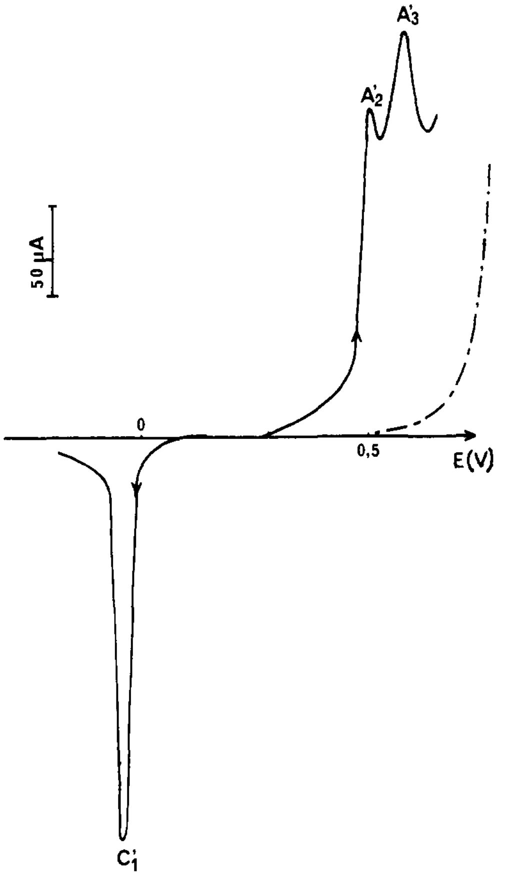

Figure 6. Voltammogram of (TTF)Br$_{0.7}$ (1.45 mg) in 1 M KBr (graphite 50 mg; scan rate 2.5 × 10^{-5} V s^{-1}). (-·-) Residual current without (TTF)Br$_{0.7}$).

tration is increased from 0.1 to 1 M; at the same time, the values of $E_{pA_{1a}'}$ and $E_{pA_{1b}'}$ become more positive as the bromide concentration decreases and plots of the peak potentials vs. log (Br$^-$) exhibit (−60 mV) slopes. These results suggest that the reactions occurring at the potential of A$_{1a}$′ or A$_{1b}$′ correspond to the formation of two different bromide salts: (TTF)Br$_\rho$ and (TTF)Br$_{\rho'}$ according to

$$\mathrm{TTF} + \rho\mathrm{Br}^- \rightarrow (\mathrm{TTF})\mathrm{Br}_\rho + \rho e^-$$

and

$$(\mathrm{TTF})\mathrm{Br}_\rho + (\rho' - \rho)\mathrm{Br}^- \rightarrow (\mathrm{TTF})\mathrm{Br}_{\rho'} + (\rho' - \rho)e^-$$

Average values of ρ and ρ' have been determined from the areas of A$_{1a}$′ and A$_{1b}$′ obtained with various amounts of TTF: $\rho = 0.046 \pm 0.004$ (peak A$_{1a}$′) and $\rho' = 0.690 \pm 0.011$ (peaks A$_{1a}$′ and A$_{1b}$′).

As a matter of fact, among the TTF bromides, those near the compositions $\rho = 0.59$ and $\rho = 0.76$ have been isolated,[24] though presently only one nonstoichiometric bromide is detected electrochemically in this ρ range. Bromides whose composition would correspond to $\rho = 0.05$ have never been observed. Our present attempts to isolate this compound have been unsuccessful, but we feel that our voltammetric results are clearly in favor of the formation of this compound.

The oxidation of TTF in the presence of bromide may then be summarized by the following reactions:

$$\mathrm{TTF} + 0.05\mathrm{Br}^- \xrightarrow{A_{1a}'} (\mathrm{TTF})\mathrm{Br}_{0.05} + 0.05e^-$$

$$(\mathrm{TTF})\mathrm{Br}_{0.05} + 0.65\mathrm{Br}^- \xrightarrow{A_{1b}'} (\mathrm{TTF})\mathrm{Br}_{0.7} + 0.65e^-$$

$$(\mathrm{TTF})\mathrm{Br}_{0.7} + 0.3\ \mathrm{Br}^- \xrightarrow{A_2'} (\mathrm{TTF})\mathrm{Br} + 0.3e^-$$

Oxidation of (TTF)Br at more anodic potentials (peak A$_3$′) probably leads to the formation of (TTF)Br$_2$, which is apparently more stable than its chloride analogue, as shown by the existence of a reduction peak, C$_3$′ (Figure 5).

Conclusion

Carbon paste electrodes can be easily and valuably used for the study of the electrochemical behavior of solid organic materials. Such studies have been carried out on a series of TTF salts as a possible example. We have characterized by this technique some previously known nonstoichiometric compounds in this series. The probable formation of a new TTF bromide salt ((TTF)Br$_{0.05}$) with an unusual composition has also been observed.

Clearly, one result of these studies is an interesting way to investigate stable intermediate phases that may occur during the redox transformations of organic solids and to determine the potential regions where these materials are electrochemically inactive and could be used as electrodes.

Further work is, however, required on an extended series of organic material to discuss more precisely the mechanism of the electron-transfer steps of these processes and to achieve rational correlations of the electrochemical behavior investigated with other solid-state physical properties.

