Registry No. (Bu$_4$N)CoPPh$_3$I$_3$, 14323-81-0; (Bu$_4$N)NiPPh$_3$I$_3$, 14320-07-1; (Bu$_4$P)CoPPh$_3$I$_3$, 27829-38-5; (Bu$_4$P)NiPPh$_3$I$_3$, 27829-39-6; (Bu$_4$N)ZnPPh$_3$I$_3$, 15037-12-4; (Bu$_4$P)ZnPPh$_3$I$_3$, 75267-71-9; (Bu$_4$N)$_2$CoI$_4$, 23324-56-3; (Bu$_4$N)$_2$NiI$_4$, 7141-63-1; (Bu$_4$N)$_2$ZnI$_4$, 21790-95-4; (Bu$_4$N)$_2$CoBr$_4$, 23324-55-2; (Bu$_4$N)$_2$NiBr$_4$, 7270-22-6; (Bu$_4$N)$_2$ZnBr$_4$, 37422-68-7.

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An *E* and *C* Analysis of Donor Numbers and Soret Band Shifts in Adducts of Zinc Tetraphenylporphine

Sir:

Previous papers have been concerned[1,2] with establishing the *E* and *C* equation as a viable means of correlating and predicting σ-bond strengths ($-\Delta H$). Two terms are needed to

$$-\Delta H = E_AE_B + C_AC_B$$

fit the data, and these relate to qualitative ideas about covalent (*C*) and electrostatic (*E*) bonding. The approach has been used in conjuction with spectroscopic and electrochemical measurements to probe intermolecular interactions.[3] With these objectives, the main concern had involved enthalpy determination and interpretation.

The data used in the *E* and *C* approach makes it a viable indicator of σ-bond strengths, and these parameters should be used to replace commonly used, invalid measures of this effect. For example, when investigators attempt to gain insights about the σ-bond contributions to some measured property by correlating or plotting it against pK_B and donor number[4] values, they are making an error. These scales are not general indicators of sigma σ-bond strength because the former contains an entropy contribution and both provide only single scale basicity orders that include solvation energy contributions.[5] We have not described in detail how the *E* and *C* approach should be used to determine if trends in measured quantities (other than enthalpies in poorly solvating solvents) are being dominated by σ-bond interactions. This is a probable cause of the continued appearance in the literature of plots of spectroscopic and thermodynamic data obtained in nonaqueous solvents with donor numbers and pK_B and also of some incorrect applications of the *E* and *C* parameters. Accordingly, we decided to prepare this paper describing the philosophy and procedure for this type of application of *E* and *C*.

One can *attempt* to interpret any spectral or reactivity parameter with the *E* and *C* model by writing

$$\Delta\chi = \text{“}E_A\text{”}E_B + \text{“}C_A\text{”}C_B \tag{1}$$

or

$$\Delta\chi + W = \text{“}E_A\text{”}E_B + \text{“}C_A\text{”}C_B \tag{2}$$

for the case where an acid is held constant and a series of bases is studied. The quotation marks imply that conversion units for converting E_B from (kcal mol^{-1})$^{1/2}$ are included in “E_A” along with the response to the quantity measured induced in the acid by the base. Equation 1 differs from eq 2 in that the latter permits incorporation of systems in which there is constant contribution to the measured parameter in all systems studied.[2]

In addition to converting the units, the quantities E_A and C_A can also include weighting factors that permit a different contribution of the two terms (E_AE_B and C_AC_B) to the measured property than is involved in the enthalpy correlation. When $\Delta\chi$ is a free energy, a successful correlation implies that the entropy term changes in a linear fashion with ΔH. The magnitudes of the “E_A” and “C_A” parameters accommodate this linear contribution as has been demonstrated for a linearly varying promotion energy.[6] Thus a successful correlation of the measured property with eq 1 implies that σ-bond strength considerations dominate the trends in the measured properties. If there are several systems that miss the attempted correlation by more than the experimental error these systems can be examined for some common property (π bonding, steric effect, etc.) that might account for the deviation.[3] Independent experiments can be designed to probe these effects.[3] If the average deviation is greater than the average error, some factor other than σ-bond strength is making an important contribution to the measured quantity. A large deviation would imply dominance by some other effect.

