J. Org. Chem. 1981, 46, 661-667

acids.[13] The first few injections of ether gave abnormally high results which we take to be the sum of the heat of hydrogenation plus the heat of adsorption of the product ether. The effect rapidly decreases and after 5 or 6 injections; a constant heat output is observed for the remainder of the experiment. We ascribe this to saturation of the adsorbant surface following which true heats of hydrogenation are obtained uncomplicated by interfering adsorption effects. The magnitude and sign of the early interference effects (2-5 kcal/mol and exothermic) are consistent with heats of fairly strong adsorption on activated charcoal.[14] No inconsistencies are observed in data sets from which the first 5 or 6 ether injections have been discarded.

9-Oxabicyclo[3.3.1]non-1-ene. The alkene was prepared from 1-hydroxy-9-oxabicyclo[3.3.1]nonane via the methanesulfonate, following the procedure of ref 15. The methanesulfonate; mp 75 °C, was recrystallized from benzene-ethyl acetate (lit.[15] mp 75 °C dec). Elimination with 2,6-di-*tert*-butylphenoxide gave the alkene, bp 67 °C (24 torr) [lit.[15] bp 67 °C (20 torr)].

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Registry No. 1, 109-92-2; 2, 3891-33-6; 3, 764-99-8; 4, 110-87-2; 5, 4454-05-1; 6, 17327-22-9; 7, 40164-27-0; 8, 1191-99-7; 9, 1708-29-8; 10, 332-77-4; 1-hydroxy-9-oxabicyclo[3.3.1]nonane, 37996-41-1; 1-hydroxy-9-oxabicyclo[3.3.1]nonanemethanesulfonate, 40164-33-8.

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[14] A. W. Adamson, "Physical Chemistry of Surfaces", 2nd ed., Interscience, New York, 1967, p 402 ff.

[15] C. B. Quinn, Ph.D. Thesis, University of Michigan, 1973, pp 159, 164.

Linear Solvation Energy Relationships. 7. Correlations between the Solvent-Donicity and Acceptor-Number Scales and the Solvatochromic Parameters π^*, α, and β

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The solvatochromic comparison method is used to examine relationships between Gutmann's solvent donicity (DN; based on ΔH_f of $SbCl_5$ complexes) and acceptor number (AN; based on ^{31}P NMR solvent shifts of Et_3PO) and the solvatochromic parameters π^*, α, and β. It is shown that the AN for nonprotonic solvents correlates well with π^* and for protonic solvents with a linear combination of π^* and α. It is therefore concluded that AN, represented as a measure of the solvent's ability to serve as an electron-pair acceptor, is, in fact, a combined measure of solvent polarity/polarizability and hydrogen bond donor ability. It is shown that DN is linear with β for oxygen bases and RCN nitrogen bases but that the correlation breaks down for pyridine. The breakdown in correlation is related to the nonlinearity between ΔH_f and ΔG_f of 4-fluorophenol complexes with HBA bases.

In earlier papers of this series,[1] we described the formulation of three scales of solvent properties (solvatochromic parameters)[2] which were used to unravel and rationalize medium effects on many types of reactivity parameters and physicochemical properties. A π^* scale of polarity/polarizabilities describes the solvent's ability to stabilize a charge or a dipole by virtue of its dielectric effect;[3] for most monofunctional aliphatic solvents, π^* values have been shown to be generally proportional to molecular dipole moments.[1,4,5] The α index of HBD (hydrogen bond donor) acidities provides a measure of the solvent's ability to donate a proton. We term this a "type-A hydrogen bond".[1,6] The β scale of HBA (hydrogen bond acceptor) basicities quantifies the solvent's ability to donate an electron pair (accept a proton). We call this participation in a type-B hydrogen bond.[1,7] Thus the terms A and B refer to the role of the solvent rather than to any major dichotomy of hydrogen bonds.

When hydrogen bonding effects are excluded, as when neither solutes nor solvents are hydrogen bond donors, correlations of medium effects with the solvatochromic parameters may take either of two forms. (1) For $p \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ electronic spectral transitions with all solvents considered together and for other properties or reactivity parameters XYZ (see below) when families of solvents with similar polarizability characteristics[4,5] are treated separately (e.g., only nonchlorinated aliphatic solvents, only polychlorinated aliphatics, or only aromatic solvents), the linear solvation energy relationships (LSER's) take the form of eq 1a, where s is a measure of the response of XYZ

$$\mathrm{XYZ} = \mathrm{XYZ}_0 + s\pi^* \qquad (1a)$$

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(1) Earlier work is summarized in: Kamlet, M. J.; Abboud, J.-L. M.; Taft, R. W. *Prog. Phys. Org. Chem.* **1980**, *13*, 485.

(2) Although eq 1-3 have been extended to cover many nonspectroscopic properties, we find it convenient to continue to refer to the method as the solvatochromic comparison method, the equations as the solvatochromic equations, the π^*, α, β, and δ terms as the solvatochromic parameters, and the s, a, b and d terms as the solvatochromic coefficients.

(3) (a) Kamlet, M. J.; Abboud, J.-L. M.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 6027. (b) Kamlet, M. J.; Hall, T. N.; Boykin, J.; Taft, R. W. *J. Org. Chem.* **1979**, *44*, 2599.

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

(5) Abboud, J.-L. M.; Taft, R. W. *J. Phys. Chem.* **1979**, *83*, 412.

(6) (a) Kamlet, M. J.; Taft, R. W. *J. Chem. Soc., Perkin Trans. 2* **1979**, 349. (b) Taft, R. W.; Kamlet, M. J. *Ibid.* **1979**, 1723.

(7) (a) Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 377. (b) Yokoyama, T.; Taft, R. W.; Kamlet, M. J. *Ibid.* **1976**, *98*, 3233. (c) Kamlet, M. J.; Solomonovici, A.; Taft, R. W. *Ibid.* **1979**, *101*, 3734. (d) Kamlet, M. J.; Jones, M. E.; Taft, R. W.; Abboud, J.-L. M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 342.

