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STRUCTURAL EFFECTS ON HYDROGEN BONDING PROPERTIES OF
NITRO COMPOUNDS(U) CALIFORNIA UNIV IRVINE DEPT OF
CHEMISTRY R W TAFT MAR 83 N60921-82-C-0039

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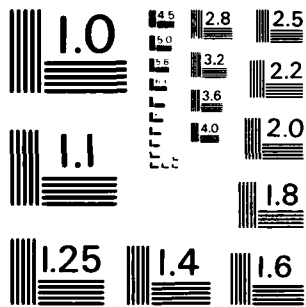
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MICROCOPY RESOLUTION TEST CHART
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Final Report for Contract N60921-82-C0039
with Naval Surface Weapons Laboratory

Professor R.W. Taft

Attn: Dr. M.S. Kamlet

Values of α , the hydrogen-bond donor ability of pure protonic solvents¹, have been obtained for 18 important solvents (cf. Table A). These values were calculated from 25 data sets which involve a significant number of both non-protonic and protonic solvents and for which the solute measurement is relatively sensitive to the solvent hydrogen bond donor ability. The individual α_i values of Table A were calculated from the correlation equation¹, $XYZ=c+s\pi^*+a\alpha$ expressed as: $\alpha_i = \frac{XYZ-c-s\pi^*}{a}$. The values were averaged to give α_{ave} values given in Table A. In Table B are given the various spectroscopic probe measurements XYZ (electronic transitions, C^{13} and P^{31} NMR shifts) used in the 25 correlations, the values of c, s , and a obtained for each correlation equation, as well as the statistical fit parameters. For protonic solvents, the π^* values used were those recently reported². Four iterations of the 25 correlations equations were carried out to obtain the "limiting" values of π_i given in Table A.

The α scale includes structural effects of solvent self-association as well as of inherent molecular hydrogen-bond donor abilities. The results for C-H acidic solvents appear to be the least affected by self-association. The order of α values found for these solvents is $(CH_3)_2CO < CH_3CN < CH_3NO_2 < CH_2Cl_2 < CHCl_3$. These are striking results since the α values reflect approximately the inherent order of molecular hydrogen bond donor abilities of these C-H acids. This order is distinctly different than that for the gas phase acidities:

$\text{CH}_2\text{Cl}_2 < \text{CHCl}_3 < \text{CH}_3\text{CN} < (\text{CH}_3)_2\text{CO} < \text{CH}_3\text{NO}_2$. Consequently, the results are important in establishing different orders of acidity for hydrogen bonding than for proton transfer. For hydrogen-bonding acidities, there appears to be little importance of resonance stabilization of the conjugate base of the C-H acid, but instead inductive electron-withdrawal which increases the positive charge on hydrogen is the dominant effect. For proton transfer acidity, on the other hand, the dominant effect tends to be resonance stabilization of the carbanionic conjugate base.

Also included in this report is a summary of interrelationships between the various solvent property scales. This work was presented in a poster session at the Euchem Conference on Correlation Analysis in Organic Chemistry, Hull, England, July 19-23, 1982.

References

1. M.J. Kamlet, J.L.M. Abboud, and R.W. Taft, *Progr. Phys. Org. Chem.*, 13, 485 (1981).
2. B. Chawla, S.K. Pollack, C.B. Lebrilla, M.J. Kamlet, and R.W. Taft, *J. Am. Chem. Soc.*, 103, 6924 (1981).

Table A. α_1 Values from Individual Data Sets and α_{ave} Values for Solvents

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
MeEtCO	.08	.08						.02	.02	.07							
Me ₂ CO	.10	.07	.06	.05	.15	.04	.01	.04	.05	.09	.10	.12	.10	.08	.10	.15	.16
MeCH	.31	.30	.28		.26	.27	.22	.23	.18	.18	.05	.08	.12	.12			
MeNO ₂	.24		.17		.18	.33	.19	.33	.32	.28	.11	.17	.12	.20	.32	.36	.20
CH ₂ Cl ₂	.11	.08		.22				.47	.46	.40		.21	.15	.27	.46	.39	.16
CHCl ₃	.21			.40							.30	.38	.29	.42			
HCONH ₂	.81	.68	.65	.70	.59	.63	.72	.83	.81	.70	.68	.67	.66	.68	.77	.69	.57
t-BuOH	.50	.60		.74	.67			.59	.59	.63	.88	.73	.84	.77	.71	.64	.72
1-PrOH	.74	.77	.62	.74	.82	.72	.74	.77	.70	.70		.79	.91	.86	.80	.73	.79
n-BuOH	.86	.85	.79	.80	.80		.76	.71	.71								
n-PrOH	.85	.83	.77	.82			.80	.76	.76	.76							
EtOH	.91	.88	.82	.81	.85	.84	.88	.85	.75	.74	.75	.89	.86	.94	.89	.81	.84
(CH ₂ OH) ₂	.84	.81		.87	.91	.84	.85	.86	.88	.85	1.04	1.04	.98	.96			
MeOH	1.09	1.02	1.03	.99	.99	1.01	1.01	.95	.84	.82	.87	.94	.97	.93	.95	.96	.92
CH ₃ CO ₂ H								1.01	1.05	1.06					1.11	1.04	1.12
H ₂ O	1.10	1.11	1.24		1.12	1.24	1.11	1.13		1.23	1.17	1.01	1.01	1.02	1.11		
CF ₃ CH ₂ OH				1.38				1.74	1.75	1.66	1.39	1.45	1.46	1.40	1.63	1.62	1.43
(CF ₃) ₂ CHOH	1.97			2.03											1.83	1.97	2.07

