Linear Solvation Energy Relationships. Part 3.[1] Some Reinterpretations of Solvent Effects based on Correlations with Solvent π^* and α Values

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Solvent polarity and hydrogen bonding effects on a number of physical and chemical properties and reaction parameters are unravelled and rationalized by means of the solvatochromic comparison method and equations of the form $XYZ = XYZ_0 + s\pi^* + a\alpha$, where π^* is a measure of solvent polarity and α a measure of solvent hydrogen bond donor acidity. XYZ's considered include E_T values for eight electronic spectral transitions, two sets of nitrogen hyperfine splitting constants, a set of fluorescence lifetimes, logarithms of rate constants for four nucleophilic substitution reactions, and the ' electrophilicity parameter,' E, of Koppel and Palm.

In combination with the π^* scale of solvent polarities,[2,3] and sometimes with the β index of solvent HBA (hydrogen bond acceptor) basicities,[1,4,5] the α scale of solvent HBD (hydrogen bond donor) acidities[6,7] is intended to serve toward rationalization of solvent effects on many types of chemical and spectroscopic properties and reactivity parameters (XYZ's). In order to demonstrate the scope and versatility of these solvatochromic parameters, we wish now to report some reinterpretations of solvent effects on the basis of correlations with π^* and α.

Where solvent effects include contributions from type-A but not type-B hydrogen bonding[†] (as when the solute species are non-hydrogen bond donors), total solvatochromic equations can take either of two forms.[8] For $p \longrightarrow \pi^*$ and $\pi \longrightarrow \pi^*$ electronic spectral transitions of uncharged molecules with all solvents considered together, and for other XYZ's if families of solvents with similar polarizability characteristics[9] are considered separately (*e.g.* only non-chlorinated aliphatics, only polychlorinated aliphatics, or only aromatic solvents), the form of the linear solvation energy relationship is

$$XYZ = XYZ_0 + s\pi^* + a\alpha \ddagger \tag{1}$$

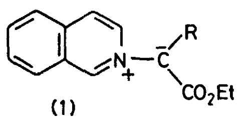
The s and a terms in equation (1) are measures of the responses of XYZ to changing solvent polarity and HBD acidity.

In formulating the α scale,[6,7] we used two versions of the solvatochromic comparison method to unravel solvent polarity and HBD acidity effects: (a) sequential single-parameter least-squares correlations with π^* and α, and (b) multiple linear-regression analysis (multiple-parameter least-squares correlations). It had been shown[1] that multiple linear-regression analysis leads to solvatochromic equations which are quite similar to those obtained by the statistically stricter sequential procedure. In the latter method, the XYZ values in non-hydrogen bonding solvents are first correlated with π^* to determine the XYZ_0 and s terms in equation (1), and the $\Delta\Delta XYZ$'s (the enhanced effects attributable to hydrogen bonding) in HBD solvents are then correlated with α to determine the a coefficient, with the r and SD measures of the goodness of statistical fit, meeting rigorous criteria of suitability in both steps.

Among the 15 XYZ's considered elsewhere[3,6,10] are Dimroth and Reichardt's $E_T(30)$ solvent polarity scale,[11] Brooker's χ_R scale,[12] Allerhand and Schleyer's G scale,[13] Brownstein's S scale,[14] Kosower's Z scale,[15] and Gutmann's ' acceptor number ' (AN) index.[16] We show that these scales, which were purported to be measures of solvent polarity (except AN, which was represented as a measure of Lewis acidity), are actually measures of combined solvent polarity and HBD acidity effects.

In order that we might use equation (1) with the more convenient method of multiple linear-regression analysis,[§] the solvatochromic comparisons in the present paper involve results in non-chlorinated aliphatic solvents only. Unless otherwise specified, all results in the cited references for which π^* and α values are known are included.

Intramolecular Charge-transfer Transitions in Isoquinolinium Ylides.—Dorohoi and his co-workers[17] have described solvent effects on transition energies of intramolecular charge-transfer bands of a series of isoquinolinium ylides. They observed poor to fair correlations with Kosower's Z scale of solvent polarities.[15]


(1)

a; R = CO_2Et
b; R = COPh
c; R = COMe

We have found that these workers' data in 11 aliphatic solvents for which the solvatochromic parameters are known (Table 1) are very well correlated by π^* and α. For the representative ylides (1a—c), for example, multiple linear-regression analysis gives the following:

$$E_T\,(1a) = 58.24 + 6.164\pi^* + 6.744\alpha, \quad r = 0.992, SD = 0.33; \tag{3}$$

$$E_T\,(1b) = 60.48 + 5.515\pi^* + 9.066\alpha, \quad r = 0.997, SD = 0.28; \tag{4}$$

$$E_T\,(1c) = 60.61 + 5.820\pi^* + 8.074\alpha, \quad r = 0.984, SD = 0.49. \tag{5}$$

[†] In type-A hydrogen bonding the solvent acts as HBD acid and the solute as HBA base. In type-B hydrogen bonding the roles are reversed.