In the course of evaluating various correlations in the literature, the routine application of correlation coefficients is a common and often misleading practice. For example, if the *E* and *C* model were applied to a data base that contained systems with some systematic exceptions, a lower correlation coefficient for an *E* and *C* fit than for some “other parameter” fit would not signal a rejection of *E* and *C*. The “other parameter” fit might mask this systematic contribution to the measured property if the data base used to derive these “other parameters” has some contribution from this variable causing the systematic deviation built into it. The application of the correlation coefficient criterion should be limited to cases in which random misses with no systematic pattern exist for all the fits being compared. In such applications, the data base must be carefully selected to give nearly equal weight to the different classes of systems that manifest the potential variables to different extents. Even then a case in which a high correlation coefficient is obtained from, for example, a data base of 15 systems with a nearly perfect fit and three with substantial, unexplained, random misses is bothersome in terms of predicting the behavior of new systems. Finally, the correlation coefficent gives no indication of the order of magnitude for the range over which the variables have been studied.

The use of the *E* and *C* equation and a critical discussion of the correlation coefficient will be illustrated by first analyzing the data referred to as donor numbers[4] (DN), i.e., enthalpies associated with the reaction of solutions of SbCl$_5$ with bases in 1,2-dichloroethane. Various investigators continue to use these parameters to estimate donor–acceptor interactions, and they report successful correlations of spectral and reactivity data. Since it was previously demonstrated[5] that there are extensive contributions to the donor numbers from solvation effects, we were interested in determining why such correlations exist and *what they mean*. In an attempt to obtain a better understanding of the relationship of donor numbers to bond strengths and to understand the limitations of a donor number correlation, an *E* and *C* analysis of this data was undertaken. Reported donor number values were substituted

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(1) For a summary see R. S. Drago, *Struct. Bonding (Berlin)*, **15**, 73 (1973); *Coord. Chem. Rev.*, **33**, 251 (1980).

(2) R. M. Guidry and R. S. Drago, *J. Am. Chem. Soc.*, **95**, 759 (1973).

(3) See, for example, R. S. Drago, S. P. Tanner, R. M. Richman, and J. R. Long, *J. Am. Chem. Soc.*, **101**, 2897 (1979).

(4) For a summary see V. Gutmann, "The Donor Acceptor Approach to Molecular Interactions", Plenum Press, New York, 1978.

(5) Y. Y. Lim and R. S. Drago, *Inorg. Chem.*, **11**, 202 (1972).

(6) O. Kolling, *Inorg. Chem.*, **18**, 1175 (1979).

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Table I. An *E* and *C* Analysis of the Donor Number Scale

Lewis base	*E* and *C* calcd $-\Delta H(\text{I})$,[a] kcal mol^{-1}	exptl $-\Delta H$, kcal mol^{-1}	*E*, *C*, and *W* calcd $-\Delta H(\text{II})$,[b] kcal mol^{-1}
CH_3CN	16.5	14.1	15.3
$O(CH_2CH_2)_2O$	21.9	14.8	
$CH_3C(=O)OCH_3$	17.4	16.5	15.9
$CH_3C(=O)OC_2H_5$	18.8	17.1	17.1
$(CH_3)_2CO$	20.1	17.0	17.9
$(C_2H_5)_2O$	21.6	19.2	18.6
$(CH_2CH_2)_2O$	23.9	20.0	20.1
$(C_2H_5O)_3PO$	24.9	23.4	22.7
$CH_3CON(CH_3)_2$	25.9	27.8	(23.0)
$(CH_3)_2SO$	26.7	29.8	(23.6)
C_5H_5N	31.2	33.1	(25.2)
$(CH_3)_2N_3PO$	31.0	38.8	(27.0)
$CH_3C_5H_4NO$		36.3	(26.3)

