# Nuclear Magnetic Resonance Studies of Hydrogen Bonding

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**Abstract:** Proton magnetic resonance spectra were obtained for 30 phenol–base systems in the solvent methylene chloride. The bases studied include amines, ethers, phosphoryl compounds, carbonyl compounds, sulfoxides, diethyl sulfide, N,N-dimethylthioacetamide, acetonitrile, and tetramethylene sulfone. Under conditions of complete phenol–base association, the position of the phenol hydroxyl proton chemical shift was found to be linearly related to $\Delta H$, the enthalpy of the hydrogen-bonding interaction. This relationship holds within ±0.5 kcal/mole or ±0.38 ppm. The equation which expresses this relationship is $\delta_{\text{obsd}} = 0.748(\Delta H) - 4.68$. Carbonyl compounds and pyridine obey this relationship only if corrections are made for anisotropic contributions from the base. It is suggested that these results present a new method for approximating enthalpies of hydrogen-bonding interactions or, if this quantity is known, for evaluating anisotropic contributions in donors.

Recently[2a] a linear relationship was established between the enthalpy of the hydrogen-bond interaction of phenol with a series of bases, $\Delta H$, and the O–H stretching frequency shift upon complexation, $\Delta\nu_{\text{OH}}$. It was of interest to investigate the change in proton chemical shift as a function of donor strength. Proton magnetic resonance signals usually shift to lower field upon formation of a hydrogen bond because of the change in the magnetic field at the proton.[2b] At room temperature the interconversion time between complexed and noncomplexed states in hydrogen-bonded systems is small (*i.e.*, $10^{-3}$ sec).[3] Consequently, the observed chemical shift, $\delta_{\text{obsd}}$ will correspond to the population weighted average for the two states as indicated in eq 1, where the weighing factor, $\alpha$, is the

$$\delta_{\text{obsd}} = \alpha\delta_{\text{A-H}} + (1 - \alpha)\delta_{\text{A-H}\cdots\text{B}} \qquad (1)$$

fraction of hydrogen-bonding acid present in the noncomplexed state and $\delta_{\text{A-H}}$ and $\delta_{\text{A-H}\cdots\text{B}}$ are the chemical shifts of the noncomplexed and the complexed state, respectively. Under conditions of complete complexation of the acid, $\delta_{\text{obsd}}$ equals $\delta_{\text{A-H}\cdots\text{B}}$. The quantity $\Delta_{\text{A-H}\cdots\text{B}}$, the "hydrogen-bond shift," as defined in eq 2, is determined primarily by contributions from the

$$\Delta_{\text{A-H}\cdots\text{B}} = \delta_{\text{A-H}\cdots\text{B}} - \delta_{\text{A-H}} \qquad (2)$$

"complexation effect" and the "donor-anisotropy effect." The complexation effect, which always gives a downfield shift, arises because the electric field of the electron-donor molecule polarizes the A–H bond of the hydrogen-bonding acid and thus alters the screening constant of the proton. The extent of this effect will be determined by the magnitude of the electric field which the hydrogen-bonding proton experiences. The donor-anisotropy effect, which can lead to upfield or downfield shifts, arises whenever anisotropic magnetic currents exist in the electron-donor atom, B, or in any part of the electron-donor molecule. The combination of these two effects suggests that the hydrogen-bond shift could be to higher or lower field. A shift to lower magnetic field is observed for all hydrogen-bonded species involving electron donors in which unusual magnetic anisotropic effects are absent.

For hydrogen-bonded systems, an increased electron-donor strength of the base would give a larger complexation effect in the proton resonance spectrum and also would lead to a larger enthalpy of hydrogen-bonding interaction. Thus a correlation between $\delta_{\text{obsd}}$ and $\Delta H$ is expected for phenol–base systems in which the donor-anisotropy effect does not prevail. Deviations are to be expected when large anisotropy effects are present in the donor. Several previous studies[4-6] have been somewhat successful in attempting to correlate quantitatively $\delta_{\text{obsd}}$ with $\Delta H$ or $\Delta\nu_{\text{O-H}}$, but in each of these studies no attempt was made to correct for donor anisotropy. The work reported in this paper demonstrates that the hydrogen-bond shift for phenol–base hydrogen-bonding interactions having $-\Delta H$ from 3 to 10 kcal/mole is linearly related to $\Delta\nu_{\text{O-H}}$ and $\delta_{\text{obsd}}$ except for donors in which large anisotropy effects are present. Corrections applied to compensate for donor anisotropy in carbonyl compounds and pyridine permit these systems to be included in the correlation.

