(34) An explanation for the fact that the reaction channel leading to inverted product is low energy could be derived by considering the time required for the inversion process to occur. Since the inversion is a relatively slow process only low energy ^{38}Cl will remain long enough in the vicinity of the substrate molecule to react with the substrate after inversion has occurred.

(35) P. S. Fredericks and J. M. Tedder, *J. Chem. Soc.*, 3420 (1961).

(36) It has been postulated that the ^{38}Cl formed as a result of the breakup of the primary reaction products is immediately scavenged via H abstraction from one of the solvent molecules (self-scavenging). This argument was used in the past to exclude the presence of caged radical-radical recombination. More recently, however, the efficiency of this self-scavenging process has been seriously questioned[37] and it seems possible that the drastic increase in the retention/inversion ratio in the presence of Br_2 is due to highly efficient scavenging of the ^{38}Cl (in the cage) by Br_2. This being the case the experimental results would suggest that the primary ^{38}Cl attack is made almost entirely by a front-side approach.

(37) For a discussion of this question see, e.g., G. Stöcklin in "Hot Atom Chemistry Status Report", IAEA, Vienna, 1975, pp 161–181, and subsequent discussion section, pp 181–190.

The Solvatochromic Comparison Method. 6. The π^* Scale of Solvent Polarities[1]

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Abstract: Seventy solvents are arranged in a π^* scale of solvent polarities, so named because it derives from and best correlates solvatochromic effects on p → π^* and $\pi \rightarrow \pi^*$ electronic spectral transitions. Solvent effects on ν_{max} values of seven primary indicator compounds are employed in the initial construction of the π^* scale, and correlations with 40 additional spectral indicators are used to expand and refine the data base. Standard deviations in the 47 correlation equations of ν_{max} with solvent π^* values average 0.11 kK, which compares well with the 0.10 kK precision limit of the solvatochromic comparison method. A number of stratagems are employed to exclude or minimize hydrogen bonding effects in determining π^* values of HBA (hydrogen bond acceptor) and amphiprotic HBA-D (hydrogen bond acceptor-donor) solvents. Values of s in the solvatochromic equation, $\nu_{max} = \nu_0 + s\pi^*$, show logical variations with indicator structure, lending confidence that this new solvatochromic parameter will come to serve as a convenient and meaningful indicator of the interaction of a chromophore with its cybotactic environment. Poor correlation of ν_{max} values for Dimroth's betaine, 4-(2,4,6-triphenylpyridinium)-2,6-diphenylphenoxide with the π^* scale is rationalized in terms of differing polarity and polarizability contributions to overall solvent effects.

In earlier papers of this series,[3-5] information obtained through solvatochromic comparisons was used to construct an α scale of solvent HBD (hydrogen bond donor) acidities and a β scale of solvent HBA (hydrogen bond acceptor) basicities.[6] These were intended to serve, together with an index (or indexes) of solvent polarity-polarizabilities (SPP's), toward rationalization of solvent effects on many free energy related properties through a schematic equation of the form,

$$\mathrm{XYZ} = \mathrm{XYZ}_0 + a\alpha + b\beta + \mathrm{SPPE} \tag{1}$$

XYZ in eq 1 may represent a reaction rate or equilibrium constant, or a position or intensity of spectral absorption; a and b are measures of the susceptibility of XYZ to changing solvent HBD acidity and HBA basicity, respectively; and SPPE denotes the solvent polarity-polarizability effect. In the present paper we direct our attention to the SPPE term in eq 1.

Koppel and Palm[7] have dealt with the SPPE problem by incorporating separate polarity and polarizability terms in the multiple parameter equation with which they have correlated solvent effects on a variety of XYZ's,

$$\mathrm{XYZ} = \mathrm{XYZ}_0 + yY + pP + eE + bB \tag{2}$$

The E and B terms in eq 2 represent solvent electrophilicity and nucleophilicity (and correspond in intent to our α and β in eq 1);[8] the Y term represents one or the other of the solvent "polarity functions", $(\epsilon - 1)/(\epsilon + 2)$ or $(\epsilon - 1)/(2\epsilon + 1)$; and the P term corresponds to the "polarizability function", $(n^2 - 1)/(n^2 + 2)$. Equation 2 has had fair to excellent success in correlating large numbers of solvent dependent properties.

In this work we have used solvatochromic comparisons of UV-visible spectral data to assemble a π^* scale which evidently combines polarity and polarizability in such a manner as to give an index of single-valued SPP parameters. This π^* scale is so named because it derives from and best correlates solvatochromic effects on p → π^* and $\pi \rightarrow \pi^*$ electronic spectral transitions. However, certain applications of the π^* scale to other types of solvent effects will also be shown. When the π^* parameters are used to quantify SPP effects in eq 1, the equation becomes,

$$\mathrm{XYZ} = \mathrm{XYZ}_0 + s\pi^* + a\alpha + b\beta \tag{3}$$

with s representing the susceptibility of XYZ to changing SPP.

We prefer this alternative, *seemingly* more empirical approach to that of Koppel and Palm for a number of reasons: (a) One fewer parameter in eq 3 compared with eq 2 allows significant simplification of the correlations and easier testing of their statistical validity. (b) The $(n^2 - 1)/(n^2 + 2)$ and $(\epsilon - 1)/(2\epsilon + 1)$ terms are interrelated ground state properties of the bulk solvent, whereas we are more concerned with effects at the molecular level which occur in solute-organized cybotactic regions (i.e., within the solvation shells)[9,10] and derive from excited or transition state dipole-dipole and dipole-induced dipole interactions. (c) Fowler, Katritzky, and Rutherford,[11] in their extensive and well-reasoned parametric analysis of solvent effect correlations, found no combination of functions of ϵ and n with other parameters which adequately correlated more than a small proportion of the XYZ's considered.

In assembling the π^* scale, we were alerted by the admonitions of other researchers in the field to avoid certain of the pitfalls encountered by earlier workers who had reported solvent polarity scales on the basis of the solvatochromic behavior of indicator solutes. In this vein, for example, Figueras[12] had presented convincing evidence that "solvent polarity scales based on shifts in λ_{max} of an indicator dye are of limited value where hydrogen bond interactions are possible", and the analysis by Katritzky and co-workers[11] confirmed that Dimroth's $E_T(30)$ scale[13] shows major dependence on solvent hydrogen bonding power. In part 2 of this series,[4] we used the solvatochromic comparison method to assess the magnitudes of these hydrogen bonding contributions to the $E_T(30)$ scale, as well as to Brooker's χ_R scale,[14] and to Kosower's Z scale.[15]

Thusly forewarned, we took care to exclude hydrogen bonding interactions from the π^* scale by the following stratagems: (a) π^* values of solvents which were neither hydrogen bond acceptors nor donors (NHB solvents) presented no problem; since $\alpha = \beta = 0$, eq 3 (XYZ = $\nu_{\max}$) reduces to,

$$\nu_{\max} = \nu_0 + s\pi^* \tag{4}$$

(b) For π^* values of solvents which were hydrogen bond acceptors (HBA, $\beta \neq 0$), but not donors (non-HBD, $\alpha = 0$), we took care to limit ourselves to nonhydrogen bond donor indicator solutes ($b = 0$), in which case eq 3 again reduces to eq 4. (c) Amphiprotic solvents (HBA-D, α and $\beta \neq 0$) presented more of a problem in that to exclude hydrogen bonding required indicator solutes which were neither hydrogen bond acceptors nor donors ($a = b = 0$, eq 3 again reduces to eq 4). As will be mentioned, such non-HBA–non-HBD dyes, with sufficiently high s values (in eq 4) to make them useful as solvent polarity indicators, are somewhat more difficult to come by. Several were found, however, and used to ascertain the π^* values of water, the alcohols, and a few additional HBA-D solvents.

Forewarned also in this further regard by the experience of earlier workers, we have constructed the π^* scale on the basis of the averaged solvatochromic behavior of a large number of indicator solutes, rather than from spectral shifts for any single compound. In this manner, we believe that we have excluded *specific* solvent effects or spectral anomalies[16] such as may contribute to dioxane in Brooker's χ_R scale[14] seemingly having polarity like diethyl ether or CCl_4 (whereas in other polarity rankings, including our own, dioxane is more like ethyl acetate or tetrahydrofuran).

In this way we may also have avoided the more serious pitfall of choosing an indicator which responds to a different mix of polarity and polarizability terms than the types of properties which it is used to correlate. As we will discuss in detail, this appears to be the case when most spectral data are compared with Dimroth's widely used $E_T(30)$ scale,[13] based on the "solvatochromiebande" of the betaine, 4-(2,4,6-triphenylpyridinium)-2,6-diphenylphenoxide. For these reasons, our initial multiple least-squares correlations for parameter optimization involved seven primary indicators, and further correlations to refine the parameters and expand the data base involved spectra of an additional 40 indicator compounds.

Results

The first step in the construction of the π^* scale involved the selection of seven primary indicator solutes which satisfied the following requirements to the greatest practicable extent: (a) positions of maxima of symmetrical, reasonably intense bands for $p \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transitions should be in experimentally accessible regions of the spectrum, i.e., as far out in the visible as practicable, so that maxima are beyond the cutoff points of maximum number of solvents; (b) $\nu_{\max}$ values in non-HBD solvents (and in HBD solvents as well, if possible) should show linear regression with high correlation; (c) positions of $\nu_{\max}$ should be influenced minimally by band overlap with high intensity higher energy bands, by lower intensity underlying bands, or by changing band shape with solvent change;[16] and (d) $\nu_{\max}$ values should show adequate responses to changing solvent polarity (high s values in eq 4) so that combined uncertainties caused by experimental precision limits and spectral anomalies (band overlap, changing band shape) should have minimal influence on π^* values (e.g., for most spectral data we consider that combined uncertainties are rarely below 0.10 kK;[16] for these to lead to uncertainties below 0.05 in π_i^* values would require that $s \geqq 2.0$).

