ethyl derivatives are slightly greater than that of 4-nitroaniline.[13] The extent of the complexation of these derivatives in di-*n*-butyl ether and diethyl ether is comparable to that for 4-nitroaniline. In these solvents the stronger acidity of the N-alkyl derivative is compensated by the N-alkyl substituent causing an even less favorable entropy contribution to adduct formation than in 4-nitroaniline.[15]

The next system to be considered is 3-nitroaniline. The fit for a limited set of solvents is shown in Table II. The calculated value for cyclohexane is 28.99 compared to an experimental value of 28.82. The Hammett substituent constant[16] for the 3-NO_2 group is 0.71 compared to 0.81 for the 4-NO_2 substituent. Accordingly, 3-nitroaniline is expected to have acceptor properties comparable to 4-nitroaniline. Consistent with this expectation, it is found that the calculated results deviate in the direction of incomplete complexation for 3-nitroaniline (Table II) and the same four solvents need to be omitted as in the 4-nitroaniline fit. In addition, the weak donor acetonitrile, not reported for the earlier systems, must be omitted. Equation 5 suggests that only about 30% of the probe is complexed in CH_3CN.

The fit for *N*-ethyl-3-nitroaniline is shown in Table II. The calculated value for the transition in cyclohexane, where specific donor–acceptor interactions are absent, is 27.12 kK compared to an experimental value of 27.06. With the possibility of enhanced contribution from the resonance form discussed above for *N*-ethyl-4-nitroaniline absent, N-ethylation of the 3-NO_2 derivative does not increase the acidity of the N–H proton. This is reflected in the necessity of eliminating all five weak donor solvents to obtain a good data fit.

The 3,5-dinitro derivative is also a weak acceptor comparable in strength to the 3-nitro derivative. The same weak donor solvents are omitted from both probe fits. The calculated value for the electronic transition in cyclohexane is 27.46, in excellent agreement with an experimental value of 27.43.

Using the extent of the complexation of acetone ($\Delta/(E_A^*E_B + C_A^*C_B)$) as an approximate criterion to indicate the free energy of complexation we obtain: 4-nitrophenol (~0% free) > 3,5-dinitroaniline (22% free) > *N*-ethyl-4-nitroaniline ~ *N*-methyl-4-nitroaniline ~ 4-nitroaniline ~ 3-nitroaniline (29% free) > *N*-ethyl-3-nitroaniline (36% free). This is a reasonable order which, coupled with the trends in donor strength of the solvents omitted from the various fits,[17] provides strong support for incomplete complexation of these probes in weak donor solvents.

The interpretation of this set of acceptor probes with eq 4, i.e., the ECS′ analysis, has provided an alternative description of the chemistry to that reported in the literature.[5] The proposal of incomplete probe complexation is supported by the data fit, which suggests elimination of donors which either are known to be weak on the basis of their *E* and *C* values or have unfavorable entropy contributions. Further support comes from the consistency of this interpretation in the comparison of all the acceptors studied and in the reasonable order deduced for the extent of the complexation of the probes.

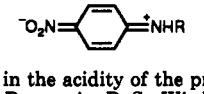
The specific donor–acceptor contributions calculated in this ECS′ analysis are determined using donor–acceptor E_B and C_B parameters that have been demonstrated to correlate enthalpies and spectroscopies for a wide range of acceptors including gas-phase ion–molecule reactions.[4] The excellent fit of these electronic transitions for moderate and strong donor solvents indicates that the component of the electronic transitions arising from specific solvation is related to solvent donor strength. The covalent and electrostatic components of the donor–acceptor contribution to the transition in all of these systems is in need of better definition. This could be provided by adding more strong nitrogen donor solvents to the data base. Normally, sulfur donors are desirable for this purpose, but incomplete complexation is expected to lead to complications with these probes. Sulfur donors are weak donors toward hydrogen-bonding acceptors.