[a] This is the combined fit of strong and weak adducts to eq 1.
[b] This is the fit of the weak adducts to eq 2 ($W = 1.0$ kcal mol^{-1}). The values in parentheses were calculated by using the E_A and C_A values obtained for the weak adducts ($E_A = 14.4$, $C_A = 1.17$, $W = 1.0$ kcal mol^{-1} in eq 2).

into eq 1 and 2 along with reported[1] E_B and C_B values. Very poor fits were obtained in the solution for E_A and C_A, but the deviations were not random. The weak adducts (DN < 22) all had positive deviations from the best fit values, and the strong adducts (DN > 25) all had negative deviations. This suggested that in attempting to compensate for large solvation effects in the strong adducts, the parameters were overcompensating the predicted enthalpies of the weak adducts. We were able to fit the donor numbers for the weakly interacting systems to eq 2 with $W = 1.0$ kcal mol^{-1}, "E_A" = 14.4, and "C_A" = 1.17. The $W = 1.0$ kcal mol^{-1} value was selected on the basis of the discrepancy found between the reported enthalpies for weak adduct formation in CCl_4 vs. 1,2-dichloroethane.[5] The bases selected for this *E* and *C* analysis and the fit obtained is shown in Table I. Since these *E* and *C* parameters fit the solvation-minimized data for ethyl acetate reported earlier and since the *E*, *C*, and *W* parameters fit the weak donors in 1,2-dichloroethane, we suggest that these E_A and C_A parameters for $SbCl_5$ replace the tentative values reported earlier.[5]

If one uses these new parameters (*E*, *C*, and *W*) for $SbCl_5$ to predict the enthalpies of adduct formation for some of the stronger donors in the donor number correlation, the values in parentheses are obtained. The deviations of experimental and calculated results are plotted vs. the predicted enthalpies in Figure 1. We propose that as the base–antimony interaction increases, the antimony–chlorine bond becomes more ionic, and the chlorines in the adduct are more extensively solvated by the solvent than is the case for weaker adducts. The abruptness of the onset of this extra stabilization is surprising. Triethyl phosphate (DN = 23.4) obeys eq 2, but DMA (DN = 27.8) does not. The data for DMF (DN = 26.6) does not fit Figure 1. Apparently, for those systems for which the *E* and *C* predicted enthalpies are in the 21–23 kcal mol^{-1} range, the donor number may or may not have extensive solvation depending upon the solvating or some unknown aspect of the coordinating properties of the base.

Little data for $SbCl_5$ is available for systems in which the $-\Delta H$ predicted by the *E* and *C* equation is above 27 kcal mol^{-1}. Donor numbers for these bases have been determined by indirect methods and they are higher than those predicted by extrapolation in Figure 1. Either the indirect method overestimates the parameter or there is even more extensive solvation in these systems than that indicated by an extrapolation of Figure 1. On the basis of these results the following conclusions written in terms of a base variation experiment can be drawn about donor number correlations. (1) For an acid with a C_A/E_A ratio of ~0.1, we expect a plot of DN vs. any property related to σ-bond strength to curve and scatter (depending on the base used) about the DMF donor number because of the solvation contribution to the donor number. (2) If a straight line is obtained when DN is plotted against some measured property, some additional effect is involved in the measurement that enhances the response of the system for strong bases above that expected from their bond strength. (3) For an acid with a C_A/E_A ratio other than ~0.1, scatter will result unless the bases employed all have similar C_B/E_B ratios. (4) If the C_A/E_A ratio of the measured property is ~0.1 or if bases with similar C_B/E_B ratios are employed, a straight-line correlation will result if only weak bases are used (DN < 24) or only strong bases are used (DN = 26–38) or bases are selected from a plot of $\Delta H_{E \text{ and } C}$ vs. Δ such that a straight line can be drawn through them. (That is, extend Figure 1 to produce a curve that includes points to DN = 16 and pick bases whose points would fall on a straight line.) These conditions either are similar to those reported to give parallel lines in an *E* and *C* determination[1] or do not permit a separation of bond strength and solvation effects. Accordingly, no significance can be assigned to either the existence of or lack of a correlation of DN with any spectral or reactivity parameter.

