Table IV. Bonding Parameters for CuL$_2{}^{2-}$ Systems

	α	β	δ	α'
Diethyldithiocarbamate[a]	0.73	0.72	0.92	0.69
Cyclopentadienedithiocarboxylate	0.77	0.70	0.72	0.64

[a] Experimental parameters needed for calculations are taken from ref 12.

It is quite obvious that the out-of-plane π bonding is much more covalent in the system investigated than in the copper-diethyldithiocarbamate system. The in-plane π and σ bondings are quite similar. Since this out-of-plane π bond is antibonding in character and is very covalent, the bonding molecular orbital is similar indicating that the dithiolate is a strong π-bonding ligand and is, in fact, a good π-acceptor ligand.[14,15] It should be noted that in Cu^{2+}, the π-bonding and antibonding molecular orbitals have two electrons each so that the transfer of electrons from metal to ligand in the antibonding orbitals is canceled by the reverse transfer in the bonding orbitals. The only effective electron transfer occurs in the B$_{1g}$ orbital where the net transfer is toward the metal cation since the bonding molecular orbital has two electrons and the antibonding molecular orbital only one electron.

This dithiolate also forms 2:1 and 3:1 ligand to metal complexes with a large number of transition and nontransition elements. We observe in a qualitative way that the stability of these complexes decreases with decreasing number of d electrons indicating the importance of the covalent π bonding in stabilizing the metal-sulfur bond.[16,17]

Registry No. $Na_2C_5H_4CS_2 \cdot C_4H_8O$, 36487-17-9; $Na_2C_5H_4CS_2 \cdot CH_3CN$, 36487-18-0; $[(C_2H_5)_4N]_2Zn(C_5H_4CS_2)_2$, 36544-15-7; $[(C_2H_5)_4N]_2Cu(C_5H_4CS_2)_2$, 36544-16-8.

Acknowledgment. We wish to thank Professor Fred Wudl of this department for many very helpful and stimulating suggestions. This work was supported by a grant (2385-G3) from the Petroleum Research Fund, administered by the American Chemical Society.

(14) F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, 3, 1398 (1964).

(15) R. R. Eley, R. R. Meyers, and N. V. Duffy, *Inorg. Chem.*, 11, 1128 (1972).

(16) B. J. Kalbacher and R. D. Bereman, in preparation.

(17) P. Savino and R. D. Bereman, in preparation.

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Calorimetric and Nuclear Magnetic Resonance Studies of Hydrogen Bonding. Quinuclidine with Various Lewis Acids[1a]

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The nmr chemical shift differences ($\Delta\omega°$) between "free" hydrogen-bonding acids and their 1:1 complexes with a Lewis base have been measured with the Lewis base quinuclidine (1-azabicyclo[2.2.2]octane) in nonpolar solvents such as cyclohexane. Enthalpies of adduct formation for this base with a series of Lewis acids enabled us to incorporate quinuclidine into our double-scale enthalpy equation. The E_B and C_B values thus obtained allowed us to predict enthalpies of adduct formation for quinuclidine with a large series of hydrogen bonding acids whose E_A and C_A numbers are known and whose nmr hydrogen bonding chemical shifts were measured. A straight-line correlation between $-\Delta H$, the enthalpy of adduct formation, and $\Delta\omega°$ was obtained for quinuclidine interacting with all the Lewis acids studied, having the form $-\Delta H = (0.95 \pm 0.04)\Delta\omega° + 3.2 \pm 0.2$ kcal/mol. This correlation is considered in light of other reported relationships between $-\Delta H$ and $\Delta\omega°$ which were obtained by keeping the acid constant and varying the base. Failure of quinuclidine to fall on these constant acid lines is discussed. This base also fails to obey constant acid enthalpy-infrared frequency shift correlations. The magnitudes of $\Delta\omega°$ for the protons in the Lewis acids upon hydrogen bonding to quinuclidine are rationalized in terms of an "electric field effect" arising from the lone-pair electrons on the nitrogen atom and the polarizability components of the Lewis acids along the hydrogen bond.

Introduction

The ability of changes in spectroscopic properties to reflect the strength and nature of the coordination of Lewis acids to Lewis bases is of considerable importance to the reliability of many conclusions drawn in inorganic chemistry. In much of the inorganic literature, it is tacitly assumed that a direct relationship exists between the strength of interaction and some spectroscopic change. Very little research has been published to verify, negate, or indicate the limitations of such assumptions. The possibility of obtaining both enthalpy data and the corresponding chemical shifts on hydrogen-bonding systems makes them particularly attractive in this regard.

It has long been known that upon hydrogen bonding of an acid to a donor, the proton magnetic resonance of the acid experiences a significant downfield contribution to the shift relative to the position of the "free" acid.[2] At room temperature, the observed chemical shift, ω_{obsd}, corresponds to the mole fraction weighted average of the complexed and free protons as indicated in

$$\omega_{\text{obsd}} = \frac{[\text{AB}]}{[\text{A}] + [\text{AB}]}\,\omega_{\text{complex}} + \frac{[\text{A}]}{[\text{A}] + [\text{AB}]}\,\omega_{\text{free}} \qquad (1)$$

for A + B $\rightleftarrows$ AB, where A denotes a hydrogen-bonding

(1) (a) Abstracted in part from the Ph.D. thesis of F. L. S., University of Illinois. (b) National Science Foundation predoctoral fellow, 1969-1972.

(2) See, for instance, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution NMR," Pergamon Press, Oxford, 1965.

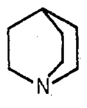
Lewis acid, B a base, and AB the complex. The hydrogen-bonding chemical shift, $\Delta\omega°$, is defined as $\Delta\omega° = \omega_{\mathrm{complex}} - \omega_{\mathrm{free}}$. A method for the simultaneous determination of $\Delta\omega°$ and K, the equilibrium constant, has been described recently,[3] permitting one to solve fast-exchange, averaged chemical shifts for $\omega_{\mathrm{complex}}$, the quantity of interest for theoretical purposes. The effects which give rise to the downfield shift of the hydrogen-bonded proton are not very clearly elucidated. There have been several attempts to attribute these shifts in the proton resonance of the complex to electric field effects which arise from the electron density of the donor.[4-7] Assuming this model, Berkeley and Hanna[8] studied the chemical shift change of the chloroform proton (CCl_3H) upon hydrogen bonding to various nitrogen donors. Using electric fields evaluated from a semiempirical MO calculation, they estimated hydrogen-bond lengths, after making corrections for donor anisotropy effects. The bond lengths were reported to increase regularly as the "basicities" of the donors decreased.

