tion was poured into 30 ml of water, yielding yellow crystals of the deuterated complex. These were collected by filtration, washed with water, and dried in a vacuum desiccator. The nmr spectrum of the complex in $CDCl_3$ revealed the presence of the dimethylglyoxime methyl protons but was free of signals due to undeuterated β-cyanoethyl(pyridine)cobaloxime. No incorporation of deuterium was observed under similar conditions at $pH < 12.5$.

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Spectral and Calorimetric Studies of Hydrogen Bonding with Pyrrole

M. S. Nozari and Russell S. Drago*

Contribution from the W. A. Noyes Laboratory, University of Illinois, Urbana, Illinois 61801. *Received April 6, 1970*

Abstract: The N–H frequency shifts and the enthalpies of hydrogen-bonding interactions between pyrrole and selected Lewis bases were experimentally determined. E and C values for pyrrole were calculated and used to estimate the enthalpies of adduct formation for pyrrole with other Lewis bases which are too weak to measure accurately. Comparison of the data for pyrrole with previously studied hydrogen-bonding hydroxy acids indicates that the ratios of the E and C parameters for all these hydrogen-bonding systems are similar. Pyrrole is a weaker acid than the phenols and 1,1,1,3,3,3-hexafluoro-2-propanol, but is stronger than *tert*-butyl alcohol. For the donors studied, the plot of $-\Delta H$ *vs.* $\Delta\nu_{N-H}$ (the change in N–H stretching frequency upon adduct formation) is found to be linear, as in the case of the hydroxy acids, and obeys the quantitative relationship: $-\Delta H = (0.0123 \pm 0.0006)\cdot\Delta\nu_{N-H} + 1.8\ (\pm 0.1)$. The enthalpy and spectral changes accompanying adduct formation are considered in the light of other reported relationships from this and other laboratories pertaining to hydrogen bonding by alcohols.

The general area of hydrogen bonding has attracted considerable interest in recent years in part owing to its importance in biological processes. Several articles[1–6] from this laboratory have been concerned with establishing correlations between the enthalpy of adduct formation and changes in the O–H stretching frequency of the hydrogen-bonding acid (various phenols and *tert*-butyl alcohol) upon complexation. The existence of such correlations is significant as a means of readily evaluating the magnitude of interactions, and the existence or lack of correlations provides insight into the fundamentals of the spectroscopic procedures employed. The studies from this laboratory have recently been extended[7,8] to provide similar relationships with the alcohols 1,1,1,3,3,3-hexafluoro-2-propanol and 2,2,2-trifluoroethanol. The correlations reported to date have been limited to alcohols interacting with various types of oxygen and nitrogen donors. It has been found recently that sulfur donors[9] do not obey the correlations of enthalpy *vs.* O–H infrared frequency shift found for the oxygen and nitrogen donors. This is consistent with an earlier claim that alkyl halides gave an incorrect trend[10,11] and suggests that caution must be employed in incorporating donors from different rows in the periodic table into our infrared correlations. We are most interested in ascertaining the limitations, if any, on the type of hydrogen bonding acid that will provide linear enthalpy–frequency shift correlations.

In biological systems, the Lewis acid involved in the hydrogen bonding system is very often an N–H functional group, as in the nucleic acids. Accordingly, we became very much interested in extending the correlations found for the alcohols to an acid with an N–H functional group. In this article, we report a successful extension of our spectroscopic correlations to the Lewis acid pyrrole.

Hydrogen bonding and other Lewis acid–base enthalpies of adduct formation have been incorporated into the general equation[12]

$$-\Delta H = C_A C_B + E_A E_B \qquad (1)$$

Empirically determined E_A and E_B, C_A and C_B parameters can be substituted into this equation to reproduce most of the known enthalpies determined in the gas phase or in poorly solvating media. It was of interest to incorporate an N–H-type functional group into this correlation and compare the E_A and C_A values for this type of acid with the alcohols.

Experimental Section

Purification of Chemicals. Reagent grade cyclohexane and carbon tetrachloride were dried over fresh Linde 4-A molecular sieves

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* Address correspondence to this author.