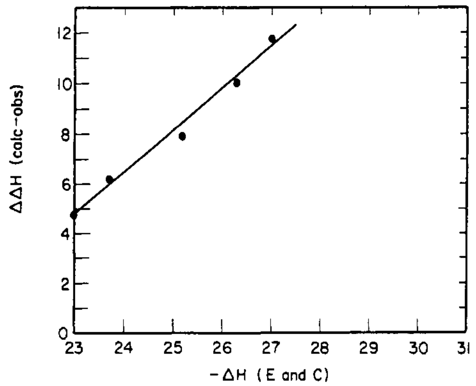

Figure 1.

One additional correlation will be analyzed in terms of *E* and *C* because the analysis and conclusion are illustrative of the strengths of the method. Attempts have been made to interpret the red shift in the Soret band of zinc tetraphenylporphine (ZnTPP) upon complexation to a series of Lewis bases.[6,7]

The Soret shifts of selected ZnTPP–donor complexes, ΔE_{TR} (see ref 8), were most recently correlated by Kolling[6] to an equation based on a combination of donor numbers and Kamlet-Taft parameters[9] (π^*). The resulting fit was only slightly superior to the one we obtained by substitution of ΔE_{TR} for $\Delta\chi$ in eq 2. Both the *E* and *C* and DN–π^* fits are shown in Table II.[10] A plot of calculated vs. experimental shifts for the DN–π^* fit represented a random scattering about the

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(7) M. Nappa and J. S. Valentine, *J. Am. Chem. Soc.*, **100**, 5075 (1978).

(8) ΔE_{TR} (kcal/mol) is calculated from the equation $\Delta E_{TR} = hc/\lambda - hc/(\lambda + \Delta\lambda)$, where $\Delta\lambda$ is the observed shift (in nm) from the noncomplexed system.

(9) J. Abboud, M. Kamlet, and R. Taft, *J. Am. Chem. Soc.*, **99**, 8325 (1977).

(10) Since there was a discrepancy for the benzene shift in ref 6, several of the shifts were remeasured. Three bases in Kolling's original fit have been deleted: cyclohexane because it is the reference standard and should not be included in calculating a correlation coefficient, acetonitrile because the totally complexed spectrum is not obtained due to base and solvent incompatibility, and benzene because K_{eq} is small and one observes spectral effects due to complex formation as well as solvation due to a large percent of benzene in solution. An isosbestic point was not observed for the ZnTPP–benzene complex formation.

Table II. Fit of Zinc(II) Tetraphenylporphine Shifts

Lewis base	$\Delta\lambda$, nm	ΔE_{TR}, kcal mol^{-1}	*E* and *C*,[a] kcal mol^{-1}	DN–π^*,[b] kcal mol^{-1}
acetone	5.6[c] (5.2[d])	0.876[e]	0.993	0.920
bridge ether	6.3[d]	1.02	1.042	1.119
chloroform	2.5[g]	0.41	*f*	0.514
diethyl ether	5.3[c] (3.7[g])	0.864	1.042	0.703
dimethylacetamide	8.8[c]	1.42	1.288	1.346
dimethylformamide	8.2[c] (8.6[g])	1.36[e]	1.206	1.425
dimethyl sulfoxide	8.6[c] (8.5[d])	1.39[e]	1.375	1.480
ethyl acetate	5.1[c] (5.3[d])	0.85[e]	0.939	0.830
hexamethylphosphoramide	10.4[d]	1.68	1.527	1.636
methyl acetate	4.7[c] (4.6[d])	0.757[e]	0.870	0.785
pyridine	10.0[c] (9.9[d])	1.61[e]	1.447	1.484
tetrahydrofuran	6.4[c] (6.2[d])	1.02[e]	1.130	0.929
triethylamine	10.1[d]	1.63	1.647	1.761
p-dioxane	5.2[c]	0.85	1.082	0.749