4-Nitroanisole (**1**), *N*,*N*-diethyl-3-nitroaniline (**2**), 4-methoxy-*β*-nitrostyrene (**3**), 1-ethyl-4-nitrobenzene (**4**), and *N*-methyl-2-nitro-*p*-toluidine (**5**) were chosen as primary indicators because, of many spectra considered, these appeared to be least influenced by type-A hydrogen bonding effects in HBD solvents,[17] while still showing an adequate response to changing solvent polarity [for **1** and **4** this involved compromising requirements a and c, and for **5** it involved compromising requirement d[18]]. *N*,*N*-Diethyl-4-nitroaniline (**6**) was selected because it had served in most of our earlier solvatochromic comparison studies,[1,3,4,9,19-21] and good spectral data in a large number of solvents were available. Finally, since **1–6** were all nitroaromatics,[22] 4-dimethylaminobenzophenone was included to ensure that we did not unwittingly incorporate into the π^* scale any solvent effects which were specific to the nitro group. In retrospect, we might properly have chosen a more representative variety of primary indicator types but, after reviewing all the correlations, we are satisfied that any other reasonable set of primary indicators would have led to very similar solvent π^* values to those reported here.

In accordance with requirement b, $\nu_{\max}$ values for **2–7** showed good linear regression with results in corresponding non-HBD solvents for **1**. The least-squares regression equations are:

$$\nu(\mathbf{2})_{\max} = 0.911\nu(\mathbf{1})_{\max} - 5.607 \text{ kK} \tag{5a}$$

with $n = 35$, r (the correlation coefficient) = 0.984, and SD (the standard deviation) = 0.11 kK;

$$\nu(\mathbf{3})_{\max} = 0.927\nu(\mathbf{1})_{\max} - 2.873 \text{ kK} \tag{5b}$$

with $n = 35$, $r = 0.988$, and SD = 0.10 kK;

$$\nu(\mathbf{4})_{\max} = 0.892\nu(\mathbf{1})_{\max} + 7.123 \text{ kK} \tag{5c}$$

with $n = 19$, $r = 0.985$, and SD = 0.11 kK;

$$\nu(\mathbf{5})_{\max} = 0.666\nu(\mathbf{1})_{\max} + 1.072 \text{ kK} \tag{5d}$$

with $n = 15$, $r = 0.996$, and SD = 0.05 kK;

$$\nu(\mathbf{6})_{\max} = 1.285\nu(\mathbf{1})_{\max} - 16.46 \text{ kK} \tag{5e}$$

with $n = 31$, $r = 0.993$, and SD = 0.11 kK; and

$$\nu(\mathbf{7})_{\max} = 0.0815\nu(\mathbf{1})_{\max} + 2.538 \text{ kK} \tag{5f}$$

with $n = 30$, $r = 0.982$, and SD = 0.13 kK.

Twenty-eight non-HBD solvents, in which spectral data for at least five of the seven primary indicator solutes were available, were next chosen as an initial solvent set, to be used with the primary indicator set in the round-robin parameter optimization program. This multiple least-squares program involved three iterations wherein multiple correlation equations were successively modified to achieve minimal least-squares deviations of all data points. Finally, best-fit $\Delta\nu_{\max}$ values were normalized and averaged to provide π^* values for the 28 solvents which were consistent with $\pi^* = 0.000$ for cyclohexane and $\pi^* = 1.000$ for dimethyl sulfoxide.

Correlation equations between π^* values and $\nu_{\max}$ values for the primary indicator solutes in the initial solvent set are given in Table II, where it is seen that this parameter optimization program has indeed resulted in significant improvements in r values and decreases in SD values compared with preliminary correlation eq 5a–f. It is also gratifying that the final SD values are in all cases no higher than probable combined

Table I. The π^* Scale of Solvent Polarities

No.[a]	Solvent	Type solvent[b]	π^{*c}	No.[a]	Solvent	Type solvent[b]	π^{*c}
1.	Hexane, heptane	NHB	−0.081	36.	Carbon disulfide		$[0.514]^2$
2.	Cyclohexane	NHB	0.000	37.	Benzonitrile	Ar-HBA	0.904
3.	Triethylamine	HBA	0.140	38.	Butyl acetate	HBA	0.460
4.	Diisopropyl ether	HBA	$(0.271)^4$	39.	Ethyl chloroacetate	HBA	0.704
5.	Di-*n*-butyl ether	HBA	0.239	40.	Tetrahydropyran	HBA	0.513
6.	Carbon tetrachloride	NHB	0.294	41.	Cyclohexanone	HBA	$(0.755)^4$
7.	Diethyl ether	HBA	0.273	42.	Tri-*n*-butyl phosphate	HBA	0.653
8.	Toluene	Ar-NHB-HBA[d]	0.535	43.	Tetrachloroethylene	NHB	0.277
9.	Dioxane	HBA	0.553	44.	1,1,2,2-Tetrachloroethane	NHB	0.948
10.	Trichloroethylene	NHB	0.534	45.	Ethyl sulfate	HBA	$(0.692)^3$
11.	Ethyl acetate	HBA	0.545	46.	Dibenzyl ether	Ar-HBA	$(0.800)^5$
12.	1,1,1-Trichloroethane	NHB	0.490	47.	Ethyl benzoate	Ar-HBA	0.739
13.	Tetrahydrofuran	HBA	0.576	48.	Tri-*n*-butylamine	HBA	0.162
14.	Benzene	Ar-NHB-HBA[d]	0.588	49.	Dimethylbenzylamine	Ar-HBA	0.494
15.	Chlorobenzene	Ar-NHB-HBA[d]	0.709	50.	Acetonitrile	HBA-HBD[e]	0.713
16.	2-Butanone	HBA	0.674	51.	Cyclopentanone	HBA	0.756
17.	Anisole	Ar-HBA	0.734	52.	Methyl acetate	HBA	$(0.503)^4$
18.	Acetone	HBA	0.683	53.	Mesitylene	Ar-NHB-HBA[d]	$(0.411)^5$
19.	Triethyl phosphate	HBA	0.715	54.	*n*-Butyl chloride	NHB	$[0.398]^1$
20.	1,2-Dichloroethane	NHB	0.807	55.	Methyl formate	HBA	$[0.561]^2$
21.	Methylene chloride	NHB	0.802	56.	Sulfolane	HBA	$(0.997)^3$
22.	1,1,2-Trichloroethane	NHB	0.829	57.	Dimethylaniline	Ar-HBA	$[0.902]^2$
23.	Dimethylacetamide	HBA	0.882	101.	2-Methyl-2-propanol	HBA-D	$(0.534)^4$
24.	Pyridine	Ar-HBA	0.867	102.	2-Propanol	HBA-D	$(0.505)^4$
25.	Dimethylformamide	HBA	0.875	103.	1-Butanol	HBA-D	$(0.503)^4$
26.	Hexamethylphosphoramide	HBA	0.871	104.	Ethanol	HBA-D	$(0.540)^4$
27.	Butyrolactone	HBA	0.873	105.	Methanol	HBA-D	$(0.586)^4$
28.	*N*-Methylpyrrolidone	HBA	0.921	106.	Phenylethanol	Ar-HBA-D	$[0.876]^2$
29.	Dimethyl sulfoxide	HBA	1.000	107.	Ethylene glycol	HBA-D	$(0.932)^4$
30.	Chloroform	NHB-HBD[e]	0.760	109.	Benzyl alcohol	Ar-HBA-D	$(0.984)^3$
31.	Nitrobenzene	Ar-HBA	$(1.029)^5$	111.	Water	HBA-D	$(1.090)^4$
32.	Nitromethane	HBA-HBD[e]	0.848	112.	1-Propanol	HBA-D	$(0.534)^3$
33.	Bromobenzene	Ar-NHB-HBA[d]	0.794	113.	Trifluoroethanol	HBD[f]	$(1.018)^4$
34.	Acetic anhydride	HBA	$(0.742)^4$	201.	Acetic acid	HBA-D	$(0.664)^3$
35.	*p*-Xylene	Ar-NHB-HBA[d]	0.426	202.	Formamide	HBA-D	$(1.118)^4$

[a] Solvent numbering is the same in all papers of this series. [b] NHB = non-hydrogen-bonding solvent; HBA = hydrogen bond acceptor; HBD = hydrogen bond donor; HBA-D = amphiprotic hydrogen bond acceptor–donor; Ar = aromatic solvents. [c] Values in parentheses are secondary values; may be used in correlations but still subject to revision. Values in brackets are tertiary values; not to be used in correlations until additional data allow promotion to secondary. Superscript numbers are number of π_i^* values averaged. [d] These aromatic solvents are usually weak hydrogen bond acceptors, but have also sometimes behaved as non-hydrogen-bonding solvents. [e] Usually act as non-hydrogen-bonding solvents, but have shown weak HBD properties with strong HBA indicator solutes. [f] Trifluoroethanol has shown no HBA properties, even with strong HBD indicator solutes.

uncertainties due to experimental precision limits and usual spectral anomalies.[16]

Solvent categories were then established as follows: (a) Initial *primary solvents* were those in which, as has been mentioned, spectral data were available for at least five primary indicator solutes; π^* values are considered to be satisfactory and not to be modified further unless warranted by the weight of additional evidence.[23] (b) *Secondary solvents* were those for which π^* values were based on spectral data for at least three indicator solutes; secondary π^* values may be used in correlations; secondary solvents may be promoted to primary when π_i^* values become available from spectral data for at least six well-behaved indicators. (c) *Tertiary solvents*, in which data for less than three indicators are available, are not to be used in correlations until promoted to secondary.

As the next step, the reciprocal equations of correlation eq 1-7 of Table II [i.e., $\pi_i^* = (\nu_{\max} - \nu_0)/s$] were used to calculate π_i^* values from $\nu_{\max}$ results where spectral data for the primary indicators were available in additional solvents. These were averaged to give 16 secondary solvent π^* values, as well as four tertiary π^* values.

Finally, the 44 primary and secondary π^* values determined from spectra of the seven primary indicators were used to correlate solvent effects on $p \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition maxima of 40 additional compounds, incorporating a wide variety of chromophore types. As before, the correlation equations, which are assembled in Table II, were employed, where appropriate, to determine additional π_i^* values, and these were used, in turn, to promote secondary to primary and tertiary to secondary π^* values. The final set of 44 primary, nine secondary, and four tertiary values, which comprises the π^* scale of solvent polarities, is assembled in Table I.