The electric field approach fails because there is difficulty associated with evaluating electric fields and more important because the model does not take into account any covalent interaction between donor and acceptor. The usual assumption made in these treatments is that the hydrogen-bonding chemical shift is affected predominantly by electrostatic interactions, and covalent interactions are ignored. Nmr contact shift experiments[9] have furnished very strong evidence for the presence of covalent contributions in the hydrogen bonding of chloroform to paramagnetic donors. Even more covalency is expected with stronger acids according to parameters determined from a proposed double-scale enthalpy equation

$$-\Delta H = E_{\mathrm{A}}E_{\mathrm{B}} + C_{\mathrm{A}}C_{\mathrm{B}} \qquad (2)$$

In this equation, the subscripts A and B indicate acceptor and donor, respectively, while E and C are two empirically derived parameters assigned to each. The product of E_{A} and E_{B} provides a rough measure of the contribution to the bonding from electrostatic interactions, while C_{A} times C_{B} provides general trends to bonding from covalent interactions in the hydrogen bonding series. A comprehensive listing of these parameters has been recently published.[10]

In view of the shortcomings described above with the electric field approach and because of the uncertainties associated with correcting for donor anisotropy, we chose to attack the general problem of understanding the hydrogen-bonding shift differently from previous investigators. Our object was to select a reference base with minimal neighbor anisotropy contributions and vary the acid X-H. With relatively slight changes in the X-H distance upon complexation, neighbor anisotropy contributions from the acid would approximately cancel when the difference in shift of the complexed and free acid is considered. Ideal requirements for a good base is one that is relatively strong, lacks large neighbor anisotropy contributions, and is soluble in inert solvents such as hexane. One base that we felt would satisfy these requirements is quinuclidine (1-azabicyclo[2.2.2]octane) (I).



I

The system described above also has the potential of providing deeper insight into correlations reported between the enthalpy of adduct formation and some infrared change in an acceptor or donor group. For limited systems, linear correlations have been established between the enthalpy of adduct formation and the change in infrared stretching frequency upon hydrogen bonding for the O–H stretching frequency in various alcohols,[11-15] the N–H stretching frequency of pyrrole,[16] and the C=O stretching frequency of ethyl acetate.[17] A similar linear correlation for the C–D stretching frequency of deuteriochloroform did not exist.[3]

Linear correlations have also been found between the enthalpy of adduct formation and the $J_{^{119}\mathrm{Sn-C-H}}$ coupling constant for trimethyltin chloride,[18] and also with the hydrogen-bonding chemical shift of the O-H proton in phenol,[19] 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP),[13] and 2,2,2-trifluoroethanol[15] after appropriate corrections were made for donor anisotropy effects.[19] Again, chloroform did not conform to an nmr proton chemical shift correlation. However, a roughly linear correlation between the chemical shift and the $J_{^{13}\mathrm{CH}}$ coupling constant of chloroform interacting with a variety of basic solvents has been recently reported.[20] The lack of understanding of and lack of information about the acid-base properties which cause these correlations to exist or fail has undermined many conclusions in inorganic chemistry based on the tacit assumption of correlations between strength of interaction and the change in some spectroscopic property.

Another goal of this research involves incorporation of enthalpies of adduct formation between quinuclidine and various Lewis acids into our double-scale enthalpy equation (eq 2). Strong reference bases which have large C/E ratios and which are convenient to work with are needed to extend the scope of this work. Finally, it is hoped that exceptions to established correlations will provide some insight into the meaning of the E and C parameters.

Experimental Section

Purification of Materials. Baker Analyzed reagent carbon tetrachloride, Baker Analyzed reagent GC-Spectrophotometric quality

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[3] F. L. Slejko, R. S. Drago, and D. G. Brown, submitted for publication.

[4] I. V. Alexandrov and N. D. Sokolov, *Dokl. Akad. Nauk SSSR*, **124**, 115 (1959).

[5] A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960).

[6] A. D. Buckingham and K. P. Lawley, *Mol. Phys.*, **3**, 219 (1960).

[7] J. I. Musher, *Can. J. Chem.*, **37**, 34 (1962).

[8] (a) P. J. Berkeley and M. W. Hanna, *J. Amer. Chem. Soc.*, **86**, 2990 (1964); (b) P. J. Berkeley and M. W. Hanna, *J. Chem. Phys.*, **41**, 2530 (1964).

[9] M. S. Rettig and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 2966 (1966).

[10] R. S. Drago, G. C. Vogel, and T. E. Needham, *J. Amer. Chem. Soc.*, **93**, 6014 (1971).

[11] R. S. Drago and T. D. Epley, *J. Amer. Chem. Soc.*, **91**, 2883 (1969).

[12] T. D. Epley and R. S. Drago, *J. Amer. Chem. Soc.*, **89**, 5770 (1967).

[13] K. F. Purcell, J. A. Stikeleather, and S. D. Brunk, *J. Amer. Chem. Soc.*, **91**, 4019 (1969).

[14] G. C. Vogel, N. O'Bryan, and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 3924 (1970).

[15] A. D. Sherry and K. F. Purcell, *J. Phys. Chem.*, **74**, 3535 (1970).

[16] M. S. Nozari and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 7086 (1970).

[17] D. G. Brown, R. S. Drago, and T. F. Bolles, *J. Amer. Chem. Soc.*, **90**, 5706 (1968).

[18] T. F. Bolles and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 5730 (1966).

[19] D. P. Eyman and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 1617 (1966).

[20] R. L. Lichter and J. D. Roberts, *J. Phys. Chem.*, **74**, 912 (1970).

cyclohexane, and Fisher Spectranalyzed reagent grade H-334 hexane were all dried over Linde 4-A molecular sieves and used without any further purifications.

Quinuclidine was kindly donated to us by Mallinckrodt Chemical Works, St. Louis, Mo., and was purified by resubliming at $\sim$0.5 Torr and 23° at least three times. Due to its hygroscopic nature, all handlings of this material were performed in a N_2-filled drybag.

Phenol (Mallinckrodt reagent grade) was resublimed twice at 0.05 Torr and 23° immediately prior to use. This same procedure was employed for the purification of *p*-fluorophenol (Aldrich Chemical Co.), *p*-chlorophenol (Eastman Chem.), *p-tert*-butylphenol (Eastman Chem.), and *p*-bromo- and *p*-iodophenol (Aldrich Chemical Co.). 1,1,1,3,3,3-Hexafluoro-2-propanol[13] (Pierce Chemical Sequanol grade), 2,2,2-trifluoroethanol[15] (Pierce Chemical), and pyrrole[16] (Aldrich Chemical Co.) were purified as previously described.

Apparatus. 1. Infrared Spectra. Infrared spectra were recorded on a Perkin-Elmer 521 spectrophotometer. The procedure used has been described previously.[14]

2. Nuclear Magnetic Resonance Spectra. The nuclear magnetic resonance spectra were measured with a Varian Associates HA-100 high-resolution nmr spectrometer operating in the field sweep mode. All chemical shifts were measured relative to the cyclohexane lock signal using a frequency counter. The precision of the chemical shifts is ±0.2 Hz or somewhat better.

3. Calorimetry. The description of the modified calorimeter and the procedure for performing the experiments and calculating the results has been reported.[12,16] The calorimeter cells and all other glassware used for the calorimetry experiments were dried and flushed with nitrogen prior to use.

Solutions. A stock solution of quinuclidine ($\sim$0.9 *M*) was made by dissolving the appropriate amount of the material in hexane. Quinuclidine dissolves with difficulty in cyclohexane, so hexane was employed. The stock solutions of the alcohols and pyrrole were made approximately 0.08 *M* in cyclohexane. Some of the phenols dissolve more readily in cyclohexane than in hexane. In some cases, a 0.08 *M* solution could not be made, so a concentration somewhat less than this was used.