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Table I. Calorimetric Data for Pyrrole–Base Systems

[Acid], *M*	[Base], *M*	(Solvent) Total vol, ml	Measured heat, cal	*K*, l. mol^{-1} (25.0°)	$-\Delta H°$, kcal mol^{-1}
Pyrrole	DMSO	(CCl_4)	*H′* [a]		
0.02733	0.05872	110.14	4.50	11.3 ± 0.4	4.2 ± 0.1
0.02752	0.08160	110.14	5.42		
0.02776	0.14315	110.14	7.43		
0.02724	0.21034	110.14	8.62		
0.02735	0.33781	110.14	9.77		
0.02692	0.67667	110.14	10.75		
Pyrrole	Pyridine	(C_6H_{12})	*H′* [b]		
0.01571	0.04402	110.15	1.54	5.5 ± 0.8	5.0 ± 0.3
0.01778	0.06731	110.15	2.44		
0.02712	0.06254	110.15	3.67		
0.02658	0.07928	110.14	4.25		
0.02740	0.08210	110.15	4.34		
0.02566	0.10274	110.15	4.89		
0.02244	0.12296	110.15	5.05		
0.02517	0.20271	110.14	6.25		
0.02540	0.29156	110.14	7.72		
0.02767	0.24373	110.14	8.28		
0.02807	0.22606	110.15	8.61		
0.02683	0.38229	110.14	8.78		
0.02500	0.54995	110.14	9.87		
0.02743	0.35640	110.14	10.10		
0.02839	0.35745	110.15	10.67		
0.02997	0.29241	110.15	10.83		
0.02712	0.45266	110.14	11.18		
0.02658	0.74484	110.14	11.57		
0.02449	0.20380	110.15	11.97		
0.02602	0.93179	110.14	12.08		
Pyrrole	Triethylamine	(C_6H_{12})	*H′* [b]		
0.02684	0.01963	110.14	1.22	4.4 ± 0.1	5.9 ± 0.2
0.02532	0.04543	110.14	2.58		
0.02508	0.06004	110.14	3.18		
0.02417	0.26132	110.14	8.24		
0.02606	0.54878	110.14	11.74		

[a] Corrected for the ΔH_{soln} (2.1 kcal mol^{-1}) of 0.14-ml aliquots of pyrrole in CCl_4. [b] Corrected for the ΔH_{soln} (3.7 kcal mol^{-1}) of 0.14-ml aliquots of pyrrole in CCl_4.

for at least 24 hr prior to use, without any further purification. Pyrrole was also dried over Linde 4-A molecular sieves and distilled from barium oxide. It was necessary to use freshly distilled pyrrole because a change in color occurred upon standing. Our attempt to stop the decomposition by storing at Dry Ice temperature in the dark was unsuccessful.

Aldrich triethylamine was dried over $LiAlH_4$ and twice distilled from CaH_2 at atmospheric pressure under argon atmosphere. Dimethyl sulfoxide and pyridine (Baker Analyzed Reagent) were both dried over BaO and distilled from BaO and CaH_2, respectively, at low pressure. In all cases, only the middle fractions were collected and tested by gas chromatography for purity.

Procedure. The experimental heats (*H′*) were measured in a twin-cell calorimeter similar in design to the one previously described.[6] The only difference is that a new sensitive constant-voltage source (Model CEA 6C 120Y251R, Berkleonics, Inc., Monrovia, Calif.) was substituted for the previously used galvanometer, potentiometer, and power supply.

Since pyrrole is very hygroscopic, all possible precautions were taken to exclude water. All solutions were prepared in a drybox or a drybag using dried glassware and syringes. The calorimeter was purged with dry nitrogen prior to every measurement. Infrared measurements were made with a Perkin-Elmer Model 521 spectrophotometer equipped with sodium chloride optics and cells. In general, the experimental procedure was similar to the one previously reported.[4,13]

Results

The concentrations, measured heats, and calculated thermodynamic parameters are presented in Table I for various donors with pyrrole. The experimental quantity *H′* is the heat evolved on adding the acid to the base corrected for the heat of solution of pyrrole in the solvent employed. The values used for this correction are 2.1 ± 0.1 and 3.7 ± 0.1 kcal mol^{-1} for CCl_4 and C_6H_{12}, respectively, over a pyrrole concentration range of 0.022–0.029 *M*. Our heat of solution is considerably different from a previously reported value of 1.4 ± 0.1 kcal mol^{-1}[14] obtained by extrapolation of results in concentrated solutions. Vinogradov and coworkers were aware of the effect of concentration, but their calorimeter design evidently imposed a limitation of about 0.9 *M* in pyrrole on the lowest concentration that could be studied. We have been able to measure the heat of solution at concentrations as low as 0.01 *M*, and our results are the average of 12–16 determinations.