We have chosen a range of 0-1.0 for the π^* values of common solvents so that, taken with an α index of solvent HBD acidities and a β index of HBA basicities which have also been scaled to range from 0 to 1.0 for the same solvents, the a/s and b/s ratios in eq 3 become useful and convenient measures of the blends of polarity and hydrogen bonding contributions to solvent effects on the XYZ's. We will show in a future paper, for example, that b/s = 1.65 for 3-nitroaniline solvatochromism, as compared with 0.92 for 4-nitroaniline, serves as important evidence regarding the nature of the hybridization on the amine nitrogens of both compounds.

π^* Values of Amphiprotic Solvents. We have mentioned that it has been quite difficult to find light-absorbing compounds which show no solvatochromic effects of type-A hydrogen bonding in HBD solvents,[17] yet meet the requirements outlined above for spectral indicators of solvent polarity. This is because

Table II. Correlations of Electronic Spectral Data with the π^* Scale of Solvent Polarities: $\nu_{max} = \nu_0 + s\pi^*$

No.	Spectrum	ν_0, kK	$-s$	r	SD	n	Solvent types	Data ref
1.	4-Nitroanisole	34.17	2.410	0.994	0.079	27[a]	NHB, HBA	*b*
1a.		34.12	2.343	0.994	0.071	51	NHB, HBA, HBA-D	*b*
2.	*N,N*-Diethyl-3-nitroaniline	25.52	2.212	0.991	0.088	28[a]	NHB, HBA	*c*
2a.		25.52	2.214	0.992	0.076	60	NHB, HBA, HBA-D	*c*
3.	4-Methoxy-β-nitrostyrene	30.00	2.329	0.992	0.084	28[a]	NHB, HBA	*c*
3a.		29.96	2.250	0.986	0.101	56	NHB, HBA, HBA-D	*c*
4.	1-Ethyl-4-nitrobenzene	37.60	2.133	0.994	0.066	18[a]	NHB, HBA	*c*
4a.		37.67	2.259	0.990	0.090	32	NHB, HBA, HBA-D	*c*
5.	*N*-Methyl-2-nitro-*p*-toluidine	23.83	1.632	0.999	0.026	14[a]	NHB, HBA	*d*
6.	*N,N*-Diethyl-4-nitroaniline	27.52	3.182	0.994	0.099	28[a]	NHB, HBA	*b*
7.	*N,N*-Dimethyl-4-aminobenzophenone	30.41	2.013	0.986	0.101	27[a]	NHB, HBA	*c*
8.	4,4′-Bis(dimethylamino)benzophenone	29.96	2.094	0.984	0.113	14	NHB, HBA	*c*
9.	Ethyl 4-dimethylaminobenzoate	33.31	1.407	0.979	0.082	30	NHB, HBA	*c*
10.	*N,N*,3,5-Tetramethyl-4-nitroaniline	27.36	2.747	0.991	0.099	42	NHB, HBA	*c*
11.	*N,N*-Diethyl-3-methyl-4-nitroaniline	27.69	3.073	0.988	0.125	37	NHB, HBA	*h*
12.	4-Dimethylamino-β-nitrostyrene	25.25	3.354	0.990	0.131	16[f]	NHB, HBA	*e*
13.	*N,N*-Dimethyl-4-nitroaniline	28.10	3.436	0.988	0.150	33	NHB, HBA	*g*
14.	4-Nitroaniline	31.10	3.138	0.988	0.207	6	NHB	*b*
15.	3,5-Dimethyl-4-nitroaniline	28.68	1.813	0.988	0.104	11	NHB	*c*
16.	3-Methyl-4-nitroaniline	31.40	3.377	0.994	0.143	9	NHB	*h*
17a.	*N*-Methyl-4-nitroaniline	29.37	3.364	0.994	0.166	6	NHB	*h*
17b.	*N*-Ethyl-4-nitroaniline	29.17	3.327	0.995	0.148	6	NHB	*h*
17c.	*N*-Isopropyl-4-nitroaniline	28.96	3.237	0.995	0.138	6	NHB	*h*
18.	*N*-Ethyl-3-methyl-4-nitroaniline	29.35	3.341	0.994	0.131	10	NHB	*h*
19.	4-Dimethylaminobenzaldehyde	30.98	1.682	0.987	0.097	12	NHB, HBA	*i*
20.	Ethyl 4-aminobenzoate	36.85	1.261	0.989	0.074	8	NHB	*c*
21.	4-Aminobenzophenone	33.09	1.682	0.983	0.111	10	NHB	*c*
22.	*N,N*-Dimethyl-2-nitro-*p*-toluidine	24.81	2.070	0.993	0.081	15	NHB, HBA	*d*
23.	2-Nitro-*p*-toluidine	25.72	1.621	0.997	0.052	6	NHB	*d*
24.	Nile blue A oxazone	20.07	1.784	0.982	0.113	17	NHB, HBA	*j*
25.	Tolyldipropyl Nile blue base	20.19	1.508	0.992	0.072	11	NHB, HBA	*j*
26.	4-Nitro-4′-dimethylaminobiphenyl	26.63	2.860	0.987	0.166	10	NHB, HBA	*k*
27.	4-Nitro-4′-dimethylaminostilbene	24.31	2.131	0.988	0.121	10	NHB, HBA	*k*
28.	3-Nitroaniline	28.87	1.664	0.986	0.100	10	NHB	*c*
29.	*N*-Ethyl-3-nitroaniline	27.10	2.030	0.992	0.093	10	NHB	*c*
30.	3,5-Dinitroaniline	27.61	1.436	0.980	0.112	9	NHB	*c*
31.	*N,N*-Dimethyl-2-nitroaniline	25.30	2.023	0.988	0.097	16	NHB, HBA	*d*
32.	*N*-Methyl-2-nitroaniline	24.59	1.593	0.993	0.055	25	NHB, HBA, HBA-D	*n*
33.	2-Nitroaniline	26.55	1.536	0.992	0.079	6	NHB	*d*
34.	*N,N*-Dimethyl-2-nitro-*p*-anisidine	23.72	2.142	0.994	0.071	15	NHB, HBA	*d*
35.	2-Nitro-*p*-anisidine	24.33	1.596	0.988	0.094	6	NHB	*d*
36.	Brooker's merocyanine	17.74	2.780	0.978	0.180	30[m]	NHB, HBA	*l*
37.	Phenol blue	18.12	1.445	0.988	0.073	21	NHB, HBA	*o*
38.	Di(*tert*-butyl) phenol blue	18.54	1.281	0.954	0.126	11	NHB, HBA	*o*
39.	*p*-Nitrosodimethylaniline	25.39	1.852	0.976	0.120	13	NHB, HBA	*c*
40.	*N*-(4-Nitrophenyl)aziridine	32.11	2.510	0.980	0.124	15	NHB, HBA	*g*
41.	*N*-(4-Nitrophenyl)pyrrolidine	27.56	3.274	0.986	0.131	16	NHB, HBA	*g*
42.	*N*-(4-Nitrophenyl)piperidine	27.93	3.405	0.988	0.126	16	NHB, HBA	*g*
43.	2-(*p*-Dimethylaminophenylimino)-3-keto-2,3-dihydrothionaphthene	20.94	1.577	0.979	0.110	14	NHB, HBA	*p*
44.	2-(*p*-Dimethylaminobenzylidine)-3-keto-2,3-dihydrothionaphthene	21.59	1.198	0.964	0.116	14	NHB, HBA	*p*
45.	2-Nitroanisole	32.56	2.428	0.977	0.195	13	NHB, HBA, HBA-D	*i*

[a] Initial round-robin multiple least-squares correlation. [b] Reference 3. [c] Present investigation. [d] Reference 5. [e] D. J. Cowley, *J. Chem. Soc., Perkin Trans. 2,* 287 (1975). [f] Solvent 7 excluded. [g] M. J. Kamlet, R. R. Minesinger, E. G. Kayser, M. H. Aldridge, and J. W. Eastes, *J. Org. Chem.*, **36,** 3852 (1971). [h] Reference 1. [i] A. E. Lutskii, V. V. Bocharova, and M. R. Kreslavskaya, *Zh. Obshch. Khim.*, **45,** 2276 (1975). [j] M. M. Davis and H. B. Hetzer, *Anal. Chem.*, **38,** 451 (1966). [k] A. E. Lutskii, V. V. Bochareva, and Z. I. Kanevskaya, *Zh. Obshch. Khim.*, **45,** 2731 (1975). [l] Reference 14. [m] Solvent 9 excluded. [n] T. Yokoyama, *Aust. J. Chem.*, **29,** 1469 (1976). [o] Reference 12. [p] M. A. Mostaslavskii and V. A. Ismailskii, *Dokl. Akad. Nauk SSSR,* **142,** 600 (1962).

to have ν_{max} out sufficiently toward the visible and sufficiently sensitive to solvent polarity, so as to be practicably useful, usually requires that the chromophore system should include at its termini polar mesomeric p- or π-electron donor and/or π-electron acceptor substituents; such substituents in conjugated systems most often act as type-A hydrogen bond acceptor sites. Nevertheless, we believe that we have found at least four indicator compounds for which $b = 0$ and $a \approx 0$ in eq 3, and which may therefore serve us to establish π^* values for the amphiprotic, hydrogen bond acceptor-donor (HBA-D) solvents.