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An *E* and *C* Modification of the β–π^* Solvation Approach

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Abstract: The specific and nonspecific interactions between a solute and polar solvent are treated by an extension of the *E* and *C* equation to incorporate nonspecific solvation. An equation of the general form $\Delta X = E_A{}^*E_B + C_A{}^*C_B + SD^*$ is offered where ΔX is the observable, E^* and C^* are parameters for the specific donor–acceptor interaction, and S and D^* are solute and solvent parameters for the nonspecific solvation interaction. The treatment is compared to the Kamlet–Taft β–π^* approach. Similarities and some very significant differences are discussed, indicating the limitations of a β–π^* analysis. The fundamental cause of the limitations reported for $\Delta\nu_{OH}$–ΔH correlations of alcohols is discussed and the correlations are shown to be more general than some reports indicate. The analysis presented lends support to the Kamlet–Taft interpretation of the meaning of $b\beta$, dramatically increases the *E* and *C* data base and provides support for the solvation minimized nature of the original *E* and *C* data base.

Introduction

The influence of solvent variation on the properties of molecules and reactions has fascinated chemists for a long time. Work from this laboratory has served to illustrate the significant point that coordinate-bond formation and nonspecific solvation are two independent solvent properties.[1,2] Though considerable success has

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been achieved in the quantitative prediction of coordinate bond strengths,[3] we have not offered quantitative scales of solvent polarity.

There have been many attempts to develop general scales of solvent polarity by choosing a single solute that undergoes large changes in some property (a spectral or reaction parameter) upon varying the solvent.[4-6] The magnitude of the change for a series of solvents provides a scale of solvation. The resulting scales have not found general applicability[7-9] because not every molecule bonds to or has similar polar interactions with the solvents.

Other approaches to predicting solvent properties involve a multiple-parameter treatment utilizing terms to correlate each different type of effect.[7-9] The most successful multiple parameter correlation has been developed by Kamlet and Taft.[9]

$$XYZ = XYZ_0 + b\beta + S(\pi^* + d\delta) \qquad (1)$$

In eq 1 *XYZ* denotes some free energy property such as a spectral transition energy, equilibrium constant, or rate of reaction; XYZ_0 is that value of the aforementioned property for a reference solvent; $b\beta$ corresponds to the amount of specific interaction (caused, for example, by hydrogen bonding) of the basic solvent, β, to a acidic solute, b; $b\beta$ is replaced by $a\alpha$ for the interaction caused by an acidic solvent, α, interacting with a basic solute a; $s(\pi^* + d\delta)$ represents the nonspecific interaction with s defining the susceptibility of the solute, π^* the solvent polarity, and $d\delta$ a correction for the polarizability of halogenated or aromatic solvents. Each solvent parameter (α, β, π^*) is based on the average effect of the solvent on a number of different solutes. The α, β, and π^* parameters that result from the empirical fitting of this extensive data set are used, often in combination with others, to account for solvent effects in a number of new systems.

The quantitative prediction of coordinate bond strengths for 1:1 neutral Lewis acid-base adducts has been demonstrated[3] with the *E* and *C* equation:

$$-\Delta H = E_AE_B + C_AC_B \qquad (2)$$

where E_A and C_A are empirical acceptor parameters and E_B and C_B are empirical donor parameters. The E_A and E_B parameters parallel our qualitative ideas of electrostatic interactions while C_A and C_B parallel ideas of covalent interactions between acceptor and donor. The data used to evaluate these parameters are relatively solvation free and therefore well suited for estimating coordinate bond strengths for neutral donor-acceptor interactions. Equation 2 can also be used[3c] in the analysis of free energies or spectral shifts to determine whether these quantities are dominated by coordinate bond strengths ($-\Delta H$). Thus, this equation should be directly applicable to the specific interactions in the systems treated by β-π^* if the interpretation[9] of $b\beta$ is correct. We shall develop an approach to test this idea for acceptor solutes in donor solvents, realizing that the extension to donor solutes in acceptor solvents is straightforward.

Equation 1 treats the donor-acceptor interaction with one term, $b\beta$. This is not a general equation for donor-acceptor interactions for reversals in a donor strength order can occur when the acceptor is varied and at least a two-term equation is required to correlate such reversals.[3] Thus, eq 1 should be rewritten as

$$XYZ = XYZ_0 + E_A{}^*E_B + C_A{}^*C_B + s(\pi^* + d\delta) \qquad (3a)$$

or for aliphatic bases or solvents

$$\Delta X = E_A{}^*E_B + C_A{}^*C_B + SD^* \qquad (3b)$$

In eq 3b we have replaced π^* with D^* to distinguish the two sets of parameters and for now will forego use of solvents that require $d\delta$. For acidic solutes in basic solvents, the reported E_B and C_B values are to be employed in eq 3b. The solute $E_A{}^*$ and $C_A{}^*$ values that one determines empirically will contain conversion units to change (kcal mol^{-1})$^{1/2}$ for E_B and C_B to those units of ΔX. For this reason, and since they do not directly refer to bond strengths, asterisks are used on the parameters. The *S* parameter refers to the susceptibility of the solute to the nonspecific interaction with the medium and the D^* parameter to the nonspecific solvation strength of the solvent. For basic solutes in acidic solvents the reported E_A and C_A values can be used in eq 3 and C_B and E_B empirically determined.

There are several advantages that accrue from an attempted fit of the Kamlet-Taft data base to eq 3b.