[‡] When solvents from the three families are considered together in the case of the other XYZ's, an additional term needs to be added to equation (1) to give a more general total solvatochromic equation of the form,

$$XYZ = XYZ_0 + s'(\pi^* + d\delta) + a\alpha \tag{2}$$

where the d term is a measure of the polarizability susceptibility of XYZ, and the polarizability parameter, δ, is assigned a value of 0.0 for all non-chlorinated aliphatic solvents, 0.5 for polychlorinated aliphatics, and 1.0 for aromatic solvents.

[§] More data than are available in most of the cited references are required to ascertain the d term in equation (2).

If the datum for DMSO is excluded in the case of (1c), the r value becomes 0.995.

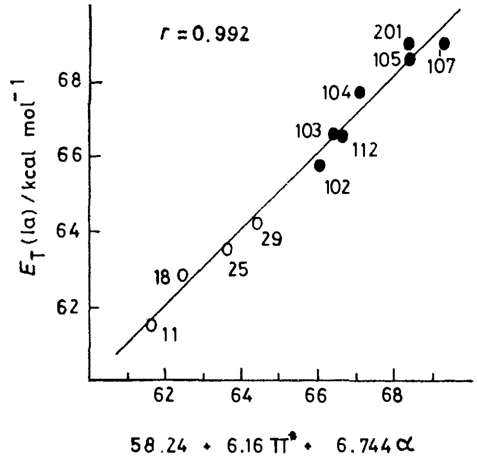


Figure 1 Observed *vs.* calculated transition energies for the ylide (1a); ● = HBD solvents and ○ = non-HBD solvents

It is seen that the coefficients of α (the a terms) increase with increasing ability of the R group to delocalize the negative charge, which suggests that ground-state hydrogen bonding by HBD solvents to (1a—c) is to the carbonyl and carboxy oxygens, rather than to the carbanion centre. The positive signs of the a terms (transition energies raised by type-A hydrogen bonding) suggest that the electronic transitions involve charge migration *from* these sites. A plot of observed *vs.* calculated E_T (1a) is shown in Figure 1.

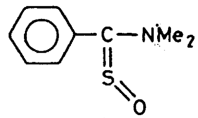
Table 1

Electronic spectral data correlated with π* and α

No.	Solvent	π*	α_{1-14} [b]	Transition energies (E_T/kcal mol^{-1}) (1a)	(1b)	(1c)	(2)	(3a)	(3b)	(4)	(5)
1	Hexane	−0.081	0.000							71.2	
2	Cyclohexane	0.000	0.000				79.9			71.0	116.3
3	Triethylamine	0.140	0.000				80.0			70.9	
7	Diethyl ether	0.273	0.000							69.9	116.3
9	Dioxan	0.553	0.000				80.8			68.9	
11	Ethyl acetate	0.545	0.000	61.5	63.5	63.2			72.5	68.8	
13	Tetrahydrofuran	0.576	0.000							68.5	
·18	Acetone	0.683	0.000	62.8	64.6	64.6	81.8	49.5	73.6	67.7	
25	Dimethylformamide	0.875	0.000	63.5	65.0	65.0	81.7				
26	Hexamethylphosphoramide	0.871	0.000							67.6	
29	Dimethyl sulphoxide	1.000	0.000	64.2	65.7	67.7	81.7	51.3	75.3		
32	Nitromethane	0.848	(0.126) [a]							66.7	
50	Acetonitrile	0.713	(0.270) [a]				82.4	51.0	74.9	66.9	119.7
101	2-Methylpropan-2-ol	0.534	0.401				84.3			67.5	
102	Propan-2-ol	0.505	0.695	65.7	69.7	69.7	84.8	55.1	75.9		
103	Butan-1-ol	0.503	0.762	66.5	70.2	69.7	84.7				121.9
112	Propan-1-ol	0.534	0.763	66.5	70.6	70.1					
104	Ethanol	0.540	0.826	67.7	70.6	70.6	85.1	57.2	77.1	66.6	122.2
105	Methanol	0.586	0.980	68.5	72.4	71.5	85.9	59.6	78.7	66.2	123.3
107	Ethylene glycol	0.932	0.796	68.9	72.8	72.4	86.0				123.8
111	Water	1.090	1.068				87.4	65.7	83.8	64.1	126.6
201	Formamide	1.118	(0.494) [a]	68.9	71.5	70.6	84.5			63.9	

[a] Secondary values. [b] Subscript indicates that 14 XYZ's were used to arrive at these α values; see ref. 10.

The ' S-Oxide ' Band of NN-*Dimethylthiobenzamide-* S-*Oxide.*—Solvent effects on an electronic transition which they characterize as the S-oxide band of (2) have been reported by Walter and Bauer.[18] They compared transition energies with Dimroth's $E_T(30)$ solvent polarity parameter[11] and found acceptable correlations only when the solvents were divided into families of hydrogen bond donors and non-hydrogen bond donors (r = 0.978 in both instances). Acetic acid fell out of line, probably because proton transfer rather than hydrogen bonding occurred in this solvent.