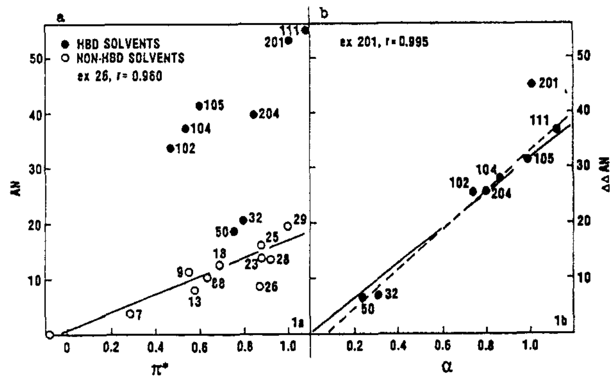

Figure 1. Solvatochromic comparison of AN with π^* and α, sequential method: AN vs. π^* (1a); $\Delta\Delta$AN vs. α (1b). The dashed line corresponds to the least-squares regression equation and the solid line to the regression equation force fitted through the origin.

to changing solvent polarity/polarizability. (2) For other XYZ's, when all solvents need to be considered together, the preferred LSER equation becomes eq 1b, where δ, a

$$\mathrm{XYZ} = \mathrm{XYZ}_0 + s(\pi^* + d\delta) \qquad (1b)$$

"polarizability correction term", equals 0.0 for nonchlorinated aliphatic solvents, 0.5 for polychlorinated aliphatics, and 1.0 for aromatic solvents, and XYZ_0 refers to the regression value in cyclohexane for that property. The XYZ term in eq 1a,b may be any solvent-dependent property, usually for a single indicator or set of reactants, such as a position or intensity of maximal absorption in an IR, NMR, ESR, UV–visible absorption, or fluorescence spectrum, an NMR coupling constant, a free energy or heat of solution or of transfer between solvents, the logarithm of a gas/liquid partition coefficient, a reaction rate, or equilibrium constant, or a fluorescence lifetime.

When solutes (but not solvents) are hydrogen bond donors, contributions of type-B hydrogen bonding must be included in the solvent effects. In these instances, total solvatochromic equations[2] also show dependences on the solvent HBA basicity parameter, β, *i.e.*, eq 2a,b.

$$\mathrm{XYZ} = \mathrm{XYZ}_0 + s\pi^* + b\beta \qquad (2a)$$

$$\mathrm{XYZ} = \mathrm{XYZ}_0 + s(\pi^* + d\delta) + b\beta \qquad (2b)$$

In the converse situation, when solvents (but not solutes) are hydrogen bond donors, type-A hydrogen bonding comes into play. Here the multiple solvent effect dependences on π^* and the solvent HBD acidity parameter, α, are expressed as in eq 3a,b.

$$\mathrm{XYZ} = \mathrm{XYZ}_0 + s\pi^* + a\alpha \qquad (3a)$$

$$\mathrm{XYZ} = \mathrm{XYZ}_0 + s(\pi^* + d\delta) + a\alpha \qquad (3b)$$

In situations where both solutes and solvents have been hydrogen bond donors, it has proven quite difficult to unravel solvent polarity/polarizability, type-B hydrogen bonding, and variable solvent self-association effects[1,6b] from (usually multiple) type-A hydrogen bonding effects. For this reason we have demonstrated total solvatochromic equations with unambiguously distinct dependences on all three solvatochromic parameters π^*, α, and β in only a few instances.[8]

Gutmann's "Donor–Acceptor" Approach. In contrast to the three solvatochromic parameter scales and the polarizability correction term which the present authors believe are required for a reasonably complete description of solvent effects, Gutmann and co-workers[9] have proposed a "donor-acceptor" approach, wherein total medium effects are described in terms of the electron donor and electron acceptor properties of the solvent.[9p] As quantitative measures of these solvent properties, they have introduced two empirical parameter scales, termed "donicity" (DN) and "acceptor number" (AN).

The donicity term (DN) was defined specifically as the negative $\Delta H°$ value in kilocalories per mole for the interaction of a basic solvent with the nonprotonic Lewis acid $\mathrm{SbCl_5}$ (**1**) in a highly diluted solution in 1,2-dichloroethane. The acceptor number (AN) was based on infinite-dilution ^{31}P NMR solvent shifts (relative to hexane) of triethylphosphine oxide (**2**) in the bulk solvents, the correction term being $-\delta_\infty^{\mathrm{corr}}(2) = \mathrm{AN}/2.349$.

Since the DN parameter is similar in concept to our β and the AN parameter resembles our α in that the former pair purports to describe electron donor properties and the latter pair electron acceptor properties, it is useful to analyze the relationships between these sets of empirical solvent parameters by means of the *solvatochromic comparison method.* Acceptor numbers and donicities for representative solvents are assembled in Table I together with corresponding values of π^*, α, and β. All solvents for which the AN and DN values and the corresponding solvatochromic parameters are known are included in Table I. The first attempt at correlation will be between AN and the solvatochromic parameters, π^* and α.

Solvatochromic Comparison of AN with π^* and α. In unravelling solvent polarity/polarizability from hydrogen bonding effects by the solvatochromic comparison method, it is necessary that three important conditions be fulfilled: (a) a plot of the property (AN in this case) against solvent π^* values for a series of nonchlorinated aliphatic solvents of varying polarity, but wherein hydrogen bonding is excluded, should show linear regression with a statistically acceptable correlation coefficient ($r > 0.90$); (b) data points representing solvents in which hydrogen bonding occurs should be displaced from the regression line all in the same direction and by statistically significant amounts; (c) the direction of the displacements should be consistent with the chemistry involved, and the relative magnitudes

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(8) Kamlet, M. J.; Dickinson, C.; Taft, R. W., submitted for publication in *Chem. Phys. Lett.*