We consider that the spectrum of 4-nitroanisole (**1**) is little influenced by solvent HBD effects mainly for the reason that $\nu(\mathbf{1})_{max}$ values in the monohydric alkanols **101–105** and **112** all fall within the narrow range 32.79–32.94 kK (data in Table III). If all of the $\Delta\nu(\mathbf{1})_{max}$ between **101** and **105** were attributable to the solvent HBD acidity effect, since α values for the alkanols vary from 0.44 for 2-methyl-2-propanol (**101**) to 0.99

Table III. Observed and Calculated ν_{max} Values for 4-Nitroanisole (**1**), *N,N*-Diethyl-3-nitroaniline (**2**), 4-Methoxy-β-nitrostyrene (**3**), and 1-Ethyl-4-nitrobenzene (**4**) in Amphiprotic Solvents

			$\nu(2)_{max}$, kK			$\nu(3)_{max}$, kK			$\nu(4)_{max}$, kK		
No.	Solvent	$\nu(1)_{max}$	Obsd	Calcd eq 5a	Δ	Obsd	Calcd eq 5b	Δ	Obsd	Calcd eq 5c	Δ
101.	2-Methyl-2-propanol	32.94	24.45	24.39	0.06	28.66	28.82	−0.16	36.42	36.52	−0.10
102.	2-Propanol	32.94	24.45	24.39	0.06	27.70	28.82	−0.12	36.63	36.52	0.11
103.	1-Butanol	32.89	24.47	24.34	0.13	28.82	28.67	0.15	36.56	36.47	0.09
104.	Ethanol	32.89	24.30	24.34	−0.04	28.72	28.67	0.05	36.50	36.47	0.03
105.	Methanol	32.79	24.15	24.25	−0.10	28.64	28.60	0.04	36.42	36.39	0.03
106.	Phenylethanol	32.15	23.50	23.67	−0.17						
107.	Ethylene glycol	31.95	23.47	23.48	−0.01	27.80	27.87	−0.07	35.65	35.64	0.01
109.	Benzyl alcohol	31.75	23.47	23.30	0.17	27.62	27.68	−0.06			
111.	Water	31.55	23.20	23.12	0.08	27.70	27.48	0.22	35.02	35.29	−0.27
112.	1-Propanol	32.79	24.33	24.25	0.08	28.69	28.68	0.01	36.63	36.39	0.24
113.	Trifluoroethanol	31.75	23.17	23.30	−0.13	27.93	27.71	0.22	35.29	35.46	−0.19
201.	Acetic acid	32.63	24.07	24.10	−0.03				36.17	36.24	−0.07
202.	Formamide	31.65	23.01	23.21	−0.20	27.47	27.58	−0.11	35.09	35.37	−0.28
		Av deviation			±0.096			±0.112			±0.129
		Av absolute deviation			−0.008			0.023			−0.038

for methanol (**105**), it follows that the *a* value (in eq 3) would be no greater than 0.27 which, taken with *s* = 2.4 (Table II), would lead to a *maximum a/s* ratio of 0.11 for 4-nitroanisole solvatochromism.

Alternatively, if we attributed all of the 0.15 kK red shift to solvent polarity effects, taken with *s* = 2.4, it would lead to a $\Delta\pi^*$ range of 0.063 covering all the alkanols. In the light of $\Delta\pi^* = 0.034$ between di-*n*-butyl and diethyl ether, and $\Delta\pi^* = 0.085$ between butyl and ethyl acetate (Table I), it seems reasonable to ascribe a major proportion of the 0.15 kK to polarity effects, in which case *a/s* would be well below 0.11; $a/s \leq 0.04$ would lead to the hydrogen bonding effects in the strongest common HBD acids ($\alpha \approx 1.0$), being below the 0.10 kK precision limit of solvatochromic comparisons.[16] Thus, although we cannot rigorously exclude the possibility that type-A hydrogen bonding contributes to the solvatochromism of **1** in HBA-D solvents, it is a reasonable working hypothesis that $a(\mathbf{1}) \approx 0$.

N,N-Diethyl-3-nitroaniline (**2**), 4-methoxy-β-nitrostyrene (**3**), and 1-ethyl-4-nitrobenzene (**4**) are considered to be non-HBA indicator solutes in HBD solvents because, in their plots of ν_{max} vs. $\nu(\mathbf{1})_{max}$, amphiprotic solvent data points are collinear with non-HBD solvent data points. This is shown in Figure 1 and Table III, where experimental $\nu(\mathbf{2\text{-}4})_{max}$ results are compared with values calculated through correlation eq 5a-c. It is seen in Table III that the average deviations of the HBA-D data points from the correlation equations are about the same for all three indicators as the SD's of the non-HBD data points, and that the absolute average deviations reflect no bathochromic trends in the HBA-D solvents.

The π^* values for the amphiprotic solvents in Table I are averages of π_i^* terms obtained through correlation eq 1-4 of Table II. Since data were available for only four non-HBA indicators,[18] these still retain the status of *secondary* π^*'s. As is seen in Table II (series 1a-4a), *r* values and SD's for the regression equations of ν_{max} vs. π^* remain about the same with the expanded data sets as with the more limited data sets.

It remains to consider why the spectra of **1-4** are so little influenced by hydrogen bonding effects in HBA-D solvents. There are three possibilities: (a) **1-4** are non-hydrogen-bond acceptors; (b) **1-4** are hydrogen bond acceptors and hydrogen bonding occurs, but is so weak as to have no appreciable effect on the spectra; and (c) **1-4** are weak hydrogen bond acceptors, but hydrogen bonding does not occur; the amphiprotic solvents achieve greater stability by remaining associated with themselves (as cyclic dimers, trimers, or tetramers), rather than by disrupting this self-association to form a bond to solute.

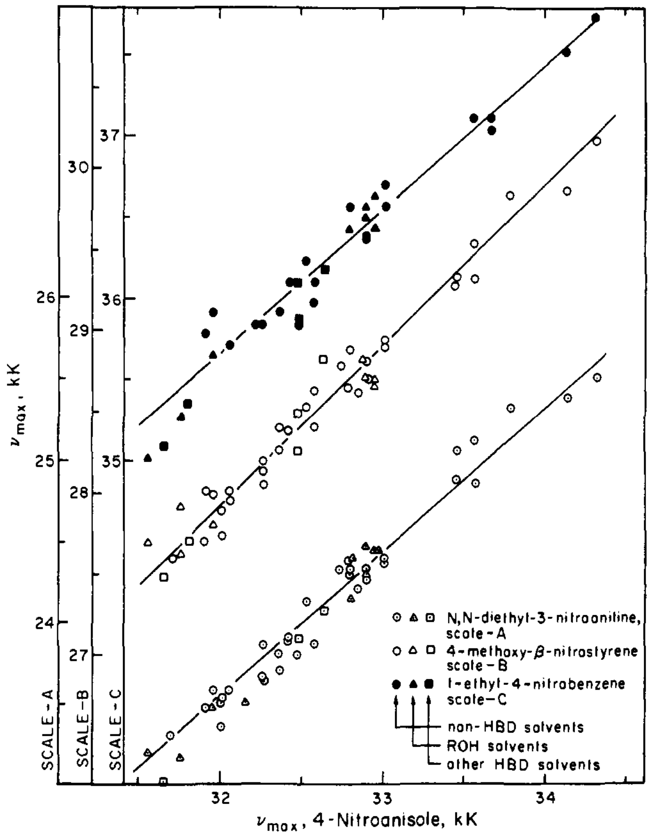


Figure 1. ν_{max} values for *N,N*-diethyl-3-nitroaniline (**2**), 4-methoxy-β-nitrostyrene (**3**), and 1-ethyl-4-nitrobenzene (**4**) plotted against results in corresponding solvents for 4-nitroanisole (**1**).

Taft and co-workers[25] have reported $pK_{HB} = 0.73$ for nitrobenzene; taken with $\Delta pK_{HB} = 0.20\text{-}0.27$ for the methoxy derivatives of benzaldehyde, acetophenone, and benzonitrile relative to the parent compounds, the pK_{HB} of **1** should be about 1.0. From the correlation equation between β and pK_{HB},[3] this corresponds to $\beta = 0.45$, making 4-nitroanisole about as strong an HBA base as methyl acetate. For this reason, and because a solvatochromic comparison study of F NMR results for *p*-fluoronitrobenzene[26] appeared to show moderate effects of hydrogen bonding by HBD solvents to the nitro oxygens (to be discussed in detail in a future paper), we consider that explanation a above can be ruled out.

Since a/s (in eq 3) is a measure of the susceptibility of XYZ to hydrogen bonding, we can evaluate the other possibilities in the light of $a/s = 0.19$ for solvent effects on the spectrum of N,N-diethyl-4-nitroaniline (indicator **6**; s value from Table II, a value calculated from $-\Delta\Delta\nu$'s in ref 19). Taken with pK_{HB}'s decreasing from 1.38 for p-dimethylaminobenzonitrile to 0.99 for p-methoxybenzonitrile to 0.79 for benzonitrile,[25] assuming that pK_{HB}'s decrease by comparable amounts for the correspondingly substituted nitrobenzenes, and assuming further that a/s ratios are strong functions of hydrogen bond acceptor strengths at the nitro termini of the chromophores, this indicates that explanation b is indeed a viable rationale. On balance, however, we prefer a combination of explanations b and c, with $a\alpha \approx 0$ for the stronger O-H HBD acid solvents a result of preferential self-association, and $a\alpha \approx 0$ for the weaker C-H HBD acid solvents deriving from relatively low a/s ratios in conjunction with low solvent α values. We will have occasion to discuss competition of R-O-H self-association with type-A bonding to indicators in greater detail in the next paper of this series.

The Correlations with π^*. The linear regression equations in Table II correlate solvatochromic shifts for the 47 indicator solutes in up to 60 solvents with solvent π^* values. In accord with the stratagems outlined above to exclude hydrogen bonding effects, 15 data sets included only NHB solvents, 26 data sets included NHB and HBA solvents, and six data sets included NHB, HBA, and HBA-D solvents. Of a total of 839 spectra, including 288 from the literature, two literature results (footnotes f and m of Table II) were excluded as probably being too strongly influenced by impurities or spectral anomalies.[16]

The average standard deviation for the 47 regression equations is 0.110 kK, which compares well with the 0.10 kK precision limit of the solvatochromic comparison method.[16] The average SD for the 33 nitro compounds in the table is 0.112 kK; this compares with SD = 0.106 for the 14 nonnitro compounds. It appears, therefore, that we have not unduly biased the π^* scale by our initial strong emphasis on nitroaromatic primary indicators. The average SD for the 27 spectral series determined at the Naval Surface Weapons Center is 0.116 kK; this compares with SD = 0.103 for 20 series of spectral results from the literature.[27]

Of the 47 correlation coefficients, r, 19 were above 0.99, 21 between 0.98 and 0.99, five between 0.97 and 0.98, and two between 0.95 and 0.97. The correlation coefficients seemed to be more strongly influenced by variations in the s terms than by the SD's (compare, for example, series 38 and 45).