(2)

Sixteen of these workers' 36 data points (excluding acetic acid) are in solvents of known π* and α (Table 1), and multiple linear-regression analysis shows quite good correlation, the regression equation being as follows:

$$E_T\,(2) = 80.07 + 1.847\pi^* + 5.045\alpha,\quad r = 0.986,\ \mathrm{SD} = 0.41 \qquad (6)$$

If the single datum for t-butyl alcohol is excluded, the r value goes up to 0.995.

The large a/s ratio suggests that type-A hydrogen bonding is to the oxygen of (2) rather than to the amide nitrogen. The positive sign of a suggests hydrogen bond weakening in the electronic excited state. Hence, electron migration in the transition must be away from oxygen. The data are plotted (observed *vs.* calculated) in Figure 2.

4-*Cyanoformyl*-1-*methylpyridinium Oximate Charge-transfer Bands.*—Mackay and Poziomak[19] have addressed themselves to solvent effects on two charge-transfer bands (3a), (3b) in the spectrum of 4-cyanoformyl-1-methylpyridinium oximate (3). Their data in eight solvents are included in Table 1.

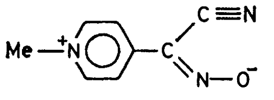
We have found that solvent effects on both bands show excellent correlations with π* and α. For the lower-energy band (3a), multiple linear-regression analysis gives,

$$E_T\,(3a) = 41.81 + 9.72\pi^* + 12.24\alpha, \quad r = 0.994,\ SD = 0.67 \quad (7)$$

and for the higher energy band (3b),

$$E_T\,(3b) = 67.53 + 8.28\pi^* + 6.42\alpha, \quad r = 0.996,\ SD = 0.40 \quad (8)$$

These results are of particular interest to us in that they provide a test of whether the relative magnitudes of the solvatochromic coefficients, *a* and *s*, can aid in band assignment.



(3)

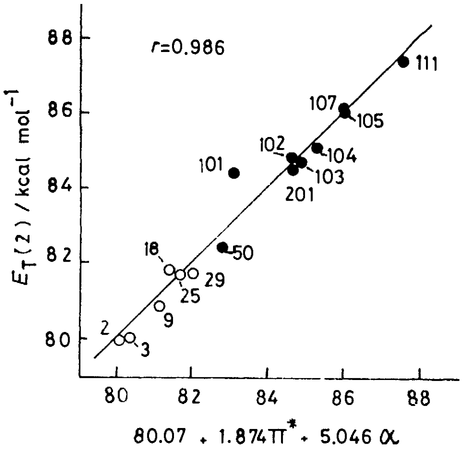


FIGURE 2 Observed *vs.* calculated transition energies for *NN*-dimethylthiobenzamide *S*-oxide; ● = HBD solvents and ○ = non-HBD solvents

Mackay and Poziomak have suggested that both bands derive from $p\rightarrow\pi^*$ transitions involving electron donation by an oxygen lone pair. Considering the most likely explanation for the two transitions to be that donation occurs from two different oxygen orbitals, they point out that ' there are three " nonbonding " electron pairs on oxygen, one pair in the 2*s* orbitals and two pairs in 2*p* orbitals (neglecting hybridization). The non-bonding *s* orbital (ns_0) is lowest in energy. One of the *p* orbitals lies in the plane of the molecule (np_0) while the other is perpendicular to the molecular plane ($np\pi_0$). The $np\pi_0$ orbital is largely localized on oxygen but does overlap with the π MO's of both the aldoximate C=N and the ring, and should thus be lower in energy than the np_0 orbitals. The two CT transitions may then be described as,

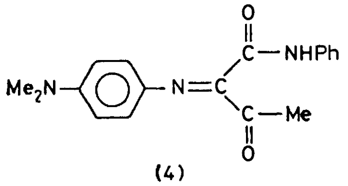
$$np_0 \xrightarrow{E(3a)} \mathrm{Py}\pi^*$$

and

$$np\pi_0 \xrightarrow{E(3b)} \mathrm{Py}\pi^*.'$$

We find that the solvent effects are completely consistent with this rationale. Ground-state type-A hydrogen bonding by HBD solvents to (3) would most likely be to the sterically more accessible non-delocalized np_0 orbital. Correspondingly, the transition involving this orbital, *E*(3a) should show the greater dependence on the solvent HBD acidity (the higher *a* value), as indeed it does.

The ' $n\rightarrow\pi^*$ *Band* ' *of* α-(p-*Dimethylaminoph-ylimino*)-*acetoacetanilide*.—Moskal and his co-workers[20] have discussed solvent effects on a band in the spectrum of (4) which they characterise as an $n\rightarrow\pi^*$ transition despite the fact that it exhibits a bathochromic shift with increasing solvent polarity (data in Table 1), and has an ε value of 10 000 (in hexane). They consider that such ' abnormal behaviour can be explained by assuming a super-donating character for the azomethine nitrogen atom.'