The final solutions were made by pipetting appropriate amounts of base and acid solutions into 25-ml volumetric flasks and diluting to the mark with cyclohexane. A similar procedure was employed for the acid dilution studies except that 10-ml volumetric flasks were used. The nmr tubes were filled by transferring the solutions from the volumetric flasks in a drybag. The nmr tubes were capped and wrapped with Parafilm to prevent evaporation, and spectra were run within a few hours after filling. For the calorimetry experiments, solutions of concentrated acid (phenol) in an appropriate solvent or the pure acid (pyrrole) were added to solutions containing different concentrations of quinuclidine in the same solvent.

Procedure. Dilution Studies. In order to obtain the chemical shift of the free -OH proton for the phenols, in an inert solvent, the shift was measured relative to cyclohexane over a concentration range of $\sim$0.070–$\sim$0.010 *M* using six to ten samples. Over this range of concentrations, the chemical shift shifted upfield by approximately 0.30 ppm. Nevertheless, when a plot was made of the chemical shift *vs.* acid concentration, a smooth curve resulted which was extrapolated easily to infinite dilution. A similar dilution study of phenol in an inert solvent has been reported[21] over a wider concentration range, down to $\sim$0.004 *M*. Even at this dilute concentration, a smooth curve could be drawn through the points. This indicated that the infinite dilution shift of the -OH proton could be obtained by extrapolation from a higher concentration. In most cases, the difference in chemical shift between the two most dilute solutions was only about 0.01–0.02 ppm. This indicates that the precision of ω_{free} is ±0.01 ppm or somewhat better.

The resonance of the broad triplet of pyrrole did not change within experimental error over the concentration range of 0.057–0.024 *M* in hexane. This result suggests that pyrrole is not significantly self-associated over this concentration range.

1,1,1,3,3,3-Hexafluoro-2-propanol in cyclohexane was similarly studied over a concentration of approximately 0.05–0.02 *M*. At this concentration, the resonance of the free -OH proton was partially obscured by the strong cyclohexane resonance. 2,2,2-Trifluoroethanol could not be studied in hexane or cyclohexane as the resonance of the -OH proton was obscured by the solvent absorptions. For this, the dilution study was carried out in CCl_4 over a concentration range of 0.060–0.013 *M*. Over this concentration range, the chemical shift of the -OH proton spanned approximately 0.20 ppm. It should be pointed out here that the chemical shift of the 2,2,2-trifluoroethanol–quinuclidine complex is measured in an inert solvent, cyclohexane. Since the resonance of the "free" alcohol is measured in CCl_4, we would expect the difference between the complex and free alcohol, $\Delta\omega^\circ$, to be somewhat smaller than the value for the case where the "free" alcohol is studied in cyclohexane.

Hydrogen-Bonding Chemical Shifts. The hydrogen-bonding chemical shifts for the phenols and the two alcohols were determined by measuring the chemical shift of the -OH proton, relative to cyclohexane, of a solution containing from 0.068 to 0.037 *M* of the alcohol and differing amounts of quinuclidine. In all cases, one concentration of alcohol was used and the concentration of base varied over a range of 0.1–3.0 equiv relative to acid concentration. When the chemical shift of the -OH proton was plotted *vs.* base concentration, a smooth curve resulted which leveled off at approximately a 1:1 ratio of acid to base. Excess amounts of base (up to 3 times the concentration of acid) changed the chemical shift only 0.02 ppm or less. This assured us that all of the acid was complexed and that excess base did not cause a medium effect on the chemical shift. Since pyrrole is a weak acid, base concentrations up to 4 times the pyrrole concentration did not complex all of the pyrrole. This manifested itself in a plot of chemical shift *vs.* base concentration. For this system, the equilibrium constant and the hydrogen-bonding chemical shift were determined simultaneously from the nmr data by a procedure previously described in conjunction with our work on chloroform.[3] For the system pyrrole–quinuclidine in hexane, the equilibrium constant was found to be 18.9 ± 0.9 l./mol at 25° and $\Delta\omega^\circ = 2.83 \pm 0.05$ ppm. This equilibrium constant agrees favorably with that measured by the calorimetric procedure (17.6 ± 0.6 l./mol) at approximately the same temperature. Attempts were made to study similarly other hydrogen-bonding Lewis acids such as thiophenol and *tert*-butyl alcohol. However, in these cases, the resonance of the free proton was obscured by the solvent resonances. Even when substantial amounts of quinuclidine were added, the resonance of the proton was still obscured by the solvent.

Results

Calorimetry. The concentrations and the heat evolved on adding the acid to the base, corrected for the heat of solution of the acids in hexane, H', and calculated thermodynamic parameters are available[22] for the interaction of quinuclidine with phenol and pyrrole. The results are summarized in Table I. An attempt to measure the enthalpy of adduct formation of quinuclidine interacting with *m*-fluorophenol in hexane failed because a gel formed when these materials were mixed.

Several enthalpies of adduct formation for quinuclidine with other Lewis acids are given in the literature. These are also listed in Table I. Since the above acids have been incorporated into our double-scale enthalpy equation,[10] we were able to calculate E_B and C_B parameters for quinuclidine. With $E_B = 0.704$ and $C_B = 13.2$ for quinuclidine, the agreement between experimental and calculated enthalpies was quite favorable (Table I). It should be emphasized that two enthalpies with two different acids, for which E_A and C_A parameters are known, are necessary to establish the E_B and C_B parameters for any base. The remaining enthalpies can serve as a check on the model although in actual practice a best fit of all the data is determined.

Nmr Chemical Shifts. The hydrogen-bonding chemical shifts, $\Delta\omega^\circ$, for a series of Lewis acids with quinuclidine are given in Table I together with the shifts of the free acid and complex measured relative to cyclohexane internal reference. In Table I are also listed the calculated enthalpies of adduct

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[21] (a) T. Gramstad and E. D. Becker, *J. Mol. Struct.*, 5, 253 (1970); (b) M. Nakano, *et al.*, *J. Phys. Chem.*, 71, 3954 (1967).

[22] Calorimetry data will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-176.

