Nuclear Magnetic Resonance Solvent Effects and Molecular Interactions. II. A Comparison of Dipolar, Hydrogen-Bonding, and Charge-Transfer Effects[1]

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Abstract: Concentration-dependent nmr shifts for hydrogen-bonding, charge-transfer, and dipolar solutes in the methylbenzenes and a few nonaromatic solvents have been analyzed using a simple collision complex model. K's, Δ's, and, in some instances, ΔH's are reported. All the interactions studied are properly classified as weak (ΔH's from 0.0 to -4.0 kcal/mol; K's from 0.03 to 4.0 l./mol; and rotational lifetimes of order 10^{-11} sec). Despite such similarities, information concerning the relative arrangement of solute and solvent for each type of interaction was obtained. Criteria are suggested to distinguish the various modes of interaction. A simple electrostatic model is suggested for the interactions of dipolar solutes with dipolar and/or polarizable solvents. The solvent effects for such solutes can be explained by electric field and magnetic anisotropy terms. Hydrogen-bonding protons show much larger solvent shifts than predicted from the electrostatic model. Various explanations are considered for anomalies in solvent shifts for charge-transfer complexes. A change of average complex geometry as the interaction strength changes is the suggested explanation.

Many intermolecular complexes in solution are a result of anisotropic forces, such as hydrogen bonding or charge transfer. In addition, interactions of polar solutes with polar and/or polarizable solvents have been proposed.[1a] Nmr methods are known to be applicable to all these systems.[1a,2,3] We have used proton nmr to determine the thermodynamic properties and the limiting chemical shifts for solutions which previous work has shown to be representative of the interactions mentioned above. Although results for some of the systems have been reported earlier, the interactions are sufficiently weak that solvent competition[4] and even the choice of units[1b,5] have raised serious questions about the direct comparison of results from different laboratories. In addition it seems desirable to compare nmr with ir and uv studies. Our work reveals that nmr measurements can be used to distinguish hydrogen-bonding, charge-transfer, and dipolar interactions and can provide some insight into the details of the mechanisms involved.

Experimental and Data Analysis

All samples were run on a Varian A60-A spectrometer equipped with a variable-temperature probe. Solvents, either reagent or spectroscopic grade, were obtained from the usual commercial sources. They were used without further purification except for drying with Drierite or molecular sieves (Matheson Coleman and Bell; "Linde" Type 4A). Metal-organic solutes were obtained from Alfa Inorganics, Inc. Chemical shifts were measured with a precision of ±0.05 Hz by procedures described elsewhere.[1a]

For the simple reaction

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{AB} \tag{1}$$

it can be shown[6] that the solvent shift δ_{obsd} is

$$\delta_{\text{obsd}} \equiv \nu_{\text{obsd}} - \nu_{\text{ref}} = \frac{1 + A_0K + B_0K - \sqrt{(1 + A_0K + B_0K)^2 - 4K^2A_0B_0}}{2KA_0}\Delta \tag{2}$$

where A_0 and B_0 are the analytical concentrations of the reactants in moles/liter, K is the equilibrium constant for eq 1, ν_{obsd} is the chemical shift of the complex, and ν_{ref} is the chemical shift of a dilute solution of A in an inert solvent. In this work ternary solutions were used. A_0 was kept below 0.2 M so that self-association of A could be neglected. B_0 was varied from 0.5 to 10.0 M. Heptane was usually used as the inert solvent. The data (δ_{obsd}, A_0, B_0) were fit to eq 2 by a least-squares computer program which yielded values of K and Δ (where $\Delta = \nu_{\text{complex}} - \nu_{\text{ref}}$). We calculated ΔH and ΔS from the temperature dependence of K in the usual manner. Equation 2 describes the concentration dependence of all systems studied to within ±0.2 Hz. Error analysis indicates that the uncertainties in K and Δ are ±10%, with larger errors in ΔH and ΔS. There was no need to postulate other equilibria (see below). For further experimental details see ref 1a.

