ring to that with a more flexible donor molecule which can better accommodate the solvent. The limited data in Table II are in accord with these assumptions.

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Association of Indole and Phenol with Diethyl Chalcogenides

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Abstract: The ir spectra of indole in solutions containing diethyl ether, diethyl sulfide, selenide, and telluride as well as those of phenol in solutions containing the first three chalcogenide compounds were obtained at 40°. The chemical shifts of the phenol hydroxyl proton were obtained for the latter three systems, at -20, 10, and 40° as a function of ether concentration. Association equilibrium constants and molar extinction coefficients were obtained for all systems, while ΔH and ΔS values were calculated for the latter three systems. The results were found to agree with the "electron vibration" model developed principally for charge-transfer (CT) complexes, if one assumes that the H-bond lengths increase in going from ether to selenide or to telluride. The thermodynamic properties and the comparison of the spectral data with literature data reported for typical CT complexes show that CT constitutes only part of the over-all H-bond interaction.

In recent years, much experimental and theoretical work has been devoted to the study of charge-transfer (CT) complexes, and in particular to their spectral properties.[1-3] To interpret the intensification of the infrared stretching vibration of the electron-acceptor molecule on CT complex formation, the so-called "electron-vibration" model was developed.[4-10] The dative or charge-transfer form contributes to the over-all state of the complex, and the relative weight of this contribution is conveniently described by the coefficient of the wave function descriptive of this dative form which enters the linear sum of terms constituting the over-all wave function of the complex.[2,3] The electron vibration model recognizes that this weighting or dative coefficient, b, varies during the electron-acceptor stretching vibration and in phase with it. This variation in turn is equivalent to a change of the over-all or effective dipole moment, again in phase with the stretching vibration, and leads to the observed intensification of the corresponding infrared band.

Interestingly, the recent and rigorous treatment of the problem by Friedrich and Person[10] should be useful to explain the intensification of typical X–H stretching vibrations on H-bonding as well. In fact, the authors recognized that there are conceptual similarities between their treatment and those presented by others who were specifically interested in H-bonding.[11-13]

A complete test of the Friedrich and Person theory as applied to H-bonding does not seem feasible at this time,[14] but accurate intensity data used in the light of the approximate results of the formal treatment[10] may well serve to estimate the relative importance of charge transfer compared to the other contributions to the H-bond strength in a series of structurally similar H-bonded complexes.

This more limited objective is the goal of the present study. Literature data alone, however extensive,[15] cannot be used to this end. For one, the methods used to determine integrated molar absorption coefficients differ widely in various laboratories,[16,17] and systematic errors cannot ordinarily be estimated and removed. Secondly, the selection of H-bonding partners is critical, even for a limited comparison of theory and experiment. Frequently, and, for example, in the case of trialkylamines, there is a definite parallelism between charge-transfer donor strength and electron-donor electrostatic action.[2] In the present series, the accumulation of negative charge on the electron-donor moiety decreases in going from O to Se or Te, while the charge-transfer tendency should increase. This means that the trends observed within series of complexes as studied here should show which of these two effects is more important, and this reasoning led to the present selection of H-bonding partners. In addition, it seemed important to get some H-bonding data for the heavier chalcogenide ethers; little work seems to have been done on these compounds.[15]

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Table I. Summary of Experimental Results