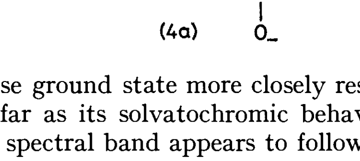
(4)

They found excellent correlation of $E_T(4)$ with the Dimroth $E_T(30)$ parameter[11] ($r = 0.994$). However, their attempts at multiple linear-regression analysis according to Krygowski and Fawcett's Lewis acid–base description of solvent effects[21] [wherein $E_T(30)$ is considered a measure of solvent Lewis acidity, and Gutmann's DN[22] a measure of Lewis basicity] led to significantly poorer correlation. They found the contribution to $E_T(4)$ from solvent acidity to be 96.5%, and that from solvent basicity to be 3.5%, with $r = 0.905$.

Our analysis leads us to somewhat different conclusions. We find the correlation equation with π^* and α to be,

$$E_T(4) = 71.3 - 4.911\pi^* - 2.715\alpha, \quad r = 0.988,\ SD = 0.35 \quad (9)$$

suggesting that most of the solvatochroism is due to solvent polarity rather than solvent acidity. The negative *a* term suggests stabilization of the electronic excited state relative to the ground state, and is consistent with hydrogen bonding to carbonyl or carboxamide oxygen, with the excited state more closely resembling canonical structure (4a), and the more charge diffuse ground state more closely resembling (4). Hence, insofar as its solvatochromic behaviour is concerned, this spectral band appears to follow the pattern



(4a)

of $p\rightarrow\pi^*$ transitions of uncharged molecules * discussed in our earlier papers.[2,6,23] Observed and calculated values of $E_T(4)$ are compared in Figure 3.

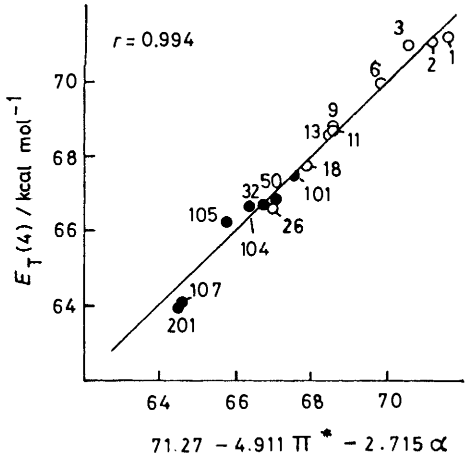
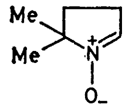


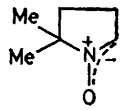
FIGURE 3 Observed *vs.* calculated transition energies for α-(*p*-dimethylaminophenylimino)acetoacetanilide; ● = HBD solvents and ○ = non-HBD solvents

5,5-Dimethylpyrroline 1-*Oxide Spectrum*.—Kaminsky and Lamchen [24] have measured the spectra of 5,5-dimethylpyrroline 1-oxide (5) in eight solvents for which π^* and α values are known, and report that hypsochromic shifts (in mμ) relative to cyclohexane are linear with Kosower's Z values.[15] We have found that, like Z, $E_T(5)$ shows excellent regression with a linear combination of π^* and α. The correlation equation is,

$$E_T(5) = 115.6 + 3.87\pi^* + 5.75\alpha, \quad r = 0.993, \text{ SD} = 0.42 \quad (10)$$

The positive signs of s and a in equation (10) are consistent with the charge on oxygen (the hydrogen bond acceptor site) being more localized in the ground state than in the electronic excited state. Our findings therefore conform with Kaminsky and Lamchen's description of the band as a $p\rightarrow\pi^*$ transition wherein the ground state resembles canonical structure (5a) and the excited state more closely resembles (5b).


(5a)


(5b)

Nitrogen Hyperfine Splitting Constants of Nitroxides.—Knauer and Napier [25] have suggested that solvent polarity scales fall into two classes: (*a*) those which involve no model reaction and which do not probe the solvent at the molecular level (in the cybotactic region) and (*b*) those which do involve a model reaction and do probe the solvent at the molecular level. As examples of the former class they cite dielectric constant, ε, and dipole moment, μ, and as examples of the latter class, Winstein and Grunwald's Y,[26] Z,[15] $E_T(30)$,[11] and Berson and Hamlet's Ω.[27] Nitrogen hyperfine splitting constants, A_N, they contend, fall into still a third category, since they involve no model reaction, but are, nevertheless, cybotactic probes [while it is not clear to us why Z and $E_T(30)$ should be regarded as involving a model reaction, while A_N for a specific indicator should not, we suppose that the π^* and α scales also fall into the third class].