Results

Our studies began with solutes and solvents whose modes of interaction were known from previous work. For example, the electron-acceptor abilities of di- and trinitrobenzene[7] and the hydrogen-bonding ability of $\mathrm{CHCl_3}$[8] and $\mathrm{CHCl_2CN}$[9] have been documented. Polar solutes that can neither hydrogen bond nor charge transfer are also available. To compare the different interactions we first used a series of common electron donors,

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[1] Preceding papers in the series: (a) I. D. Kuntz, Jr., and M. D. Johnston, Jr., *J. Am. Chem. Soc.*, **89**, 6008 (1967); (b) I. D. Kuntz, Jr., F. P. Gasparro, M. D. Johnston, Jr., and R. P. Taylor, *ibid.*, **90**, 4778 (1968).

[2] P. Laszlo in "Progress in Nuclear Magnetic Resonance Spectroscopy," Vol. III, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., Pergamon Press, London, 1967, Chapter 6.

[3] (a) M. W. Hanna and A. L. Ashbaugh, *J. Phys. Chem.*, **68**, 811 (1964); (b) R. Foster and C. A. Fyfe, *Trans. Faraday Soc.*, **62**, 1400 (1966).

[4] (a) S. Carter, J. N. Murrell, and E. J. Rosch, *J. Chem. Soc.*, 2048 (1965); (b) S. Carter, *ibid.*, *A*, 404 (1968); (c) R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, 80, 2778 (1958); (d) M. Tamres, *J. Phys. Chem.*, 65, 654 (1961); (e) J. M. Corkill, R. Foster, and D. L. Hammick, *J. Chem. Soc.*, 1202 (1955).

[5] (a) P. J. Trotter and M. W. Hanna, *J. Am. Chem. Soc.*, **88**, 3724 (1966); (b) R. L. Scott, *Rec. Trav. Chim.*, **75**, 787 (1956).

[6] P. Pineau, N. Fuson, and M. L. Josien, *J. Chim. Phys.*, **55**, 464 (1958).

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[8] C. J. Creswell and A. L. Allred, *J. Phys. Chem.*, **66**, 1469 (1962).

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the methylbenzenes. It also proved profitable to examine a few nonaromatic solvents.

Although our choices of solutes and solvents were governed by *a priori* assumptions of the modes of interaction, in most cases these proved to be sufficiently well-founded so that it is profitable to separate the results into the following sections.

1. Dipolar Solutes. We first consider the interaction of polar solutes with aromatic hydrocarbons. Brown and Stark[10] first suggested that the set of group IV compounds, $(CH_3)_{4-n}MCl_n$, would be ideal for investigating dipolar interactions because of (1) similar geometries and sizes, (2) the wide range of available dipole moments, and (3) the inability of these compounds to participate in other interactions.[9] Thermodynamic and nmr parameters for these solutes in the methylbenzenes and α-methylnaphthalene are given in Table I. Results for other common polar molecules are also included. A general trend of increasing interaction strength as the solute polarity increases is observed. Interestingly, both *K*'s and Δ's are reasonably constant for a given solute with any of the methylbenzenes.

Table I. Polar Solutes in the Methylbenzenes (40 ± 1°)

Solute	Solvent	*K*, l./mole	Δ, Hz	Δ*G*°, kcal/mole	−Δ*H*°, kcal/mole	−Δ*S*°, eu
$MeCCl_3$	Benzene	0.06	76	1.76		
$MeSiCl_3$		0.08	74	1.60		
$MeSnCl_3$		0.17	102	1.12		
Me_2CCl_2		0.065	52	1.69	0.84	8.1
Me_2SiCl_2		0.065	53	1.69		
Me_2GeCl_2		0.11	56	1.38	1.40	8.9
Me_2SnCl_2		0.16	59	1.14	1.7	9.1
$MeCCl_3$	Toluene	0.06	77	1.71	1.3	9.7
$MeSiCl_3$		0.07	82	1.67	1.3	9.6
$MeGeCl_3$		0.10	93	1.40		
$MeSnCl_3$		0.16	103	1.14	1.8	9.5
Me_2CCl_2		0.07	51	1.63		
Me_2SiCl_2		0.07	51	1.63		
Me_2GeCl_2		0.11	54	1.37		
Me_2SnCl_2		0.16	57	1.12		
Me_3SiCl		0.07	26	1.67		
Me_3SnCl		0.11	31	1.37		
Me_2GeCl_2	Xylene[a]	0.10	58	1.40		
Me_2CCl_2	Mesitylene	0.07	58	1.65	1.0	8.6
Me_2SiCl_2		0.06	64	1.75		
Me_2GeCl_2		0.09	65	1.48	1.0	7.9
Me_2SnCl_2		0.14	61	1.23		
Me_2GeCl_2	Durene	0.095	71	1.46		
Me_2CCl_2	α-MN[b]	0.13	74	1.28		
Me_2SiCl_2		0.11	76	1.35		
Me_2GeCl_2		0.19	80	1.03		
Me_2SnCl_2		0.40	69	0.57		
$MeNO_2$	Benzene	0.18	97	1.07		
	Toluene	0.19	93	1.04		
	Xylene[a]	0.20	93	1.00	1.6	8.0
	Mesitylene	0.21	93	0.96	1.4	7.6
	Durene	0.29	85	0.76		
	α-MN[b]	0.33	125	0.70	1.2	6.1