Table A (cont) n_D Values from Individual Data Sets and n_{ave} Values for Solvents

Solvent	19	20	21	22	23	24	25	n_{ave}	SD	n
MeELCO	.11	.12	.01	.01	.04	.05	.04	.06	.04	11
Me ₂ CO	.13	.00	.01		.02	.06	.04	.08	.05	23
MeOH	.13	.07	.10	.10	.16	.28	.19	.19	.08	20
MeNO ₂	.20	.17	.06	.17	.16	.37	.27	.22	.09	22
CH ₂ Cl ₂	.21	.34	.30	.31	.04	.30	.30	.30	.11	17
CHCl ₃	.56	.53	.53	.59	.56	.45	.39	.44	.10	11
HCOOH ₂	.61	.75	.88	.77	.92	.56	.78	.71	.09	24
t-BuOH	.79	.60	.68	.61	.65	.33	.61	.68	.09	20
i-PrOH	.81							.76	.07	18
n-BuOH								.79	.06	8
n-PrOH	.74	.76	.78	.78	.77	.57	.57	.78	.03	12
EtOH	.87	.81	.80	.79	.77	1.15	1.12	.83	.05	23
(CH ₂ OH) ₂								.90	.08	13
MeOH	.92	.87	.79	.90	.85	.62	.69	.93	.08	24
CH ₃ CO ₂ H	1.22	1.16	.96	1.24	1.30			1.12	.11	11
H ₂ O	1.12	1.24	1.32	1.43	1.28	1.15	1.20	1.17	.11	20
CF ₃ CH ₂ OH	1.44	1.47	1.39	1.45	1.40	1.51	1.62	1.51	.12	18
(CF ₃) ₂ CHOH	1.93	1.94	2.06	1.77	1.88	2.11	1.92	1.96	.10	12

Table B Data Sets Used to Define α Values by Correlation Eqns, $XYZ = c + a/s + R^3$ SEE%⁴ SEE⁵

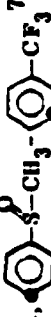

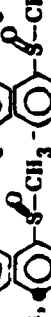
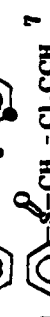






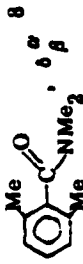

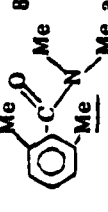
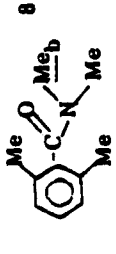
Property	n	c	a	a/s	SEa ¹	SEa ²	R ³	SEE% ⁴	SEE ⁵	Excluded
1. E _T (30) (cf. Fig. 47) ⁶	27	30.58	14.31	14.97	1.05	1.06	0.82	4.9	1.58	CF ₃ CH ₂ OH
2. E _T (cf. Fig. 53). ⁶ Kosower's Z	16	51.25	18.29	21.01	1.15	2.41	0.99	4.8	1.94	HOAc
3. E _T (cf. Fig. 54) ⁶	14	40.23	8.01	9.09	1.14	1.03	0.51	5.3	.76	t-BuOH, dioxane
4. E _T (cf. Fig. 55) ⁶	11	61.11	4.34	8.80	2.03	0.44	0.23	2.9	.27	
5. E _T (cf. Fig. 56) ⁶	17	79.84	1.68	5.10	3.00	0.32	0.23	4.9	.37	HOAc, CHCl ₃
6. E _T (cf. Fig. 57) ⁶	17	67.61	7.31	6.62	0.91	0.58	0.26	3.4	.60	
7. ν_{max} (cf. Fig. 49a) ⁶	13	14.11	0.89	1.50	1.70	0.10	0.06	3.3	.08	
8. P ¹ Shift Et ₃ PO, Gutmann's AN	17	0.63	16.17	32.47	2.01	1.21	0.85	2.5	1.36	HOAc
9. C ¹³ Shift, 	25	1.38	0.01	1.36	226.	0.10	0.06	5.1	.13	CCl ₄ , CHCl ₃ , (CF ₃) ₂ CHOH
10. C ¹³ Shift, 	26	-1.37	-0.51	1.35	-2.64	0.09	0.06	4.9	.12	CHCl ₃ , (CF ₃) ₂ CHOH
11. C ¹³ Shift, 	25	1.05	0.36	0.75	2.06	0.04	0.02	3.2	.05	CH ₂ Cl ₂ , CHCl ₃ , (CF ₃) ₂ CHOH
12. C ¹³ Shift, 	15	-3.83	-0.28	-1.31	4.70	0.13	0.08	6.8	.14	
13. C ¹³ Shift, 	20	11.65	0.44	0.98	2.20	0.07	0.04	4.6	.08	HOAc, (CF ₃) ₂ CHOH
14. C ¹³ Shift, 	20	15.31	-1.33	-2.95	2.22	0.27	0.18	6.1	.34	HOAc, (CF ₃) ₂ CHOH
15. C ¹³ Shift, 	19	3.35	0.00	2.02	-	0.11	0.07	4.6	.13	HOAc, (CF ₃) ₂ CHOH
16. C ¹³ Shift, Tropone 	17	57.66	1.49	2.75	1.84	0.22	0.11	4.0	.25	
17. C ¹³ Shift, Tropone, δ_{α}	17	43.01	2.86	3.42	1.19	0.24	0.11	3.1	.27	
18. C ¹³ Shift, Tropone, δ_{β}	17	9.25	-3.96	-3.91	0.99	0.28	0.13	2.9	.31	
19. C ¹³ Shift, Tropone, δ_{γ}	17	0.27	1.20	1.35	1.12	0.08	0.04	2.7	.09	
20. C ¹³ Shift, 	21	32.58	0.73	4.01	5.5	0.23	0.11	3.1	.26	
21. C ¹³ Shift, 	21	-8.52	0.36	2.38	6.6	0.27	0.13	5.7	.30	