(9) (a) Gutmann, V. *CHEMTECH* **1977**, 255 and the following references cited therein: Gutmann, V.; Wychera, E. *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 257; (b) Gutmann, V. "Coordination Chemistry in Non-Aqueous Solvents"; Springer Wien, New York, 1968; (c) Gutmann, V.; Mayer, U. *Monatsh. Chem.* **1969**, *100*, 2048; (d) Gutmann, V. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 843; (e) Gutmann, V. *Coord. Chem. Rev.* **1975**, *15*, 207; (f) Mayer, U.; Gutmann, V.; Gerger, W. *Monatsh. Chem.* **1975**, *106*, 1275; (g) Gutmann, V. *Electrochim. Acta* **1976**, *21*, 661; (h) Gutmann, V. *Chem. Br.* **1971**, *7*, 102; (i) Gutmann, V.; Schmid, R. *Coord. Chem. Rev.* **1974**, *12*, 263; (j) Gutmann, V. *Ibid.* **1975**, *15*, 207; (k) Mayer, U.; Gutmann, V. *Monatsh. Chem.* **1970**, *101*, 912; (l) Gutmann, V.; Gritzner, G.; Daksagmuller, K. *Inorg. Chim. Acta* **1976**, *17*, 81; (m) Gutmann, V.; Schmid, R. *Monatsh. Chem.* **1969**, *100*, 2113; (n) *Ibid.* **1971**, *102*, 1217; (o) Mayer, U.; Gutmann, V.; Lodzinska, A. *Ibid.* **1973**, *104*, 1045. (p) In this paper we use the terms *donor* and *acceptor* to refer to a variety of ways that a solute can offer electron pairs to or accept electron pairs from a solvent. Our correlations include the following: thermodynamic properties, for which the terms *acid* and *base* would be suitable;[9q] kinetics, for which *electrophile* and *nucleophile* should apply;[9q] spectral, for which no accepted terminology known to us exists to describe the tendency to donate or accept electrons increasingly or decreasingly in going from an initial state to an excited state. Charge transfer of electrons in a Franck–Condon transition obviously involves different factors than those for a simple acid–base equilibrium. Even within acid–base properties there are clear differences between those involving hydrogen bonding, Brønsted proton transfer, and Lewis-type coordination. Again free-energy properties need not correspond to enthalpy terms such as DN. However, since electron donation and acceptance is the principal common factor in all of the properties correlated here, we encompass them all by referring to the roles of the solvent as electron pair *donor* (hydrogen bond acceptor) and electron pair *acceptor* (hydrogen bond donor). (q) Gold V. *Pure Appl. Chem.* **1979**, *51*, 1725.

Table I. Comparison of the Solvent-Donicity (DN) and Acceptor-Number (AN) Scales with the Solvatochromic Parameters π^*, α, and β

no.[a]	solvent	π^{*b}	α^c	β^d	DN[e]	AN[e]
1	*n*-hexane	−0.08	nil	nil		nil
3	triethylamine	0.14	nil	0.71	30.7[g]	
6	carbon tetrachloride	0.29	nil			8.6
7	diethyl ether	0.27	nil	0.47	19.2	3.9
9	dioxane	0.55	nil	0.37	14.8	10.8
11	ethyl acetate	0.55	nil	0.45	17.1	
13	tetrahydrofuran	0.58	nil	0.55	20.0	8.0
14	benzene	0.59	nil	0.10	0.1	8.2
18	acetone	0.68	0.10	0.48	17.0	12.5
20	1,2-dichloroethane	0.81	nil	nil	nil	
23	*N*,*N*-dimethylacetamide	0.88	nil	0.76	27.8	13.6
24	pyridine	0.87	nil	0.64	33.1	14.2
25	dimethylformamide	0.88	nil	0.69	26.6	16.0
26	hexamethylphosphoramide	0.87	nil	1.05	38.8	10.6
28	*N*-methylpyrrolidone	0.82	nil	0.77	27.3	13.3
29	dimethyl sulfoxide	1.00	nil	0.76	29.8	19.3
31	nitrobenzene	1.01	nil	nyd[i]	4.4	14.8
32	nitromethane	0.80	0.29	nyd[i]	2.7	20.5
37	benzonitrile	0.90	nil	0.41	11.9	15.5
50	acetonitrile	0.76	0.22	0.31	14.1	19.3
52	methyl acetate	0.56	nil	0.42	16.5	
61	1,2-dimethoxyethane	0.53	nil	0.41	20.0[h]	
88	bis(2-methyoxyethyl) ether	0.64	nil			10.2
102	2-propanol	0.47	0.77			33.5
104	ethanol	0.54	0.85			37.1
105	methanol	0.60	0.98			41.3
111	water	1.09	1.10			54.8
201	acetic acid	(0.48)[f]	(1.01)[f]			52.9
204	formamide	0.85	0.77			39.8

[a] Solvent numbering is the same in all papers of this series. [b] Reference 3. [c] Reference 1; these numbers have been changed somewhat from values used in ref 6a,b. [d] Reference 7. [e] Reference 9. [f] Relatively uncertain. [g] Revised from Gutmann's value of 61.0; see text. [h] Reference 19. This is different from the value reported in ref 9. [i] nyd = not yet determined.

should reflect a reasonable order of solvent hydrogen bond donor strengths in the case of solvent to solute (type-A) bonding or solvent hydrogen bond acceptor strengths where the effects derive from solute to solvent (type-B) hydrogen bonds.

The plot of AN vs. solvent π^* values is shown in Figure 1a, wherein it may be seen that the first condition is satisfied. AN values for the non-HBD or very weak HBD aliphatic solvents [hexane, Et_2O, dioxane, THF, acetone, DMA, DMF, NMPy, Me_2SO, and $(MeOCH_2)_2$; excluding HMPA (solvent **26**)[10]] are nicely linear with corresponding π^* values. The correlation equation, represented by the regression line in Figure 1a, is as shown in eq 4, with r (the correlation coefficient) = 0.960 and σ (the standard deviation) = 1.7. If the datum for hexamethylphosphoramide is included, r becomes 0.934, and σ becomes 2.0.