## Experimental Section

**Apparatus.** The chemical shift data were determined from proton magnetic resonance spectra obtained on a Varian Model A-60 high-resolution nuclear magnetic resonance spectrometer with temperature regulating accessories. The instrument settings used were the following: frequency response, 1 cps; radiofrequency field, 0.2 mg; sweep time, 250 sec; sweep width, 500 cps; sweep offset, 300 cps; spectrum amplitude, 8. At very low temperatures (*i.e.*, below −40°), it was necessary to increase the spectrum amplitude to as high as 30 for the amine bases, depending upon the extent of $\text{N}^{14}$ quadrupolar broadening of the proton resonance signal. The temperatures were determined using a methanol sample and the calibration data furnished by Varian Associates.

**Materials.** Mallinckrodt analytical reagent phenol was distilled at atmospheric pressure. The middle fraction, collected and stored in a desiccator over calcium chloride, was sublimed at atmospheric pressure just prior to use.

No attempt was made to obtain ultrapure bases for the proton magnetic resonance experiments. However, at least one purification step was performed on all of the bases except Columbia Organic Chemicals triphenylphosphine oxide, Eastman White Label diethyl sulfide, and the N-methyl lactams.[7] A qualitative gas chromato-

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[1] Abstracted in part from the Ph.D. thesis of D. P. Eyman, University of Illinois, Urbana, Ill., 1964.

[2] (a) M. D. Joeston and R. S. Drago, *J. Am. Chem. Soc.*, **84**, 3817 (1962); (b) C. M. Huggins, G. C. Pimentel, and J. N. Schoolery, *J. Phys. Chem.*, **60**, 1311 (1956).

[3] J. A. Pople, W. G. Schneider, and J. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 15.

[4] R. Kaiser, *Can. J. Chem.*, **41**, 430 (1963).

[5] E. A. Allan and L. W. Reevers, *J. Phys. Chem.*, **66**, 613 (1962).

[6] I. Granacher, *Helv. Phys. Acta*, **34**, 272 (1961).

[7] The N-methyl lactams were furnished by Dr. David M. Hart of Oklahoma City University, who prepared and purified them by the

graphic analysis was performed on each of the liquid bases. Mallinckrodt analytical reagent acetone was dried over Linde 4-A molecular sieves and used without further purification. Mallinckrodt analytical reagent ethyl acetate was used after being purified in the same way. Eastman White Label triethylamine was dried over Linde 4-A molecular sieves and then distilled twice at atmospheric pressure.

Mallinckrodt analytical reagent diethyl ether was dried over calcium hydride for 2 days and distilled from fresh calcium hydride at atmospheric pressure. Baker Analyzed reagent acetonitrile was dried over phosphorus pentoxide for 1 week and then distilled from fresh phosphorus pentoxide. The distillate was stored over calcium hydride for 2 days and then distilled from fresh calcium hydride at atmospheric pressure. Eastman White Label acetamide was purified by sublimation at atmospheric pressure and 85°. Eastman White Label *p*-dioxane was purified by the method of Hess and Frahm.[8]

Mallinckrodt analytical reagent pyridine was dried over barium oxide for 2 days and distilled from fresh barium oxide at atmospheric pressure. Big Ben Chemicals tetrahydrofuran was treated with solid potassium hydroxide, decanted, and distilled at atmospheric pressure from calcium hydride. Trimethylphosphine oxide, prepared by the method of Burg and McKee,[9] was sublimed at about 75° (100 mm) just prior to use. The N,N-dimethyltrichloroacetamide was prepared and purified by the method of Brintzinger, *et al.*[10]

The N,N-dimethyltrifluoroacetamide was prepared and purified by the procedure of Bissell and Finger.[11] The N,N-dimethylthioacetamide was prepared by the method of Hofmann[12] and purified by recrystallization from water. The N,N-dimethylbenzamide was prepared and purified as previously reported.[13]