Table B (cont)

Property	n	c	s	a	a/s	SEs ¹	SEa ²	R ³	SEE ⁴	SEE ⁵	Excluded
22. C ¹³ Shift, 	21	31.52	1.18	4.23	3.6	0.42	0.20	.984	5.8	.47	(CH ₃) ₂ CO
23. C ¹³ Shift, 	21	~10.25	0.40	2.63	6.5	0.30	0.14	.979	6.4	.33	CH ₂ Cl ₂
24. C ¹³ Shift, 	20	17.81	0.53	1.00	1.90	0.14	0.07	.974	6.2	.15	t-BuOH, n-PrOH, EtOH
25. C ¹³ Shift, 	20	14.64	0.34	1.01	3.0	0.11	0.05	.982	5.7	.12	n-PrOH, EtOH, MeOH

(1) Standard Error of s

(2) Standard Error of a

(3) Multiple Correlation Coefficient

(4) Standard Error of Estimate as % of the range of XYZ

(5) Standard Error of Estimate

(6) cf. figures given in Kamlet, Abboud, and Taft, *Prog. Phys. Org. Chem.*, **13**, 485 (1981).

(7) B. Chawla, S. K. Pollack, M. Fujio, L. Simanyi, C. Lebrilla, and R. W. Taft, unpublished.

(8) C. W. Fong and H. G. Grant, unpublished.

INTERRELATIONSHIPS BETWEEN THE VARIOUS SOLVENT PROPERTY SCALES

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THE SOLVATOCHROMIC EQUATIONS AND PARAMETERS

$$1. \text{XYZ} = \text{XYZ}_0 + s(\pi^* + D\delta) + A\alpha + B\beta + H\delta_H + E\xi^2$$

π^* IS A SCALE OF SOLVENT DIPOLARITY/POLARIZABILITY.

α IS A SCALE OF SOLVENT HYDROGEN BOND DONOR (HBD) ACIDITY.

β IS A SCALE OF SOLVENT HYDROGEN BOND ACCEPTOR (HBA) BASICITY.

δ IS A "POLARIZABILITY CORRECTION FACTOR" EQUAL TO 0.0 FOR NON-CHLORINATED ALIPHATIC SOLVENTS, 0.5 FOR POLYCHLORINATED ALIPHATICS AND 1.0 FOR AROMATIC SOLVENTS

δ_H , THE HILDEBRAND SOLUBILITY PARAMETER, IS A MEASURE OF SOLVENT-SOLVENT INTERACTIONS WHICH ARE INTERRUPTED IN CREATING A CAVITY FOR THE SOLUTE.

ξ IS A COORDINATE COVALENCY PARAMETER, EQUAL TO -0.20 FOR P=O BASES, 0.0 FOR C=O, S=O AND N=O BASES, 0.2 FOR SINGLE BONDED OXYGEN BASES, 0.6 FOR PYRIDINES, AND 1.0 FOR ALKYLAMINE BASES.

THE S, D, A, B, AND H COEFFICIENTS MEASURE THE RELATIVE SUSCEPTIBILITIES OF XYZ TO THE INDICATED SOLVENT PROPERTIES. THE D TERM IS NIL FOR ELECTRONIC SPECTRA WHICH ARE SHIFTED BATHOCHROMICALLY WITH INCREASING SOLVENT DIPOLARITY, AND IS FINITE AND (USUALLY) NEGATIVE FOR OTHER XYZ'S.