1. Support for their proposal that $b\beta$ (or $a\alpha$) represents specific donor-acceptor interaction parameters will be obtained if our E_B and C_B parameters (determined from enthalpies under solvation minimized conditions) agree with their estimate of this effect. Note that since reported[3] E_B and C_B values based on enthalpies of adduct formation are to be used in our fit of these spectroscopic shifts, this new data base is fit by four unknowns: $E_A{}^*$, $C_A{}^*$, S, and D^*. The same number of unknowns are employed in the $b\beta$ analysis of this spectroscopic data base for the solvents selected.
2. A fit of this data base will significantly increase the data base for *E* and *C* and enhance the usefulness of this approach.
3. A fit of this data base will provide further support for the solvation minimized character of the *E* and *C* parameters.
4. Utilization of the more general eq 3 in place of eq 1 will permit the extension of solvation effect predictions to systems with donor order reversals. As we shall see, incorrect interpretations can result when certain systems are incorrectly forced to fit eq 1.

With these objectives in mind, the UV-visible spectral shifts of a number of substituted aniline indicators used to determine β and π^* were fit to eq 3b using a computer program designed to find the best fit $E_A{}^*$, $C_A{}^*$, S, and D^* values.

Calculations

Hexane was chosen as the reference solvent instead of cyclohexane so all the solvent solvation parameters (D^*) have the same sign. Expressed in kcal mol^{-1} (2.86 kcal mol^{-1} = 1 kK) the spectroscopic data are the bathochromic shift from hexane, $\Delta\nu$, of a series of solutes and are summarized in Table M-1 of the microfilm edition. These data were fit to a three-term, six-parameter equation with programs designed to find the best fit E^*, C^*, S for solutes and D^* for solvents using both a "linearized" least-squares method[3a] or a round-robin multiple least-squares regression. Both programs converge to the same solution, and the resulting parameters are reported in Table I. The computations were done on a Digital Vax 11/780 computer in double precision.

The experimental error in most of the shifts was taken to be 0.3 kcal/mol (~0.10 kK). A weighting scheme was devised to prevent systems, in which aggregation or self-association was suspected, from introducing error into the noninteracting systems.

The following errors, σ_i, were assigned to these systems in cyclohexane: 0.4 kcal mol^{-1} to shifts where the maximum value in hexane is obtained by extrapolation; 0.5 kcal mol^{-1} to shifts involving polar solutes in cyclohexane where some aggregation is suspected (the results show little or no effect from association as reported[9]); 0.7 kcal mol^{-1} to shifts in cyclohexane where

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Table I

solutes	E_A	C_A	S
1. 2-nitroaniline	0.657 0.097	0.055 0.052	2.282 0.620
2. *N*-methyl-2-nitroaniline[a]	−0.602 0.066	−0.028 0.036	2.238 0.048
3. *N*,*N*-dimethyl-2-nitroaniline	0.00	0.00	2.152 0.113
4. *N*-ethyl-3-nitroaniline	2.125 0.248	0.077 0.199	2.095 0.162
5. 4-nitroaniline	4.425 0.150	0.085 0.065	3.434 0.193
6. *N*-methyl-4-nitroaniline	2.088 0.124	0.096 0.053	3.422 0.294
7. *N*,*N*-diethyl-4-nitroaniline	0.00	0.00	3.457 0.825
8. 3-methyl-4-nitroaniline	4.992 0.146	0.008 0.057	3.280 0.111
9. *N*-ethyl-3-methyl-4-nitroaniline	2.130 0.086	0.081 0.040	3.273 0.058
10. *N*,*N*-diethyl-3-methyl-4-nitroaniline	0.00	0.00	3.215 0.559
11. 3,5-dinitroaniline[a]	4.458 0.224	−0.018 0.087	1.502 0.399
12. 2-nitro-*p*-toluidine	0.572 0.092	0.077 0.052	2.205 0.117
13. *N*,*N*-dimethyl-2-nitro-*p*-toluidine	0.00	0.00	2.133 0.911
14. 2-nitro-*p*-anisidine	0.766 0.169	0.106 0.084	1.848 0.219
15. *N*,*N*-dimethyl-2-nitro-*p*-anisidine	0.00	0.00	2.193 0.204
16. 4-nitrophenol	3.197 0.119	0.074 0.053	2.498 0.155
17. 4-nitroanisole	0.00	0.00	2.612 0.096
18. 4-aminobenzophenone	2.406 0.172	0.023 0.086	2.367 0.111
19. ethyl 4-aminobenzoate			
20. *N*-(4-nitrophenyl)aziridine	0.00	0.00	2.759 0.286
21. *N*-(4-nitrophenyl)pyrrolidine	0.00	0.00	3.431 0.233
22. *N*-(4-nitrophenyl)piperidine	0.00	0.00	3.363 .248
23. 3-nitroaniline[b]	4.130 0.756	0.098 0.063	1.716 0.354

solvents	E_B	C_B	D^*
1. C_6H_{12}	0.00	0.00	0.190 0.059
2. CCl_4	0.00	0.00	0.813 0.054
3. C_2Cl_4	0.00	0.00	0.846 0.059
4. C_5H_5N	1.17	6.40	2.443 0.047
5. $(C_2H_5)_3N$	0.991	11.09	0.525 0.065
6. $HC(O)N(CH_3)_2$ (DMF)	1.23	2.48	2.557 0.074
7. $CH_3C(O)N(CH_3)_2$ (DMA)	1.32	2.58	2.521 0.082
8. $CH_3C(O)OC_2H_5$	0.975	1.74	1.537 0.087
9. $(CH_3)_2O$ (acetone)	0.987	2.33	2.04 0.118
10. $(C_2H_5)_2O$	0.963	3.25	0.932 0.053
11. $(CH_2)_4O$ (THF)	0.978	4.27	1.692 0.072
12. $(CH_2)_5O$ (THP)	0.949	3.91	1.586 0.070
13. $(CH_3)_2SO$ (Me_2SO)	1.34	2.85	2.830 0.058
14. $(C_2H_5O)_3PO$	1.36	1.81	2.140 0.060