$$\mathrm{AN} = 0.40 + 16.4\pi^* \tag{4}$$

That the second condition is satisfied is also seen in Figure 1a. Data points for protonic solvents which participate in $Et_3PO\cdots HBD$ hydrogen bonds are displaced from the regression line, all in the same direction and by statistically significant amounts. Values of $\Delta\Delta\mathrm{AN}(2\text{-}\pi^*)^{\mathrm{A}}{}_{\rightarrow \mathrm{O=P}}$, corresponding to vertical displacements of the HBD solvent data points from the non-HBD solvent regression line[11] and calculated from eq 5 are as follows (solvent, ΔΔAN): MeCN, 6.4; $MeNO_2$, 7.0; 2-PrOH, 25.4; EtOH, 27.8; MeOH, 31.1; $HCONH_2$, 25.5; H_2O, 36.6; HOAc, 44.6. Thus, the effects on AN of the type-A hydrogen bonds range from 3.8 to 26.2 standard deviations of eq 4. Further, the direction of the displacements is consistent with hydrogen bonding by protic solvents to the P=O oxygen, leading to electron withdrawal from phosphorus, with a correspondingly increased downfield ^{31}P shift and an increased AN value.

$$\Delta\Delta\mathrm{AN}(2\text{-}\pi^*)^{\mathrm{A}}{}_{\rightarrow \mathrm{O=P}} = \mathrm{AN}^{\mathrm{obsd}}\ (\text{ref } 9) - \mathrm{AN}^{\mathrm{calcd}}\ (\text{eq } 4) \tag{5}$$

That the third condition for solvatochromic comparison is fulfilled is shown in Figure 1b. ΔΔAN terms attributable to hydrogen bonding by protonic solvents are nicely linear with and almost proportional to solvent α values. If the point for acetic acid (solvent **201**), whose π^* and α values are still relatively uncertain,[1,6b] is excluded, the correlation equation, force-fitted through the origin to reflect the necessary direct proportionality between ΔΔAN and α, is given by eq 6, with $n = 7$, $r = 0.995$, and $\sigma = 1.2$. The solid regression line in Figure 1b corresponds to eq 6.[12] If the HOAc result is included, $r = 0.952$ and $\sigma = 4.4$, which still represents an acceptable correlation.

$$\Delta\Delta\mathrm{AN}(2\text{-}\pi^*)^{\mathrm{A}}{}_{\rightarrow \mathrm{O=P}} = 31.3\alpha \tag{6}$$

Total Solvatochromic Equation for AN. The intercept and slope in eq 4 correspond to the XYZ_0 and s terms in eq 3a, and the proportionality constant in eq 6

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[10] Hexamethylphosphoramide (solvent **26**), which was specifically excluded from *the select solvent set* (for which π^* is very nearly proportional to the molecular dipole moment),[4] has occasionally shown anomolous behavior in solvatochromic comparison studies. While it usually fits a π^* value of about 0.9, in a number of occasions (as in the correlation of AN with π^*) effects consonant with a π^* value of 0.4–0.6 have been reported. See also ref 27.

[11] In the system of nomenclature which we have used in this series of papers, which makes descriptions of solvent effects much easier when multiple hydrogen bonding interactions occur simultaneously, the ΔΔ term indicates an enhanced or reduced effect due to hydrogen bonding, the 2-π^* indicates that the effect is observed for indicator **2** relative to a correlation with the π^* scale, the superscript A indicates that the effect is attributed to type-A hydrogen bonding, and the subscript $\rightarrow$O=P indicates that the bonding is by the solvent to the indicator oxygen.

[12] The dashed line represents the least squares equation not force fitted through the origin.

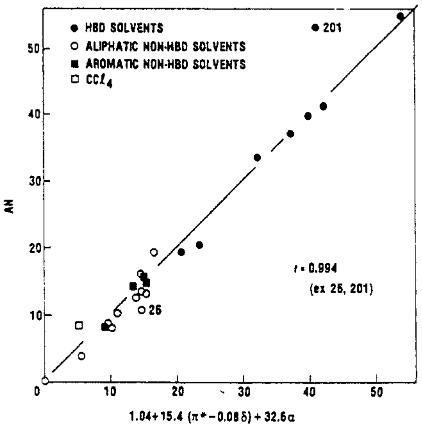

Figure 2. Solvatochromic comparison of AN with π^* and α, multiple linear regression method.

corresponds to the *a* coefficient. Combining the appropriate terms from eq 4 and 6, we therefore obtain the total solvatochromic equation for acceptor numbers of aliphatic solvents (eq 7a; $n = 17$, $r = 0.994$, $\sigma = 1.6$).

$$\mathrm{AN} = 0.40 + 16.4\pi^* + 31.3\alpha \qquad (7a)$$

An alternative route to the total solvatochromic equation is by the method of multiple-parameter least-squares correlation (multiple linear regression analysis), which has become quite convenient with the recent accessibility of inexpensive programmable computers. In this one-step procedure, correlation of the AN values with the aliphatic solvent π^* and α parameters (excluding HOAc and HMPA) leads directly to eq 7b, with $n = 17$, $r = 0.996$, and $\sigma = 1.5$. If the HMPA and HOAc results are included,

$$\mathrm{AN} = 0.04 + 16.2\pi^* + 33.0\alpha \qquad (7b)$$

r becomes 0.985 and σ becomes 2.7. Considering that seven solvent π^* values which served as input to eq 7b did not contribute to the determination of *s* in eq 7a, the fact that the agreement between the two equations is well within the precision of the individual NMR solvent shift determinations must be regarded as highly satisfactory.

For extension of the description of solvent effects on AN to include the aromatic and polychloroaliphatic solvents in a total solvatochromic equation of the form of eq 3b, the *d* term is calculated to be –0.08.[13] Multiple-parameter least-squares correlation of AN with ($\pi^* - 0.08\delta$) and α then leads to the *all solvent* equation (excluding HMPA and HOAc) given by eq 8 ($n = 22$, $r = 0.994$, $\sigma = 1.7$). If

$$\mathrm{AN} = 1.04 + 15.4(\pi^* - 0.08\delta) + 32.6\alpha \qquad (8)$$

the results for HMPA and HOAc are included, $r = 0.984$ and $\sigma = 2.8$. A plot of AN values reported by Gutmann[9] against values calculated through eq 8 is shown in Figure 2.