BY A JUDICIOUS CHOICE OF SOLVENTS AND REACTANTS OR INDICATORS, IT IS USUALLY POSSIBLE TO REDUCE EQ 1 TO A MORE MANAGEABLE ONE OR TWO TERM EQUATION. FOR EXAMPLE, FOR CERTAIN BASICITY DEPENDENT PROPERTIES,

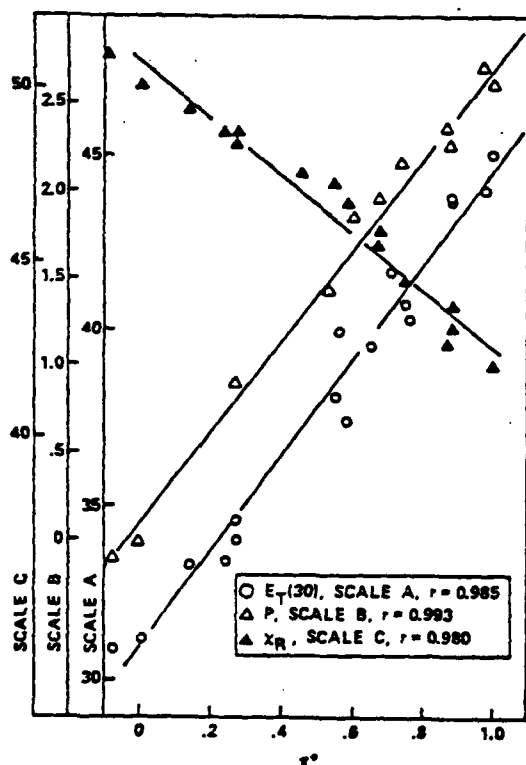
$$2. \text{XYZ} = \text{XYZ}_0 + B\beta + E\xi^2$$

XYZ IN EQ 1 IS, FOR EXAMPLE, THE LOGARITHM OF A RATE OR EQUILIBRIUM CONSTANT, A FLUORESCENCE LIFETIME, OR A GLC PARTITION COEFFICIENT, A POSITION OR INTENSITY OF MAXIMAL ABSORPTION IN AN NMR, ESR, IR, OR UV/VISIBLE SPECTRUM, AN NMR COUPLING CONSTANT, OR A FREE ENERGY OF SOLUTION OR OF TRANSFER BETWEEN SOLVENTS OF A DIPOLAR SOLUTE.

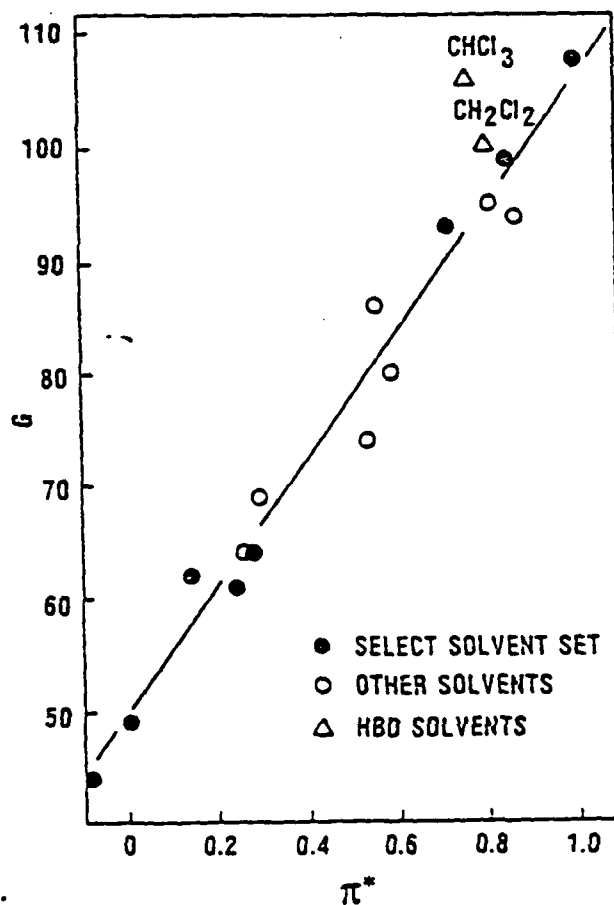
XYZ IN EQ 2 IS, FOR EXAMPLE, AN IR FREQUENCY SHIFT (FREE MINUS HYDROGEN BONDED), AN ENTHALPY OF FORMATION OF A HYDROGEN BONDED OR LEWIS ACID/BASE COMPLEX, OR THE FREE ENERGY OF TRANSFER OF A PROTON TO AQUEOUS BASE FROM AQUEOUS NH_4^+ (THE LATTER QUANTITY BEING LINEAR WITH pK_A).

TABLE II. CORRELATION COEFFICIENTS FOR LINEAR REGRESSION EQUATIONS WITH π^* (SELECT SOLVENTS).