Proton donor	Proton acceptor	$A_f \times 10^{-4\,a,b}$		$A_c \times 10^{-4\,a,b}$			K (at 40°),[b] l./mole				Δe^{eff},[d] from eq 6	$\Delta\nu$, cm^{-1}	$\Delta k/k$, from eq 7
		A	C	A	B	C	A	B	C	From nmr data and eq 5			
Phenol in CCl$_4$	Ether	1.03	1.05	7.03	6.88	6.92	4.30	4.50	4.50	4.61	2.42	274	0.146
	Sulfide		1.00	5.83	6.18	6.15	0.86	0.80	0.80	0.83	2.16	251	0.134
	Selenide		1.03	6.08	5.82	6.01	0.63	0.67	0.62	0.63	2.14	236	0.126
	Telluride			5.30[c]			0.5[c]				1.93[c]	213[c]	0.114[c]
Indole in n-hexane	Ether	1.07	1.07	4.58	4.84	4.56	1.70	1.53	1.72		1.65	155	0.86
	Sulfide		1.09	3.36	3.48	3.43	0.73	0.68	0.72		1.22	136	0.76
	Selenide			3.41	2.97	2.99	0.60	0.72	0.69		1.09	132	0.74
	Telluride			3.20	2.88	3.11	0.50	0.57	0.48		1.04	130	0.73

[a] Molar absorptivity (cm^{-1} cm^2/mmole) of the non-H-bonded, A_f, and H-bonded OH or >N–H group, A_c. Here $A \equiv (2.303/cl) \int \log (I_0/I) \int d\nu$, where c is the actual concentration of non-H-bonded or H-bonded group, respectively, in moles/l., l is the cell path length in cm, ν is the wave number, and I/I_0 is the experimental transmittance. The integration extends over the entire band in question. [b] Methods of evaluation (A, B, or C) from ir data of K, A_c, and A_f are discussed in the text. Δe^{eff} is the additional effective charge, see eq 6. $\Delta k/k$ and $\Delta\nu/\nu$ are the relative change in force constant and in frequency on H-bonding, respectively; see eq 7. [c] The experimental errors in these two cases are larger than normal (see below) because of the instability of phenol in CCl$_4$ in the presence of telluride. [d] Δe^{eff} calculated from the averages of A_c. Relative standard deviations of K and A_c are 0.03–0.05 and 0.02–0.03 in phenol, and 0.05–0.10 and 0.03–0.05 in indole, respectively.

Experimental Section

Materials. The solvents used, carbon tetrachloride and n-hexane, were Matheson Spectroquality grade. n-Hexane was used without further treatment, but carbon tetrachloride was dried over P_2O_5 and then distilled. The phenol used was Mallinckrodt reagent grade; it was distilled under vacuum and stored in the dark in a tightly closed vessel. The indole was obtained from Eastman; it was recrystallized from isooctane, dried under vacuum, and stored like the phenol. Diethyl ether, used as one of the H-bonding partners, was Mallinckrodt reagent grade; it was distilled over sodium shortly before use. Diethyl sulfide and selenide were obtained from K & K Laboratories, dried over sodium, and then distilled.

All distillations, except that of the telluride, were carried out in a very efficient column, previously purged with prepurified nitrogen. Diethyl telluride from K & K Laboratories was distilled shortly before use in a small column under 15 mm pressure of nitrogen. The distillates were always protected from atmospheric moisture, and telluride from atmospheric oxygen as well. The purity of the sulfide, selenide, and telluride was checked by gas chromatography.

Infrared Measurements. Stock solutions of proton acceptors were prepared gravimetrically, their densities measured at 40°, and molarities calculated therefrom. These solutions were used to prepare gravimetrically the ternary solutions containing both H donor and acceptor.

Most of the above manipulations were carried out under nitrogen to prevent the absorption of moisture from the air. The slight changes of the base line in the infrared spectrum afforded a sensitive test on the efficiency of the technique.

The concentration ranges (moles/liter) used were as follows: phenol, 0.005–0.01; indole, 0.005–0.04; ether, 0.08–1.2; other proton acceptors, 0.2–1.5. The spectra were obtained on a Beckman IR-9 prism-grating spectrophotometer between 3000 and 3700 cm^{-1}. The spectrum of each ternary solution, containing H donor, H acceptor, and solvent, was taken in a single near-infrared quartz cell without solvent compensation. After that, the spectrum of the stock solution was taken in the same sample cell under identical conditions. In this fashion, the mismatching of the cells was rendered harmless. The path lengths were 1 and 5 mm, for the phenol and indole solutions, respectively. The very small difference in concentration of H acceptor in the binary stock solution and in the ternary solution prepared from it was shown to be of no consequence.