In the present study, it was not possible to investigate weaker donors than those reported because of the very small enthalpies and equilibrium constants for these systems. Very large concentrations are required to study weak donors, and this large excess of base in effect changes the solvent properties from those of CCl_4 or cyclohexane, leading to enthalpies that contain interaction and solvation terms. The enthalpies for these donors were calculated by a previously reported[12] double-scale enthalpy equation. After determining the enthalpy of interaction of preferably three or more donors of known E_B and C_B values with a new acid,

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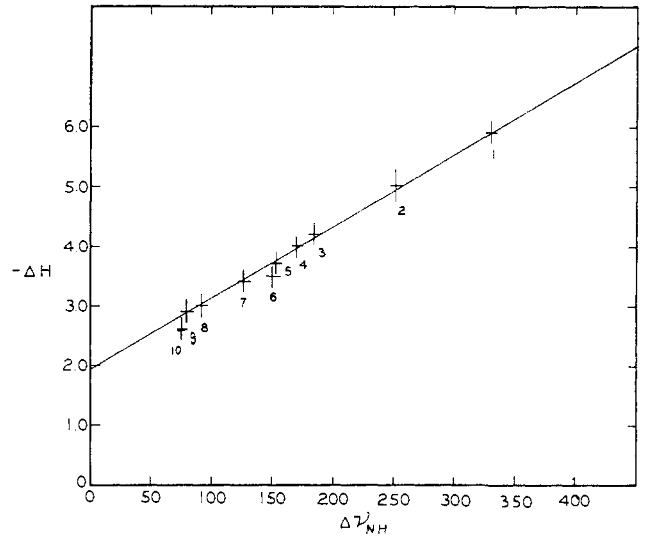

Figure 1. A plot of $-\Delta H$ (kcal mol^{-1}) *vs.* $\Delta\nu_{N-H}$ (cm^{-1}) for different pyrrole–base interactions: 1, triethylamine; 2, pyridine; 3, DMSO; 4, DMA; 5, THF; 6, ethyl ether; 7, dioxane; 8, acetone; 9, ethyl acetate; 10, acetonitrile.

one is able to calculate the E_A and C_A values of the new acceptor, using eq 1.

In the present study, the heats of interaction of pyrrole with three Lewis bases, DMSO, pyridine, and triethylamine, were determined. The C_B and E_B values[15] are 10.91 and 1.03, 6.36 and 1.21, 2.86 and 1.36 for triethylamine, pyridine, and DMSO, respectively. This enabled us to calculate a set of E and C values for pyrrole as follows: $E_{\text{pyrrole}} = 2.43$, $C_{\text{pyrrole}} = 0.318$. Substituting these values and the refined donor C_B and E_B values into eq 1, we were able to estimate the heat of interaction of pyrrole with several additional bases. Based on the results from other hydrogen-bonding systems, the calculated values are expected to be accurate to ± 0.2 kcal mol^{-1}. The measured and calculated enthalpies as well as the measured N–H frequency shifts are reported in Table II. The frequency shifts reported here are considerably different from previously reported values.[16–18] The discrepancy can be attributed to the concentration dependence of the frequency shifts. For example, if to a 25-ml volume of CCl_4, 0.015 ml of pyrrole and 0.5 ml of DMSO are added, the observed frequency shift is 200 cm^{-1} compared to an extrapolated value of 184 ± 3 cm at infinite dilution. Most of the previously reported values were measured in neat solutions, whereas all our reported shifts are checked for the concentration dependence and the values reported are for infinitely dilute solutions.

Table II. Measured and Calculated Enthalpies and N–H Frequency Shifts of Pyrrole with Various Lewis Bases

Numbering system	Base	$-\Delta H°$, kcal mol^{-1}	$\Delta\nu_{N-H}$ (cm^{-1})^{c,d} of pyrrole
1	Triethylamine	5.9 ± 0.2^a	331 ± 5
2	Pyridine	5.0 ± 0.3^a	252
3	DMSO	4.2 ± 0.1^a	184
4	DMA	4.0 ± 0.2^b	170
5	THF	3.7 ± 0.2^b	153
6	Ethyl ether	3.5 ± 0.2^b	150
7	Dioxane	3.4 ± 0.2^b	127
8	Acetone	3.2 ± 0.2^b	92 ± 5
9	Ethyl acetate	2.9 ± 0.2^b	80
10	Acetonitrile	2.6 ± 0.2^b	77
11	Xylene		49
12	Benzene		30

[a] Measured calorimetrically. [b] Calculated from eq 1. [c] Error limit = ±3 unless otherwise specified. [d] Frequency shifts measured in CCl_4.