SOLVENT SCALE OR PROPERTY	R	N
DIPOLE MOMENT, μ	0.985	23
REICHARDT AND DIMROTH'S $E_T(30)$, UV/VIS BETAINE	0.987	12
BROOKER'S X_{R2} , UV/VIS MERCOCYANINE	0.987	16
LASSAU AND JUNGERS' $\log K(\text{MEI} + \text{PR}_3\text{N})$	0.985	13
WALTHER'S E_{K2} , UV/VIS MOLYBDENUM COMPLEX	0.977	9
NAPIER AND KNAUER'S A_{N1} , ESR NITROXIDE	0.978	6
ALLERHAND AND SCHLEYER'S G , IR SHIFTS	0.993	8
TAFT'S P , ^{19}F -NMR 4-F- $\text{C}_6\text{H}_4\text{-N=O}$	0.989	12
BROWNSTEIN'S S (EXTENSION OF KOSOWER'S Z)	0.981	19
SNYDER'S P , GAS/LIQUID PARTITION COEFFICIENTS	0.991	21
GUTMANN'S ACCEPTOR NUMBER, A_N , ^{31}P -NMR SHIFTS OF $\text{Et}_3\text{P=O}$	0.960	10



DIMROTH'S $E_T(30)$, BROOKER'S X_R , AND THE NMR-BASED SOLVENT POLARITY PARAMETER, P , FOR SELECT SOLVENTS PLOTTED AGAINST CORRESPONDING SOLVENT π^* VALUES. SELECT SOLVENT ARE NON-CHLORINATED ALIPHATIC SOLVENTS FOR WHICH π^* IS PROPORTIONAL TO MOLECULAR DIPOLE MOMENT.



Allerhand and Schleyer's G Values Plotted against π^*

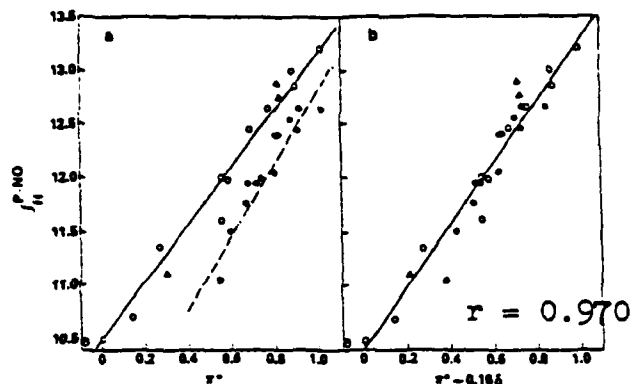


Figure 3. \int_{π}^{NO} for *p*-fluoronitrosobenzene plotted (a) against π^* and (b) against $(\pi^* - 0.16\delta)$. Symbols for the solvent families are as in Figure 1.

TAFT'S P PLOTTED AGAINST π^* AND AGAINST $(\pi^* - 0.16\delta)$

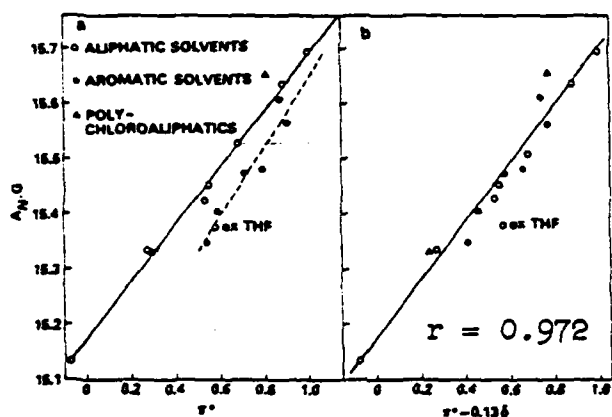


Figure 4. ΔN for di-*tert*-butyl nitroxide plotted (a) against π^* and (b) against $(\pi^* - 0.13\delta)$.

NAPIER AND KNAUER'S A_N PLOTTED AGAINST π^* AND AGAINST $(\pi^* - 0.13\delta)$

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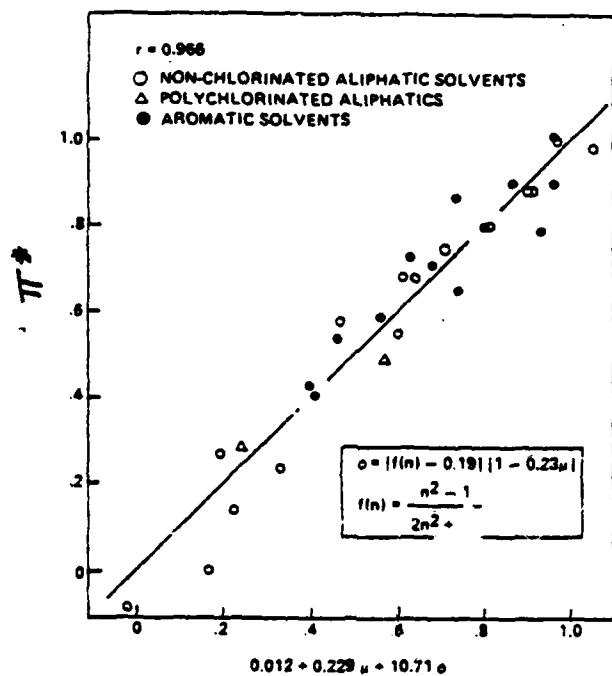


Figure 8. Correlation of π^* with μ and ϕ .