[a] Most negative values are within error limits of being zero or have limited data and are statistically insignificant. A negative value is not an impossibility.[3] [b] These parameters were not part of the original master fit but calculated afterwards using the best fit E_B, C_B, and D^* parameters.

self-association via hydrogen bonding is suspected (the results show little or no effect from association as reported[9]).

Errors of 0.1 kcal/mol were assigned to shifts involving noninteracting solutes in cyclohexane. The equation

$$\text{weight}_i = \sigma_i^{-2} \Big/ \frac{1}{N}\sum_{j=1}^{N} \sigma_j^{-2}$$

was used to weight the data in the least-squares fit.

The solvents and solutes in which specific acid–base interactions are not expected were given respectively E_B and C_B or E_A and C_A values fixed at 0. These systems are shown in Table I. The other donor solvents have E_B and C_B values fixed at the literature values.[3] The original guesses for the S and D^* parameters were the reported π^* values.[9] The criterion for convergence is change in χ^2 (sum of the squared deviations) of less than 0.01% upon successive iterations.

The multiple linear regression method, though less statistically rigorous, facilitates the detection of systematic errors. The first attempted data fit contained all solvents with known E_B and C_B values that have at least three spectral data points. During the initial fits, it was found that the solvents *p*-dioxane, CH_3CN, and hexamethylphosphoramide show large (>0.3 kcal/mol) deviations between the experimental and calculated shifts. The β–π^* analysis of other reported systems[9] caused Kamlet and Taft to conclude that these are unusual solvents.[9d,e] In the E and C approach we find *p*-dioxane and HMPA work well with ΔG, ΔH, ΔS, and $\Delta\nu_{OH}$, but not with the UV indicator shifts or the ^{19}F shifts. The basic solvent benzene is an aromatic system and is excluded because the solutes are also aromatic and a specific π–π intermolecular interaction is possible. Not enough data are available to parameterize these π–π effects and check the parameterization. Furthermore, in weakly basic solvents like benzene which do not fully complex the solute, a broad band will result from free and complexed solute whose average position will not reflect the full contribution from specific interactions. When these systems and acidic, chlorinated hydrocarbons are excluded, the remaining data set is comprised of 212 shifts for 22 solutes and 14 solvents.

Results and Discussion

The overall χ^2 of the fit of the spectroscopic data to eq 3b is 5.409 and the standard deviation 0.16 kcal mol^{-1}. Perhaps a better way of judging such a fit is its ability to reproduce the data in the set within experimental error. In this fit, only 17 of the 212 calculated shifts miss by more than 0.3 kcal mol^{-1} and most of these miss by less than 0.5 kcal mol^{-1}. The best fit E_A^*, C_A^*, S, and D^* parameters are listed in Table I along with their conditional standard deviations. Though based on different reference shifts, the comparison between D^* and π^* shows that they are essentially the same parameter. This similarity is shown by a plot of D^* vs. π^* which fits to the linear equation $D^* = (2.86/1.07)\ \pi^* + 0.161$, with a correlation coefficient $r = 0.9973$. Thus, the β–π^* breakup of the total shift in these systems into specific and nonspecific interactions is fully consistent with an E and C prediction of the specific interaction.

The parameters also show there is a strong correlation between E_B and D^* for the specific interacting donors. This is not unexpected as the E_B parameters of donors parallel ideas about the ability of that donor to undergo an electrostatic interaction with an acceptor, and Abboud, Kamlet, and Taft[9f] have shown

Table II. Chemical Shifts of Fluorine with Respect to Fluorobenzene (ppm)[14]

solvent	3-fluorophenylmercury acetate		4-fluorophenylmercury acetate		bis(4-fluorophenylmercury)		bis(3-fluorophenylmercury)	
	exptl	calcd[b]	exptl	calcd[c]	exptl	calcd[d]	exptl	calcd[e]
cyclohexane					−1.21	*f*	−0.31	*f*
tetrahydrofuran	−0.52	−0.60	−0.51	−0.52	0.51	0.47	0.47	0.49
acetone	−0.73	−0.64	−0.76	−0.72	0.50	0.50	0.56	0.52
ethyl acetate	−0.61	−0.59	−0.95	−0.96	0.32	0.32	0.45	0.48
acetonitrile[a]	−0.83	−0.87	−1.00	−1.02	0.45	0.39	0.41	0.47
dimethyl sulfoxide	−0.05	−0.08	0.17	0.17	1.06	1.12	0.87	0.83
pyridine	−0.37	−0.34	0.33	0.33	0.94	0.98	0.67	0.67

[a] D^* value calculated from $D^* = 2.67\pi^* + 0.161$. [b] $\delta = 1.97E_B + 0.004C_B - 0.167D^* - 2.25$, $r = 0.978$. [c] $\delta = 1.73E_B + 0.156C_B + 0.246D^* - 3.29$, $r = 0.999$. [d] $\delta = 1.03E_B + 0.042C_B + 0.294D^*$, $r = 0.991$. [e] $\delta = 0.68E_B - 0.002C_B + 0.083D^*$, $r = 0.984$. [f] These correlations were done as the extent of the shift from cyclohexane.

their π^* parameter is correlated to the dipole moment of the donors. Correlation between "independent" variables of multiple linear regression can cause problems in obtaining a well-defined minimum. In order to reduce this problem, solvents with a wide range of C/E, E/D^*, and C/D^* ratios must be used. This can best be accomplished by using a set of solvents that include a wide range of specific interacting solvents as well as nonspecific ones. These conclusions are supported by an analysis of the inter-"independent" variable correlation coefficients.