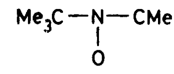
Since A_N values for specific indicators correlated poorly with ε and μ, but fairly well with $E_T(30)$, Z, and Ω, Knauer and Napier suggested that it is more important that a solvent polarity scale should be a cybotactic probe than that it should involve a model reaction.† They suggested also that A_N might serve as a useful solvent polarity parameter, especially in cases where values for the other parameters cannot be obtained because of solubility limitations, spectral interference, *etc.*

We have found, however, that, as with $E_T(30)$ and Z, A_N values for protic solvents are more measures of solvent HBD acidity than of solvent polarity. Thus, the total solvatochromic equation for the nitrogen hyperfine splitting constants (in G) of di-t-butyl nitroxide (6) in 17 aliphatic solvents (data in Table 2) is

$$A_N(6) = 15.034 + 0.715\pi^* + 0.916\alpha, \quad r = 0.963, \text{ SD} = 0.106 \quad (11)$$

and that for 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (7) is

$$A_N(7) = 15.177 + 0.631\pi^* + 0.789\alpha, \quad r = 0.971, \text{ SD} = 0.101 \quad (12)$$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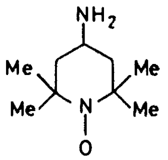
(7)

For reasons which we cannot now explain, but which probably relate to a specific solvent effect, the data points for water fall out of line on the high side in a consistent manner for all the nitroxides studied by Knauer and Napier. If these data are excluded, the correlation equations become

$$A_N(6) = 15.151 + 0.545\pi^* + 0.785\alpha, \quad r = 0.988, \text{ SD} = 0.054 \quad (13)$$

and

$$A_N(7) = 15.263 + 0.506\pi^* + 0.693\alpha, \quad r = 0.988, \text{ SD} = 0.052 \quad (14)$$

Observed $A_N(6)$ values are plotted against values calculated through equation (13) in Figure 4.

Reactions of Thiophen-2-sulphonyl Chloride with

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* Note that for $p\rightarrow\pi^*$ transitions of charged or zwitterionic molecules such as (1), (3), and (5), usually referred to as intramolecular charge-transfer bands, the converse effects of solvent polarity and type-A hydrogen bonding are observed, *i.e.* positive signs of both s and a.

† For our views on this subject see ref. 9.

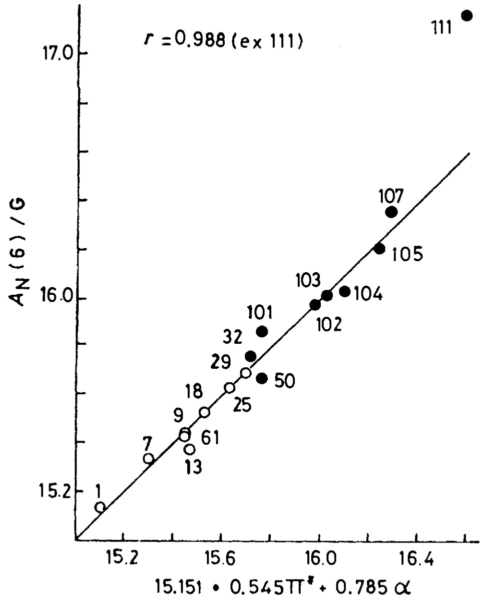


FIGURE 4 Observed *vs.* calculated nitrogen hyperfine splitting constants for di-t-butyl nitroxide; ● = HBD solvents and ○ = non-HBD solvents

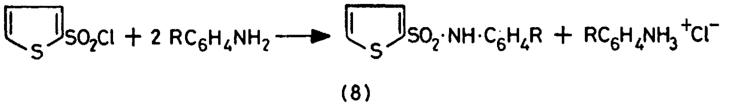
Anilines.—Arcoria and his co-workers[28] have studied solvent effects on the kinetics of the reactions of thiophen-2-sulphonyl chloride with a series of ring-substituted aniline derivatives. Attempts at multiple-parameter correlations of the log k values using the Palm–Koppel[29] or Krygowski–Fawcett[21] models were unsuccessful, but they did find sets of 'satisfactory' single-parameter corrections with ε, one for protic solvents with positive slope, another for aprotic solvents with negative slope.

TABLE 2

Physical and chemical properties correlated with π* and α

	Solvent [a]	A_N/G (6)	A_N/G (7)	3 + log k (8a)	3 + log k (8b)	3 + log k (8c)	3 + log k (9)	log τ (10)	log ε (11)	E
1	Hexane	15.134	15.219						0.80 [d]	
7	Ethyl ether	15.334	15.421							
9	Dioxan	15.452	15.539						1.46	
13	Tetrahydrofuran	15.373	15.465							
61	1,2-Dimethoxyethane [b]	15.424	15.525							
18	Acetone	15.527	15.621	−0.040	−0.585	−1.721		3.410	1.74	
25	Dimethylformamide	15.635	15.672					3.340	2.10	
29	Dimethyl sulphoxide	15.692	15.771				0.750		2.31	
32	Nitromethane	15.759	15.858							5.1
50	Acetonitrile	15.666	15.761	0.631	0.079	−1.071	−1.394	3.377	2.09	5.2
101	2-Methylpropan-2-ol	15.680	15.912				−1.388	3.093	2.48	5.2
102	Propan-2-ol	15.973	16.044	0.577	0.262	−0.563	−1.063	2.989	2.72	8.7
103	Butan-1-ol	16.018	16.038	0.722	0.198	−0.489	−0.964	2.888		10.3
112	Propan-1-ol			0.601	0.272	−0.432	−0.890	2.869		10.8
104	Ethanol	16.030	16.075	0.806	0.498	−0.276	−0.783	2.869	3.06	11.6
105	Methanol	16.210	16.199	1.130	0.750	−0.011	−0.457	2.735	3.32	14.9
107	Ethylene glycol	16.364	16.298				0.128	2.682		15.0
111	Water	17.175	16.990	3.088	2.851	2.130	0.886	2.072		21.8
210	Formamide							2.836		15.4
202	Acetic acid [c]									14.6