Structural Effects. Nature of Auxichrome. The s terms in the correlation equations of Table II show reasonable trends with systematic variations in indicator structure; these lend confidence that this new s parameter may serve as a convenient and meaningful indicator of the interaction of a chromophore with its cybotactic environment.[10]

Thus, for example, it has long been known that spectral maxima for $[^+X{=}C(1) \rightarrow C(4){=}Y^-]$ electronic transitions are shifted to lower energies with increasing electron donor ability of X and electron acceptor ability of Y. As is shown in Table IVA for para complementary substituted nitrobenzene derivatives, such a progressive red shift in the ν_0 terms is accompanied by a progressive increase in the magnitudes of the s terms. Indeed, as can be seen in Figure 2, there appear to be reasonably good linear correlations of both ν_0 and s for p-$XC_6H_4NO_2$ with σ^+ of X. The correlation equations are

$$\nu_0 = 6.390\sigma^+ + 39.50 \text{ kK} \qquad (6)$$

with $n = 8$, $r = 0.992$, and SD = 0.65 kK, and

$$s = 1.021\sigma^+ - 1.685 \qquad (7)$$

with $n = 8$, $r = 0.994$, and SD = 0.09. We have used eq 6 and 7 to estimate a σ^+ value for the p-aziridinyl substituent; the value is included in Table IV.

Other workers, including Bagal[28] and Rao,[29] have reported correlations between ν_{max} values of para complementary substituted nitrobenzene derivatives and various of the σ substituent constants. However, Brownlee and Topsom[30] have pointed out that these correlations have limited scope and significance, and break down when electron withdrawing para substituents are included. Similar limitations are probably applicable to the correlation of s with σ^+ (eq 7).

Electron-Acceptor Terminus of Chromophore. The limited scope of ρ-σ relationships involving electronic spectral data is also evident from the results in Table IVB for chromophores containing the $(CH_3)_2N$- auxichrome at one terminus, and various electron-acceptor substituents, Y, at the other. Although the general trends of decreasing transition energy and increasing sensitivity to solvent polarity with increasing electron withdrawing ability of Y are readily seen (except for the -N=O substituent), we were unable to discern any satisfactory correlations of either s or ν_0 with any of the various σ sets.

In both the p-$XC_6H_4NO_2$ and p-$YC_6H_4N(CH_2)_3$ series, the trends are toward increasing s values with increasing quinoidal character of the electronic excited states. These trends probably reflect greater stabilization by more polar solvents of charge-concentrated excited states relative to charge-diffuse ground states.

Chromophore Length. The effects of increasing the lengths of chromophores on sensitivities of transition energies to solvent polarity are shown in Table IVC. Incorporation of a -CH=CH- or $-C_6H_4-$ moiety into a chromophore leads to more charge separation in the electronic excitation, a result being to shift transition maxima to lower energies. However, in contradistinction to the trends of increasing $-s$ with decreasing ν_0 in the earlier examples, the red shifts are here accompanied by *lowered* $-s$ values. The increased distances between centers of maximum and minimum electron density in the excited state molecules are evidently accompanied by charge delocalization from (or less charge concentration at) these centers in the electronic excitation. The net effects are to lessen both the energy of the transition and the dependence of that energy on solvent polarity.

The effects are not necessarily of parallel magnitudes, however. Comparing the $\Delta\nu_0$ and $-\Delta s$ values on going from N,N-dimethyl-4-nitroaniline (**13**) to 4-dimethylamino-4′-nitrobiphenyl (**26**) and 4-dimethylamino-β-nitrostyrene (**12**), the vinylene group causes the greater bathochromic shift, but the phenylene group causes the greater decrease in $-s$. How these effects relate to relative charge separation vs. charge delocalization in the electronic excited states requires further study.

Insulation of Chromophore from Solvent. The effects of N-alkylation and N,N-dialkylation of 4-nitroaniline (**14**) on ν_0 and s are relatively easily unraveled (Table IVD). On going from **14** to the N-methyl derivative (**17a**), and thence to the N,N-dimethyl derivative (**13**), we see progressive decreases in ν_0 and increases in $-s$; these trends reflect the $(CH_3)_2N- > CH_3NH- > H_2N-$ order of electron donor ability of these auxichromes.

On going from the N-methyl (**17a**) to the N-ethyl (**17b**) and N-isopropyl (**17c**) derivatives, and from N,N-dimethyl (**13**) to N,N-diethyl (**6**), we see further bathochromic displacements of ν_0, again reflecting the substituent electron donor orders: $(CH_3)_2CHNH- > CH_3CH_2NH- > CH_3NH-$ and $(CH_3CH_2)_2N- > (CH_3)_2N-$. Here, however, the effects of the ethyl and isopropyl groups relative to methyl are to *decrease* the s values. The rationale obviously involves a steric effect. By virtue of their greater steric requirements, these substituents serve both to increase the size of the solvent cavity

Table IV. Structural Effects on Solvatochromic Parameters

A. Electron Donor Ability of Auxichrome

No.	*p*-$XC_6H_4NO_2$, X =	σ^{+a}	ν_0, kK[g]	$-s$
13.	$(CH_3)_2N$-	−1.67	28.10	3.44
14.	H_2N-	−1.47	31.10	3.14
1.	CH_3O-	−0.79	34.17	2.41
4.	CH_3CH_2-	−0.31	37.60	2.13
b	F-	−0.08	38.89	1.70
c	H-	0.00	39.58	1.69
40.	CH_2CH_2N-	[−0.99 ± 0.17][d]	32.11	2.51

B. Electron Acceptor Terminus of Chromophore

No.	*p*-$YC_6H_4N(CH_3)_2$, Y =	ν_0, kK	$-s$
11.	$COOC_2H_5$	33.31	1.41
19.	CH=O	30.97	1.68
7.	COC_6H_5	30.41	2.01
13.	NO_2	28.10	3.44
39.	N=O	25.39	1.85

C. Chromophore Length

p-$RC_6H_4XNO_2$,

No.	R =	X =	ν_0, kK	$-s$
13.	$(CH_3)_2N$-	Direct bond	28.10	3.44
12.		-CH=CH-	25.25	3.35
26.		$-C_6H_4$-	26.63	2.86
27.		$-CH{=}CHC_6H_4$-	24.31	2.15
1.	CH_3O-	Direct bond	34.17	2.41
3.		-CH=CH-	30.00	2.33

D. Insulation of Chromophore by N-Alkylation

p-$RR'NC_6H_4NO_2$,

No.	R =	R′ =	ν_0, kK	$-s$
14.	H-	H-	31.10	3.14
17a.	H-	CH_3-	29.37	3.36
17b.	H-	CH_3CH_2-	29.17	3.33
17c.	H-	$(CH_3)_2CH$-	28.96	3.24
13.	CH_3-	CH_3-	28.10	3.44
6.	CH_3CH_2-	CH_3CH_2-	27.52	3.18

E. Ortho, Meta, Para

No.	$XC_6H_4NO_2$, X =	ν_0, kK	$-s$
6.	4-$(CH_3CH_2)_2N$-	27.52	3.18
2.	3-$(CH_3CH_2)_2N$-	25.52	2.21
31.	2-$(CH_3)_2N$-	25.30[e]	2.02[e]
17b.	4-CH_3CH_2NH-	29.17	3.33
29.	3-CH_3CH_2NH-	27.10	2.03
17a.	4-CH_3NH-	29.37	3.36
32.	2-CH_3NH-	24.59[f]	1.59
14.	4-H_2N-	31.10	3.14
28.	3-H_2N-	28.87	1.66
33.	2-H_2N-	26.55[f]	1.54
1.	4-CH_3O-	34.17	2.41
45.	2-CH_3O-	32.56	2.43

[a] J. Hine, "Structural Effects on Equilibria in Organic Chemistry", Wiley, New York, N.Y., 1975, p 72. [b] By correlation of results of W. M. Schubert, J. Robins, and J. L. Haun [*J. Am. Chem. Soc.*, **79**, 910 (1957)] for nitrobenzene (NB) with our results in corresponding solvents (including HBA-D solvents) for **4**. The correlation equation was $\nu(NB) = 0.811\nu(\mathbf{4}) + 9.09$ kK, $n = 8$, $r = 0.991$, SD = 0.10 kK. [c] By correlation of results of W. M. Schubert, H. Steadly, and J. M. Craven [*J. Am. Chem. Soc.*, **82**, 1353 (1960)] for *p*-fluoronitrobenzene (FNB) with earlier results for nitrobenzene. The correlation equation was $\nu(FNB) = 1.005\nu(NB) - 0.89$ kK, $n = 6$, $r = 0.995$, SD = 0.09 kK. [d] Average of values back-calculated through eq 6 and 7. [e] Includes effects of steric inhibition of resonance. [f] Includes effects of intramolecular amine → nitro hydrogen bonding. [g] 1 kK = 2.86 kcal transition energy.

and to interpose themselves between the chromophore and solvent molecules; both effects should reduce the interactions of the chromophore with its cybotactic environment. In comparing **17a** or **13** with **14**, the greater electron donor ability overcomes the steric effect, and the net result is to increase the $-s$ term in accordance with eq 7; in going from methyl to

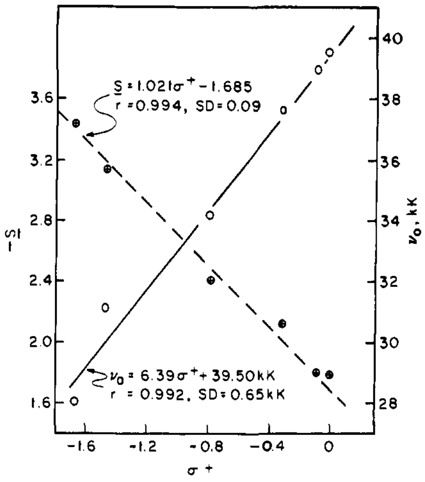


Figure 2. Solvatochromic parameters for p-$XC_6H_4NO_2$ plotted against σ^+ of X.