The trends in the magnitude of the specific acid–base interaction with acid variation are reasonable when compared to Hammett substituent effects. Graphs of $E_A{}^*E_B + C_A{}^*C_B$ for the three *singly* substituted anilines, 3-nitroaniline, 4-nitroaniline, and 4-aminobenzophenone, fit well to straight-line plots of the Hammett parameters. This behavior is expected, since the Hammett approach is a restricted form of the *E* and *C* equation.[3a] Ethyl 4-aminobenzoate has not been studied with a wide enough range of different solvents to permit a unique determination of its parameters. The 2-nitro derivatives are intramolecularly hydrogen bonded and weaker acids than expected on the basis of the inductive effect of the substituents. Most of the *S* coefficients obtained in our fit are very close to the reported Kamlet–Taft *s* values. The agreement provides a very strong endorsement for the ability of the *E* and *C* parameters to predict coordinate bond strengths and strengthens our claim that the data set used for *E* and *C* is solvation minimized.

***E* and *C* vs. β.** To test β against *E* and *C*, the same data set used in the master fit that determined the compatibility of *E* and *C* with π^* was fit to Kamlet and Taft's double-scale, four-parameter equation

$$\Delta\nu = b\beta + s\pi^* \tag{4}$$

In this case, β is fixed at literature values while *b*, *s*, and π^* are allowed to vary. The *b* parameter for noninteracting solutes is fixed at 0 as in the *E* and *C* fit. The overall χ^2 value of 5.598 is comparable to that for the *E* and *C* fit. This β–π^* fit misses 18 shifts by more than 0.3 kcal mol^{-1}. The nonspecific solvation parameters for the solvents and solutes are very close (within a standard deviation) to the values obtained in the *E* and *C* fit. This brings up the question, why use the *E* and *C* equation when β appears to be sufficient?

We have shown previously[10] that when a series of donors are investigated toward acceptors with similar C_A/E_A ratios, the *E* and *C* equation reduces to a one-term equation. Dividing $\Delta H = E_AE_B + C_AC_B$ by E_A gives

$$\frac{\Delta H}{E_A} = E_B + \frac{C_AC_B}{E_A} = E_B + kC_B = P_B \tag{5}$$

(that is, $E_B + kC_B$ is a function only of the base). Therefore, $\Delta H = E_AP_B$.

Since most of the acids in this spectroscopic data set have similar C_A/E_A ratios, a one-term ($b\beta$) analysis of the specific interactions will work. However, it is to be emphasized that the parameters can be used only on new systems with this same C_A/E_A ratio. It can be shown[11] that this one-parameter treatment is expected to work for solutes with a C_A/E_A ratio of 0.0287.

How problems can arise with β and why it seems to work for acids with C_A/E_A different from 0.0287 can be explained by manipulation of the *E* and *C* equation. If some measured property, y_i (ΔH, $\Delta\nu$, etc.) fits to *E* and *C*, two equations can be written:

$$y_i = E_AE_{B_i} + C_AC_{B_i}$$

$$\beta_i = 0.509E_{B_i} + 0.0146C_{B_i}$$

An equation relating y_i and β_i can be obtained[12] (given $\beta \neq 0$)

$$y_i = \frac{E_A}{0.509}\left[\frac{E_{B_i}/C_{B_i} + C_A/E_A}{E_{B_i}/C_{B_i} + 0.0287}\right]\beta_i \tag{6}$$

Equation 6 can be written as $y_i = kq_i\beta_i$, where $k = E_A/0.509$ and $q_i = (E_{B_i}/C_{B_i} + C_A/E_A)/(E_{B_i}/C_{B_i} + 0.0287)$. Therefore, y_i will be linear with β_i if and only if q_i is constant for all bases. This can be true only when $C_A/E_A = 0.0287$ as then q_i is identically 1. However, q_i will be approximately constant and therefore y_i and β_i close to linear if at least one of three criteria is met: (1) $C_A/E_A \simeq 0.0287$; (2) $E_B/C_B >> C_A/E_A$ and 0.0287 for all bases; (3) the bases used have very similar E_B/C_B ratios. Under the first condition, $E_B/C_B + C_A/E_A \simeq E_B/C_B + 0.0287$ and therefore $q_i \simeq 1$ for all E_B/C_B. Condition 2 reduces both the numerator and denominator of q_i to $\sim E_B/C_B$ and therefore $q_i \simeq 1$ once again. With condition 3, E_{B_i}/C_{B_i} is approximately constant for the bases used and q_i becomes a constant, but not necessarily 1. Note that conditions 1 and 2 produce a slope of $E_A/0.509$, the same as the