Comparison of the ECS′ and β–π^* Approaches. The data sets in Tables I and II are part of a more extensive data base that has been used by Kamlet, Taft, and coworkers to derive β parameters to treat the specific interaction and π^* parameters to treat the nonspecific interactions in polar solvents.[5d] Complete complexation of the probe is assumed, and the β and π values are empirically determined by fitting this and other data (p$k\beta$'s, $\Delta\nu$'s, ΔG's) whose trends are determined by essentially electrostatic interactions. The frequencies in Tables I and II would be calculated with the β–π^* model using eq 6.

$$\nu = \beta_S\beta_P + \pi_S^*\pi_P + W \qquad (6)$$

Using the refined set[5d] of β and π^* values, all of these data, including those solvents whose misses in the ECS′ analysis are attributed to incomplete complexation, are fit very well with equation 6.

(13) The increased acceptor strength of the N–H proton of the N-alkyl substituent is contrary to the inductive effect of the alkyl groups which would cause the N–H to be a poorer acceptor. NMR coupling constants suggest[5,14] that nitrogen hybridization is between sp^3 and sp^2 in aniline. N-Methylation and *N*-ethylation lead to an increase in the s-character toward sp^2. An increase in s-character in the 4-nitroaniline system would lead[5] to a more favorable contribution from the resonance form



and lead to an increase in the acidity of the proton as observed.

(14) (a) Axenrod, T.; Pregonsin, P. S.; Wieder, M. J.; Becker, E. D.; Bradley, R. B.; Milne, G. W. A. *J. Am. Chem. Soc.* **1973**, *93*, 6536 and references cited therein. (b) Paolillo, L.; Becker, E. D. *J. Magn. Res.* **1970**, *2*, 168. (c) Wasylishen, R. E. *Can. J. Chem.* **1976**, *54*, 533.

(15) Pyridine appears to be well behaved in these fits. Unfortunately, shifts for donors with large C_B/E_B ratios are not available to determine the C_A^*/E_A^* ratio more accurately and confirm the data fit to pyridine.

(16) Exner, O. In *Correlation Analysis in Chemistry*; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978; Chapter 10.

(17) The donor solvent hexamethylphosphoramide has not been included in these analyses. This solvent has consistently caused problems in spectral correlations involving acceptor molecules, but is well behaved when donor probes are studied in donor solvents.[1] Toward acceptor probes with large E_A^* and C_A^* values, the deviations are greater than 600 kK and in the direction of shifting more than calculted. This could arise from primary coordination at oxygen with an added contribution to the observed shift from specific or nonspecific interaction with the nitrogen lone pair. This interaction makes a minor contribution to the enthalpies of adduct formation because this donor is well behaved in enthalpy fits. The limited data available make it difficult to rationalize the spectral deviations for this donor with confidence.

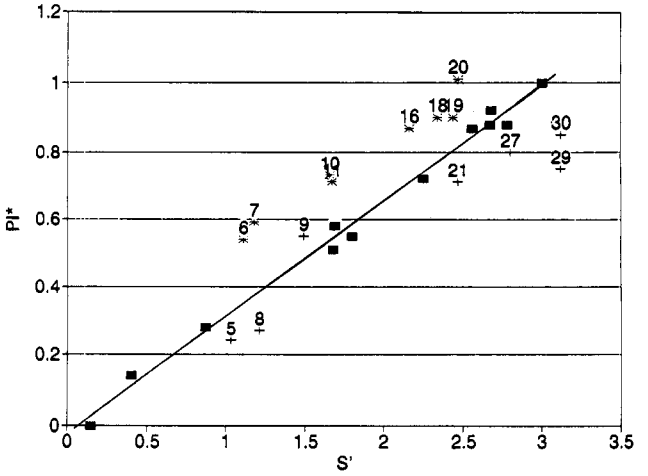


Figure 1. Comparison of the nonspecific solvation parameters S' and π^* for donor solvents. The numbering scheme corresponds to the numbers listed in Table I of ref 1. The asterisks refer to solvents that contain a π-system. The + symbols refer to weak donor solvents that are proposed to incompletely complex many of the β–π^* probe molecules.