In a recent report on the limitations of calorimetry,[19] it was pointed out that the concentration of both reactants should be varied widely. In the present work, we were able to vary the concentration of base over a large range. However, as far as the acid concentration was concerned, we were quite limited by intermolecular association of pyrrole.[20–22] The association cannot be explained by a simple monomer–dimer equilibrium, and solutions of pyrrole more concentrated than 0.030 *M* have an appreciable concentration of polymer. On the other hand, with our apparatus the very small enthalpies of interaction of pyrrole with even the strong donors set a lower limit of concentration of about 0.01 *M* on systems we can study.

Discussion

Prior to this study, there were two sets of literature values for the pyridine–pyrrole interaction. In contrast to our value of 5.0 ± 0.3 kcal mol^{-1}, Vinogradov[14] reported a value of 3.8 kcal mol^{-1}. The lower value results in part from the use of CCl_4 as solvent with the donor pyridine. We have earlier reported[4] that pyridine–CCl_4 interactions lead to low enthalpies. Another potential cause of the lower result is the high pyrrole concentrations utilized in the reported study. In the second literature report of an attempt to determine the heat of interaction of pyridine with pyrrole, an nmr technique was employed to determine the temperature dependence of the equilibrium constant leading to a value of 4.3 kcal mol^{-1} in cyclohexane as solvent. This is again lower than our measured enthalpy. The nmr technique is extremely sensitive to self-association. Very slight association can cause the chemical shift of the free material to be very temperature and concentration dependent. This could introduce error into the reported enthalpy in the nmr study.

Previous studies from this laboratory[3,4,6] demonstrated that a linear relationship exists between the magnitude of the OH frequency shift of an alcohol upon adduct formation, $\Delta\nu_{O-H}$, and the enthalpy of adduct formation. As Figure 1 illustrates, the same type of relationship is observed for pyrrole. The equation for the least-squares line is

$$-\Delta H = (0.0123 \pm 0.0006)\Delta\nu_{N-H} + 1.8\ (\pm 0.1) \qquad (2)$$

This equation can be used to predict the heat of interaction of various oxygen and nitrogen donors with

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Table III. Reported $-\Delta\nu_{X-H}$ Relationships and E_A and C_A Parameters for Various Acids

Acid	$-\Delta H$ *vs.* $\Delta\nu_{K-H}$ relation	E_A	C_A	C_A/E_A	Ref
Phenol[a]	$-\Delta H = (0.0105 \pm 0.0007)\Delta\nu_{OH} + 3.0\ (\pm 0.2)$	4.35	0.405	0.093	4
tert-Butyl alcohol	$-\Delta H = (0.0106 \pm 0.0005)\Delta\nu_{OH} + 1.65\ (\pm 0.09)$	2.04	0.287	0.140	6
HFIP	$-\Delta H = (0.0115 \pm 0.0008)\Delta\nu_{OH} + 3.6\ (\pm 0.3)$	5.52	0.500	0.091	7
2,2,2-Trifluoroethanol	$-\Delta H = (0.0121 \pm 0.0005)\Delta\nu_{OH} + 2.7\ (\pm 0.2)$	3.95	0.444	0.113	8
Pyrrole	$-\Delta H = (0.0123 \pm 0.0006)\Delta\nu_{NH} + 1.8\ (\pm 0.1)$	2.43	0.318	0.131	

[a] Also applicable for the substituted phenols.

pyrrole from the measured infrared frequency shift. Figure 2 also indicates that the enthalpies of interaction of pyrrole with Lewis bases fall on the same constant-base line as those of donors with hydroxy acids.

Table III contains a summary of the reported enthalpy-frequency shift correlations for the various hydrogen-bonding acids studied.