The remainder of the bases were all purified by the same general procedure. After drying over barium oxide for several days, each base was fractionally distilled under vacuum from fresh barium oxide. The bases purified in this way included Eastman White Label N,N-dimethylformamide, N,N-dimethylacetamide, N,N-di-*n*-propylacetamide, N,N-dimethylpropionamide, triethyl phosphate, and diethyl phosphite; Wateree Chemical Co. tetramethylene sulfoxide; Fisher hexamethylphosphoramide; Phillips Petroleum Company tetramethylene sulfone; Aldrich Chemical trimethyl phosphate; and Baker Analyzed reagent dimethyl sulfoxide.

Baker Analyzed reagent methylene chloride and Fisher Spectranalyzed carbon tetrachloride were dried over Linde 4-A molecular sieves and used without further purification.

**Procedure.** The solutions to be studied were prepared in Varian nmr tubes. After weighing the bases, both solids and liquids, in the nmr tubes, an aliquot of a stock solution of phenol in methylene chloride was added. After the addition of tetramethylsilane (*ca.* 0.05 ml), the final volume of each solution was determined by measuring the height of the liquid in the tube and applying a previously determined calibration factor. Each nmr tube was capped with a polyethylene cap and sealed with wax to prevent solvent loss at higher temperatures or condensation of water at lower temperatures.

The chemical shifts were all determined relative to the internal standard tetramethylsilane. Whenever the phenol hydroxy proton peak occurred in the vicinity of the phenol ring proton peaks, small temperature changes (*ca.* 5°) permitted identification.

A dilution study of phenol in methylene chloride was performed in order to determine the chemical shift associated with monomeric phenol. This study covered the concentration range 0.005–0.5 *M* phenol and was done at a constant temperature of 38°.

A comparison of the solvents methylene chloride and carbon tetrachloride was made for phenol–base systems having large formation constants. This was done in order to establish that the behavior of the phenol–base system is nearly the same in these solvents.

In order to establish complete phenol–base complexation at −60°, a study was made of the temperature dependence of the phenol hydroxy proton chemical shift. This was done on systems with a range of formation constants.

For purposes of detecting adduct–adduct association or 2:1 or higher complexes, phenol concentrations were varied from 0.2 to 0.6 *M* while the base concentrations varied from 0.7 to 2.3 *M*. The lower limit of the phenol concentrations was established by the detection limits of the nmr spectrometer. The approximate base concentrations required for complete phenol–base complexation at lower temperatures were calculated using available thermodynamic data[2a] and the integrated form of the Van't Hoff equation.

**Anisotropy Calculations.** The anisotropy correction applied for the pyridine system is that suggested by Howard, Jumper, and Emerson[14] who assumed an N···H bond distance of 3.2 A. Their calculated correction is 1.0 ppm. The anisotropy correction applied for the carbonyl compounds is based on Narasimhan and Rogers[15] values of the principal magnetic susceptibility of the carbonyl moiety. These workers calculated the following anisotropies under the assumption that the magnetic dipole of the carbonyl moiety is on the oxygen atom.

$$\Delta\chi_1 = \chi_{zz} - \chi_{yy} = -2.5 \times 10^{-6}$$

$$\Delta\chi_2 = \chi_{zz} - \chi_{xx} = +6.6 \times 10^{-6}$$

In these expressions the *z* axis corresponds to the C–O bond axis and the *y* axis is perpendicular to the trigonal carbonyl plane. In order to calculate the magnetic contribution of the carbonyl moiety to the proton shielding constant in a hydrogen-bonded species, eq 3 is used.

$$\Delta\sigma = \frac{1}{3L_0R^3}\left(-\Delta\chi_2 + \Delta\chi_1(2 - 3\cos^2\theta)\right) \qquad (3)$$

In this equation, *R* is the radius vector between the hydrogen-bonded proton and the point magnetic dipole of the C–O bond (*i.e.*, the oxygen atom), $\theta$ is the acute angle between the C–O bond axis and *R*, and $L_0$ is Avogadro's number. This expression is used when the bond in question is not magnetically axially symmetric (*i.e.*, $\chi_{zz} \neq \chi_{yy} \neq \chi_{xx}$) provided the axis can be chosen so that *R* lies in the trigonal plane of the carbonyl group or perpendicular to it. Since a hydrogen-bonded proton will be aligned with an oxygen lone pair which is coplanar to the trigonal carbonyl moiety, this expression can be used here. The values of *R* and $\theta$ used in this correction are 1.7 A and 60°, respectively. These are based on the most common values of these parameters reported in crystallographic studies of similar systems.[16] The applied correction is 1.1 ppm.