[a] π* and α values given in Table 1. [b] π* = (0.526). [c] π* = 0.664, α = (0.756). [d] Iso-octane.



(8)

a; R = p-Me
b; R = H
c; R = p-Cl

Using the data in the eight of their solvents which are aliphatic and whose solvatochromic parameters are known (Table 2) we have found correlations with π* and α to be excellent. For the representative reaction where R = p-Me,

$$\log k(8a) = -5.27 + 3.42\pi^* + 1.52\alpha, \quad r = 0.996, \ \mathrm{SD} = 0.09 \qquad (15)$$

for R = H,

$$\log k(8b) = -5.93 + 3.51\pi^* + 1.80\alpha, \quad r = 0.996, \ \mathrm{SD} = 0.10 \qquad (16)$$

and for R = p-Cl,

$$\log k(8c) = -6.96 + 3.29\pi^* + 2.30\alpha, \quad r = 0.995, \ \mathrm{SD} = 0.12 \qquad (17).$$

There appears to be an unmistakeable trend toward increasing coefficients of α (a values) with decreasing basicity of the aniline derivative. This can be rationalized in terms of a 'push–pull' mechanism where the lower the nucleophilicity of the attacking group, the greater is the importance of type-A hydrogen bonding (electrophilic assistance) to the leaving group. Equations (15)—(17) may also include minor rate-decelerating effects of type-A hydrogen bonding to the anilines, which should lessen their nucleophilicity, with the effect being greater the more basic the amine.

Benzylation of Aniline.—Acceleration of a nucleophilic substitution reaction by type-A hydrogen bonding is also seen in the kinetics of benzylation of aniline, as reported by Maccarone and co-workers.[30] Data in 10 aliphatic solvents are included in Table 2.

$$\mathrm{PhCH_2Cl + H_2NPh \xrightarrow[50\,^{\circ}C]{k(9)} PhCH_2\text{-}NHPh}$$

These workers noted a rather poor correlation of $k(9)$ (the second-order rate constant) with the Dimroth–Reichardt $E_T(30)$ parameter,[11] but found that the fit of the data improved somewhat in a multiple-parameter correlation with $E_T(30)$ and the $(\varepsilon - 1)/(2\varepsilon + 1)$ function. We have found that correlation is quite good in multiple linear-regression with π^* and α. The regression equation is

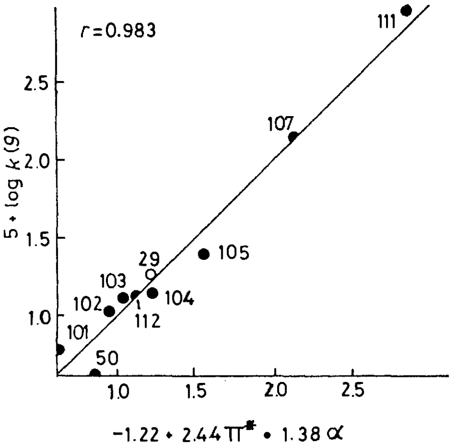


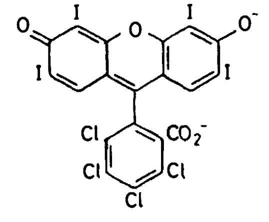
FIGURE 5 Observed *vs.* calculated rate constants for the benzylation of aniline; ● = HBD solvents and ○ = non-HBD solvents

$$\log k(9) = -6.52 + 2.44\pi^* + 1.38\alpha, \quad r = 0.983, \mathrm{SD} = 0.13 \quad (19).$$

As in the previous examples, the dependence on α is consistent with a 'push-pull' mechanism wherein hydrogen bonding by protic solvents provides 'electrophilic assistance' to the leaving halide. In a future paper on Menschutkin reactions we will report that type-A hydrogen bonding by protic solvents to the attacking trialkylamine nucleophile tends to slow down the reaction and offset the accelerating effect of hydrogen bonding to the leaving halide. That the accelerating effect in ROH solvents shows a relatively clean dependence on α in the present instance suggests that aniline is insufficiently basic for its nucleophilicity to be influenced markedly by hydrogen bonding. The same probably applies to the thiophensulphonyl chloride–aniline reactions discussed earlier.

Observed values of log $k(9)$ are plotted against calculated values in Figure 5.