Table I. Nmr Chemical Shift and Thermodynamic Data for Quinuclidine–Acid System

Acid	ω_{free},[a] ppm	ω_{AB},[a] ppm	$\Delta\omega°$,[c] ppm	ΔH, kcal/mol		E_A[g]	C_A[g]
				Exptl	Calcd[d]		
C_6H_5OH	2.63	8.73	6.10	9.03 ± 0.08	8.9	4.33	0.442
p-FC_6H_4OH	2.52	8.85	6.35		8.8	4.17	0.446
p-ClC_6H_4OH	2.61	9.26	6.65		9.4	4.34	0.478
p-BrC_6H_4OH	2.67	9.19	6.52		9.4	4.34[j]	0.478[j]
p-IC_6H_4OH	2.64	9.08	6.44		9.0	4.4[j]	0.45[j]
p-t-BuC_6H_4OH	2.68	8.01	5.33		8.0	4.06	0.387
$CHCl_3$[e]	5.64	6.79	1.15 ± 0.12 (0.08)[l]	4.1 ± 0.1	4.1	3.02	0.159
Pyrrole	5.94	8.77	2.83 ± 0.05 (0.01)[l]	5.55 ± 0.18	5.7	2.54	0.295
CF_3CH_2OH[b]	0.27	6.17	5.90 ± 0.05		8.6	4.00	0.434
HFIP	0.811	8.78	7.97 ± 0.05	11.36 ± 0.07[k]		5.56	0.509
$CF_3(CF_2)_5CF_2H$[f]	4.397	5.70	1.30 ± 0.11 (0.01)[l]	4.4 ± 0.2	4.4	2.51	0.200
I_2				13.9[h]	13.9	1.00	1.00
$B(CH_3)_3$				19.94[i]	26.8	6.14	1.70

[a] Referenced to cyclohexane internal reference; precision is ±0.01 ppm. [b] "Free" -OH chemical shift measured in CCl_4. [c] Unless otherwise noted, precision is ±0.03 ppm or somewhat better. [d] Calculated using eq 2 and $E_B = 0.704$ and $C_B = 13.2$ for quinuclidine. The precision expected in these heats is ±0.2 kcal/mol. [e] See reference 3. [f] F. L. Slejko and R. S. Drago, to be submitted for publication. [g] See ref 10. [h] A. M. Halpern and K. Weiss, *J. Amer. Chem. Soc.*, **90**, 6297 (1968). Spectrophotometric enthalpy measured in *n*-heptane. [i] H. C. Brown, *J. Chem. Soc.*, 1248 (1956). [j] Tentative *E* and *C* parameters based on enthalpies of adduct formation for these phenols with various Lewis bases predicted from correlations with Hammett substituent constants. See R. S. Drago and T. D. Epley, *J. Amer. Chem. Soc.*, 91, 2883 (1969). [k] R. M. Guidry and R. S. Drago, to be submitted for publication. [l] Whenever $\Delta\omega°$ and *K* are solved simultaneously, the errors given are the marginal standard deviation. The values in parentheses are the conditional standard deviations. The ratio of the marginal to the conditional is a measure of the "goodness of the fit." For a thorough discussion on the procedure utilized for obtaining these errors, see ref 3.

formation, utilizing eq 2, for quinuclidine with these hydrogen-bonding acids together with their respective E_A and C_A parameters. The concentrations and observed chemical shifts for the system quinuclidine–pyrrole for which $\Delta\omega°$ and K were solved simultaneously appear in the microfilm edition of this journal.[22]

Infrared Frequency Shifts. The frequency shifts for the N-H stretching frequency of pyrrole and the O-H stretching frequency of *tert*-butyl alcohol are 251 and 240 cm^{-1}, respectively. These shifts are defined as the difference in the stretching frequency between the free and the complexed acid. These were measured in hexane and extrapolated to infinitely dilute solution in accord with previous work from our laboratory.[16] The error limit for these values is ±3 cm^{-1}.

Discussion

E_B and C_B Parameters for Quinuclidine. A close examination of the enthalpies of adduct formation given in Table I will show a remarkable agreement between the experimental values and those predicted by eq 2. The boron trimethyl–quinuclidine adduct apparently does not fit this correlation. It has been shown that the $(CH_3)_3B \cdot N(CH_3)_3$ complex has sufficient F strain to cause a discrepancy between the experimental and calculated heats of 6.9 kcal/mol.[23] This agrees well with the magnitude of this strain energy, predicted to be 7.8 kcal/mol, by Brown[24] from heat of combustion data on a hydrocarbon which is structurally analogous to this adduct.[23,24] With quinuclidine, we also observe a discrepancy between calculated and experimental heats of 6.9 kcal/mol.

With C_B and E_B parameters of 13.2 and 0.704, respectively, the ratio of C_B to E_B for quinuclidine is 18.73, making it much larger than that for triethylamine ($C_B/E_B = 11.19$) but not as large as for the sulfur donors such as diethyl sulfide ($C_B/E_B = 21.84$).[10] However, the magnitude of both the C_B and E_B parameters is larger for quinuclidine than for the sulfur donors. In defining the E_A and C_A numbers for a new acid, bases with a wide range of C_B/E_B ratios must be employed so quinuclidine will be a useful reference base in this regard. Experimentally, this base is ideal in that it is very easily purified, does not have an offensive odor, and is readily soluble in inert solvents such as hexane.

Enthalpy–Spectral Correlations. Although much effort has been made to obtain correlations between infrared -OH stretching frequency changes upon hydrogen bonding and the enthalpy of adduct formation, only a few attempts have been made to correlate the hydrogen-bonding chemical shift, $\Delta\omega°$, with the enthalpy of adduct formation. Eyman and Drago[19] correlated these quantities for phenol with various Lewis bases. Similar relationships have been found for 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)[13] and 2,2,2-trifluoroethanol.[15] One drawback which exists in these constant acid lines is that each donor may contribute different amounts to the chemical shift of the complex, ω_{AB}, from neighbor anisotropy effects. Corrections for the magnetic anisotropy of pyridine and the carbonyl group have been made[19] utilizing eq 3. Applying this equation to

$$\Delta\omega°_{anis} = \frac{(-\Delta\chi_2 + \Delta\chi_1)(1 - 3\cos^2\theta)}{3L_0R^3} \qquad (3)$$

the carbonyl group, R is the radius vector between the hydrogen-bonded proton and the point magnetic dipole of the C=O bond, θ is the acute angle between the C=O bond axis and R, and L_0 is Avogadro's number. The values of R and θ were chosen to be 1.7 Å and 60°, respectively, yielding a downfield contribution of 1.1 ppm. Similarly, a contribution of 1.0 ppm was calculated for pyridine.

These corrections are assumed[13,15] to be transferrable from one system to another as long as the hydrogen-bond length remains approximately the same (*i.e.*, 1,1,1,3,3,3-hexafluoro-2-propanol and 2,2,2-trifluoroethanol). Apparently, this assumption cannot be extended to the system base-$CHCl_3$ as this correction in some cases is larger than the observed hydrogen-bonding chemical shift.[3] For phenol hydrogen bonded to pyridine, the contribution to the deshielding of the proton from the anisotropy of the pyridine ring, evaluated at the center, is 1.0 ppm,[19] for an N- - -H bond distance of 1.8 Å. Contributions to the hydrogen-bond energy as a function of hydrogen-bonding distances have been calculated and were used to estimate distance changes for varying strength of interaction.[25] The values, though rough, do serve as a guide for estimating the deshielding of the proton

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(23) R. S. Drago and B. B. Wayland, *J. Amer. Chem. Soc.*, **87**, 3571 (1965).

(24) H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

from the neighbor anisotropy as a function of $-\Delta H$ as would occur when the acid is varied with an anisotropic donor. A stronger interaction, say 14 kcal/mol, may correspond to an N-H distance of approximately 1.6 Å, in which case the contribution from the pyridine anisotropy would be 1.2 ppm. For a relatively large N-H bond length of 2.4 Å, corresponding to an interaction of 1.7 kcal/mol, the donor anisotropy at the proton is expected to contribute 0.60 ppm. In view of the uncertainty in donor-proton distances in most adducts and in view of the demonstrated significant shielding contribution, linear plots are not expected when the acid is varied toward donors with anisotropic groups.