## Results and Discussions

The choice of methylene chloride rather than carbon tetrachloride as a solvent in this study was made because of a desire to collect the data at low temperatures where complexation of relatively dilute phenol–base systems would be nearly complete. The use of relatively dilute systems should decrease the possibility of significant interference by adduct–adduct association or 2:1 or higher complex formation. Since most of the $\Delta\nu_{\text{O-H}}$ values have been determined in carbon tetrachloride, it would have been the ideal solvent to use in this study. However, its relatively high freezing point (*i.e.*, −228°) precludes its use in lower temperature studies. Data on the comparison of the solvents methylene chloride and carbon tetrachloride for phenol adducts with the base dimethyl sulfoxide, N,N-dimethylacetamide, and pyridine are reported in Table I.

The difference of 0.2–0.4 ppm at 30° is probably due to small differences in the phenol–base formation constants in the two solvents. At −20° where these adducts are nearly completely associated, the chemical

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procedure outlined in the following reference: C. D. Schmulbach and D. M. Hart, *J. Org. Chem.*, **29**, 3122 (1964).

[8] K. Hess and H. Frahm, *Ber.*, 71, 2627 (1938).

[9] A. B. Burg and W. E. McKee, *J. Am. Chem. Soc.*, **73**, 4590 (1951).

[10] H. Brintzinger, K. Pfannsteil, and H. Koddebusch, *Chem. Ber.*, **82**, 389 (1949).

[11] F. R. Bissell and M. Finger, *J. Org. Chem.*, **24**, 1256 (1959).

[12] A. W. Hofmann, *Ber.*, **11**, 338 (1878).

[13] R. L. Carlson and R. S. Drago, *J. Am. Chem. Soc.*, **84**, 2320 (1962).

[14] B. B. Howard, C. F. Jumper, and M. T. Emerson, *J. Mol. Spectry.*, **10**, 117 (1963).

[15] P. T. Narasimhan and M. T. Rogers, *J. Phys. Chem.*, **63**, 1388 (1959).

[16] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

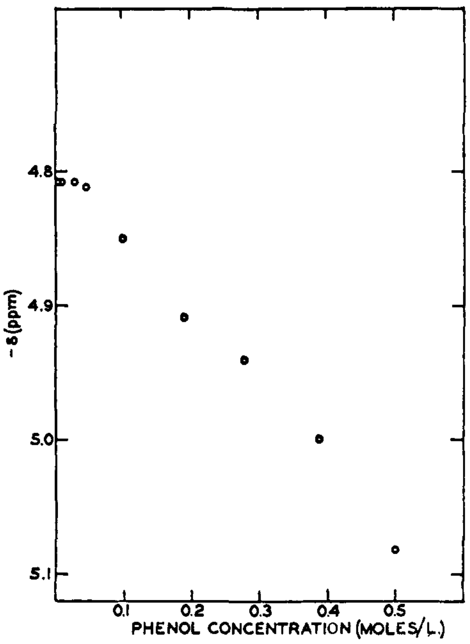

Figure 1. Dilution study of phenol in methylene chloride.

shifts all vary by less than 0.03 ppm. It is concluded that under conditions of nearly complete complexation the hydrogen-bond shift of phenol-base systems will be the same in these two solvents.

Table I. Solvent Effects on the Hydrogen-Bond Shift

| | δ, ppm[a] | | | |
|---|---|---|---|---|
| | 30° | | −20° | |
| Base | $CCl_4$ | $CH_2Cl_2$ | $CCl_4$ | $CH_2Cl_2$ |
| $(CH_3)_2SO$ | 8.68 | 8.90 | 9.20 | 9.20 |
| $CH_3C(O)N(CH_3)_2$ | 9.25 | 9.45 | 9.85 | 9.87 |
| $C_5H_5N$ | 10.48 | 10.88 | 11.40 | 11.43 |

[a] Relative to tetramethylsilane.