[a] Calculated with "E_A" = 0.831 and "C_A" = 0.0743. [b] Calculated with the equation $\Delta E_{TR} = 0.0270(\mathrm{DN}) + 0.236\pi^*$. [c] Shift from this work. [d] Shift reported from ref 12. [e] ΔE_{TR} calculated from average of the two reported shifts. [f] Chloroform is an acid in the *E* and *C* system. [g] Shift reported from ref 6.

least-squares line (a correlation coefficient squared of 0.94 was obtained), whereas a similar plot for the *E* and *C* fit (a correlation coefficient of 0.91 was obtained) revealed a trend in the deviation. Calculated shifts for those donors with small donor numbers were greater than experimental shifts while calculated shifts for those donors with large donor numbers were less than experimental shifts (with the exception of triethylamine). Thus no significance can be assessed from the correlation coefficient criterion for these fits.

The data base upon which *E* and *C* is founded provides us with predictions of what the ΔE_{TR} values would be if they were dominated by metal–donor σ-bond strength effects. Examination of the deviations from this predicted trend (Table II) fails to reveal a single systematic effect that could account for the observed deviations. Though the observed shift is too large for the polar donor dimethyl sulfoxide, it is also too large for the poorly solvating donor pyridine.[11] The complexity of the ΔE_{TR} values is fully appreciated when all of the data[12] are considered. When the reported ΔE_{TR} values for sulfur bases[12] are included, this data fails to fit either the DN–π^* or the *E* and *C* equation. Since the enthalpies of adduct formation with the sulfur donors obey *E* and *C*,[12] we must conclude that there are additional unknown factors besides those related to σ-bond strength and solvation that contribute to the ΔE_{TR} values. This was recognized in the early report[12] of a lack of correlation of the Soret shift and enthalpy of adduct formation for sulfur donors. However, the generalized *E* and *C* fit (eq 1 or 2) shown above illustrates that in addition to not paralleling the enthalpies, there are no combinations of covalent or electrostatic contributions to the bond strength that rationalize all the ΔE_{TR} values. Clearly, more data is required before the contributions to the spectral shifts are understood.

It is to be emphasized that, if the property being investigated is influenced by covalent and electrostatic bonding interactions in a way that is different from their influence on bond energy, the property will fit eq 1 or 2 if it is a matter of changing the relative importance of C_AC_B and E_AE_B contributions. However, if electrostatic or covalent effects have a different functional dependence (for example, $C_AC_B{}^n$), the property will not be fit by eq 1 or 2 even if solvation and unusal bonding effects are absent. The NMR shifts in the proton resonances upon hydrogen bonding of a series of acids to a base illustrate the various transformations of the *E* and *C* parameters that may be needed to account for spectral shifts.[13]

The DN–π^* fit does not reflect any trends in the deviations of the calculated and observed quantities. The meaning of the observed correlation is difficult to assess. The Soret shifts are measured in cyclohexane with excess base. It is not clear how this relates to donor numbers which include coordination as well as 1,2-dichloroethane solvation and π^* numbers which are a property of the pure base as solvent. In terms of the utility of the correlation for predicting ΔE_{TR} values for new systems, one would have to expect agreement no better than the 12–19% errors in the *p*-dioxane and diethyl ether systems, for the causes of these deviations are not understood. Clearly, the conclusion from this study that the trends in ΔE_{TR} values are dominated by polarizability considerations (dominance by the C_B term) is open to question.

The above analysis illustrates the point that there are enough parameters and scales in the literature to fit almost any restricted set of reactivity or spectral results. However, other than giving a good fit, meaningful information is not obtained by finding such a fit. Reference scales derived from data which may have solvation and other effects hidden in them will usually fail to show when these effects are present in the results being analyzed. The decided advantage of the *E* and *C* reference scale (which is derived from solvation-minimized, σ-type interactions) is that evidence for or against domination of a trend by σ-type bonding interactions can be ascertained. Patterns in the deviations of donors (or acceptors) from a σ order can provide evidences for interesting bonding effects.

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