Normally, much of the absorbance in the sample beam was compensated by placing rotating sectors in the reference beam. This procedure made it possible to use the variable-scale expansion of the absorbance scale and to prove that the slight nonlinearity of the comb in the reference beam, and of the potentiometer connected to it, was of no consequence.

The mechanical slit width was four times the standard value to make for high photometric precision. The corresponding spectral slit width is approximately 4.0 cm^{-1} near 3500 cm^{-1}.[18]

The absorption of solvent and of traces of water present at times caused difficulties in the determination of solute absorbances. The overlap of the absorption bands of free phenol OH groups and the H-bonded OH groups was resolved by assuming the former band to be symmetrical in shape. Separate experiments showed that in the concentration range used here, phenol dimer formation was negligibly small. In the case of indole, there is a low-frequency shoulder on the absorption band related to the free >N–H group, presumably due to Fermi resonance.[19] In this case the overlap of bands related to bonded and nonbonded species was accounted for by first establishing the average shape of the free >N–H band at different indole concentrations and in the absence of electron-donor molecules, and then redrawing it at the appropriate height in the actual experimental spectra. The absorbances measured at very low concentrations followed Beer's law very well (Figure 1). In a few cases, indole dimer formation was noticeable and was accounted for by a graphical procedure. Very often, the (small) overlap with C–H vibrations had to be taken into account.

The sample temperature was controlled to within ±0.1° using a thermostat around the sample cell.

Nmr Measurements. A stock solution containing 1.6% by weight tetramethylsilane (TMS) and approximately 0.006 mole/l. of phenol and a second stock solution containing the H acceptor were prepared gravimetrically, using carbon tetrachloride as solvent. The densities of these solutions were measured at several temperatures to calculate molarities. Much care was used to keep the solutions dry.

The phenol hydroxyl proton chemical shifts were measured using a Varian Model HA-100 nmr spectrometer with a frequency counter, in frequency sweep operation, using the proton side-band resonance technique.[20] The sample temperature was kept constant to within better than 1° using the variable temperature accessory of the spectrometer. The precision of the chemical shifts is ±0.2 cps or somewhat better.

Results

Evaluation of Association Equilibrium Constants, *K*, from Infrared Data. The results as shown in Table I were obtained by three different methods.

A. The absorbance of the free –OH and >N–H group vibrations, A_f' ($\equiv 2.303 \int \log (I_0/I)\, d\nu$) were measured as a function of initial concentration of H donor and acceptor, a_0 and b_0, respectively. The integrated molar absorption coefficient of the free X–H group vibration, A_f, and the optical path length, l, were determined in separate series of experiments. From

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(18) Operating Manual of the Beckman IR-9 spectrophotometer, Beckman Instruments Co., Fullerton, Calif., 1965.

(19) H. Fritzsche, *Ber. Bunsenges. Physik. Chem.*, **68**, 459 (1964).

(20) W. A. Anderson, *Rev. Sci. Instr.*, **33**, 1160 (1962).

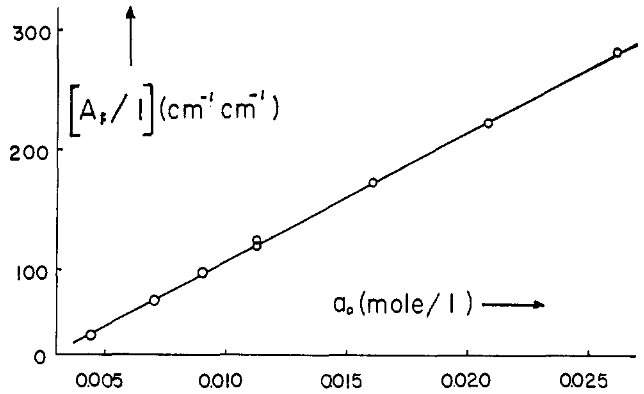

Figure 1. Test of Beer's law for indole in *n*-hexane. A_f' ($\equiv A_f a_0 l$) is 2.303 times the absorbance of the non-H-bonded indole >N–H absorption band, l is the cell thickness, and a_0 is the indole concentration.