The conclusion of incomplete complexation in the ECS′ analysis has profound implications on the β–π^* parameters. In this section, we shall assume incomplete complexation occurs in order to examine these implications. Incomplete complexation averages incorrect shift data mostly into the values of β. However, when the data for N,N-dialkyl derivatives are combined with the data for the NH_2, NHR, and OH systems to provide a best fit, π^* accommodates some of the error in the π^* parameters for weak donor solvents. Figure 1 illustrates the differences in the treatment of nonspecific solvation with eq 4 and 6. The numbering scheme corresponds to that in Table I and uses S' values determined from donor probes in donor solvents.[1] Those systems in which the probe molecule is thought to be incompletely complexed are indicated with a plus sign in Figure 1. In all instances, except for dioxane, the points fall below the line. The largest deviations occur for the most weakly basic solvents where the extent of complexation is least, i.e., CH_3CN and CH_3NO_2. Thus, in the β–π^* averaging procedures, incomplete complexation is being compensated for with a small π^* value. This permits a larger component of the shift to be fit by the β-parameter. Averaging aids in obtaining an excellent fit of the data at the cost of making the parameters less meaningful for interpreting specific (β) and nonspecific (π^*) contributions.

Solvents that contain an aromatic ring have been indicated with a star in Figure 1. The measured shifts of these solvents toward the aromatic nitroaniline probes used in the β–π^* data set have been shown[1] to have a contribution from charge-transfer complexation, i.e., a specific donor–acceptor interaction. Fitting this data to a π^* value attributes these specific interactions to nonspecific interactions. As seen in Figure 1, in every instance this leads to a π^* value that is too large when compared to S'.

The π^* values for the remaining systems, which are devoid of charge-transfer or incomplete complexation complications, fall on the line in Figure 1 and are in excellent agreement with the S' values. In order for CH_3NO_2 and CH_3CN to be consistent with π^*, their S' value would have to be 2.6 and 2.2, respectively. These S' values would lead to large errors in the fit of most of the nine donor probes used[1] to derive S'. In order to circumvent misses by these solvents in β–π^* analyses, these solvents are claimed[5c] to be hydrogen bonding toward certain probes. In the analysis with eq 4, these solvents are well-behaved donor solvents showing no tendency to hydrogen bond. Thus, not only are there differences in the magnitude of the parameters in the two approaches, but most importantly, there are differences in the interpretation of the chemistry that is taking place in these solvents and in other systems where the β–π^* parameters have been used on weak donors and π solutes for data interpretation.

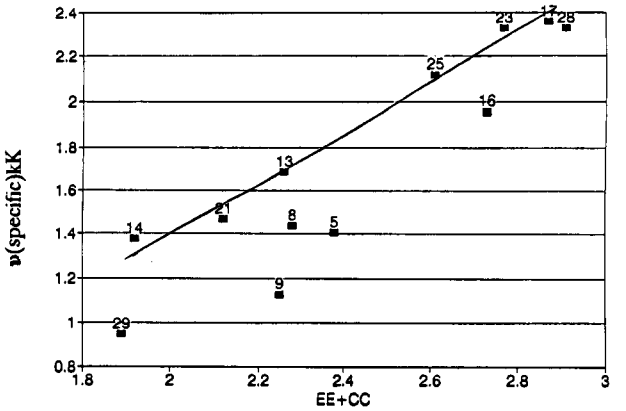


Figure 2. Plot of the specific donor–acceptor contribution to the shift in the electronic absorption spectrum of 3-nitroaniline calculated with β-parameters and E_B, C_B parameters.