CORRELATION OF π^* WITH THE SOLVENT DIPOLE MOMENT, μ , AND THE "REDUCING FUNCTION" ϕ .

THE P/F RATIO IN THE RELATIONSHIP, $XYZ = XYZ_0 + F\mu + P\phi$ IS LINEAR WITH THE D TERM IN $(\pi^* + D\delta)$, WITH THE D TERM BECOMING INCREASINGLY NEGATIVE AS THE POLARIZABILITY CONTRIBUTION BECOMES LESS IMPORTANT.

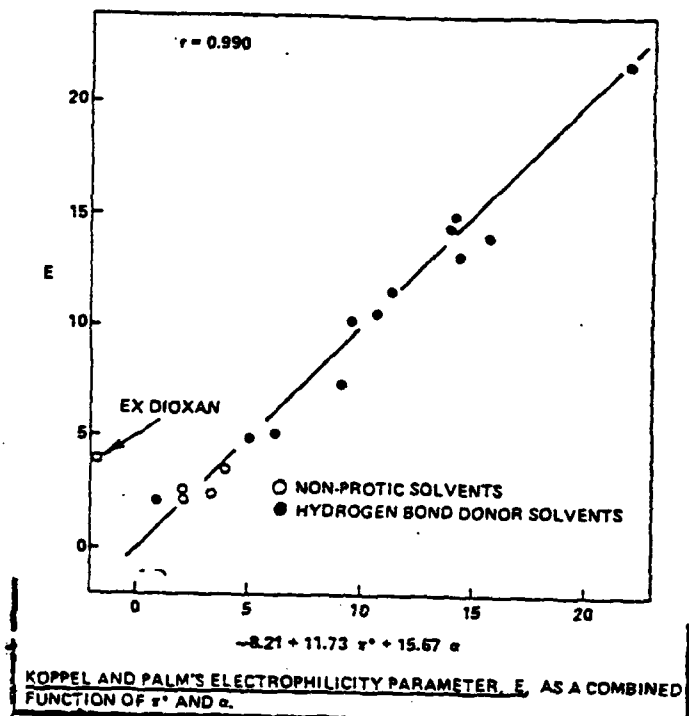
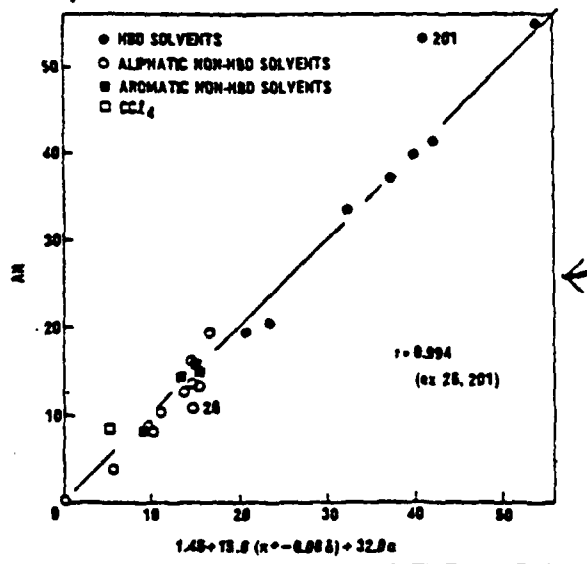
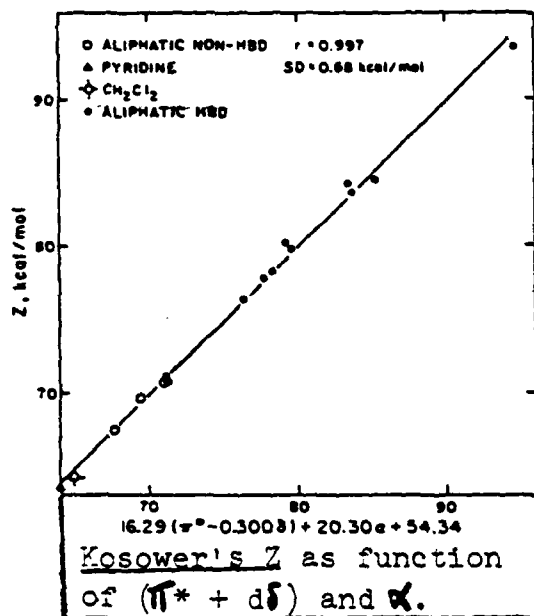
HBD SOLVENTS. CORRELATIONS WITH π^* AND α .