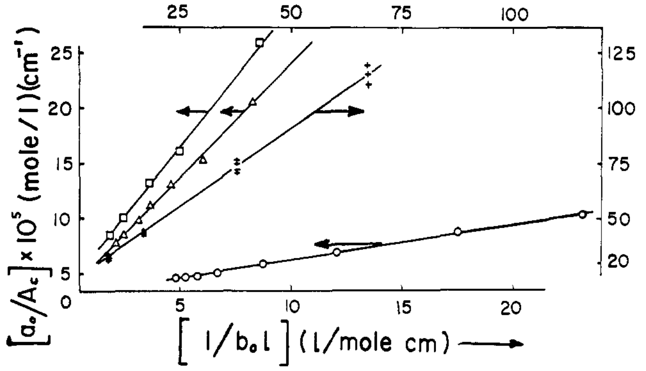

Figure 2. Benesi–Hildebrand plot for several systems: ○, △, □, phenol with diethyl ether, diethyl sulfide, and diethyl selenide, respectively; +, indole with diethyl ether. A_c' ($\equiv A_c a_0 l$) is 2.303 times the absorbance of the H-bonded OH or >N–H absorption band, l is the cell thickness, and a_0 and b_0 are the initial concentrations of H donor and acceptor, respectively.

the law of mass action one obtains

$$K = \frac{a_0 - (A_f'/A_f l)}{(A_f'/A_f l)(b_0 - a_0 + A_f'/A_f l)} \qquad (1)$$

Thus K can be calculated from A_f and l plus experimental values of A_f'. Next, the integrated molar absorption coefficient of the bonded species, A_c, can be calculated from

$$A_c = \frac{A_c'[KA_f' + A_f l]}{KA_f' l b_0} \qquad (2)$$

Here A_c' ($\equiv 2.303 \int \log (I_0/I) \, d\nu$) is the absorbance of the bonded species. Arithmetic averages of K and A_c calculated by this method are given in Table I.

B. Secondly, K and A_c were determined simultaneously using the Benesi–Hildebrand equation[21]

$$\frac{a_0}{A_c'} = \frac{1}{KA_c l}\frac{1}{b_0} + \frac{1}{A_c l} \qquad (3)$$

for equilibria involving phenol (see Figure 2), and the Rose and Drago method[22] in the case of indole. Obviously only A_c' values are used; thus the resulting K values are entirely independent of those obtained by method A.

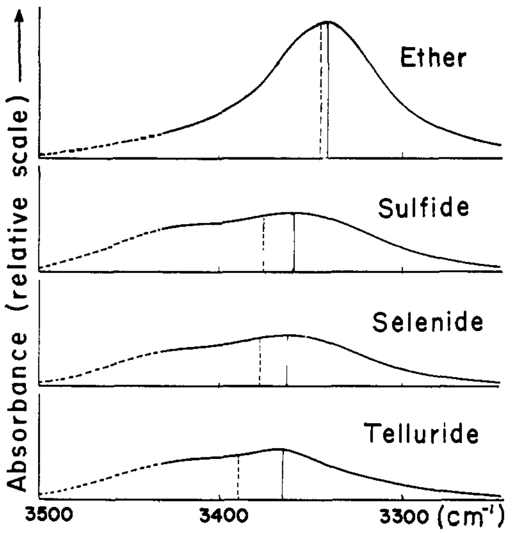

Figure 3. Absorption bands of H-bonded >N–H of indole with four diethyl chalcogenides. Concerning the vertical lines, see legend to Figure 5.