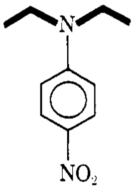
Table V. Effects of Steric Inhibition of Resonance on Solvatochromic Parameters

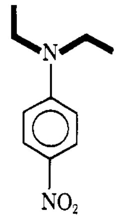
No.	Aniline derivative	ν_0, kK	Steric $\Delta\nu_0$, kK[a]	$-s$
14.	4-Nitro-	31.10		3.14
16.	3-Methyl-4-nitro-	31.40	0.3	3.38
15.	3,5-Dimethyl-4-nitro-	28.68	−2.4	1.81
6.	*N,N*-Diethyl-4-nitro-	27.52		3.18
11.	*N,N*-Diethyl-3-methyl-4-nitro-	27.69	0.2	3.07
13.	*N,N*-Dimethyl-4-nitro-	28.10		3.44
10.	*N,N*,3,5-tetramethyl-4-nitro-	27.36	−0.7	2.74
33.	2-Nitro-	26.55		1.54
32.	*N*-Methyl-2-nitro-	24.59		1.59
31.	*N,N*-Dimethyl-2-nitro-	25.30	1.5[b]	2.02

[a] Spectral shift attributable to steric inhibition of resonance. [b] See text.

higher alkyl, however, the increase in para donor ability is smaller, and the steric effect dominates.

It is also of some interest that, in comparing *N*-(4-nitrophenyl)pyrrolidine and piperidine (**41** and **42** of Table II) with the dimethyl and diethyl derivatives (**6** and **13**), the increasing bulk of the N-substituents leads to much smaller decreases in $-s$. This may be because **41** and **42** exclude conformations like **6a–b**, which more effectively shield the chromophore from the solvent. A steric effect quite similar to that discussed above is seen on ring alkylation of phenol blue (examples **37** and **38** of Table II).


6a


6b

1,2-, 1,3-, and 1,4-Aminonitrobenzenes. In comparing the solvatochromic parameters for the aminonitrobenzenes and their *N*-alkyl and *N,N*-dialkyl derivatives (Table IVE), it is seen that in all instances the progressions of decreasing ν_0 and decreasing $-s$ are in the order: para > meta > ortho. We are tempted to take these regular progressions, with meta values intermediate between those for ortho and para, as evidence supporting Murrell's contention[31] that the 3-nitroaniline band in the 350–400-nm region arises from an electronic transition similar in nature to those leading to the lowest energy bands of 2- and 4-nitroaniline (as contrasted with the view that meta must be different because we cannot write quinoidal resonance structures, as with ortho and para).[32]

The progressions in Table IVE are not completely unambiguous, however, because, in comparing 2- and 4-nitroanisole, we see the lower ν_0 value for the ortho derivative, but not the lower $-s$. This raises the question of whether, in the absence of internal amine → nitro hydrogen bonding as with **32** and **33**, or steric inhibition of resonance as with **31**, the ortho-meta-para progression would prevail for the aminonitro compounds. Since an *o*-nitroaniline derivative which is neither internally hydrogen bonded nor suffers steric inhibition of resonance is almost necessarily hypothetical, we see no easy way of resolving this question.

Steric Inhibition of Resonance. Compounds of Table II which suffer steric inhibition of resonance to a greater or lesser extent are the *N,N*-dimethyl-2-nitroaniline derivatives (**22, 31, 34**), 3-methyl- and 3,5-dimethyl-4-nitroaniline (**16, 15**), *N,N*-diethyl-3-methyl-4-nitroaniline (**11**), and *N,N*,3,5-tetramethyl-4-nitroaniline (**10**). In all of the above instances, the effects of twisting one or both of the terminal substituents of the chromophore from planarity are to decrease absorption intensities. Representative extinction coefficients for sterically hindered nitroanilines and planar reference compounds, and angles of twist of the nitro groups from planarity, calculated from the $\cos^2\theta = \epsilon/\epsilon_0$ relationship,[33] are:

$$\epsilon(\mathbf{31})/\epsilon(\mathbf{33}) = 2950/5250,^{34}\ \theta = 41°^{35}$$

$$\epsilon(\mathbf{16})/\epsilon(\mathbf{14}) = 13\,200/15\,500,^{36}\ \theta = 23°$$

and

$$\epsilon(\mathbf{15})/\epsilon(\mathbf{14}) = 4840/15\,500,^{36}\ \theta = 56°$$

Values of ν_0 and s for some sterically hindered indicators and reference compounds are assembled in Table V, where it is seen that, in contradistinction to their predictable behavior regarding ϵ_{max} values, there appear to be no consistent trends in the solvatochromic parameters. Before discussing these, however, we must first unravel steric from other effects, as follows.

On going from 2-nitroaniline (**33**) to *N*-methyl-2-nitroaniline (**32**), both of which are planar and intramolecularly hydrogen bonded, the electronic effect of N-methylation is to shift ν_0 bathochromically by 1.96 kK; on going from **32** to *N,N*-dimethyl-2-nitroaniline (**31**), the effect of introducing the second methyl group is hypsochromic by 0.71 kK. Assuming a slightly smaller bathochromic electronic effect for the second methyl group than for the first (as is the case with the 4-nitroaniline derivatives),[37] the joint effect of steric inhibition of resonance and exclusion of the intramolecular hydrogen bond is hypsochromic by about 2.5 kK. Estimating a ca. 1.0 kK bathochromic effect for the internal hydrogen bond (about like the $-\Delta\Delta\nu$ resulting from an external hydrogen bond by **33** to one of the stronger HBA bases),[5] we arrive at a residual value of ~1.5 kK as the hypsochromic effect, which we can attribute to twisting the dimethylamino and nitro substituents of **31** from planarity by combined angles of about 40°.[34]

The effect of twisting the nitro group in the 1,4-aminonitrobenzene chromophore by small angles is also slightly hypsochromic [e.g., $\Delta\nu_0(\mathbf{14} \rightarrow \mathbf{16}) = 0.30$ kK; $\Delta\nu_0(\mathbf{6} \rightarrow \mathbf{11}) = 0.17$ kK], but larger angles of twist lead to moderate to very large *bathochromic* effects [e.g., $\Delta\nu_0(\mathbf{13} \rightarrow \mathbf{10}) = -0.74$ kK; $\Delta\nu_0(\mathbf{14} \rightarrow \mathbf{15}) = -2.42$ kK]. The spectral shifts on displacing the nitro group in the above instances parallel those described by

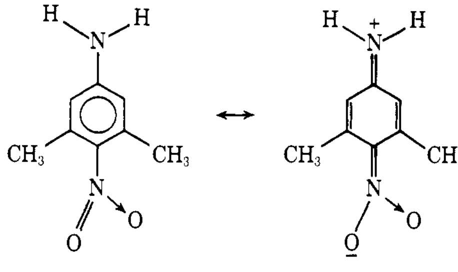
Murrell[38] when either substituent in *N,N*-dimethyl-4-nitroaniline is twisted from planarity, i.e., small θ's leading to hypsochromic displacements, larger θ's to bathochromic displacements.

Although the reasons for the dramatic reversals from hypsochromic to bathochromic displacements, as the angles of twist in the 4-nitroaniline series increase are not yet completely understood,[36,38] they do help to explain the effects of steric inhibition of resonance on the s values. It may be seen in Table V that the relative s values vary systematically with the $\Delta\nu_0$(steric) terms as follows: (a) minor changes in s accompany small $\Delta\nu_0$'s [e.g., **6** → **11**, $\Delta\nu_0$(steric) = 0.2 kK, $s/s_0 = 0.96$; **14** → **16** $\Delta\nu_0$(steric) = 0.3 kK, $s/s_0 = 1.08$]; (b) an increase in $-s$ accompanies a larger hypsochromic effect [**32** → **31**, $\Delta\nu_0$(steric) = 1.5 kK, $s/s_0 = 1.27$]; and (c) decreases in $-s$ accompany bathochromic steric effects [**13** → **10**, $\Delta\nu_0$(steric) = −0.7 kK, $s/s_0 = 0.80$; **14** → **15**, $\Delta\nu_0$(steric) = −2.4 kK, $s/s_0 = 0.54$]. Indeed, although we would hesitate to attribute too much significance to this in the light of the approximations involved, there appears to be a good linear relationship between the $\Delta\nu_0$(steric) and s/s_0 quantities,

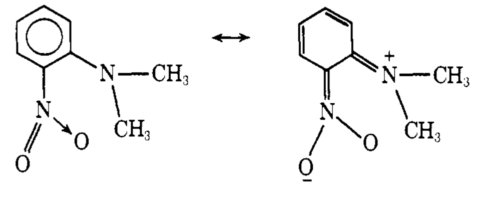
$$s/s_0 = 0.19\Delta\nu_0 + 0.97 \qquad (8)$$

$n = 5$, $r = 0.988$, SD = 0.05.

We rationalize these results in terms of changing angles of noncoplanarity with changing solvent polarity. The angles of twist in **15** and **31** are determined by competing influences. Atom to atom repulsions favor noncoplanarity; resonance effects (**15** ↔ **15a**, **31** ↔ **31a**) favor planarity. To whatever extent more polar solvents stabilize the charge-separated quinoid resonance structures **15a** and **31a** as ground-state contributors, increasing solvent polarity should lead to decreasing angles of twist (and does).[39]



15 **15a**



31 **31a**

A decreasing angle of twist with increasing solvent polarity is a bathochromic influence with **31** (reducing a hypsochromic effect of noncoplanarity) and a hypsochromic influence with **15** (reducing a bathochromic effect of noncoplanarity). Adding these effects to the normal bathochromic trends with increasing solvent polarity, the increase in $-s$ from **33** to **31** is attributed to increased coplanarity reinforcing the normal solvatochromic effect; the decreases in $-s$ from **14** to **15** and from **13** to **10** are attributed to increased coplanarity opposing normal solvatochromic effects. The self-consistent way in which the $\Delta\nu$(steric) and s terms go hand in hand reinforces our conviction that the new s parameter will come to serve as a convenient and meaningful indicator of the interaction of a chromophore with its cybotactic environment.