The results of the dilution study are presented in Figure 1. This study suggests that below a concentration of 0.03 *M*, phenol in methylene chloride exists in only one state, probably the monomeric form. Assuming this to be the case, the value of $\delta_{A-H}$, the chemical shift of uncomplexed monomeric phenol relative to tetramethylsilane, is −4.81 ppm.

The chemical shift data for 30 phenol-base systems studied in methylene chloride at various temperatures are presented in Table II. This table also includes $\Delta\nu_{O-H}$ values and enthalpy values calculated using eq 4, which expresses the established correlation between $\Delta\nu_{O-H}$ and $\Delta H$. The $-\delta_{obsd}$ values in parentheses at

$$-\Delta H_{calcd} = 0.016\Delta\nu_{OH} + 0.63 \qquad (4)$$

−60° have had the anisotropy corrections applied.

Twenty of these phenol-base systems were studied at two phenol-base concentrations. Since all of the systems were found to vary less than ±0.06 ppm with concentration variations, it is concluded that there is no evidence for extensive adduct-adduct association or the formation of 2:1 or higher complexes.

It is observed that for 18 of these systems, the average change in going from −30 to −60° is 0.28 ppm. For eight of the systems which were studied at −50°, the change in the chemical shift upon going to −60° is 0.06 ppm or less, with the average being about 0.03 ppm. This is interpreted as evidence for nearly complete phenol-base complexation in the temperature range −50 to −60°. Thus the chemical shifts recorded at −60° are considered to represent $\delta_{obsd}$ or $\delta_{A-H \cdots B}$ as defined in eq 1.

The data in Table II suggest that there is a relationship between $\delta_{obsd}$ and $\Delta\nu_{O-H}$ or $\Delta H$. This is more obvious if the data are presented as a plot of $\delta_{obsd}$ *vs.* $\Delta H_{calcd}$ as in Figure 2. In this plot it is seen that all of

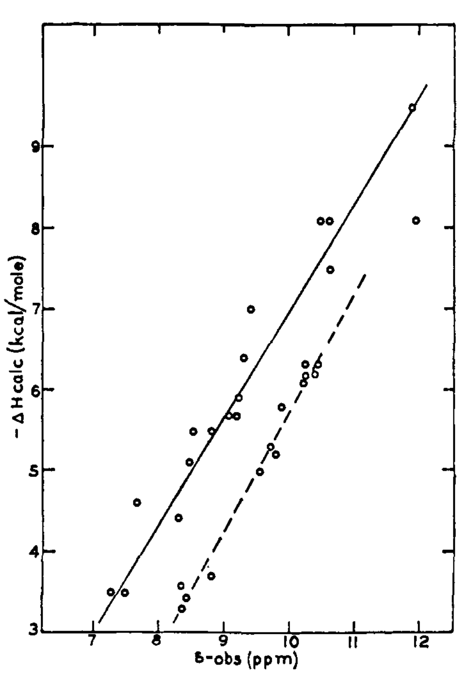

Figure 2. Enthalpy *vs.* observed chemical shift, $\delta_{obsd}$ (ppm), for adducts of bases with phenol.

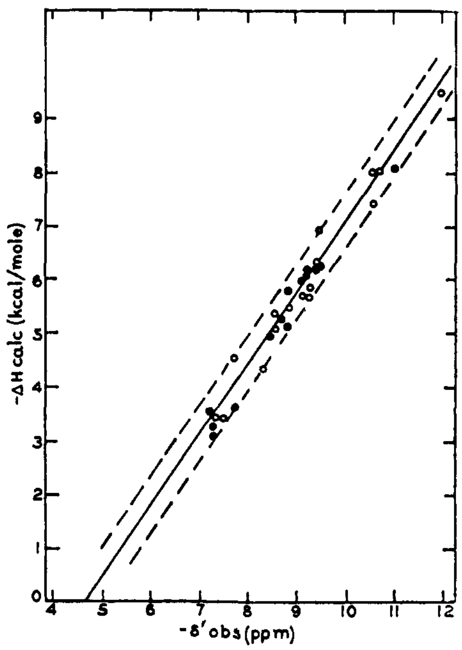

Figure 3. Enthalpy *vs.* chemical shifts corrected for certain donor anisotropies in adducts of bases with phenol (the dark circles represent corrected points; the open circles are those on the solid line in Figure 2).