C. Using the mass balance condition on the proton donor, one can show that

$$\frac{A_c'}{A_f'} = \frac{a_0}{A_f'}A_c l - \frac{A_c}{A_f} \qquad (4)$$

Using a least-squares fit based on this equation and pairs of experimental A_c', A_f' values, one obtains A_c and A_f simultaneously. K can then be obtained through a least-squares fit of modified eq 2.

Infrared Absorption Band Shapes. The absorption band of the phenol OH group H-bonded to ether is by far not as broad as that H-bonded to sulfide, selenide, and telluride, while the band shape changes little. The indole >N–H band, however, becomes broader, as one goes from ether to heavier electron-donor molecules, and at the same time a shoulder appears, as shown in Figure 3. The band shape appears independent of concentration, so that higher order (1:*n*) complexes are not likely to be present, even though the existence of more than one 1:1 complex is conceivable. This shoulder is due more likely, however, to an overtone or combination frequency.

Nmr Results and Their Treatment. The chemical shifts measured for different systems and at different temperatures are presented in Figure 4 and Table II. The extrapolated chemical shift for the bonded species is defined as $\Delta\delta_{\text{assoc}} \equiv \delta_2 - \delta_1$, where δ_2 is the (extrapolated) value of the chemical shift for the H-bonded OH group, and δ is that of the non-H-bonded species. It is found that $\Delta\delta_{\text{assoc}}$ is less temperature dependent than has been found by others. This is in good agreement with the recent work of Muller and Simon.[23]

Evaluation of the Association Equilibrium Constants from Nmr Data. One can write[24]

$$\delta = \frac{\delta_1 a + \delta_2(a_0 - a)}{a_0} \qquad (5)$$

where δ is the observed chemical shift, a is the equilib-

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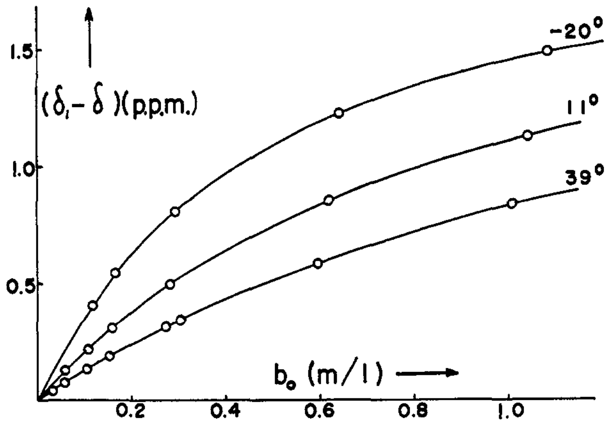

Figure 4. Chemical shift of phenol OH proton in solution with diethyl selenide at different temperatures: $(\delta_1 - \delta)$, chemical shift relative to non-H-bonded value; b_0, concentration of selenide. The drawn-out curves are calculated, using the best estimates of K, δ_1, and δ_2, the equilibrium constant of association, and the (extrapolated) chemical shifts of the completely non-H-bonded and H-bonded OH group, respectively.

rium concentration of free phenol, and a_0 is the total phenol concentration, as above. From this expression and the law of mass action, K and $\Delta\delta_{\text{assoc}}$ were obtained by trial and error. Calculated values of $\Delta\delta_{\text{assoc}}$ agree closely for proton-acceptor concentrations up to about 1 mole/l. Above this concentration medium effects become appreciable and lead to the divergence of calculated and experimental values of $(\delta_1 - \delta)$, as shown in Table II.