A similar calculation to that described above may be made for the contribution to the deshielding of a proton due to the anisotropy of the C-N bonds in quinuclidine. Taking the anisotropy of the C-N bond to be roughly that of a C-C bond, evaluated at the midpoint of the C-N bond, and using reasonable values for bond lengths and angles in quinuclidine, we find a contribution of 0.10 ppm for an N-H distance of 2.4 Å and 0.30 ppm for an N-H distance of 1.6 Å. In light of the relatively large values for $\Delta\omega^\circ$ obtained in this work (see Table I), we can safely say that this contribution from the neighbor anisotropy of quinuclidine would result in only a few per cent error in $\Delta\omega^\circ$. Moreover, these anisotropy corrections are to be taken as upper limits. As the N-H bond becomes shorter, the X-H bond of the acid becomes longer. The neighbor anisotropy contribution to the deshielding from the X group would decrease, thus to some extent counterbalancing the deshielding from the anisotropy of quinuclidine.

Although these calculations are only crude estimates, the upper limits of the contribution to $\Delta\omega^\circ$ from the neighbor anisotropy of the C-N bonds in quinuclidine is expected to be negligible in the systems we studied. A plot of $-\Delta H$ *vs.* $\Delta\omega^\circ$ is shown in Figure 1. A straight line results having the form

$$-\Delta H = (0.95 \pm 0.04)\Delta\omega^\circ + 3.2 \pm 0.2 \text{ kcal/mol}$$

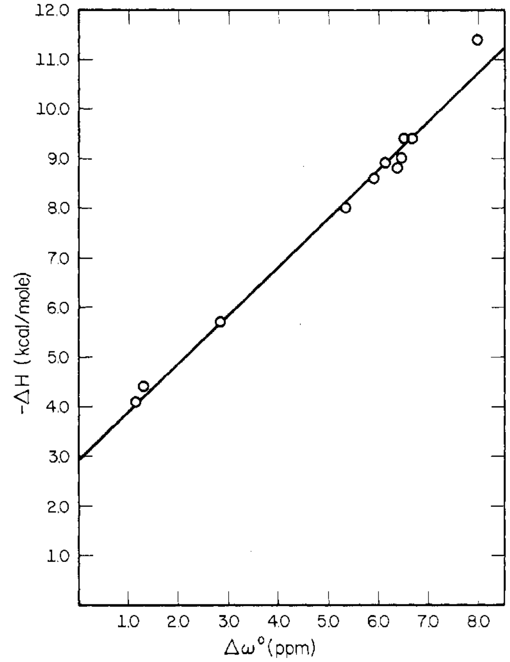

Figure 1. Plot of $-\Delta H$ *vs.* $\Delta\omega^\circ$ for the system quinuclidine-acid.

Table II. Comparison of Enthalpies for Quinuclidine Adduct Formation Based on Spectroscopic Correlation and the *E* and *C* Equation

Acid	$-\Delta H$,[a] kcal/mol Predicted	$-\Delta H$,[a] kcal/mol Calcd (eq 2)
Phenol	7.3[b]	8.9
CF_3CH_2OH	7.6[c]	8.6
HFIP	9.9[d]	11.36[g]
Pyrrole	4.8[e]	5.7
tert-Butyl alcohol	4.2[f]	5.4

[a] Precision in these heats is ±0.2 kcal/mol. [b] Obtained from $-\Delta H$ *vs.* ω_{AB} correlation; see ref 19. [c] Obtained from $-\Delta H$ *vs.* $\Delta\omega^\circ$ correlation; see ref 15. [d] Obtained from $-\Delta H$ *vs.* $\Delta\omega^\circ$ correlation; see ref 13. [e] Obtained from $-\Delta H$ *vs.* $\Delta\nu_{NH}$ correlation; see ref 16. [f] Obtained from $-\Delta H$ *vs.* $\Delta\nu_{OH}$ correlation; see ref 14. [g] Measured calorimetrically: R. M. Guidry and R. S. Drago, to be submitted for publication.

Since we are correlating $\Delta\omega^\circ = \omega_{AB} - \omega_{free}$ with the enthalpy, it is crucial that ω_{free} for each acid be determined in an inert solvent such as hexane or cyclohexane. For the constant acid nmr lines reported in the literature, the shift of the free acid, ω_{free}, is a constant and its value need not be accurately known. In this study, all of the free acids used have different chemical shifts so a great deal of effort was made to obtain accurate values of ω_{free} in an inert solvent such as cyclohexane. The fact that the resonance frequency of "free" phenol is different in cyclohexane than in CCl_4 or CH_2Cl_2 suggests that phenol interacts to some degree with these halogenated hydrocarbons. This idea has been supported in a recent publication by Gramstad and Becker,[21a] who showed that the chemical shift of the -OH proton in phenol, extrapolated to infinite dilution, appears 0.20 ppm downfield in CCl_4 relative to the value obtained in cyclohexane. Unfortunately, ω_{free} for 2,2,2-trifluoroethanol could not be measured in cyclohexane. The value reported in Table I was measured in CCl_4. However, the chemical shift of the complex was calculated from the equilibrium in cyclohexane. In general, ω_{free} for an alcohol is at lower field in CCl_4 than in hexane.[21] One would then expect that if this is operative with 2,2,2-trifluoroethanol, $\Delta\omega^\circ$ should be ~0.20 ppm larger than the 5.90 ppm reported in Table I.

It is intriguing that quinuclidine falls of established constant acid lines ($-\Delta H$ *vs.* $\Delta\omega^\circ$ and $-\Delta H$ *vs.* $\Delta\nu$) by a considerable amount. Table II gives the values of $-\Delta H$ which would be calculated by assuming that quinuclidine obeys these correlations. In calculating the enthalpies given in Table II from reported spectroscopic correlations, the data were corrected to the conditions used to establish the correlation. For example, our cyclohexane data were converted to chemical shifts based on ω_{free} measured in CH_2Cl_2 or CCl_4 by applying the appropriate correction. In all cases, the difference between predicted and experimental enthalpies is substantial, 0.9-1.6 kcal/mol. This apparent anomaly for quinuclidine is not surprising in view of the fact that sulfur donors also fail to obey these correlations.[26] It has been suggested[14] that the large C_B/E_B ratio of the sulfur donors is responsible for their anomalous behavior. In view of the high C_B/E_B ratio found for quinuclidine (*vide supra*), this anomaly might be expected. However, this does not explain the fact that this deviation for quinuclidine is in the opposite direction of that for the sulfur donors. The lack

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(25) F. B. Van Duijnevelt and J. N. Murrell, *J. Chem. Phys.*, **46**, 1759 (1967).

(26) G. C. Vogel and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 5347 (1970).

of a readily available explanation for these discrepancies emphasizes the need of a more theoretical basis for these spectroscopic correlations so their limitations can be more readily anticipated. Nevertheless, the sulfur donors and quinuclidine share one property in common. Although both fall off established constant acid correlations, they do give rise to constant base lines[26] as evidenced in Figure 1 for quinuclidine.