**Table II.** Chemical Shifts and Frequency Shifts for Phenol–Base Adducts

| Base | $\Delta\nu_{O-H}$, cm$^{-1}$ | Ref | $-\Delta H_{calcd}$, kcal/mole | $-\delta_{obsd}$, ppm[a] 30° | -30° | -50° | -60° |
|---|---|---|---|---|---|---|---|
| $(C_2H_5)_3N$ | 556 | 2 | 9.5 | 10.45 | 11.33 | . . . | 11.88 |
| $[(CH_3)_2N]_3PO$ | 467 | *b* | 8.1 | 10.20 | 10.50 | 10.61 | 10.63 |
| $C_5H_5N$ | 465 | 2 | 8.1 | 10.88 | 11.55 | 11.87 | 11.93 (10.93) |
| $(CH_3)_3PO$ | 464 | 2 | 8.1 | 10.00 | . . . | 10.47 | 10.48 |
| $(C_6H_5)_3PO$ | 430 | *c* | 7.5 | 10.10 | 10.50 | . . . | 10.63 |
| $(CH_2)_4SO$ | 400 | *d* | 7.0 | 8.93 | 9.28 | . . . | 9.43 |
| $(CH_3)_2SO$ | 359 | *b* | 6.4 | 8.90 | 9.25 | 9.37 | 9.35 |
| $\underline{(CH_2)_4C(O)N}CH_3$ | 357 | *e* | 6.3 | 9.58 | . . . | . . . | 10.47 (9.37) |
| $CH_3C(O)N(C_3H_7)_2$ | 353 | *b* | 6.3 | 9.45 | 9.95 | . . . | 10.27 (9.17) |
| $\underline{(CH_2)_5C(O)N}CH_3$ | 350 | *e* | 6.2 | 9.50 | . . . | . . . | 10.36 (9.26) |
| $CH_3C(O)N(CH_3)_2$ | 345 | 2 | 6.2 | 9.45 | 9.95 | 10.21 | 10.27 (9.17) |
| $\underline{(CH_2)_3C(O)N}CH_3$ | 341 | *e* | 6.1 | 9.42 | . . . | . . . | 10.25 (9.15) |
| $(C_2H_5O)_3PO$ | 332 | *b* | 5.9 | . . . | . . . | . . . | 9.23 |
| $C_2H_5C(O)N(CH_3)_2$ | 325 | 2 | 5.8 | 9.27 | . . . | . . . | 9.90 (8.80) |
| $(CH_3O)_3PO$ | 315 | *c* | 5.7 | 8.35 | . . . | . . . | 9.10 |
| $(C_2H_5O)_2POH$ | 310 | *c* | 5.7 | 8.53 | . . . | . . . | 9.22 |
| $(CH_2)_4O$ | 305 |  | 5.5 | 8.05 | 8.57 | . . . | 8.83 |
| $CH_3C(S)N(CH_3)_2$ | 301 | *f* | 5.5 | 7.83 | . . . | . . . | 8.57 |
| $HC(O)N(CH_3)_2$ | 294 | 2 | 5.3 | 9.03 | 9.55 | . . . | 9.73 (8.63) |
| $C_6H_5C(O)N(CH_3)_2$ | 283 | *b* | 5.2 | 9.15 | . . . | . . . | 9.83 (8.73) |
| $(C_2H_5)_2O$ | 279 | 2 | 5.1 | 7.63 | 8.25 | 8.48 | 8.52 |
| $CH_3C(O)NH_2$ | 270 | *b* | 5.0 | . . . | . . . | . . . | 9.57 (8.47) |
| $(C_2H_5)_2S$ | 250 | 2 | 4.6 | 6.27 | 7.22 | . . . | 7.70 |
| $(CH_2)_4O_2$ | 236 |  | 4.4 | 7.55 | 8.05 | . . . | 8.32 |
| $(CH_3)_2CO$ | 193 | 2 | 3.7 | 7.87 | 8.53 | 8.77 | 8.82 (7.72) |
| $CF_3C(O)N(CH_3)_2$ | 185 | *g* | 3.6 | 7.33 | . . . | . . . | 8.33 (7.23) |
| $(CH_2)_4SO_2$ | 181 | *b* | 3.5 | 6.93 | 7.32 | . . . | 7.50 |
| $CH_3CN$ | 178 | 2 | 3.5 | 6.62 | 7.08 | . . . | 7.30 |
| $CCl_3C(O)N(CH_3)_2$ | 172 | 2 | 3.4 | 7.35 | . . . | 8.33 | 8.38 (7.28) |
| $CH_3C(O)OC_2H_5$ | 164 | 2 | 3.3 | 7.83 | 8.03 | . . . | 8.38 (7.28) |