Fluorescence Lifetimes of Rose Bengal Dye.—Cramer and Spears [31] have suggested that solvent dependent fluorescence lifetimes, τ_{fl} of Rose Bengal dye (10) may be effective measures of solvent hydrogen bond donor abilities. They report that log $\tau(10)$ values in a series of eight alcohols are linear with $\Delta_{\bar{\nu}}$ of the O–H vibrations from complexation of the same alcohols with pyridine in non-hydrogen bonding solvents



(10)

We have found that log $\tau(10)_{fl}$ values in picoseconds in 12 aliphatic solvents for which the solvatochromic parameters are known (data in Table 2) show good correlation with a combination of π^* and α. The multiple linear-regression equation is

$$\log \tau(10)_{fl} = 3.95 - 0.663\pi^* - 0.917\alpha, \quad r = 0.967, \mathrm{SD} = 0.094 \quad (19)$$

These data are plotted (observed *vs.* calculated) in Figure 6. Although the correlation coefficient here is lower than for our other correlations, we consider it quite acceptable in the light of the sensitivity of fluorescence lifetimes to minor amounts of impurities.

Absorption Intensity of the 400 *nm Band of* N-*Salicylidenebutylamine.*—Kazitsyna and Mischenko [32] have reported that, in going from iso-octane to more polar solvents, there appears in the spectrum of *N*-salicylidenebutylamine (11) a new band near 400 nm whose intensity increases with increasing solvent polarity (Table 2). In disagreement with earlier workers,[33] these Russian authors have discounted the possibility that a chemical change contributes to the appearance of this band. They consider instead that the increasing $\varepsilon_{\max.}$ is physical in nature and derives from an increase in the degree of allowance of a forbidden transition as a function of the character of the solvent.

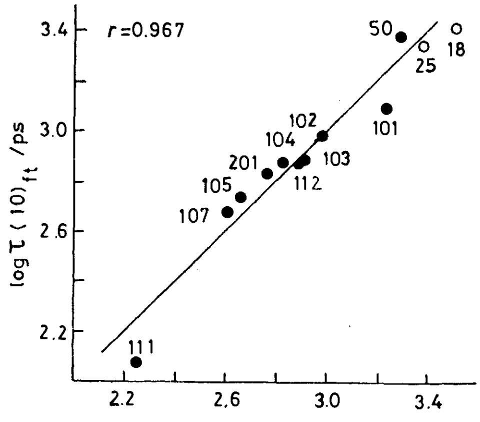
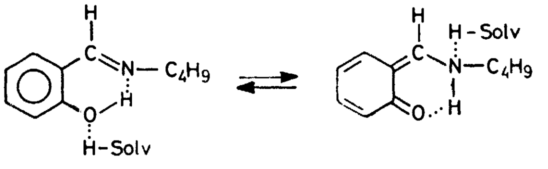


FIGURE 6 Observed *vs.* calculated fluorescence life-times for Rose Bengal dye; ● = HBD solvents and ○ = non-HBD solvents

There is an intrinsic inexactness in the $\varepsilon_{\max.}$ of this band due to overlap with the tail of a higher intensity band with a maximum near 300 nm. Nevertheless, $\varepsilon(11)_{\text{max.}}^{400\text{ nm}}$ seemed an interesting property which was completely different from the other XYZ's considered in these papers [6,10] and involved a question which could be addressed by the solvatochromic comparison method. We have, therefore, carried out a multiple-parameter least-squares correlation of log $\varepsilon(11)_{\text{max.}}^{400\text{ nm}}$ with π^* and α, and arrived at the regression equation,

$$\log \varepsilon(11) = 0.87 + 1.34\pi^* + 1.74\alpha, \quad r = 0.988, \text{ SD} = 0.12 \quad (20)$$

The a/s ratio of 1.3 in equation (20) seems strong evidence that, the conclusion of Kazitsyna and Mischenko notwithstanding, type-A hydrogen bonding markedly influences $\varepsilon(11)_{\text{max.}}^{400\text{ nm}}$.



(11a) (11b)

It is tempting to rationalize the appearance of the new band in (11) in terms of an equilibrium between (11a) and (11b), with the stronger type-A hydrogen bond in (11b) pulling the equilibrium in the direction of the quinoid structure. The Russian workers have also argued against the possibility of such an equilibrium on the basis of i.r. and n.m.r. studies, but the evidence in this regard may also be equivocal.

Koppel and Palm's E *Parameter*. Koppel and Palm [34,35] have proposed a multiple-parameter model which rationalizes solvent effects in terms of four properties of the medium:

$$XYZ = XYZ_0 + yY + pP + eE + bB \quad (21)$$

The Y term represents one or the other of the solvent 'polarity functions,' $(\varepsilon - 1)/(\varepsilon + 2)$ or $(\varepsilon - 1)/(2\varepsilon + 1)$; the P term corresponds to the 'polarizability function' $(n^2 - 1)/(n^2 + 2)$; the B parameter is a solvent nucleophilicity term, corresponding in intent to our β parameter,* and based on the $\Delta\nu_{\text{OD}}$ (relative to gas phase) of C_6H_5OD or CH_3OD in the solvent; and the E term is a solvent electrophilicity parameter, similar in intent to our α.