It has been shown that when $\Delta\nu$(phenol) is plotted *vs.* $\Delta\nu_{OH}$ for a different hydrogen-bonding acid with a given series of Lewis bases, a straight-line correlation results. This is even true for the sulfur donors which do not obey the constant acid $-\Delta H$ *vs.* $\Delta\nu$ correlations.[14,26] Quinuclidine is also normal in this respect and falls on the plot of $\Delta\nu$(*tert*-butyl alcohol) *vs.* $\Delta\nu$(pyrrole). With stronger hydroxyl acids, the shift is so large that overlap with C-H vibrations renders its measurement impossible.

A similar straight-line correlation exists when $\Delta\omega°$ for one acid is plotted *vs.* $\Delta\omega°$ for another, except, of course, for chloroform.[3] When one plots $\Delta\omega°(CF_3CH_2OH)$[15] *vs.* $\Delta\omega°$-(HFIP),[13] a straight line with zero intercept results, and the quinuclidine data fall on it. Here, our values for $\Delta\omega°$ were corrected such that the "free" OH resonance frequency is that corresponding to the one in the solvent used to establish the correlations.[13,15] Surprisingly, quinuclidine misses the similar lines for $\Delta\omega°$(phenol) *vs.* $\Delta\omega°$(HFIP) by 0.8 ppm and the $\Delta\omega°$(phenol) *vs.* $\Delta\omega°(CF_3CH_2OH)$ correlation by 0.5 ppm. All other donors, except triethylamine, fell on these lines. Some of these discrepancies may result from the fact that these correlations utilize literature values of $\Delta\omega°$ obtained in different solvents.

Origin of the Hydrogen-Bonding Chemical Shift. The total chemical shift of a hydrogen-bonded system is believed to be due to the effects[27]

$$\omega_{AB} = \omega_g + \omega_b + \omega_w + \omega_a + \omega_e + \omega_c$$

where ω_g is the gas-phase chemical shift of the free acid, ω_b is the contribution due to the bulk susceptibility of the solvent, ω_w is due to dispersion (or van der Waals) forces which distort the electronic environment about the proton, ω_a is the contribution from solvent anisotropic susceptibilities, ω_e is due to reaction field effects, and ω_c is the contribution due to specific interactions.

By using an internal reference, working in cyclohexane or hexane solvent, and comparing the difference in free and complexed acid, the above equation reduces to

$$\omega_{AB} = \omega_g + \omega_e + \omega_c$$

or

$$\Delta\omega_{AB} = \omega_{AB} - \omega_g = \omega_e + \omega_c$$

Buckingham[28] showed that in the presence of a uniform electric field $\vec{E}_z$ an atom in an S state is distorted such as to affect the diamagnetic and paramagnetic shielding of the nucleus. Due to symmetry requirements, the shielding for a proton in an X-H bond will be proportional to the first power of the component of the field along the bond and the second power of the field perpendicular to it (see eq 4).

$$\Delta\omega = K_E \times 10^{-12}\vec{E}_z - K_E' \times 10^{-18}\vec{E}^2 \qquad (4)$$

Values of K_E from -3.4 to -2.6 have been used in the literature.[8a] This term is negative since an electric field along X-H would repel the bonding electrons toward X. K_E' was given a value of 0.738 by Musher.

A polar molecule, when dissolved, polarizes the medium, and this polarization results in a "reaction field" at the solute. For the Onsager[29] model, in which the solute is represented by a sphere of radius r containing a point dipole of moment μ at its center and the solvent by a continuum of dielectric constant ϵ, the reaction field R is

$$R = \frac{2(\epsilon - 1)(M^2 - 1)\mu}{3(2\epsilon + M^2)\alpha}$$

where $\alpha = [(M^2 - 1)/(M^2 + 2)]r^3$ is the polarizability of the sphere and M is the refractive index of the pure solute. There are several reasons why this is not really a good approximation.[30] Diehl and Freeman have treated the reaction field effect for elliptical cavities.[31] This approach was used by Abraham[32] to explain solvent shifts of methyl iodide in several non-hydrogen-bonding solvents. In all cases, the reaction field was less than 0.10 ppm. Furthermore, cyclohexane and hexane had the smallest solvent effects on the proton chemical shift. Since our studies were all carried out in either cyclohexane or hexane, we feel that we can safely neglect any reaction field effects on the $\Delta\omega°$ values given in Table I. To confirm these conclusions, we measured the resonance of the OH proton in the series of hydrogen-bonded phenols both relative to an internal reference (cyclohexane) and with the "double internal reference" technique which uses the midpoint of the aromatic proton absorption as the reference. It is believed that any reaction field effects should influence all protons in the phenol molecule, so double internal referencing to a noninteracting hydrogen should cancel out the reaction field contributions. We observed no difference within experimental error in our value of $\Delta\omega°$ when the two referencing techniques were used, suggesting either that the reaction field effect is the same for the free and complexed phenols or that this effect is negligible. The electric field effect which makes a contribution to ω_c differs from the "reaction field effect" in that the origin of the electric field is not the polarized solvent medium surrounding a polar solute but the presence of a Lewis base in the proximity of the proton, such as in the hydrogen bond. Since it is our feeling that quinuclidine contributes a nearly constant and small amount to the chemical shift of the proton due to neighbor anisotropy, most of the magnitudes of the $\Delta\omega°$ values given in Table I must be explained in terms of the electric field effect.

Several attempts have been made to explain the chemical shift for various hydrogen-bonding Lewis acids with the aid of eq 4.[7,33-36]

The coefficient for the term linear in the field, K_E, of eq 4 is believed to be related to the bond polarizability, while the coefficient for the term quadratic in the field, K_E', is usually taken[8a,34] to be constant and to have the hydrogen atom value, 0.738 esu^{-2}. This corresponds to all of the proton deshielding contributions from the bond polarizability being assigned to the term linear in base electric

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(27) J. Ronayne and D. H. Williams, *Annu. Rev. NMR Spectrosc.*, 2, 83 (1969).

(28) A. D. Buckingham, *Can. J. Chem.*, 38, 300 (1960).

(29) L. Onsager, *J. Amer. Chem. Soc.*, 58, 1486 (1936).

(30) P. Lazlo and J. I. Musher, *J. Chem. Phys.*, 41, 3906 (1964).

(31) P. Diehl and R. Freeman, *Mol. Phys.*, 4, 39 (1961).

(32) R. J. Abraham, *Mol. Phys.*, 4, 369 (1961).

(33) T. Yonemoto, *Can. J. Chem.*, 44, 223 (1966).

(34) (a) R. D. Green and J. S. Martin, *J. Amer. Chem. Soc.*, 90, 3659 (1968); (b) R. D. Green, J. S. Martin, W. B. McG. Cassie, and J. B. Hyne, *Can. J. Chem.*, 47, 1639 (1969).

(35) I. Granacher, *Helv. Phys. Acta*, 34, 272 (1961).

(36) J. I. Musher, *J. Chem. Phys.*, 35, 1989 (1961).

field $\vec{E}$. The contribution to the deshielding from the permanent dipole moment of the X-H bond interacting with the base electric field is assigned a quadratic dependence in $\vec{E}$. In studies[34] of chloroform and various alcohols complexed to halide ions, the constant K_E for the -O-H and -C-H bonds in these complexes was evaluated. The ratio of the bond polarizabilities for the OH and CH bonds is approximately 1.8, the OH bond being more polarizable.