Table II. Comparison of Experimental $(\delta_1 - \delta_{\text{exptl}})$ and Calculated $(\delta_1 - \delta_{\text{calcd}})$ Chemical Shifts of the Phenol OH Signal on N-Bonding with Diethyl Ether at 37.5° in CCl_4 at Various Total Ether Concentrations, b_0[a]

b_0, M	$\delta_1 - \delta_{\text{calcd}}$, ppm	$\delta_1 - \delta_{\text{exptl}}$, ppm	Complexed phenol, %	a_0, M
0.05187	0.626	0.625	20.2	0.00614
0.1017	1.030	1.030	33.3	0.00610
0.2315	1.653	1.656	53.3	0.00602
0.5420	2.252	2.250	72.7	0.0131
0.7753	2.461	2.459	79.4	0.00568
1.029	2.589	2.587	83.5	0.1037
1.952	2.810	2.821	90.6	0.0147
3.916	2.949 (3.100)[b]	3.000 (∽3.250)[b]	95.1 (100.0)[b]	0.0133

[a] a_0 is the initial phenol concentration. Here K = 4.99 moles/l. and $\Delta\delta_{\text{assoc}} = \delta_2 - \delta_1 = 3.10$ ppm (see Table III). δ_1 is the chemical shift of the free OH group and δ_2 is the (extrapolated) value for the bonded group. [b] Values are extrapolated. Note the discrepancies between $\delta_1 - \delta_{\text{calcd}}$ and $\delta_1 - \delta_{\text{exptl}}$ in the last three rows, due to the medium effect.

Discussion

From the above agreement of the results obtained by the nmr and ir methods, as shown in Table I, one may gain confidence in the values of K, the equilibrium constants of association. Deviations from Beer's law[25] are unimportant over the entire concentration ranges used here; one example of this is shown in Figure 1. The effect of solute-solvent association likewise is of little consequence[26] since the K values are not very small. Finally, Person's criteria for getting reliable association constants are met as well,[27] at least over most of the range investigated.

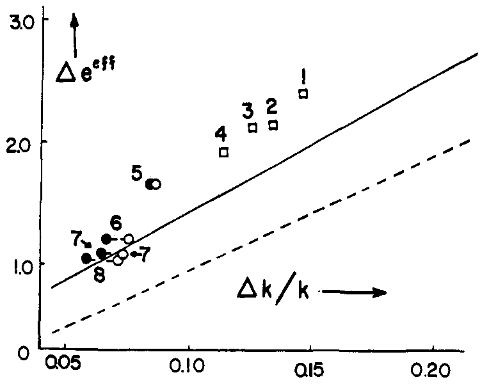

Figure 5. Plot of the additional effective charge Δe^{eff}, calculated from eq 6 against the relative change in force constant $\Delta k/k$, obtained from eq 7: □, phenol; ○ and ●, indole as H donor. Points 1 and 5, diethyl ether; 2 and 6, diethyl sulfide; 3 and 7, diethyl selenide; 4 and 8, diethyl telluride as H acceptors. ○, $\Delta k/k$ calculated from the position of the absorption band maximum (drawn-out vertical lines of Figure 3); ●, based on the position of the midpoint of the absorption band area (dashed vertical lines of Figure 3). The drawn-out line represents the correlation for typical charge-transfer complexes,[8] while the dashed line corresponds to the early Person model mentioned in the text.[7,8]

Having obtained reliable K values, one obtains equally reliable values of A_c and thus of Δe^{eff}, the additional effective charge. This quantity can be calculated from[28]

$$\Delta e^{\text{eff}}\,(\text{D}/\mathring{\text{A}}) = \left(\frac{3000c^2}{\pi N}\right)^{1/2}\sqrt{\mu_{\text{red}}}(\sqrt{A_c} - \sqrt{A_f}) \qquad (6)$$

Here, c is the velocity of light, N is Avogadro's number, μ_{red} is the reduced mass, and the quantities A_c and A_f are the integrated molar extinction coefficients defined above.

To facilitate the discussion, Δe^{eff} is plotted in Figure 5 against the fractional change of the force constant on H-bond formation, $\Delta k/k$. This is given to a good approximation by[10]

$$\frac{\Delta k}{k} = \frac{\nu_0{}^2 - \nu_c{}^2}{\nu_0{}^2} \simeq \frac{2\Delta\nu}{\nu_0} \qquad (7)$$

Here, ν_0 and ν_c are the wave numbers of the free and H-bonded X–H species, respectively.