Dimroth's Betaine. In marked contrast to the very good linear regressions of the ν_{max} positions of indicators **1–45** with solvent π^* values, a solvatochromic comparison of spectral data for Dimroth's betaine, 4-(2,4,6-triphenylpyridinium)-2,6-diphenylphenoxide (**46**), with the π^* scale shows relatively much poorer correlation. Taking the data in all 32 non-HBD solvents for which $\nu(\mathbf{46})_{max}$ and solvent π^* values are available,[13,40] a plot (Figure 3) shows considerable scatter. The linear regression equation is,

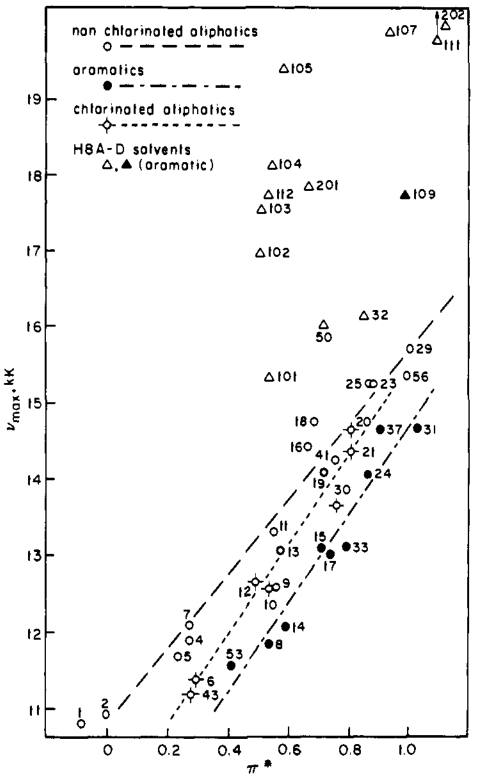
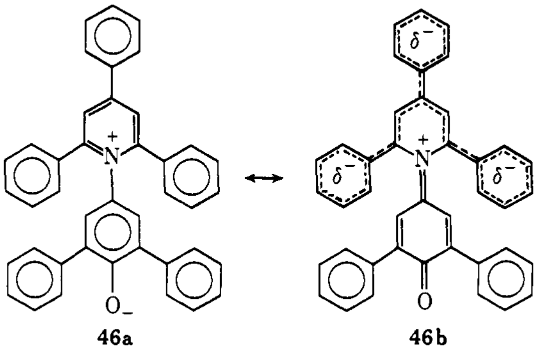


Figure 3. Solvatochromic comparison of ν_{max} values for Dimroth's betaine with solvent π^* values.

$$\nu(\mathbf{46})_{max}{}^{\text{all non-HBD's}} = 4.652\pi^* + 10.42 \text{ kK} \qquad (9)$$

with $r = 0.905$ and SD = 0.63 kK. In view of the fact that Dimroth's $E_T(30)$ scale, based on solvatochromic shifts for **46**,



46a **46b**

has been the most frequently cited index of solvent polarity for over 13 years, the much less satisfactory correlation in this instance cannot be lightly dismissed.[41]

For this reason, we have subjected the data for **46** to somewhat more detailed analysis, and found that the correlations improve significantly when we restrict the solvatochromic comparisons to solvent sets which have common structural features. thus, for example, if the aromatic solvents are excluded, the regression equation for the aliphatic solvents becomes,

$$\nu(\mathbf{46})_{max}{}^{\text{aliphatics}} = 5.001\pi^* + 10.50 \text{ kK} \qquad (10)$$

Table VI

For indicators	Increased solvent	Stabilizes the electronic	Relative to the electronic
1–45	Polarity	Excited state	Ground state
	Polarizability	Excited state	Ground state
46	Polarity	Ground state	Excited state
	Polarizability	Excited state	Ground state

with $n = 23, r = 0.957$, and SD = 0.46 kK. For the aromatic solvents, taken alone, the regression equation is,

$$\nu(\mathbf{46})_{\max}{}^{\text{aromatics}} = 5.820\pi^* + 8.88 \text{ kK} \qquad (11)$$

with $n = 9, r = 0.967$, and SD = 0.32 kK. On detailed examination of the plot in Figure 3, it is seen that the chlorinated solvents seem to follow a somewhat different trend from the other aliphatics. If we exclude these, the correlation equation for the nonchlorinated aliphatic solvents becomes

$$\nu(\mathbf{46})_{\max}{}^{\text{non-Cl-aliphatics}} = 4.836\pi^* + 10.80 \text{ kK} \qquad (12)$$

with $n = 16, r = 0.974$, and SD = 0.39 kK; and for the chlorinated aliphatic solvents, taken alone, the regression equation is

$$\nu(\mathbf{46})_{\max}{}^{\text{Cl-aliphatics}} = 5.930\pi^* + 9.56 \text{ kK} \qquad (13)$$

with $n = 7, r = 0.985$, and SD = 0.26. The regression lines in Figure 3 correspond to eq 11–13.

The correlation is subject to even further refinements. In company with nitromethane (**32**) and acetonitrile (**50**), whose behavior as HBD acids is readily evident in Figure 3, acetone (**18**) and 2-butanone (**16**) also appear to be showing weak hydrogen bond donor properties with the very strong HBA base, **46.** If we exclude these from the correlation, as well as dioxane (**9**), which has acted atypically in other regards,[42] the correlation equation for the select solvent set becomes

$$\nu(\mathbf{46})_{\max}{}^{\text{select aliphatics}} = 4.750\pi^* + 10.80 \text{ kK} \qquad (14)$$

with $n = 13, r = 0.990$, and SD = 0.26 kK.

It is seen that, on going from eq 9 to eq 14, each successive structural constraint on the scope of the correlation has led to a statistically significant increase in the r factor and decrease in the SD. When similar structural constraints were imposed on the correlations involving **1–45** we saw no similar improvements in r or SD. It remains, therefore, to consider why the total π^* scale was satisfactory for the solvatochromic comparisons involving indicators **1–45,** while separation into families of structurally similar solvents is necessary to obtain statistically acceptable correlations with indicator **46.**

The chromophores of **1–45** have in common, and differ from **46,** in that increasing solvent polarity leads to a bathochromic shift of $\nu_{\max}$. This is consistent with a series of p → π^* and π → π^* transitions, which go from relatively charge-diffuse ground states to excited states wherein electronic charges are more concentrated and the charge centers are more separated. Hence, more polar solvents stabilize the electronic excited states relative to the ground states, with the effect of shifting $\nu_{\max}$ to lower energies (corresponding to negative signs of s in eq 4 for **1–45**).

By way of contrast, the "solvatochromiebande" of Dimroth's betaine arises from an electronic transition to an excited state, wherein the electronic charge is more diffuse than in the ground state. The ground state is best depicted by canonical structure **46a,** while the excited state is usually represented as more closely resembling structure **46b,** with the negative charge delocalized over the several aromatic rings. The result is that the more polar solvents stabilize the ground relative to the excited state, leading to an increase in the electronic transition energy, and a hypsochromic displacement of $\nu_{\max}$ (i.e., the sign of s is positive for **46**). Such a **46a** ($h\nu$) → **46b** representation of the electronic transition is also consistent with the strong hypsochromic effect of type-A hydrogen bonding by HBD solvents to **46,** which we reported earlier.[4]

Another difference between **46** and **1–45,** not unrelated to the above, is in the orientations and relative magnitudes of ground and electronic excited state dipoles. For **1–45,** charge displacements in the electronic excitations are in the same directions (and usually on the same axes) as the permanent ground-state dipoles of the indicator molecules; hence, they increase the magnitudes, but do not change the orientations of those dipoles. For the betaine, on the other hand, the excitation leads to electron migration in the converse direction, resulting in an excited state dipole which is opposed in orientation to, and smaller in magnitude than, the ground state dipole moment. This provides the basis for the following as a possible explanation for the difference between **46** and **1–45** in their solvatochromic behavior with the π^* scale.

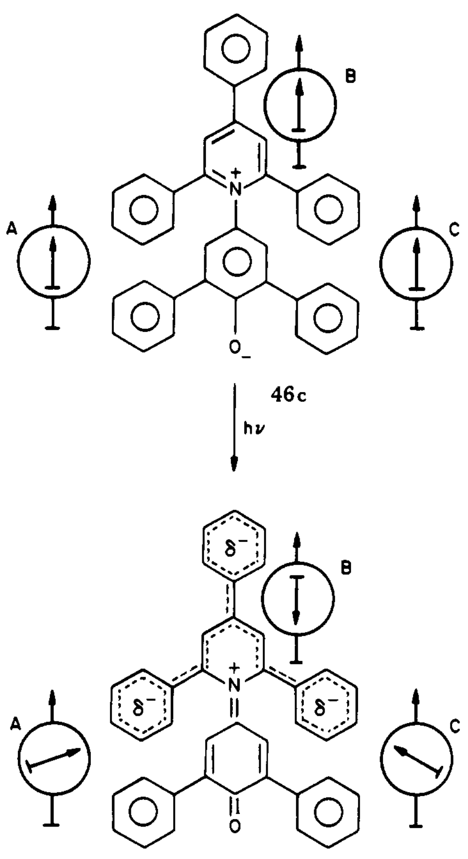
Since solvent molecules which are best oriented to solvate the ground states of **1–45** are also very nearly optimally positioned for solvation of the electronic excited states, *incremental increases* over polarity and polarizability contributions to ground state solvation stabilization are brought into play *during the electronic excitations.* The fact that a scale of single-valued π^* terms rationalizes the spectral consequences of this enhanced solvation stabilization for such diverse chromophores suggests that there may be a *usual or average blend of polarity and polarizability contributions to both ground and excited state solvation stabilization,* which applies to most p → π^* and π → π^* transitions of uncharged molecules.

In the case of **46,** the differing directions of the ground and electronic excited state dipoles leads to a radically different situation. Solvent molecules which are best oriented to solvate the ground state are poorly oriented to solvate the excited state, and solvent reorganization in the time frame of the electronic excitation is ruled out by the Franck-Condon principle. Insofar as stabilization of the excited state of **46** is concerned, this inability to redistribute charge in the cybotactic environment[10] by molecular reorganization places a greater premium on the ability of the solvent to effect such charge redistribution by electronic reorganization (which is not ruled out by the Franck-Condon principle). Hence we can readily rationalize a blend of polarity and polarizability contributions to solvatochromic effects on $\nu(\mathbf{46})_{\max}$ which is quite different from that which applied for **1–45,** i.e., Table VI. As a result, in the correlation of $\nu(\mathbf{46})_{\max}$ values with the π^* scale (Figure 3), we see the separation into families of structurally similar solvents (or solvents with similar polarizability characteristics).

The direction of the separation into families in Figure 3 is consistent with such a rationale. Enhanced solvation stabilization of the electronic excited state by more polarizable solvents should be a bathochromic influence, leading to a reduced hypsochromic effect; such a reduced hypsochromic effect is indeed observed for **46** in the more polarizable aromatic and polychlorinated aliphatic solvents relative to the less polarizable aliphatic solvents.