Equations 6–8 tell us that for nonprotonic solvents the AN parameter is a measure of solvent polarity/polarizability (SPP) and that for HBD solvents AN measures a linear combination of effects attributable to SPP and type-A hydrogen bonding ability. In consequence, all properties which have been reported by Gutmann and others to be linear with AN should be rationalized as well through multiple-parameter correlations with π^* and α.

For example, Gutmann has pointed out[9] that a fair relationship exists between acceptor numbers and Kosower's Z values,[14] with exceptions being found for solvents with low dielectric constants.[15] On this basis, he has commented as follows: "Thus the Z values bear a close relationship to the electrophilic solvent properties rather than representing a general measure of the polarity or of the ionizing properties of a solvent. It has been rather unfortunate that Kosower's otherwise correct ideas about the formation of molecular adducts as a result of solute–solvent interactions could not be applied widely, as he had failed to recognize the chemical meaning of his polarity scale as an approximate guide for the relative electrophilic character of the solvents. His frequent use of the terms, "solvent polarity" and "ionizing power of the solvent" as synonomous expression has been particularly unfortunate and misleading since there is no general relationship between solvent polarity and ionizing properties. The latter have clearly been shown to depend both on the nucleophilic and electrophilic properties of the solvent toward the substrate. It is therefore important to recognize the two functions involved and to estimate their respective contributions".

As with AN, we have reported that Kosower's Z parameter for protonic solvents measures a linear combination of SPP and HBD properties, the correlation equation with π^* and α of aliphatic solvents being eq 9 ($n = 13$, r

$$Z = 51.46 + 19.4\pi^* + 20.5\alpha \qquad (9)$$

$= 0.998$, $\sigma = 1.06$), with no exceptions being necessary for low dielectric constant solvents.[1,15] Thus, the contrasting views of Kosower, that Z measures solvent polarity, and of Gutmann, that AN (and hence Z) measures solvent "electrophilicity",[9p] are reconciled in the present approach to solvent effects, which finds that Z and AN measure somewhat different linear combinations of both properties.

Where hydrogen bonding effects are excluded, "solvent polarity" and Kosower's conception of "ionizing power of the solvent" are indeed synonomous [as was convincingly shown by linear correlations of heats of transfer of the $Et_4N^+I^-$ ion pair into non-HBD solvents with solvent π^* values ($r = 0.985$ for aliphatic solvents)[3b,16]]. Where type-A hydrogen bonding is possible, the "ionizing power of the solvent" does indeed also depend, frequently predominantly, on the ability of the solvent to serve as an electron-pair acceptor.

As a further example, Parker, Gutmann, and co-workers[17] have recently reported that there is a good correlation between solvent acceptor numbers and solvolysis rates of *p*-methoxyneophyl tosylate[18] [rates expressed in terms of free energies of transfer of the transition state from acetonitrile, $\Delta G^*_{tr}(S_N1)$] but have not given the correlation equation or any measure of the goodness of the statistical fit. It is therefore of interest to compare correlations by the two methods of the results in the ten solvents for which AN, π^*, and α values are known (**7**, **18**, **25**, **29**, **32**, **50**, **104**, **105**, **111**, and **201** of Table I).

The correlation equation with AN is given by eq 10 (r

$$\Delta G^*_{tr}(S_N1) = 13.2 - 0.57\mathrm{AN}\ \text{kcal/mol} \qquad (10)$$

$= 0.878$, $\sigma = 5.7$ kcal/mol). For comparison, the multi-

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[13] The *d* term is estimated through the equation $d = 2\Delta XYZ/[s(\mathrm{al}) + s(\mathrm{ar})]$, where ΔXYZ is the difference between values calculated through the regression equations for aliphatic and aromatic solvents at $\pi^* = 0.7$, and s(al) and s(ar) are the slopes of those regression equations.

[14] Kosower, E. M. *J. Am. Chem. Soc.* **1958**, *80*, 5253; Kosower, E. M. "An Introduction to Physical Organic Chemistry"; Wiley: New York, 1968; p 301.

[15] The nonconformance of the less polar solvents to Gutmann's AN vs. Z relationship should not be unexpected in the light of the differing a/s ratios in eq 3a: a/s for AN is 2.05; a/s for Z is 1.06.

[16] Abraham, M. H. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1343.

[17] Parker, A. J.; Mayer, U.; Schmid, R.; Gutmann, V. *J. Org. Chem.* **1978**, *43*, 1843.

[18] Smith, S. G.; Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1961**, *83*, 618.

Table II

	$-\Delta H°$ of complex,[a] kcal/mol	lit.[9,19] DN values
pyridine	34.1 ± 0.4	33.1
tetrahydrofuran	21.4 ± 0.5	20.0
triethylamine	31.7 ± 0.6	61.0

[a] $SbCl_5/CH_2Cl_2$, −55 °C.

ple-parameter least-squares regression equation with the solvatochromic parameters is given as eq 11 (r = 0.987, σ = 2.6 kcal/mol).

$$\Delta G^{\ddagger}_{tr}(S_N1) = 24.5 - 26.5\pi^* - 18.9\alpha \text{ kcal/mol} \quad (11)$$

If the result for water, which is an approximate value extrapolated from water–solvent mixtures and rightly considered suspect by the original authors,[18] is excluded, r becomes 0.993. The relatively poor correlation between $\Delta G^{\ddagger}_{tr}(S_N1)$ and AN is readily explained by the differing a/s ratios (in eq 3a) of 2.05 for eq 7b and 0.71 for eq 11.

Donor Number of Triethylamine. Before examining the relationship between Gutmann's donicities and the β scale, we found it necessary to reevaluate the important donor number reported by Gutmann for triethylamine. The basis for this value, given as 61.0, was uncertain. In his recent book on the donor–acceptor approach,[19] Gutmann had indicated that it had been determined indirectly from a correlation of donicities with ^{23}Na NMR chemical shifts of $NaClO_4$, but the Erlich and Popov paper[20] which was cited as the source of this datum contained no mention of triethylamine. Further, on the basis of many calorimetric measurements for complexing of tertiary amines with $SbCl_4$ and SbF_5, we felt certain that this 61.0 value was far too high.