As a first major feature of the data presented in Figure 5, one notes that the intensification, or Δe^{eff}, is distinctly smaller for the selenide or telluride complexes than for those involving ether. Since the electrostatic theory of H-bonding has not been successful in accounting for the intensification of the X–H stretching vibration,[29–31] while the "electron vibration" model has been partially successful, in the case of typical charge-transfer complexes,[10] one may assume that the decrease in question

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(25) P. H. Emslie, R. Foster, C. A. Fyfe, and I. Horman, *Tetrahedron*, **21**, 2843 (1965).

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(30) G. M. Huggins and G. C. Pimentel, *J. Phys. Chem.*, **60**, 1615 (1956).

(31) M. Van Thiel, E. D. Becker, and G. C. Pimentel, *J. Chem. Phys.*, **27**, 486 (1957).

is primarily due to a decrease in b, that is, to a lessening of the charge-transfer interaction in going from complexes involving ether to those of selenide or telluride. The decrease of $\Delta k/k$ in these series leads to the same conclusion, since $\Delta k/k \simeq b^2$.[10]

From the decrease of the ionization potentials in the series of chalcogenide ethers, one would expect the opposite trend, that is, an increase of the CT effect, either using the simplified results of Friedrich and Person's treatment[32] or the crude approximations given by Szczepaniak and Tramer.[33] For example, the equilibrium constant of CT complex formation of diethyl selenide with iodine is much larger than that of diethyl sulfide.[34]

The unexpected trend observed here may well be due to an increase of the H-bond lengths in this same series. The recent model calculations of Duijneveldt and Murrell[35] show that such a change could more than balance the effect of decreasing ionization potentials.

The data plotted in Figure 5 show that Δe^{eff} increases monotonically with $\Delta k/k$, but the two quantities do not follow a good linear correlation, as predicted by the approximate eq 22 of Friedrich and Person.[10] This may be due to the approximations involved, or perhaps, and less likely so, to the simultaneous existence of several 1:1 complexes, as discussed above.

As a second feature of the present data, one notes that the enthalpies of H-bond formation (Table III) decrease even more strongly than the Δe^{eff} or $\Delta k/k$, in the series ether, sulfide, selenide. Probably ΔH contains several contributions of opposite sign, according to Duijneveldt and Murrell's results.[35] As discussed in the introductory section, and judging from the calculated results of these authors, one would expect the contributions to the H-bond strength other than CT to decrease at least as much as the CT effect itself. This in turn is in agreement with the strong decrease of ΔH. The agreement presented here ignores the changes in hybridization which are not as yet estimated by model calculations[35] but can be demonstrated to exist experimentally.[36,37]

Table III. Enthalpies, Entropies, Association Equilibrium Constants, and Extreme Chemical Shifts, $\Delta\delta_{\mathrm{assoc}}$, on H-Bonding of Phenol with Ethers in CCl_4 at Different Temperatures[a]

Proton acceptor	$-\Delta H$, kcal/mole	$-\Delta S$, eu	K, l./mole	$\Delta\delta_{\mathrm{assoc}}$, ppm	Temp, °C
Ether	5.63	14.9	4.99	3.10	37.5
			11.2	3.15	12
			43.5	3.19	−21
Sulfide	3.35	11.1	0.84	2.36	39
			1.44	2.39	11.5
			2.95	2.39	−20
Selenide	3.15	11.0	0.63	2.15	39.5
			1.06	2.16	11
			2.04	2.17	−20

[a] δ_1, the chemical shift of the free phenol hydroxyl group, is 4.23 ppm at 40°, and increases slightly with decreasing temperature.

Acknowledgment. The authors are indebted to Mr. A. Torrison of this department for his effective administrative support of this work. The work was supported by the U. S. Public Health Service under Grant GM-13977.

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(32) See eq 22 of ref 10.

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