The estimated error limits on the slopes and the intercepts of these lines are merely representative of the randomness of the points involved, and do *not* include the inherent errors in the frequency shifts and the enthalpies. If the latter uncertainties had been accounted for, it would have been impossible to detect any significant difference in the slopes of the lines for the different H-bonding acids studied. Even in their present form, with a conservative estimate of the error in the slope of the constant-acid line, pyrrole has the same slope as that of 2,2,2-trifluoroethanol and HFIP. We conclude that the slopes of the constant-acid lines for the hydrogen-bonding acids in Table III do not differ within our experimental ability to detect differences. On the other hand, the differences in the intercepts are, in most cases, significant. HFIP has the largest intercept and *tert*-butyl alcohol the smallest, while those for phenol and 2,2,2-trifluoroethanol are larger than that for pyrrole. The magnitude of the intercept is apparently related to the acidity of the hydrogen-bonding acid. Pyrrole is a weaker Lewis acid than phenol, HFIP, and 2,2,2-trifluoroethanol, but is slightly stronger than *tert*-butyl alcohol. Owing to the higher electronegativity of oxygen than nitrogen, pyrrole is expected to be weaker acid than phenol. The higher acidity of pyrrole than most amines is attributed to the inductive properties of the two attached sp^2 carbons in pyrrole and delocalization of the nitrogen lone pair into the π system. These effects make pyrrole a much stronger hydrogen-bonding acid than dimethylamine and cause withdrawal of enough electron density off the nitrogen to make pyrrole more acidic than *tert*-butyl alcohol. Comparison of E_A and C_A values of the acids in Table III[15] also reveals that the E_A and C_A values of pyrrole are significantly smaller than those of phenols, HFIP, and 2,2,2-trifluoroethanol and somewhat larger than those of *tert*-butyl alcohol. On the basis of this study, we predict that for all Lewis bases the order of donor strength toward an N–H hydrogen-bonding interaction should be the same as toward that of an alcohol. This is mainly due to the fact that *both* E_A and C_A for pyrrole are smaller than those for phenol, 2,2,2-trifluoroethanol, or HFIP, and *both* parameters are larger than the corresponding values for *tert*-butyl alcohol. Reversals in donor orders are expected when the magnitudes of E_A and C_A for two acids do not both change in the same direction.

Another way of looking at this is if, for a series of acids, the C/E ratio is about the same, similar trends in donor–acceptor behavior toward a series of bases is expected. Conversely, if the C/E ratio of two acids is quite different, then by proper selection of the donors, reversals in donor orders toward the two acids will be observed. Note that the C/E values of hydroxy acids and pyrrole are all about 0.1 compared to a value of 1.0 for iodine. Thus, we expect hydrogen bonding to the N–H proton of pyrrole by donors which have not yet been studied to give a similar donor order to that observed for alcohols.

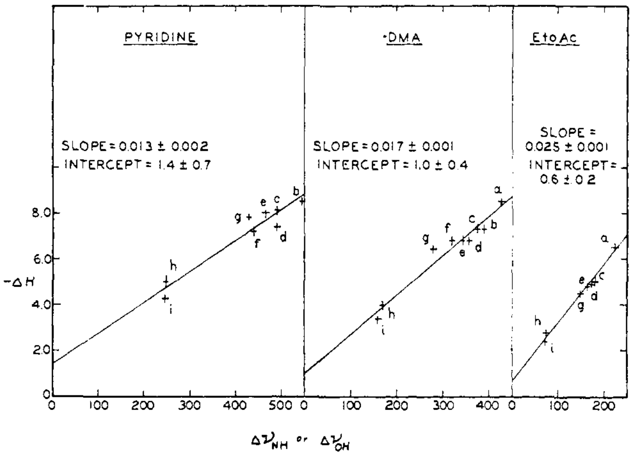

Figure 2. Constant-base lines for the interaction of selected Lewis bases with hydrogen-bonding acids: a, HFIP; b, *m*-trifluoromethylphenol; c, *p*-chlorophenol; d, *p*-fluorophenol; e, phenol; f, *p*-*tert*-butylphenol; g, 2,2,2-trifluoroethanol; h, pyrrole; i, *tert*-butyl alcohol.

In an earlier report from this laboratory,[6] it was shown that a series of constant-base lines (*i.e.*, when the base is fixed, ΔH *vs.* $\Delta\nu_{OH}$ for a series of acids gives a straight-line plot) passes through the series of constant-acid lines. It was demonstrated that *if* constant-acid and constant-base relationships *exist* for a new alcohol, X, and if the slopes of the constant-acid lines are the same, a straight-line plot of $\Delta\nu_{OH}(X)$ *vs.* $\Delta\nu_{OH}$(phenol) must result with zero intercept.[6] As can be seen by examination of Figure 1, a constant-acid line exists for pyrrole, whose slope does not differ from that of the hydroxy acids, in Table III, by any significant amount. Pyrrole, also fits on the constant-base lines equally as well as any of the above mentioned alcohols (Figure 2). It is of interest to point out that in a previous report,[6] it was shown that the constant-base lines should go through zero. However, one should examine the consequences of the nonzero intercepts and their implications upon the $\Delta\nu_{O-H}$ *vs.* $\Delta\nu_{N-H}$ plots. Following the notations in ref 6, we can write the equation for con-