Accordingly, we determined this value directly by measuring the heat of formation of the $Et_3N–SbCl_5$ complex. Since we considered that at 25 °C in 1,2-dichloroethane (the conditions for the direct determination of most DN values) we might encounter the $SbCl_5$-catalyzed Menschutkin reaction of the trialkylamine with the alkyl halide solvent, the measurement was carried out in methylene chloride at −55 °C, and comparison measurements under the same conditions were made for the $SbCl_5$ complexes with pyridine and tetrahydrofuran. The results are as shown in Table II. As is seen, the $-\Delta H°$'s for pyridine and THF at −55 °C in CH_2Cl_2 are about 1 kcal/mol higher than the values determined at 25 °C in $ClCH_2CH_2Cl$, and on this basis the DN value for triethylamine in Table I is given as 30.7.[21]

Correlation of Gutmann's DN with β. Turning now to the relationship between Gutmann's donicities and the β scale, values of both parameters are known for 18 solvents (Table I). A plot of DN vs. β is shown in Figure 3, where it is seen that if the result for pyridine (solvent **24**) is excluded, linear correlation is quite good. The linear regression equation is given by eq 12 (n = 17, r = 0.976, σ = 2.3). If the result for pyridine is included, the r value falls to 0.958.

$$\mathrm{DN} = -0.17 + 38.4\beta \quad (12)$$

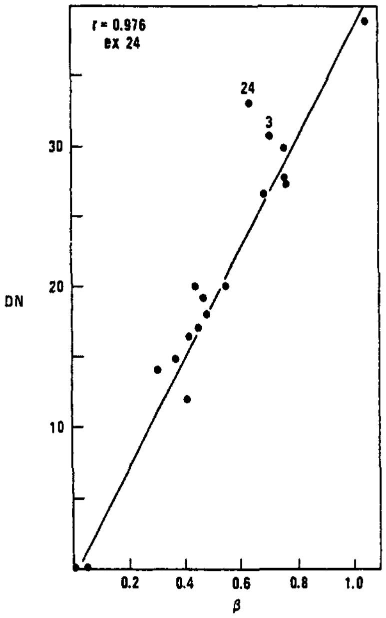

Figure 3. Correlation of Gutmann's donicity numbers with solvent β values.

We do not consider that the out of line behavior of pyridine in Figure 3 results from normal scatter of the data but believe rather that it is reminiscent of the separations into families of HBA bases in an aqueous pK_a vs. pK_{HB} plot[22] and in an infrared $\Delta\nu$ (phenol, free minus bonded) vs. β plot reported earlier.[7c] In the former instance, the separation into families was attributed to differing electronegativities on the acceptor atoms and in the latter to different geometries of the hydrogen bonds or electron mobilities on the HBA atoms. The nonconformance of pyridine to eq 12 may arise from similar differences.[23]

The behavior of pyridine is also reminiscent of a plot reported some years ago[24] wherein a very poor correlation (indeed a scatter diagram) resulted for a plot of $\Delta H_f°$ for complexes of 4-fluorophenol with a large variety of types of hydrogen bond acceptors against $\Delta G_f°$ for the same HBD acid with the same HBA bases. However, when families of bases with similar types of acceptor sites were considered separately, a series of crudely parallel lines was observed.

This raises a fundamental question regarding the scope and applicability of the DN scale, or, for that matter, any other acid–base scale based on a single compound. If the ΔG_f's of 4-fluorophenol complexes with a series of HBA bases are not linear with the ΔH_f's *of the same complexes* when bases with different types of HBA sites are considered together, why should they or any other free energy-proportional solvent-dependent properties be linear with ΔH_f's of Lewis acid–base complexes of $SbCl_5$?[9a,p] It is of considerable interest in this regard to compare correlations with DN and with the solvatochromic parameters of properties which, like DN, depend on interactions between nonprotonic Lewis acid indicators and bases. Preferably, the comparisons should involve solvent sets which include pyridine, the out of line solvent in Figure 3.

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(19) Gutmann, V "The Donor-Acceptor Approach to Molecular Interactions"; Plenum Press: New York, 1978; Chapter 2.

(20) Erlich, R. H.; Popov, A. I. *J. Am. Chem. Soc.* **1971**, *93*, 5620.

(21) In this paper and in previous ones we have followed the usual practices of accepting published thermodynamic, kinetic, and spectral properties at face value. The large discrepancy in the present case is a remainder that poor correlations may occasionally be due to experimental errors in the data rather than to the incursion of a new physical or chemical "effect".

(22) Taft, R. W.; Gurka, D.; Joris, L.; Schleyer, P. v. R.; Rakshys, J. W. *J. Am. Chem. Soc.* **1969**, *91*, 4801.

(23) Usually, where we see such family behavior, tertiary amines are even more out of line than pyridines. That triethylamine seems to conform to eq 12 may be a result of a compensating steric effect, which lessens the $Et_3N–SbCl_5$ formation energy and offsets the tendency toward out of line behavior.

(24) Arnett, E. M.; Mitchell, E. J.; Murty, T. S. S. R. *J. Am. Chem. Soc.* **1974**, *96*, 3875.