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(11) The β parameter can be fit to the *E* and *C* equation producing $\beta = 0.509E_B + 0.0146C_B$ ($r = 0.920$) for a range of β values from 0.446 to 0.774. Thus, to convert β to a P_B-type of expression, we obtain $(\beta/0.509) = E_B + (0.0146/0.509)C_B = P_B$. A more correct expression relating β's to *E* and *C* is $\beta = 0.741E_B + 0.0216C_B - 0.290$. This nonzero intercept may be a result of the same type of factors that cause nonzero intercepts of $-\Delta H$ vs. $-\Delta\nu_{OH}$ plots. However, the C_A/E_A value for β obtained from this equation is 0.0291, not noticeably different from 0.0287. If we attempt two linear correlations, one with β, the other with $\beta + 0.290$, $y = b\beta + y_0$, $y = b(\beta + 0.290) + y_0$, the only result will be a different y_0 value; the slope or *b* value will be the same. For most of these solutes, the difference between the two intercepts is within experimental error.

(12) Given the two equations, $y_i = E_AE_B + C_AC_B$ and $\beta_i = 0.509E_B + 0.0146C_B$, and the condition $\beta_i \neq 0$, we can write

$$y_i = \left[\frac{E_AE_B + C_AC_B}{\beta_i}\right]\beta_i = \left[\frac{E_AE_B + C_AC_B}{0.509E_B + 0.0146C_B}\right]\beta_i$$

Dividing both numerator and denominator by C_B gives

$$y_i = \left[\frac{E_A(E_B/C_B) + C_A}{0.509(E_B/C_B) + 0.0146}\right]\beta_i$$

Now factoring E_A from numerator and 0.509 from denominator yields

$$y_i = \frac{E_A}{0.509}\left[\frac{(E_B/C_B) + (C_A/E_A)}{(E_B/C_B) + 0.0287}\right]\beta_i$$

slope if $C_A/E_A = 0.0287$, but condition 3 does not. So β is still a "good", but incomplete, donor scale under conditions 1 and 2 but fails under condition 3.

For the acceptor solutes in the master fit, only three have C_A/E_A ratios sufficiently different from 0.0287 (2-nitroaniline, $C_A/E_A = 0.084$; 2-nitro-*p*-toluidine, $C_A/E_A = 0.135$; 2-nitro-*p*-anisidine, $C_A/E_A = 0.137$) to test the generality of β. For each of these acids, the range of E_B/C_B values for the donors is limited. Though this satisfies one of the criteria for β to show linear behavior even when $C_A/E_A \neq 0.0287$, it must be pointed out these parameters cannot generally be employed. A complete characterization of the specific interaction must utilize donors with as wide a range of C_B/E_B ratios as possible in order to have the minimum well determined. Since this is not true in any of these cases, the reported C_A/E_A values must be labeled "tentative". These solutes need to be studied with nitrogen donors such as pyridine and triethylamine to better determine their E_A and C_A parameters as well as tested for possible breakdowns of correlations with β.

Applications of Eq 1 and 3b. The shifts in ^{19}F NMR spectra relative to fluorobenzene of 4-fluorophenylmercury acetate ($FC_6H_4HgO_2CCH)_3$, 3-fluorophenylmercury acetate, bis(4-fluorophenyl)mercury [$(FC_6H_4)_2Hg$], and bis(3-fluorophenyl)mercury were measured in pure basic solvents with fluorobenzene as an internal reference.[14] Kamlet and Taft have shown that the acceptor bis(4-fluorophenyl)mercury correlates well in the β–π^* approach ($r = 0.985$). We have correlated all four of these acceptors using β, π^*, E, C, D^*, and E- and C-type analyses. The E, C, D^* fits are listed in Table II.

The latter three acceptors show equivalent fits to the E, C, D^*, and β–π^* treatments with correlation coefficients greater than 0.975 for each fit. All of the C_A^*/E_A^* ratios of these acceptors are close enough to 0.03 to allow the two-parameter β–π^* equation to correlate the breakup of specific and nonspecific as well as the three-parameter E, C, D^* equation does. In these three cases, E, C, D^* provide a sufficiently better correlation to the data than a simple E and C approach showing the need of a nonspecific solvation term in the correlation.

The acceptor 4-fluorophenylmercury acetate shows a different correlation to the E, C, D^*, and β–π^* approaches, however. In this case, the correlation coefficient of the β–π^* fit is 0.932 compared to 0.999 in the E, C, and D^* approach. The F tests of these fits shows the E, C, D^* approach to be 1219 (significant at >99% level) compared to 9.94 for β–π^* (significant at 95% level). The C_A^*/E_A^* ratio of this acceptor is 0.092. The 4-fluorophenylmercury acetate fit to β–π^* has two of the six shifts (those in pyridine and $(CH_3)_2SO$) missing the measured value well outside of experimental error. The obvious problem for the β–π^* fit of these data is the reversal of magnitude of the $(CH_3)_2SO$ ($\Delta\delta = 0.17$) and pyridine ($\Delta\delta = 0.33$) shifts toward this acceptor than toward the other mercury derivatives. Since $(CH_3)_2SO$ has a greater β and π^* than pyridine, it will always have a larger predicted shift than pyridine. The E, C, and D^* equation is able to correlate such reversals as are observed in the 4-fluorophenylmercury acetate data. Pyridine and $(CH_3)_2SO$ will undergo a reversal in the magnitude of the donor–acceptor interaction when an acid with a C_A/E_A of 0.03 is compared to another acid with a ratio of 0.09.