WHEN THE SET OF SOLVENTS CONSIDERED INCLUDES ALSO PROTONIC SOLVENTS, EFFECTS OF SOLVENT HBD (HYDROGEN BOND DONOR) ACIDITY MUST ALSO BE INCLUDED IN THE SOLVATOCHROMIC EQUATIONS. MULTIPLE LINEAR REGRESSION EQUATIONS IN π^* AND α OR $(\pi^* + D\delta)$ AND α SHOW THAT THE EARLIER SOLVENT PROPERTY SCALES, REPRESENTED AS MEASURES OF EITHER SOLVENT POLARITY (IONIZING POWER) OR SOLVENT ELECTROPHILICITY (ACIDITY) ARE, IN FACT, MEASURES OF LINEAR COMBINATIONS OF BOTH PROPERTIES.

THUS, FOR REICHARDT AND DIMROTH'S BETAINE,

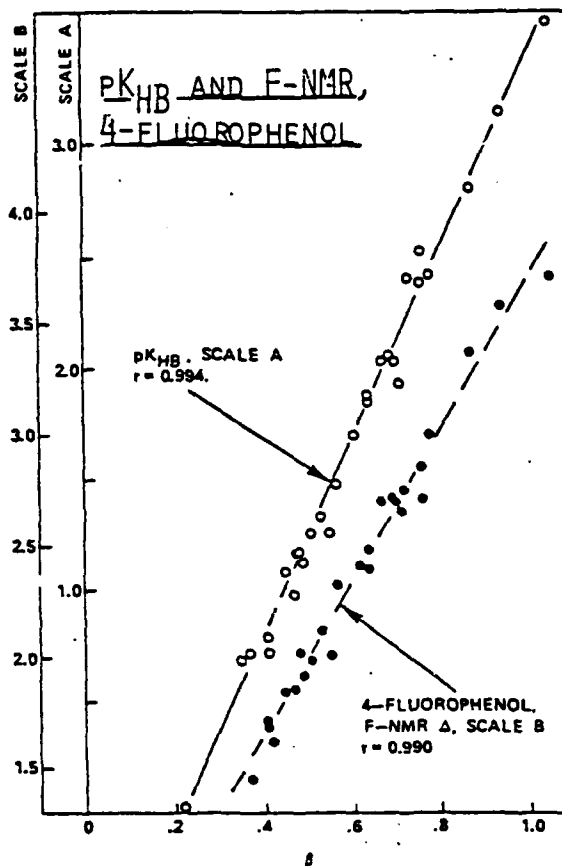
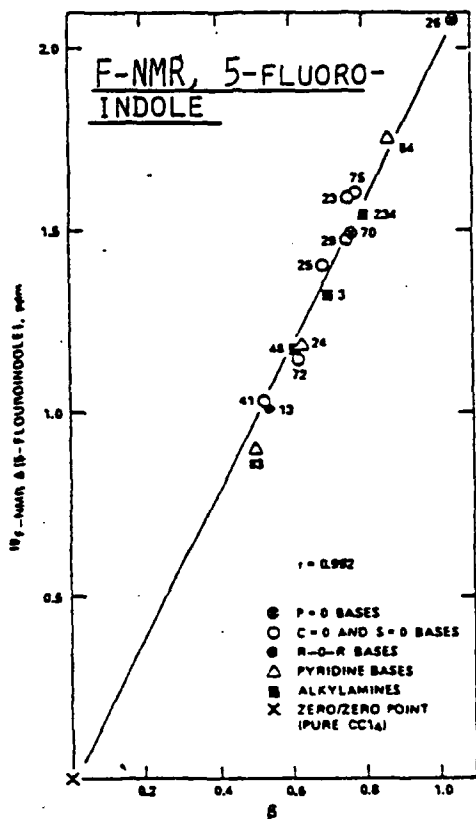
$$E_T(30) = 30.3 + 14.6(\pi^* - 0.23\delta) + 16.4\alpha, \quad N = 44, R = 0.993$$