NMR Coupling Constant of Me_3SnCl. The $J(^{119}Sn-CH_3)$ coupling constant of $(CH_3)_3SnCl$, reported by Bolles and Drago,[25] represents such a solvent-dependent property. Coupling constants in ten solvents including pyridine (solvents **6**, **7**, **13**, **18**, **23**, **24**, **26**, **29**, **50**, and toluene) show a fair correlation with β (eq 13a; $r = 0.938$, $\sigma = 1.8$ Hz).

$$J(^{119}Sn-CH_3) = 57.1 + 14.6\beta \text{ Hz} \qquad (13a)$$

If we allow also a partial dependence on π^*, the goodness of the fit is improved significantly (eq 13b, $r = 0.980$), and

$$J(^{119}Sn-CH_3) = 54.2 + 7.8\pi^* + 10.2\beta \text{ Hz} \qquad (13b)$$

the correlation is improved even more if we include a $d\delta$ term with a d value of about -0.20 in a total solvatochromic equation of the form of eq 2b (eq 13c, $r = 0.988$).

$$J(^{119}Sn-CH_3) = 54.8 + 8.8(\pi^* - 0.20\delta) - 8.5\beta \text{ Hz} \qquad (13c)$$

DN numbers have been reported for eight of Bolles and Drago's solvents (Table I), and we have assigned DN = 0 (like $ClCH_2CH_2Cl$) to CCl_4 and DN = 0.1 (like benzene) to toluene in order that the comparison with eq 13a–c not be biased in favor of the solvatochromic parameters. The correlation equation with DN for the coupling constants in these ten solvents is given by eq 14a ($r = 0.922$, $\sigma = 2.0$ Hz).

$$J(^{119}Sn-CH_3) = 57.9 + 0.342\text{DN Hz} \qquad (14a)$$

Acceptor numbers have also been reported for the solvents treated above (again we will use the benzene AN number for toluene), which allows a multiparameter treatment according to Gutmann's donor–acceptor approach to solvent effects. In the light of the near proportionality between AN and π^* for non-HBD solvents shown in eq 4, this is roughly comparable to a multiple-parameter correlation with DN and π^*. The correlation equation with Gutmann's parameter is given by eq 14b (r = 0.956).

$$J(^{119}SN-CH_3) = 55.5 + 0.309\text{DN} + 0.257\text{AN Hz} \qquad (14b)$$

On comparison of eq 13a–c with eq 14a,b, it is seen that the correlations with the solvatochromic parameters are somewhat better (but not overwhelmingly so) than with Gutmann's parameters. It is therefore also useful to compare the J values calculated by the two-multiparameter equations with the observed coupling constant for pyridine, the out of line data point in Figure 3. The results are as follows: J(eq 13c) = 66.1 Hz, J(eq 14b) = 69.4 Hz, J(exptl) = 67.0 Hz. These seem to indicate that, although the indicator is a Lewis acid similar to $SbCl_5$, this property shows β-type rather than DN-type behavior.

^{19}F NMR Spectrum of Bis(4-fluorophenyl)mercury. Another comparison of the two sets of solvent parameter scales involves ^{19}F NMR shifts of $(4-FC_6H_4)_2Hg$ relative to fluorobenzene as internal standard.[26] Results are available in 12 solvents for which both β and DN are known or can be estimated (**6**, **9**, **11**, **13**, **14**, **18**, **24**, **26**, **29**, **50**, and **61**; we assume DN = 0 for cyclohexane).

The least-squares regression equation of the ^{19}F NMR shifts with solvent β values is given by eq 15a ($r = 0.974$,

$$\delta = -0.96 + 2.85\beta \text{ ppm} \qquad (15a)$$

$\sigma = 0.22$ ppm). With the allowance of a partial dependence on π^* also, the multiple linear regression equation becomes eq 15b ($r = 0.985$). For comparison, the correlation

$$\delta = -1.22 + 0.83\pi^* - 2.27\beta \text{ ppm} \qquad (15b)$$

equation with DN is given by eq 16a ($r = 0.953$, $\sigma = 0.28$

$$\delta = 0.90 + 0.067\text{DN ppm} \qquad (16a)$$

ppm), and the multiple-parameter correlation with AN and DN (above solvents except **11** and **61**, for which AN is not known) is shown in eq 16b ($r = 0.965$).

$$\delta = 1.06 + 0.063\text{DN} + 0.022\text{AN ppm} \qquad (16b)$$

As before, the solvatochromic parameters give somewhat better correlations (but not overwhelmingly so) than AN and DN, so that a comparison of the results in pyridine is again appropriate. The results are δ(eq 15b) = 0.96 ppm, δ(eq 16b) = 1.34 ppm, and δ(exptl) = 0.94 ppm. Again, although the indicator is a nonprotonic Lewis acid, the property shows β-type rather than DN-type behavior.[27]

Solvent–Cation Complexation Parameter, L_s. Also of interest are the effects of pure solvents on the ^{19}F NMR spectra of a series of *m*- and *p*-fluorophenyl alkyl- and aryl-substituted "onium" ions (ammonium, carbonium, phosphonium, sulfonium) as reported by Rakshys and Taft.[28] The solvent effects were found to be well correlated by the product of a solvent–cation complexation parameter, L_s, and a cation sensitivity parameter, M_{R^+}. L_s was considered to be an approximate measure of the stability of a generalized class of weak organic cation–molecule complexes which appeared specifically not to involve hydrogen bonding interactions (although for certain of the *p*-fluorophenyl onium ions such as $4-FC_6H_4S^+(CH_3)_2$, the possibility of HBD acidity of a proton on the alkyl group cannot be excluded).

Correlation is quite good between the L_s values for nine solvents (**23**–**26**, **28**, **29**, and **50**; trimethyl phosphate, β = 0.73; tetramethylurea, β = 0.78) and corresponding β values (eq 17a; $r = 0.984$, $\sigma = 0.12$). Here, however, the high r

$$L_s = 1.85 + 3.30\beta \qquad (17a)$$

value for eq 17a may mask an important contribution of solvent polarity to medium effects on L_s. Multiple linear regression analysis (excluding TMP and TMU, whose π^* values are not yet known) leads to eq 17b (r = 0.990).

$$L_s = 0.79 + 1.41\pi^* + 3.05\beta \qquad (17b)$$

For comparison, the correlation equation between L_s and DN (above solvents except TMU; DN of TMP = 23.0[19]) is given by eq 18a ($r = 0.796$, $\sigma = 0.45$), and the correlation

$$L_s = 2.13 + 0.075\text{DN} \qquad (18a)$$

equation with AN and DN is shown in eq 18b ($r = 0.836$).

$$L_s = 2.32 - 0.018\text{AN} + 0.076\text{DN} \qquad (18b)$$

By any reasonable standards, the r values for eq 18a,b represent a statistically unsatisfactory correlation.