In Figure 2, the specific interaction contribution to the shift of 3-nitroaniline, calculated with $E_A{}^*E_B + C_A{}^*C_B$, is plotted versus that calculated with $\beta_S\beta_P$. Again a good trend exists for those non-aromatic solvents in which the probe is fully complexed. Relative to E and C, the β parameters of CH_3CN, dioxane, diethylether, and di-n-butylether underestimate the specific donor acceptor interaction. Thus, incomplete complexation is being averaged over both β and π^* to fit the data. The $\beta_S\beta_P$ contribution to pyridine is below the trend line to compensate for the large π^* value that results from charge-transfer complexation of pyridine with π-probes. Thus, the good fit of the data set used to derive β and π^* is obtained at the expense of producing parameters that mask the subtle effects of incomplete complexation and charge-transfer interaction. The averaging distributes these effects in a complex way over both β and π^*. This analysis does not imply that the β–π^* parameters will not fit experimental data sets. For those systems that fall on the line in Figures 1 and 2, the same essential conclusions will result in β–π^* and ECS′ analyses. When weak donor solvents are employed on new systems that also are not fully complexed by the solvent, a better fit to β–π^* than to eq 4 could result. When π-solutes are studied in π-solvents, charge-transfer interactions can lead to a better fit of the data to β–π^* than to eq 4. However, the full understanding of these systems will be lost in the complacency of a good correlation.

In addition to differences in the estimates of specific and nonspecific solvation with the two approaches, differences exist in many instances in the interpretation of the chemistry. One example is the unsubstantiated labeling of acetonitrile and nitromethane as hydrogen-bonding acids[5] as discussed above. The π^* scale correlates poorly with the Dimroth–Reichardt, $E_T(30)$, scale,[18] and this has been attributed to differences in polarity and polarizability contributions to overall solvent effects. The E–C analysis attributes the differences in π^* values and the Dimroth–Reichardt parameters to averaging in incomplete complexation and charge-transfer effects in the former while they are much less important in the latter. In support of this conclusion, it is reported[5c] that elimination of aromatic

(18) Reichardt, C. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 29.

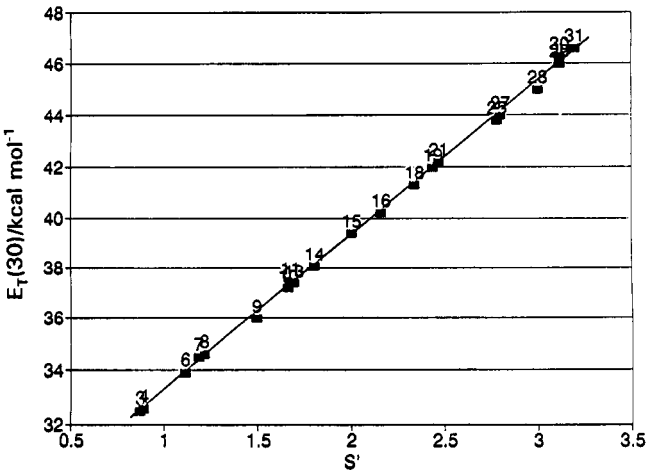


Figure 3. Comparison of the nonspecific solvation parameters, S', with Dimroth–Reichardt's $E_T(30)$ scale (kcal mol^{-1}).

solvents, chlorinated aliphatic solvents, CH_3NO_2, CH_3CN, and $(CH_3)_2CO$ lead to a good correlation of $E_T(30)$ and π^*. The excellent correlation of $E_T(30)$ and S' for all these systems, shown in Figure 3, suggests that the problems lie with π^*.

The β–π^* analysis attributes differences in the β parameters for N-alkyl-3-nitroaniline and 3-nitroaniline to the existence of 2:1 donor–acceptor adducts in the former.[5b,c] If some of the strong donor solvents formed 2:1 complexes with 3-nitroaniline and medium donor-strength solvents did not, the data would not fit E and C. With such a low K for the 1:1 adduct of dioxane and with the large size of *N,N*-dimethylacetamide, it is highly unlikely that any 2:1 adduct would form in these solvents. Furthermore, both the decrease in partial positive charge and probability considerations would lead to a very low K for a 2:1 adduct.