[a] Relative to tetramethylsilane. [b] M. D. Joesten, Ph.D. Thesis, University of Illinois, 1962. [c] G. Aksnes and T. Gramstad, *Acta Chem. Scand.*, **14**, 1485 (1960). [d] R. S. Drago, B. Wayland, and R. L. Carlson, *J. Am. Chem. Soc.*, **85**, 3125 (1963). [e] J. H. Bright, R. S. Drago, D. M. Hart, and S. K. Madan, *Inorg. Chem.*, **4**, 18 (1965). [f] R. J. Niedzielski, R. S. Drago, and R. L. Middaugh, *J. Am. Chem. Soc.*, **86**, 1694 (1964). [g] R. L. Middaugh, R. S. Drago, and R. Niedzielski, *ibid.*, **86**, 388 (1964).

the carbonyl compounds fall along the arbitrarily positioned dashed line and all of the other compounds, with the exception of pyridine, are distributed about the arbitrarily positioned solid line. For the pyridine system, the expected downfield shift is observed. The fact that the 13 carbonyl compounds show nearly a constant deviation from the solid line suggests that for this series of compounds the most significant donor-anisotropy effect arises from the carbonyl moiety. Thus, a donor-anisotropy correction involving only the magnetic anisotropy of the carbonyl moiety should give shifts which do not deviate significantly from the shifts of other compounds in which the donor-anisotropy effect is inoperative.

The corrected chemical shifts, $-\delta'_{obsd}$, for phenol adducts of pyridine and the carbonyl compounds are given in parentheses in Table II. These corrected values along with the other uncorrected values are plotted *vs.* $-\Delta H_{calcd}$ in Figure 3. In this plot the corrected and uncorrected points all seem to be distributed about one line. In order to establish a statistically significant line, a regression analysis was performed on these data.[17]

The slope of this line was found to be $-1.340 \pm 0.086$ kcal/mole ppm at the 95% confidence level. Thus by incorporating eq 2, it is concluded that a linear correlation exists between the hydrogen-bond shift and the frequency shift for phenol–base adducts. Since it has been demonstrated that frequency shifts are linearly related to the enthalpy for phenol–base interactions, this study establishes a linear relationship between the hydrogen-bond shift and the enthalpy. The equation defining this correlation is

$$\delta'_{obsd} = 0.748(\Delta H_{calcd}) - 4.68 \qquad (5)$$

The abscissa intercept, which occurs at $-4.68$ ppm, compares favorably with the experimentally determined $\delta_{A-H}$ of monomeric phenol in methylene chloride which was found to be $-4.81$ ppm. The close agreement between these values suggests that the correlation of $\delta_{obsd}$ and $\Delta H_{calcd}$ is good over the range 0 to 10 kcal/mole. All of the points in Figure 3 vary from the statistically determined line by less than $\pm 0.5$ kcal/mole or $\pm 0.38$ ppm as indicated by the dashed lines. Under the assumptions of complete complexation and no interference from more complex interactions, these deviations probably are attributed to experimental error in $\Delta H$ and to minor anisotropic contributions from the donor molecules.

**Acknowledgment.** The authors thank the Chemistry Branch of the Atomic Energy Commission for their generous support of this research through Contract No. AT(11-1)758.

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(17) H. A. Laitenen, "Chemical Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 547.