The mechanism of solvation of **46** by polarizable solvents is depicted schematically by solvated canonical structures **46c** and **46d,** where A, B, and C represent variously positioned solvent molecules. The longer arrows are intended to denote the orientations of the polarity components of the overall SPP effects, and the arrows within the circles the orientations of the polarizability components before and during the interaction of **46** with the photon.

According to such a mechanism, solvation effects on ground and electronic excited states of **46** should depend not only on relative magnitudes of solvent polarities and polarizabilities, but also on whether the polarizability effects are uni- or mul-



46c

46d

tidirectional (i.e., whether the solvent molecule allows charge displacement only back and forth along the axis of its permanent dipole, or whether electron density may also be displaced normal to the ground-state dipole). Thus, in **46d,** the anisotropy of polarizability should not influence the solvating ability of solvent molecule B, but should markedly effect solvation stabilization by A and C. The separate trends for the aromatic and polychloroaliphatic families of solvents in Figure 3 may exist because these compounds allow multidirectional polarization, whereas polarizabilities of monofunctional aliphatic compounds are largely unidirectional and coincident with ground state dipoles.

Although the above solvation mechanism nicely explains the relative solvent effects on the spectrum of **46,** and closely parallels the reasoning of Irving, Byers, and Leermakers[43] in their cogent analysis of solvent effects on the spectrum of *all trans*-retinylpyrrolidinium perchlorate, there is reason to believe that the final word on this question has not yet been spoken. This is because, as we will have occasion to show in future papers of this series, large numbers of reaction rates and equilibria, and IR, NMR, and n → π^* electronic spectra exhibit behavior more or less like **46** in their correlations with the π^* scale (i.e., very good to excellent linear regressions with π^* values when only aliphatic or only aromatic solvents are compared, but with statistically significant separations between the aliphatic and aromatic solvent regression lines). It will be shown that the usual trends of the reactivity results are toward *lower* reaction rates in the aromatic relative to the aliphatic solvents at comparable π^* values. Such trends are inconsistent with mechanisms like the above, which would call for increased transition-state stabilization (hence *higher* reaction rates) with increased solvent polarizability. Indications are that multiple solvation mechanisms may be required to rationalize differing polarizability effects in the correlations of the various XYZ's with the π^* scale.

In conclusion, lest the above comment (regarding similar separations of aliphatic and aromatic solvent regression lines) be construed as indicating that the $E_T(30)$ scale might be more appropriate than the π^* index for correlating solvent effects on IR, NMR, and reactivity results, we wish to present now the following additional preliminary information. In future papers, a general equation (of which eq 4 is a special case) will be shown to correlate SPP effects on dozens of spectral and reactivity properties of many types. Where solvent hydrogen bonding effects have been excluded or accounted for, this equation takes the form

$$\mathrm{XYZ} = \mathrm{XYZ}_0 + s(\pi^* + d\delta) \qquad (15)$$

The polarizability parameter, δ, equals 0.00 for all nonhalogenated aliphatic solvents, 0.50 for all polyhalogenated aliphatics, and 1.00 for all aromatic solvents; the d term is a measure of the differential susceptibility to solvent polarizability between XYZ and $\pi \rightarrow \pi^*$ electronic spectral transitions.[44] Some representative solvatochromic parameters in eq 15 are as follows: (a) As has been shown, very good to excellent correlations are obtained with $d = 0$ for most p → π^* and $\pi \rightarrow \pi^*$ electronic transitions. (b) For XYZ = $\nu(\mathbf{46})_{\max}$, XYZ_0 = 10.60 kK, $s = 5.120$, and $d = -0.231$ ($n = 32$, $r = 0.971$, and SD = 0.35 kK). (c) For a representative Menschutkin reaction, tripropylamine plus methyl iodide at 20 °C,[45] XYZ = log k (L mol^{-1} min^{-1}), $\mathrm{XYZ}_0 = -4.114$, $s = 4.464$, $d = -0.053$ (n = 29, $r = 0.987$, SD = 0.18 log unit). (d) For the solvolysis of *tert*-butyl chloride at 120 °C,[46] XYZ = Y′ = 1.800[log k_{solvent}(120 °C) − log $k_{\text{gas phase}}$(120 °C)] kcal/mol, XYZ_0 = 5.97, $s = 8.745$, $d = -0.279$ ($n = 13$, $r = 0.987$, SD = 0.52 kcal/mol). (e) For Taft and co-workers solvent polarity scale based on F NMR shielding results,[47] XYZ = the polarity parameter, P, $\mathrm{XYZ}_0 = -0.055$, $s = 2.814$, $d = -0.185$ (n = 25, $r = 0.977$, SD = 0.18 unit).

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(6) There has been some confusion in the literature as to whether the terms hydrogen bond donor and acceptor refer to the donation and acceptance of the proton or the electron pair. In the present series of papers, HBD (hydrogen bond donor) and HBA (hydrogen bond acceptor) refer to donation and acceptance of the proton.

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(16) The effects of band overlap (usually with higher intensity, higher energy bands), of hidden underlying lower intensity bands, and of changing band shape with changing solvent, all of which we include in the term *spectral anomalies*, can cause shifts in ν_{max} of as much as 0.4–0.5 kK. We have attempted to minimize such complications by taking ν_{max} as the midpoint between the two positions on the spectrum where OD (optical density) = $0.90OD_{max}$. We consider that for "well behaved" spectra, combined uncertainties in ν_{max} due to *usual spectral anomalies* and experimental precision limits in determining the spectra are about 0.10 kK.

(17) In type-A hydrogen bonding the solvent acts as proton donor and the solute as proton acceptor; the converse applies in type-B bonding.[24]

(18) It was later decided that weak type-A hydrogen bonding by HBD solvents to the nitro oxygens might slightly influence the spectrum of **5**; for this reason and because of the low *s* value, which would increase the consequence of such an effect on π_i^*, the results for **5** were not included in determining the π^* values for the amphiprotic solvents.

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(22) This emphasis reflects the NSWC's interest in properties and spectra of *nitro compounds*.

(23) As examples of the latter type, primary solvents of the initial set whose π^* values were changed when π_i^* results for at least 20 indicators were averaged were: CCl_4, 0.317 → 0.294; $ClCH_2CH_2Cl$, 0.783 → 0.807.

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(34) M. J. Kamlet, H. G. Adolph, and J. C. Hoffsommer, *J. Am. Chem. Soc.*, **86**, 4018 (1964).

(35) The nitro and dimethylamino groups are probably both twisted from planarity, in phase and with combined angles of about 40°.[34]

(36) H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy", Wiley, New York, N.Y., 1962, p 414; B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **76**, 335 (1957).

(37) For example, $\Delta\nu_0(\mathbf{14} \rightarrow \mathbf{17a}) = 1.73$, $\Delta\nu_0(\mathbf{17a} \rightarrow \mathbf{13}) = 1.27$ kK; $\Delta\nu_0(\mathbf{14} \rightarrow \mathbf{17b}) = 1.93$, $\Delta\nu_0(\mathbf{17b} \rightarrow \mathbf{6}) = 1.65$ kK.

(38) Reference 31, pp 242 ff.

(39) We shall give evidence in this regard in terms of ϵ/ϵ_0 values as functions of solvent polarity and solvent HBA basicity in future papers. As a preliminary example, $\epsilon(\mathbf{15})/\epsilon(\mathbf{14}) = 0.315$, $\theta(\mathbf{15}) = 56°$ in Me_2SO; $\epsilon(\mathbf{15})/\epsilon(\mathbf{14}) = 0.166$, $\theta(\mathbf{15}) = 66°$ in CCl_4.

(40) Additional $E_T(30)$ values were taken from Fowler, Katritzky, and Rutherford's collection,[11] and converted to $\nu(\mathbf{46})_{max}$ values. Acetonitrile and nitromethane were treated as HBA-D solvents.

(41) We have pointed out in an earlier paper[4] that type-A hydrogen bonding effects strongly influence the $E_T(30)$ values of HBA-D solvents.

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A 1,3-Hydride Shift in the Rearrangement of (1-Phenylallyl)oxyacetic Acid to 2-Ethyl-2-phenyl-1,3-dioxolan-4-one[1]

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Abstract: Condensation of the sodium salt of α-ethenylbenzenemethanol (**1a**) with sodium chloroacetate in DMF gave **2a** which upon treatment with 2 N HCl solution in the presence of ether gave 2-ethyl-2-phenyl-1,3-dioxolan-2-one (**3a**). When the same sequence of reactions was carried out starting with the deuterated allyl alcohols **1b**, **1c**, or **1d** the rearrangement gave in each case the monodeuterated product **3b**. When **2a** was treated with DCl another monodeuterated compound **3c** was isolated. From a 1:1 mixture of **1b** and **1c** only **3b** was obtained. These results are consistent with a 1,3-hydride shift in an open-chain system (**2a**) with formation of **3a**. A chiral product (+)-**3a** was isolated starting with chiral alcohol (+)-**1a** consistent with a concerted mechanism for the rearrangement.

The 1,3-hydride shifts seem to play only a minor role in organic chemistry. They are observed in bicyclic systems, e.g., norbornyl[2] cations, where they can compete with Wagner-Meerwein rearrangements and where two consecutive 1,2-hydride shifts would require the intermediacy of a bridgehead carbonium ion. The same may be said about the reported 1,3-hydride shifts observed in adamantane.[3] In open-chain systems, 1,3-hydride shifts do not compete favorably with 1,2-hydride shifts under thermodynamic control,[4] but can account for 15–30% of the substitution products under kinetically controlled conditions.[5] In this paper we report some of our observations regarding 1,3-hydride shifts under hydrolytic conditions.

In the course of our investigation[6] of the 2,3-sigmatropic rearrangement of allyloxy acetic acids to 2-oxy-5-pentenoic acids[1] we wanted to prepare (1-phenylallyl)oxyacetic acid starting with the sodium salt of the known 1-phenylallyl alcohol[7] (**1a**) and the sodium salt of chloroacetic acid in absolute DMF. Upon acidification of the crude condensation product with dilute (2 N) hydrochloric acid in a two-phase system we isolated a neutral compound $C_{11}H_{12}O_3$ in good yield which we assigned structure **3a**. The NMR spectrum of this novel