Koppel and Palm obtained their E values from Dimroth's $E_T(30)$ results [11] according to the equation,

$$E = E_T(30) - E_T^{\circ} - yY - pP \quad (22)$$

where $E_T^{\circ} = 25.10 \pm 1.06$, $y = 14.84 \pm 0.74$, and $p = 9.59 \pm 3.70$. The latter values were determined by least-squares correlation of $E_T(30)$ with Y and P for a special set of non-specifically solvating, not strongly dipolar, aprotic reference solvents. Using this scheme, they formulated a scale of E values which, for HBD solvents ranged from 5.1 for nitromethane, 5.2 for acetonitrile, and 5.2 for t-butyl alcohol to 14.9 for methanol, 15.0 for ethylene glycol, and 21.8 for water (Table 2). A seeming weakness in their treatment was that small but significant E values were assigned to a number of solvents for which it is difficult to rationalize HBD or Lewis acid type electrophilic properties, *e.g.* *N*-methylpyrrolidone, 1.3; dimethylformamide, 2.6; dioxan, 4.2.

We point out in other papers [6,10] that Dimroth's $E_T(30)$ values correlate quite well ($r = 0.987$) with a linear combination of the π^* and α parameters. It follows therefore that if our $(E_T^{\circ} + s\pi^*)$ quantities and Koppel and Palm's $(E_T^{\circ} + yY + pP)$ quantities account equally well for solvent polarity–polarizability effects, the E values for electrophilic solvents should be proportional to corresponding α parameters. E Values for HBD solvents are plotted against corresponding α's in Figure 7, where it is seen that the proportionality applies in only a very rough way, the r value of the linear regression equation being only 0.881.

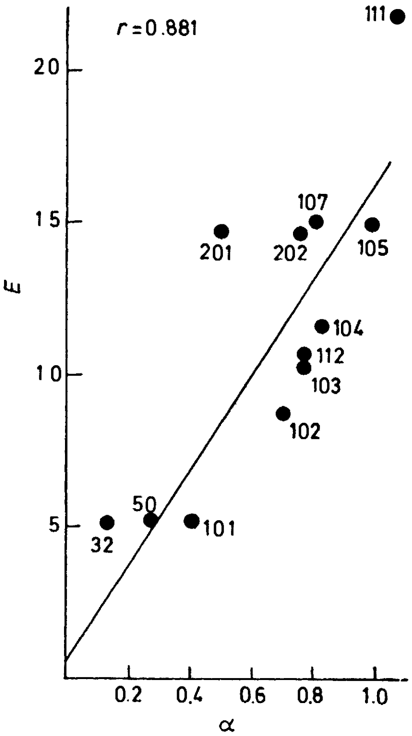


FIGURE 7 Koppel and Palm's E parameter plotted against solvent α values

In marked contrast, multiple-parameter correlation of E with π^* and α leads to quite a good statistical fit, with respectable $(E_0 + s\pi^*)/a\alpha$ ratios for all solvents indicating that there are still significant polarity–polarizability components included in the E terms. The correlation equation is

$$E = -7.15 + 12.20\pi^* + 14.97\alpha, \; n = 12, \quad r = 0.986, \text{ SD} = 0.87 \quad (23).$$

If the data point for acetic acid is excluded, the r value goes up to 0.996.

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* However, for reasons which we will discuss in a future paper, correlation between B and β is relatively poor unless confined to families of HBA bases with similar functional groups.

The Koppel–Palm E parameters for HBD solvents are plotted against a linear combination of π^* and α [from equation (23)] in Figure 8. On the basis of equation (23) we conclude not only that the E parameters do not correctly reflect the relative HBD acidities of the solvents, but also that the yY and pP terms do not adequately account for solvent polarity–polarizability effects.

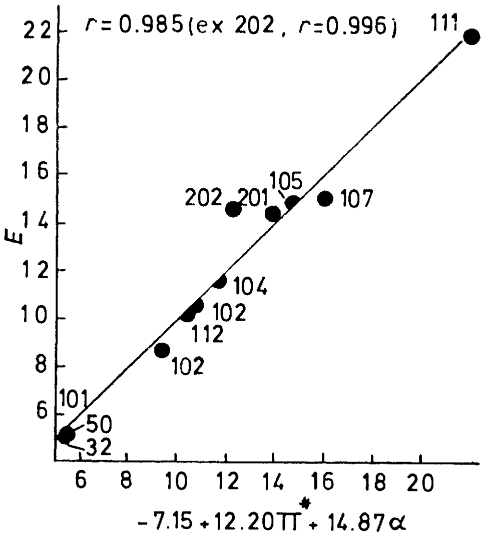

FIGURE 8 Koppel and Palm's E parameter as a combined function of α and π σ

[8/456 *Received*, 13*th March*, 1978]

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