The studies have a direct bearing on our interpretation of the $\Delta\omega^\circ$ values in Table I. The electric field can be assumed to originate from the lone-pair electrons of the donor, *e.g.*, quinuclidine. Since the hydrogen-bond length does not change drastically for many O-H acids, one would expect that with a given donor approximately the same value for the electric field could be used in eq 4.

Including anisotropy terms, we have

$$\Delta\omega^\circ = K\alpha_{\mathrm{XH}}\vec{E} + \Delta\omega_{\mathrm{a}} + 0.738 \times 10^{-12}\vec{E}^2$$

where α_{XH} is the polarizability of the Lewis acid along the X-H bond and K is some proportionality constant. $\Delta\omega_{\mathrm{a}}$ is the donor anisotropy contribution which may be positive or negative. The constant K is chosen such that a positive $\Delta\omega^\circ$ indicates a downfield shift in the resonance of the hydrogen-bonded proton.

For a constant base experiment, such as in our own work, $\Delta\omega^\circ$ should be linearly related to the polarizability of the Lewis acid along the X-H bond

$$\Delta\omega^\circ = a\alpha_{\mathrm{XH}} + b \qquad (5)$$

where a and b are some constants. Unfortunately, the polarizabilities for the Lewis acids reported in Table I are not available. However, our initial work on the E and C correlation (eq 2) indicates that the C_{A} parameters give an indication of the susceptibility of an acid to undergo covalent interaction so that an acid with a high C_{A} value should be more polarizable than one with a low C_{A} value. It should be emphasized that at this point a quantitative correlation between $\Delta\omega^\circ$ and C_{A} cannot be taken too literally, since we have no direct supporting evidence to allow us to identify α_{XH} directly with the C_{A} parameter. We are presently involved in studies from which we hope to gather physical meaning about the factors contributing to the C and E parameters. Nevertheless, a qualitative correlation between $\Delta\omega^\circ$ and C_{A} is shown in Table I. It is gratifying to note that the ratio of the C_{A} number for chloroform ($C_{\mathrm{A}} = 0.150$) to that for an alcohol, say, *tert*-butyl alcohol ($C_{\mathrm{A}} = 0.300$),[10] is close to the ratio for the polarizabilities of the C-H and O-H bonds as predicted by Green and coworkers.[34]

It might also be pointed out here that the above treatment would also hold if we were to assume that the coefficient for the term quadratic in the electric field of eq 4 depends on the bond polarizability and that the coefficient for the term linear in the field (giving rise to the approximately constant term of eq 5) is related to the permanent atomic dipole at the proton.[33] The net deshielding then becomes related to the total X-H dipole moment made up of the permanent ($\vec{u}_{\mathrm{p}}$) and induced ($\vec{u}_{\mathrm{I}} = \alpha_{\mathrm{XH}}\vec{E}$) dipole moments. Then interaction of the total dipole moment with the electric field gives

$$\Delta\omega^\circ = (a'\alpha_{\mathrm{XH}}\vec{E} + b'\vec{u}_{\mathrm{p}})\vec{E}_{\mathrm{B}}$$

where a' and b' are proportionality constants. We feel that this is a more reasonable interpretation of Yonemoto's results.[33] Furthermore, by assuming that the base electric field remains constant and that for a series of closely related hydrogen-bonding Lewis acids the permanent atomic dipole at the proton does not differ significantly, we still obtain an expression relating $\Delta\omega^\circ$ to α_{XH} having the form of eq 5.

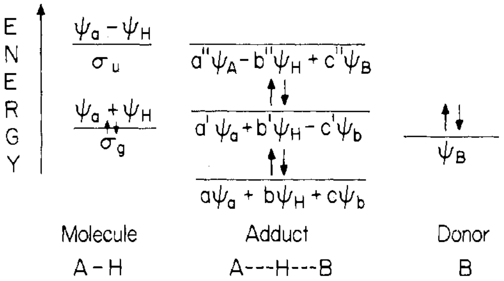

Figure 2. Molecular orbital representation of the hydrogen bond B- - -H- - -A (for a strong interaction).

Table III.

Substituent	δ_{p}	$\Delta\omega^\circ$, ppm	Substituent	δ_{p}	$\Delta\omega^\circ$, ppm
p-t-Bu	−0.20	5.33	I	0.18	6.44
H	0.00	6.10	Br	0.23	6.52
F	0.06	6.35	Cl	0.23	6.65

Correlation with Hammett Substituent Constants. We have seen above that the hydrogen-bonding chemical shift for a series of Lewis acids with quinuclidine could be interpreted in terms of the polarizability along the X-H bond of the Lewis acid. A similar conclusion can be reached by a molecular orbital description for the system A-H - - - - B illustrated in Figure 2. A symmetrical (B - - -H- - -B) three-centered bond is the limit approached for strong interaction in which the base strength of A is equal to the base strength of B. Here, all three atoms make appreciable contribution to the molecular orbitals and the two bonding electrons are delocalized over three atoms while the two nonbonding electrons reside on the B's. This results in a lower fraction of electron density residing on the proton than in the free acid which corresponds to a decrease in chemical shielding. For weak interactions, where the basicity of A (*e.g.*, $C_6H_5O^-$) is much greater than B, one pair of electrons will occupy an orbital which corresponds with essentially an A-X bond.

For para-substituted phenols, the basicity of the phenoxide anion is reduced by an electron-withdrawing substituent X. The overall description of the hydrogen bond, for a given base that is weaker than phenoxide, will approach the three-center bond description and will result in a greater reduction of charge around the proton with a corresponding increase in $\Delta\omega^\circ$. A measure of the ability of the group X to decrease the basicity of the phenoxide anion is reflected by the published Hammett substituent constants obtained from the ionization of benzoic acids.[37] Indeed a trend is observed (Table III) between the magnitude of the substituent constant and $\Delta\omega^\circ$ (or ω_{AB}) for the quinuclidine adducts. A similar correlation of ω_{AB} has been reported for DMSO interacting with a series of substituted phenols.[38]

Registry No. C_6H_5OH, 108-95-2; *p*-FC_6H_4OH, 371-41-5; *p*-ClC_6H_4OH, 106-48-9; *p*-BrC_6H_4OH, 106-41-2; *p*-IC_6H_4OH, 540-38-5; *p-t*-BuC_6H_4OH, 98-54-4; $CHCl_3$, 67-66-3; CF_3CH_2OH, 75-89-8; HFIP, 920-66-1; $CF_3(CF_2)_5CF_2H$, 375-83-7;

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(37) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 80, 4979 (1958).

(38) R. Ouellette, *Can. J. Chem.*, 43, 707 (1965).