A very significant difference in ECS′ and β–π^* arises in those cases where correlations to β–π^* give rise to family-dependent properties, i.e., different linear plots for C=O, ether, amine, etc. families of compounds. The concept of families is foreign to the EC approach and was shown to occur with β–π^* when the property correlated had larger contributions from covalency than those used to derive the parameters.[19] This was subsequently recognized,[20,21] and an additional term was added to β–π^*. The analysis in this paper suggests this modification of β–π^* will only provide additional opportunity to average in effects not related to specific and nonspecific solvation. The enthalpy-based data set, which includes donors and acceptors of widely varying covalent and electrostatic bonding contributions, fixes the E_B and C_B values and prevents this from happening in E and C analyses. This is evidenced by the fact that the weak donor systems in this article cannot be averaged into E_A^* and C_A^* for the nitroaniline probes.

In conclusion, the β–π^* and the ECS′ approaches are very different. The wider range of donor–acceptor systems that are accurately correlated in the latter is its main advantage. A broad data base does not permit deviant systems to be averaged in, but identifies them as involving unusual effects. It is hoped that this analysis will stimulate further research to determine which of these two very different interpretations is correct. Is incomplete complexation an incorrect proposal or does the limited data set for β–π^* average in deviant systems introducing errors in the parameters? Using both approaches in data analyses may reveal patterns consistent with those reported here and provide more details about the subtle, important, interesting chemistry occurring in solution.

Registry No. *p*-$NO_2C_6H_4OH$, 100-02-7; *p*-$NO_2C_6H_4NH_2$, 100-01-6; *p*-$NO_2C_6H_4NHMe$, 100-15-2; *p*-$NO_2C_6H_4NHEt$, 3665-80-3; *m*-$NO_2C_6H_4NH_2$, 99-09-2; *m*-$NO_2C_6H_4NHEt$, 4319-19-1; 3,5-$(NO_2)_2C_6H_3NH_2$, 618-87-1.

(19) Doan, P. E.; Drago, R. S. *J. Am. Chem. Soc.* **1982**, *104*, 4524.
(20) Kamlet, M. J.; Gal, J. F.; Maria, P. C.; Taft, R. W. *J. Chem. Soc., Perkin Trans 2* **1985**, 1583.
(21) Maria, P. C.; Gal, J.-F.; de Franceschi, J.; Fargin, E. *J. Am. Chem. Soc.* **1987**, *109*, 483.

Rearrangements of Organosilicon Compounds Using Organoaluminum Reagents. Conversion of Phenyl- and Alkenyl(chloromethyl)silanes to Benzyl- and Allylsilanes

Paul F. Hudrlik,* Yousef M. Abdallah, Ashok K. Kulkarni, and Anne M. Hudrlik

Department of Chemistry, Howard University, Washington, D.C. 20059

Received June 16, 1992

Various (chloromethyl)silanes undergo Wagner–Meerwein-type rearrangements using a catalytic amount of $EtAlCl_2$ in dichloromethane. The resulting chlorosilanes have been converted to alkyl(or aryl)silanes with RMgX and/or to fluorosilanes with NH_4HF_2. In this way phenyl-, alkenyl-, and allyl(chloromethyl)silanes were converted to benzyl-, allyl-, and homoallylsilanes, respectively. Attempted rearrangements of methyl-, alkynyl-, and furyl(chloromethyl)silanes under these conditions were not successful.

In general, nucleophilic displacements at silicon in R_3SiX are considerably more facile than those at carbon in RX. We have therefore initiated a program to explore the possibility of making carbon–carbon bonds by first attaching two organic groups (which might be difficult to join by conventional methods) to silicon and forming the carbon–carbon bond in an intramolecular process. The silicon, having served as a template, could subsequently be removed, or used as a site for further useful reactions.

Rearrangements of α-substituted organosilicon com-

0022-3263/92/1957-6552$03.00/0