SIMILARLY,

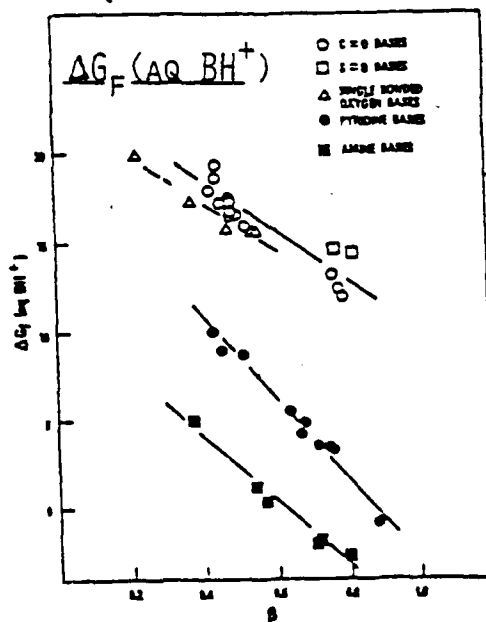
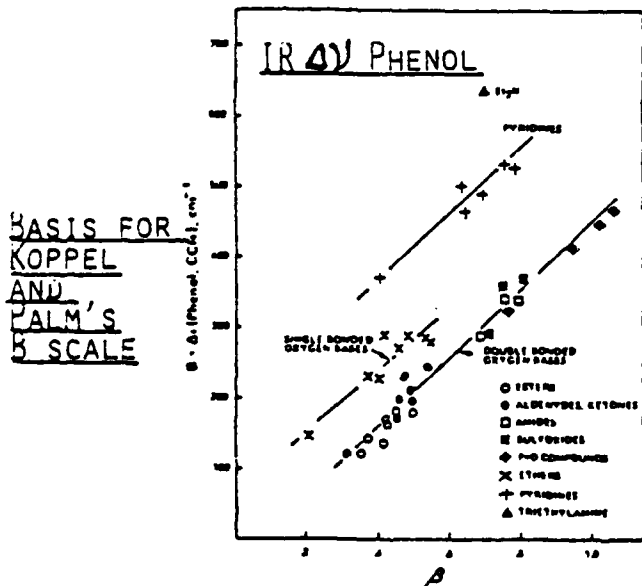


Gutmann's Acceptor Number (AN) as a function of $(\pi^* + d\delta)$ and α .

EXAMPLES OF FI CORRELATIONS



EXAMPLES OF FD CORRELATIONS



ΔG_F (AQ BH⁺) IS LINEAR WITH PK_A

Table I. Correlations of Basicity Dependent Properties with E_B/C_B and β/ξ

Family Independent Properties	$XYZ = XYZ_O + E_A E_B + C_A C_B$		$XYZ = XYZ_O + \beta\beta + e\xi$	
	n	C_A/E_A r	n	e/b r
1. $-\Delta\Delta\nu_{max}$, 3,5-(NO ₂) ₂ - ϕ -NH ₂ in pure base	14	0.027 0.926	14	-0.035 0.995
2. ΔG_f , 4-F- ϕ -OH:HBA in CCl ₄	14	0.044 0.891	14	-0.026 0.982
3. ¹⁹ F-NMR Δ , 5-fluoroindole:HBA in CCl ₄	8	0.015 0.951	14	-0.010 0.983
Family Dependent Properties	average	0.922		0.987
4. ΔH_f , n-BuOH:HBA in CCl ₄ or C ₆ H ₁₂	9	0.060 0.984	14	0.225 0.982
5. ΔH_f , 4-F- ϕ -OH:HBA in pure base	13	0.076 0.968	23	0.244 0.974 ^b
5a. " " in CCl ₄	8	0.058 0.973 ^c	23	0.310 0.966 ^d
6. ΔH_f , ϕ -OH in CCl ₄ or C ₆ H ₁₂	17	0.112 0.986	17	0.444 0.967
7. Log k/k ₀ , catalyzed n-butylaminolysis of 4-NO ₂ - ϕ -O-CO-CF ₃ in ClCH ₂ CH ₂ Cl	5	0.169 0.989	8	0.460 0.985 ^f
8. ΔH_f , CF ₃ CH ₂ OH:HBA in CCl ₄ or C ₆ H ₁₂	10	0.106 0.992	10	0.485 0.984
9. $\Delta\nu$ (O-D), MeOD:HBA in pure base	13	0.122 0.987	25	0.570 0.988
10. ΔG_f , I ₂ :HBA in heptane	15	0.175 0.950	34	0.570 0.982
11. ΔH_f , BF ₃ :HBA in CH ₂ Cl ₂	13	0.110 0.953	34	0.577 0.978
12. $\Delta\nu$ (O-II), ϕ -OH:HBA in CCl ₄	17	0.129 0.991	43	0.611 0.989
13. ¹⁹ F-NMR Δ , 4-F- ϕ -SO ₃ ⁻ BIH ⁺ ion pair in CH ₂ Cl ₂			10	0.642 0.953
14. ΔH_f , 4-F- ϕ -SO ₃ ⁻ BIH ⁺ ion pair in CH ₂ Cl ₂	11	0.217 0.994	10	0.744 0.993
15. $\Delta\nu$ (C-I), I-CN:HBA in CCl ₄	10	0.253 0.995	25	0.787 0.981
16. ΔH_f , I ₂ :HBA in heptane	14	0.210 0.978	23	0.859 0.989
17. ΔG_f , Aq BIH ⁺ in water	average	0.980	36	0.859 0.992
			average	0.980

a) r' is β/ξ correlation coefficient for same data set as was used with E/C . b) ex diphenyl ether and 1,2-dimethoxyethane; if these are included $r = 0.969$. c) Ex tetramethylurea; if included $r = 0.813$. d) Ex tetramethylurea and triphenyl phosphate; if the latter is included $r = 0.926$. e) Ex 4-dimethylaminopyridine and quinuclidine; if included $r = 0.971$. f) Ex 4-dimethylaminopyridine; if included $r = 0.973$.

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