C_6H_5OH-quinuclidine, 36578-79-7; *p*-FC_6H_4OH-quinuclidine, 36578-80-0; *p*-ClC_6H_4OH-quinuclidine, 36578-81-1; *p*-BrC_6H_4OH-quinuclidine, 36578-84-4; *p*-IC_6H_4OH-quinuclidine, 36578-83-3; *p*-*t*-BuC_6H_4OH-quinuclidine, 36578-78-6; $CHCl_3$-quinuclidine, 36578-76-4; CF_3CH_2OH-quinuclidine, 36578-82-2; HFIP-quinuclidine, 36578-85-5; $CF_3(CF_2)_5CF_2H$-quinuclidine, 36578-86-6; I_2-quinuclidine, 23290-15-5; $B(CH_3)_3$-quinuclidine, 36578-88-8; quinuclidine, 100-76-5; pyrrole, 109-97-7; pyrrole-quinuclidine, 36578-77-5.

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The Nature of Trimethylamine-Dimethylalane

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The nature of trimethylamine-dimethylalane ($H(CH_3)_2Al{\cdot}N(CH_3)_3$) has been examined in detail in order to resolve a recent controversy. All of our data are consistent with the hypothesis that trimethylamine-dimethylalane is a discrete compound which exists as an equilibrium mixture of monomeric and more associated species. Tensimetric titrations between pure dimethylalane and $N(CH_3)_3$ establish the formation of only a 1:1 adduct. The reaction between $H(CH_3)_2Al{\cdot}N(CH_3)_3$ and $N(CH_3)_2H$ provides even more conclusive evidence that $H(CH_3)_2Al{\cdot}N(CH_3)_3$ is a discrete compound. The only aluminum-containing product from this reaction is $[(CH_3)_2Al{\cdot}N(CH_3)_2]_2$. Solution- and gas-phase molecular weight studies demonstrate that an equilibrium exists between monomeric and more associated species. Furthermore, the ^1H nmr data are also consistent with the existence of an equilibrium between monomeric and associated species.

The nature of trimethylamine-dimethylalane, $H(CH_3)_2Al{\cdot}N(CH_3)_3$, has been the subject of recent controversy. Originally the compound[1] was believed to exist as a mixture of monomeric and dimeric species. More recently, the nmr spectrum of a benzene or cyclohexane solution of the material,[2] considered to be $H(CH_3)_2Al{\cdot}N(CH_3)_3$, has been interpreted in terms of a disproportionation equilibrium involving $H_3Al{\cdot}N(CH_3)_3$, $H_2(CH_3)Al{\cdot}N(CH_3)_3$, and $(CH_3)_3Al{\cdot}N(CH_3)_3$ as products. If $H(CH_3)_2Al{\cdot}N(CH_3)_3$ does indeed readily disproportionate in solution, then much of the synthetic chemistry involving organoaluminum hydrides would have to be reconsidered and evaluated. Therefore, we felt that this controversy had to be resolved.

In order to understand the nature of $H(CH_3)_2Al{\cdot}N(CH_3)_3$ we have examined its chemical, physical, and spectral properties. The compound was prepared directly from dimethylalane and trimethylamine. The previous workers[1,2] synthesized their samples of $H(CH_3)_2Al{\cdot}N(CH_3)_3$ by an exchange reaction involving $(CH_3)_3Al{\cdot}N(CH_3)_3$ and $H_3Al{\cdot}N(CH_3)_3$. This type of preparative reaction introduces ambiguities, which must be eliminated.

Experimental Section

Materials. All compounds described in this investigation were manipulated in a vacuum line or a purified nitrogen atmosphere. All solvents were dried by conventional procedures. The dimethylalane was prepared from $LiAlH_4$ and $B(CH_3)_3$ in a sealed tube according to a previously published procedure.[3] The yields of dimethylalane, based on the $LiAlH_4$, were usually 70%. The physical properties of the dimethylalane were identical in every respect with those previously reported.[3] (Vapor pressure: 1.75 mm at 24.0°; lit.[3] 1.8 mm at 24.7°.) The trimethylboron was prepared by the reaction of methylmagnesium iodide with $BF_3{\cdot}O(C_4H_9)_2$ in *n*-butyl ether according to a previously published procedure.[4] The trimethylamine was dried with P_4O_{10} and distilled.

It should be noted that dimethylalane is an extremely viscous liquid which is difficult to transfer quantitatively on a vacuum line. Thus, all quantitative transfers were accomplished by pumping the material into the appropriate vessel cooled to −196°.

Tensimetric Titrations between Dimethylalane and Trimethylamine. The nature and stoichiometry of the reaction between dimethylalane and $N(CH_3)_3$ were established by titrating samples of dimethylalane with $N(CH_3)_3$ tensimetrically. The titrations, which were conducted according to standard procedures,[5] were either run neat or run as *n*-heptane solutions at 25, −23, and −46°. In all titrations 1.00 ± 0.02 mol of $N(CH_3)_3$ reacted per mole of $(CH_3)_2AlH$. All subsequent preparations of $H(CH_3)_2Al{\cdot}N(CH_3)_3$ were accomplished by allowing the two reagents to react at −78° in a 1:1 mole ratio and then allowing the product to warm slowly to room temperature.

Physical Properties of $H(CH_3)_2Al{\cdot}N(CH_3)_3$. The compound $H(CH_3)_2Al{\cdot}N(CH_3)_3$ has a melting point of 17-25°. At room temperature one frequently observes the material to be a mixture of a liquid and solid. Above the melting point the material is a mobile liquid. The compound has a reproducible vapor pressure of 5.0 mm at 0° and is thermally stable at temperatures up to 100°. Thermal stability was monitored for the pure compound as well as a refluxing heptane solution, bp 98°. The vapor pressure of the compound as a function of temperature is given in Figure 1.

Analysis of $H(CH_3)_2Al{\cdot}N(CH_3)_3$. A sample of $H(CH_3)_2Al{\cdot}N(CH_3)_3$ of sufficient size for analysis was prepared from dimethylalane and $N(CH_3)_3$. The entire sample was then divided into two parts by a vacuum distillation. Each part was then analyzed separately. Nitrogen was determined by the standard Kjeldahl method, whereas aluminum was measured by an EDTA titration.[6] *Anal.* Calcd. for $H(CH_3)_2Al{\cdot}N(CH_3)_3$: N, 12.0; Al, 23.1. Found (first fraction removed): N, 12.0; Al, 22.7. Found (second fraction): N, 12.0; Al, 23.1.

Molecular Weight Studies. The molecular weight of $H(CH_3)_2Al{\cdot}N(CH_3)_3$ was measured in cyclopentane solution by vapor pressure depression and in the gas phase by vapor density. The results are given in Table I.

The molecular weight studies of the solution and gas phases require comment. The molecular weight studies of the solution were designed to provide data which would be directly comparable with the nmr data. Therefore, the measurements in cyclopentane at room temperature required vapor pressure depression as the mole-

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(1) F. M. Peters, B. Bartocha, and A. J. Bilbo, *Can. J. Chem.*, 41, 1051 (1962).

(2) A. Storr and V. G. Wiebe, *Can. J. Chem.*, 47, 673 (1969).

(3) T. Wartik and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 75, 835 (1953).

(4) H. C. Brown, *J. Amer. Chem. Soc.*, 67, 374 (1945).

(5) D. F. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969, p 61.

(6) G. E. Coates and J. Graham, *J. Chem. Soc.*, 233 (1963).