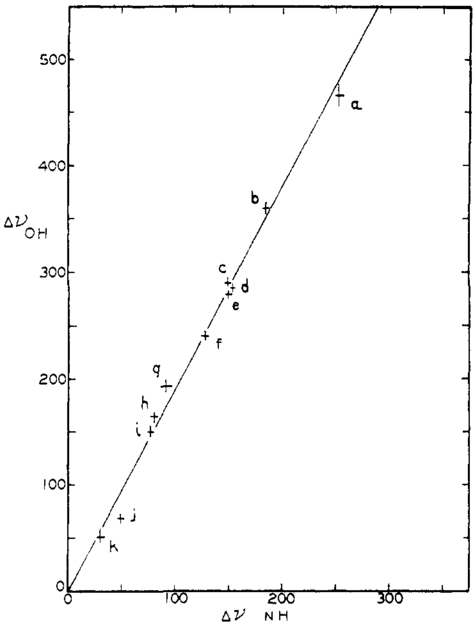

Figure 3. Linear plot of $\Delta\nu_{O-H}$ for phenol adducts *vs.* $\Delta\nu_{N-H}$ for pyrrole adducts: 2, pyridine; 3, DMSO; 4, DMA; 5, THF; 6, ethyl ether; 7, dioxane; 8, acetone; 9, ethyl acetate; 10, acetonitrile; 11, xylene; 12, benzene.

stant-base plots, giving an intercept as follows

$$-\Delta H_{ij} = k_j \Delta\nu_{ij} + L_j \tag{3}$$

where i and j refer to an acid and a base, respectively, *k* is the slope, and *L* is the intercept for the constant-base line. Substituting this equation in the general equation for constant-acid lines gives

$$\Delta\nu_{aj} = \frac{(n_a - L_j)\Delta\nu_{bj}}{(m_b - m_a)\Delta\nu_{bj} + n_b - L_j} \tag{4}$$

where a and b refer to two different acids, *n* is the intercept, and *m* is the slope of a given constant-acid line. For the condition when $m_b = m_a$, the slope of the $\Delta\nu_{aj}$ *vs.* $\Delta\nu_{bj}$ plot is given by

$$\frac{n_a - L_j}{n_b - L_j}$$

In order to get a straight-line plot for a series of different bases, L_j, which depends on the base, must either be the same for all bases or be zero. If the intercept is other than zero for a constant-base plot, this value must be subtracted from the slope of the $\Delta\nu$ *vs.* $\Delta\nu$ plot to obtain the intercept in the constant-acid plot.[6]

The least-squares treatment of the data for the interaction of several Lewis acids and bases (Figure 2) give intercepts greater than zero. We believe these nonzero intercepts are caused by the large errors inherent in the reported frequency shifts with weak donors where large base concentrations are needed to measure the shift. Small changes in the frequency shifts of systems at the ends of the lines can change the intercepts considerably. At any rate, the pyrrole system described satisfies all of the mathematical requirements previously stated[6] for constant-base lines with zero intercepts. Consequently, effects leading to our observed nonzero intercepts are not great enough to destroy the mathematical relationships previously derived which lead to prediction of the intercept in the constant-acid plot. Figure 3 demonstrates that a plot of $\Delta\nu_{OH}$(phenol) *vs.* $\Delta\nu_{N-H}$ is linear with a zero intercept. (Triethylamine is not included in this figure, because of the great uncertainty in its frequency shift.) Thus, the same relationships[6] that exist for alcohols also are operative in the case of pyrrole. For pyrrole or any other hydrogen-bonding acid, found to lie on our constant-base lines with two or three donors, a straight-line plot of $\Delta\nu_{N-H}$(X) *vs.* $\Delta\nu_{O-H}$(phenol) with zero intercept requires a $\Delta\nu_{N-H}$(X) *vs.* ΔH(X) relation whose slope is the same as phenol's.[6] From the slope, *m*, of the $\Delta\nu_{NH}$ *vs.* $\Delta\nu_{OH}$(phenol) line, the intercept, n_2, for the pyrrole $\Delta\nu_{N-H}$ *vs.* ΔH plot can be calculated[6]

$$m = \frac{3.0\ (+0.2)}{n_2}$$

Using a slope, *m*, from Figure 3 of 1.91 (±0.07), an intercept of 1.6 (±0.1) is predicted, compared to the experimental value of 1.8 (±0.1). Clearly, the systems of acids and bases described here obey the relationships previously reported well enough to predict slopes, intercepts, and enthalpies as accurately as they can be measured.

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