A final and very illustrative example of the limitations of β and misinterpretations that result from its application to systems where the C/E ratio of the acid solute is not 0.0287 is shown in the analysis of the shifts in the OH stretching frequency of phenols upon base coordination. There is much debate in the literature about the linearity of $\Delta\nu_{OH}$ with ΔH or other thermodynamic functions of the 1:1 phenol–base adducts. Reports from this laboratory have shown a linear correlation for ΔH and $\Delta\nu_{OH}$ for oxygen and nitrogen donors[15]

$$-\Delta H\ (\text{kcal mol}^{-1}) = 0.00103\Delta\nu\ (\text{cm}^{-1}) + 3.08 \qquad (7)$$

This correlation breaks down[16] when applied to sulfur donors, and this deviation was attributed to problems caused by the high polarizability of sulfur.

Table III. OH Stretching Frequency Shifts of Phenol-Base Adducts (cm^{-1})

donor	C_B/E_B	$\Delta\nu_{OH}$ (exptl)	$\Delta\nu_{OH}$ (calcd)	diff	ref
ethyl acetate	1.78	181	183	2	*a*
dimethylformamide	2.02	291	304	13	*a*
dimethylacetamide	1.95	343	339	−4	*a*
hexamethylphosphoramide	2.33	454	471	17	*a*
acetone	2.36	224	216	−8	*a*
dimethyl sulfoxide	2.13	362	359	−3	*a*
triethyl phosphate	1.33	314	331	17	*a*
diethyl ether	3.37	280	253	−27	*a*
diisopropyl ether	2.87	293	300	7	*a*
di-*n*-butyl ether	3.11	285	289	4	*a*
p-dioxane	2.18	237	253	16	*a*
tetrahydrofuran	4.37	287	309	22	*a*
tetrahydropyran	4.12	290	282	−8	*a*
dimethyl sulfide	21.7	257	253	−4	*b*
diethyl sulfide	21.8	256	252	−4	*c*
trimethylene sulfide	19.4	246	229	−17	*b*
tetrahydrothiophene	23.2	278	274	−4	*c*
pentamethylene sulfide	19.7	264	264		*b*
chloroacetonitrile	0.56	111	111		*b*
dimethylcyanamide	1.65	222	228	6	*b*
pyridine	5.47	472	479	7	*a*
triethylamine	11.2	650	653	3	*a*

[a] Reference 17. [b] Reference 3a. [c] Reference 16.

Kamlet, Solomonovici,[17] and Taft investigated correlations of $\Delta\nu_{OH}$ with their β parameter. They find that no general linear correlation exists for β and $\Delta\nu_{OH}$ with oxygen and nitrogen donors, but when the bases are separated into donor families (double-bonded oxygens, single-bonded oxygens, pyridines, etc.), linear behavior results. The curve for each family has a slightly different slope with different intercepts. This behavior is similar to that reported by Gramstad[18] in plots of $\Delta\nu_{OH}$ against the thermodynamic functions ΔG and ΔS for the formation of phenol–base adducts. The lack of a single correlation for the oxygen and nitrogen donors was rationalized[17] as resulting from differing geometries causing the dipole moment of the base to interact differently with respect to the axis of O–H vibration. For example, the acetone adduct has an angular O-H-O bond and the triethylamine adduct a linear N-H-O bond.

We attempted an E, C, W fit (W for the nonzero intercept) of the 22 donors in Table III including various oxygen and nitrogen donors as well as sulfur donors. An excellent correlation is obtained for the equation

$$\Delta\nu_{OH}\ (\text{cm}^{-1}) = 333.1E_B + 49.71C_B - 228.5 \qquad (8)$$

A standard deviation of 12 cm^{-1} and a correlation coefficient of 0.9947 result. Note that the C/E ratio for the acid frequency shift from eq 8 is 0.149. Thus the β correlation fails not because there is anything fundamentally different about the geometries of the different families of base adducts but because the C/E ratio of 0.149 differs from the 0.0287 that is appropriate for a β analysis. Restricting the donors to those in a given family can restrict the range of C_B/E_B involved in a plot and enables one to get a straight line even though the C_A/E_A ratio represented by β is incorrect for this system (condition 3 described earlier). The best correlation of the donor families was obtained for double-bonded oxygens, which have the smallest C_B/E_B ratio of the donors reported, thereby masking the difference between the β and actual C_A/E_A

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ratios (condition 2 described earlier).

It is interesting to note that the C_A/E_A ratio for the enthalpy of base adduct formation with phenol is 0.102 while the $C_A{}^*/E_A{}^*$ ratio for the phenol adduct frequency shift is 0.149. Note that the $C_A{}^*/E_A{}^*$ ratio is not a fundamental acceptor property of the acid but includes in it the response of the acid property being measured. It is possible to have two different properties of an acid obey the E and C equation but not give a straight line when plotted against each other if their $C_A{}^*/E_A{}^*$ ratios are different. Since the C_A/E_A and $C_A{}^*/E_A{}^*$ ratios are closer to each other than those for $C_A{}^*/E_A{}^*$ and β (0.0287), a more general straight line plot of $\Delta\nu_{OH}$ vs. $-\Delta H$ is obtained which will be valid as long as bases with a C_B/E_B ratio of 1.5 to 6 are employed. Thus this analysis extends our earlier proposal that this correlation is of more general applicability than reported[19,20] and that the high polarizability of sulfur donors cause them to deviate from the $-\Delta H$ vs. $\Delta\nu_{OH}$ relation. We now clearly understand what the limitations of the $-\Delta H$ vs. $\Delta\nu_{OH}$ relation are, and when it can be used with confidence to predict enthalpies.