From the comparisons it appears quite clear that, for the properties discussed here (admittedly a limited sam-

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[25] Bolles, T. F.; Drago, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 3255.

[26] Kravtsov, D. N.; Kvasov, B. A.; Fedin, F. N.; Faingor, B. A.; Golovchenko, L. S. *Izv. Akad. Nauk SSSR* **1969**, 536.

[27] Since the data point for hexamethylphosphoramide (**26**) was out of line in the correlations of AN with π^* and with π^* and α (eq 4, 7, and 8), it is also of interest to compare observed values of $J(^{119}Sn-CH_3)$ and δ of bis(4-fluorophenyl)mercury with values calculated by using the two parameter sets. The results are as follows: $J(\pi^*,\beta)$ = 71.6; J(AN,DN) = 70.2; J(exptl) = 71.6; $\delta(\pi^*,\beta)$ = 1.90; δ(AN,DN) = 1.62; δ(exptl) = 1.93. Thus, while solvent no. **26** has been anomalous in a number of correlations with the solvatochromic parameters, it is seemingly worse with AN and DN insofar as the present correlations are concerned.

[28] (a) Rakshys, J. W., Jr. Ph.D. Thesis, University of California, Irvine, CA, June 1967. (b) The material is adequately summarized in ref 22.

pling), nonprotonic Lewis acid–base type solvent effects parallel type-B hydrogen bonding (proton sharing) effects in their dependence on β. Moreover, it may also be noted that for the 50-odd correlations of properties of protonic indicators or reactants which we have carried out in connection with the HBA basicity scale, the demonstrated fits with β or with β and π^* were better than corresponding correlations with DN or with AN and DN. Indeed, from our evaluation of the latter parameter, we conclude that DN is a reasonably good measure of the ability of the solvent to serve as an electron-pair donor to solutes when only oxygen bases (and a few R–CN nitrogen bases) are considered but that the correlations of solvent effects on free-energy-proportional properties are likely to break down if the solvent sets include single bonded nitrogen or pyridine bases.

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Systematic Conformational Analysis. General Method for Rapid Conformational Evaluation. Its Application to the Hydroazulene System

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A simple yet general method for conformational analysis of cyclic systems, with present focus on the seven-membered ring, is outlined. From a two-dimensional structure, with stereocenters indicated by wedged and hashed bonds, a semiquantitative conformational evaluation is rapidly performed by hand. Central in the procedure stands the identification of torsion-constraining structural features and the analysis of the constraints in terms of allowed signs and magnitudes of endocyclic torsion angles. The matching of the so-defined constraints against a set of basic unsubstituted ring forms allows for the derivation of a primary set of allowed conformations or, via simultaneous assessment of conformational energies (i.e., strain energies of the unsubstituted ring form and axial substituents), a secondary set of probable forms. The final prediction of the preferred conformation(s) proceeds via supplementary energy and torsional constraint evaluations. Examples are given dealing with the hydroazulene system.

Molecular model examination is extremely popular among synthetic chemists because it can yield both qualitative (e.g., evaluation of steric environment) and quantitative (e.g., interatomic distances) information that may otherwise be difficult to arrive at. A prerequisite to the effective use of models, however, is the knowledge of the preferred geometry of the molecule. Hence a problem arises when dealing with systems that can adopt several conformations. Indeed, the sole manipulation of a model does not indicate which among the considered forms is the preferred one, nor can it ensure that all possible conformations have been examined. The present paper describes a conformational procedure that intends to help in resolving that problem in a ready and systematic way.

At the origin of this work stands the observation of some remarkable stereo- and regioselective reactions in the hydroazulene field.[2] In contrast with the six-membered-ring case,[3-5] the conformational analysis of seven-membered rings and other flexible systems is generally regarded as tentative. A conformational procedure for cycloheptane derivatives with particular attention to the natural perhydroazulenes has already been reported by Hendrickson.[6] A refinement of his procedure has presently led to a general yet simple method for the semiquantitative conformational analysis of cyclic systems. Starting from a two-dimensional structure with stereocenters indicated by the conventional wedged (β, up)/hashed (α, down) bond notation, one can perform the analysis rapidly by hand. In this paper I describe the essential features of the method with focus on the seven-membered ring.

As a working hypothesis I assume that the analysis of the torsional constraint imposed upon a cyclic system must enable the deduction of a primary set of "allowed" basic conformations (Chart I, entry 9). A basic conformation refers to a geometrically well-defined (usually symmetry related) form. Structural features which may impose a torsion constraint on the endocyclic bonds include fusions with other rings, bridgings, and anchoring substituents (e.g., *tert*-butyl) located off the ring (entry 5). The consideration of the strain energies[7,8] of the unsubstituted ring forms and of the various substituents (entry 10) in the allowed forms leads to a secondary set of "probable" low energy conformations (entry 12). Further energy and torsion constraint evaluations (entries 13 and 14) eventually yield the preferred geometry of the molecule (entry 15). Torsion constraints may restrict both the sign and the magnitude of internal torsion angles of a ring and are

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[1] Bevoegdverklaard Navorser of the Belgian Nationaal Fonds voor Wetenschappelijk Onderzoek.

[2] For recent syntheses of pseudoguaianolides, see: (a) Demuynck, M.; De Clercq, P.; Vandewalle, M. *J. Org. Chem.* **1979**, *44*, 4863; (b) Kok, P.; De Clercq, P.; Vandewalle, M. *Ibid.* **1979**, *44*, 4553; (c) Wender, P. A.; Eissenstat, M. A.; Filosa, M. P. *J. Am. Chem. Soc.* **1979**, *101*, 2196; (d) Grieco, P. A.; Ohfune, Y.; Majetich, G. *Tetrahedron Lett.* **1979**, 3265. (e) Grieco, P. A.; Ohfune, Y.; Majetich, G. *J. Org. Chem.* **1979**, *44*, 3092. (f) Roberts, M. R.; Schlessinger, R. H. *J. Am. Chem. Soc.* **1979**, *101*, 7626; (g) Quallich, G. J.; Schlessinger, R. H. *Ibid.* **1979**, *101*, 7627.

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