With this work we have provided a set of parameters to be used in conjunction with the equation:

$$\Delta X = \text{“}E_A\text{”}E_B + \text{“}C_A\text{”}C_B + SD^* \tag{9}$$

Since in a new system, one does not know if the C_A/E_A ratio will be 0.0287, we feel it is first appropriate to determine if the observation, ΔX, is related to coordinate bond strengths and a relatively simple solvation model (eq 9). If the E, C, and D^* analysis indicates a C/E ratio close to 0.0287, the very extensive compilation of β parameters can be used with confidence for solvents for which E_B and C_B values are not determined. In interpreting deviations from an attempted fit of a data set to eq 9, one must remember that the parameters have been derived for dilute solutes undergoing specific and nonspecific interactions with varying solvents. As the observation that one is attempting to correlate, ΔX, becomes more complex and has more independent factors contributing to it, the chance diminishes for a successful correlation. Lack of a correlation does not mean that the model is incorrect but suggests that factors other than coordinate bond strength and this simple solvation model dominate the chemistry. Bulk solvation effects are a complex phenomenon coupled to the structure of the liquid state. Though a theoretical rationalization of the SD^* type of analysis has been provided,[20] a wider range of systems must be studied to determine the limitations of the treatment of this effect by the SD^* term.

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Registry No. 2-Nitroaniline, 88-74-4; *N*-methyl-2-nitroaniline, 612-28-2; *N,N*-dimethyl-2-nitroaniline, 610-17-3; *N*-ethyl-3-nitroaniline, 4319-19-1; 4-nitroaniline, 100-01-6; *N*-methyl-4-nitroaniline, 100-15-2; *N,N*-diethyl-4-nitroaniline, 100-23-2; 3-methyl-4-nitroaniline, 611-05-2; *N*-ethyl-3-methyl-4-nitroaniline, 52177-09-0; *N,N*-diethyl-3-methyl-4-nitroaniline, 52177-26-1; 3,5-dinitroaniline, 618-87-1; 2-nitro-*p*-toluidine, 89-62-3; *N,N*-dimethyl-2-nitro-*p*-toluidine, 52262-63-4; 2-nitro-*p*-anisidine, 96-96-8; *N,N*-dimethyl-2-nitro-*p*-anisidine, 60049-83-4; 4-nitrophenol, 100-02-7; 4-nitroanisole, 100-17-4; 4-aminobenzophenone, 1137-41-3; ethyl 4-aminobenzoate, 94-09-7; *N*-(4-nitrophenyl)aziridine, 30855-79-9; *N*-(4-nitrophenyl)pyrrolidine, 10220-22-1; *N*-(4-nitrophenyl)piperidine, 6574-15-8; 3-nitroaniline, 99-09-2; C_6H_{12}, 110-82-7; CCl_4, 56-23-5; C_2Cl_4, 127-18-4; C_5H_5N, 110-86-1; $(C_2H_5)_3N$, 121-44-8; $HCON(CH_3)_2$, 68-12-2; $CH_3CON(CH_3)_2$, 127-19-5; $CH_3COOC_2H_5$, 141-78-6; $(CH_3)_2CO$, 67-64-1; $(C_2H_5)_2O$, 60-29-7; $(CH_2)_4O$, 109-99-9; $(CH_2)_5O$, 142-68-7; $(CH_3)_2SO$, 67-68-5; $(C_2H_5O)_3PO$, 78-40-0.

Supplementary Material Available: Table M-1, spectroscopic data (bathochromic shifts from hexane) of a series of solutes (12 pages). Ordering information is given on any current masthead page.

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Unusual Bonding in Trans-Bent Digermene

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Abstract: Ab initio calculations using pseudopotentials have been carried out on the two singlet isomers of Ge_2H_4 at both SCF (double ζ + d basis set) and CI levels. Digermene ($H_2Ge{=}GeH_2$) is 5 kcal/mol more stable than germylgermylene ($H\ddot{G}e{-}GeH_3$). Its trans-bent geometry does not depend strongly on correlation effects; the wagging angle of the GeH_2 groups is 39° while the planar form stands 3–4 kcal/mol higher in energy. The type of bonding occurring in digermene can be described as two semipolar bent bonds between two singlet germylenes.

1. Introduction

Considerable interest arises from π-bonded silicon[2-10] and germanium[11-13] compounds. A recent extensive investigation of the Si_2H_4 potential surface[14] has confirmed (i) the singlet character of both disilene and silylsilylene ground states and (ii) the trans-bent geometry of singlet disilene. Although the organometallic chemistries of silicon and germanium are quite different, the available calculations on model compounds containing silicon or germanium atoms[11,12,15] do not show tremendous distinctions between the two series. Within our studies of π-bonded germanium compounds[11-13] we present here the study of the two Ge_2H_4 singlet isomers, namely, digermene ($H_2Ge{=}GeH_2$) and germylgermylene ($H\ddot{G}e{-}GeH_3$). In the light of the theoretical investigations on Si_2H_4[14] and on simple germylenes,[15] it can be

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