[a] Averaged for *o*-, *m*-, and *p*-xylenes. [b] α-MN = α-methylnaphthalene.

A second set of experiments (Table II) shows the interactions of polar solutes in polar solvents. Again increasing interactions are observed as the dipole moment (Table VI) of either solute or solvent increases.

Table II. Polar Solutes in Polar Solvents (40 ± 1°)

Solute	Solvent	*K*, l./mole	−Δ, Hz	Δ*G*°, kcal/mole
$MeCCl_3$	Me_3CCl	0.055	11	1.80
$MeSiCl_3$		0.06	16	1.78
Me_2CCl_2		0.05	9	1.80
Me_2SiCl_2		0.06	10	1.71
Me_2GeCl_2		0.08	14	1.57
Me_2SnCl_2		0.11	16	1.38
Me_2GeCl_2	Me_3SnCl	0.32	10	0.72
Me_2SnCl_2		0.64	14	0.29
MeCN	$MeCCl_3$	0.07	29	1.65
	Me_3CCl	0.09	15	1.47
	Me_3SnCl	0.48	16	0.45
$MeNO_2$	1-Fluorohexane	0.04	13	2.04
	1-Chlorobutane[a]	0.09	17	1.49
	Me_3CCl	0.08	18	1.54
	Me_3SnCl	0.46	11.5	0.48
	Me_3CBr	0.10	21.5	1.41
	1-Bromoalkanes[a]	0.11	20	1.37
	2-Bromopentane	0.09	22	1.49
	MeI[a]	0.09	28	1.49
	Me_3CI	0.10	29	1.41
Me_2SnCl_2	CH_2Cl_2	0.09	24	1.50
	CH_2Br_2	0.11	30	1.37
	CH_2I_2	0.14	39	1.21

[a] See ref 1a.

2. Hydrogen Bonding. Hydrogen-bonding association constants, limiting chemical shifts, and enthalpies and entropies of formation have been determined for CH_2Cl_2, $CHCl_3$, and $CHCl_2CN$ with some of the methylbenzenes, α-methylnaphthalene, and dioxane (Table III). Some data for $CH(NO_2)_3$[11] and phenol[12] are included for comparison. For a given solute *K*, Δ, and Δ*H* increase with the number of methyl groups on the solvent.

3. Charge Transfer. In Table IV[13] are similar data for charge-transfer systems involving 1,3,5-trinitrobenzene (TNB) and 1,4-dinitrobenzene (DNB) as acceptors and the methylbenzenes and α-methylnaphthalene as donors. Our results are in good agreement with those of Foster and Fyfe[3b,7] when their units are converted to molar units. The choice of units influences *K*, Δ, Δ*H*, and Δ*S*.[1b,14] *K* and Δ*H* increase in the series benzene to hexamethylbenzene, but Δ decreases. The former trend is explainable by the decreasing ionization potentials of the donors. A possible explanation for the latter, observed by other workers,[3,15] is deferred until later.

4. Comparison with Dielectric Measurements. A recent dielectric study[16,17] of the chloroethanes in aromatic solvents and dioxane provided free energies of interaction which can be directly compared to the free energies determined by nmr (Table V). The agreement is reasonably good, but the nmr values are slightly higher (Figure 1).

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(10) T. L. Brown and K. Stark, *J. Phys. Chem.*, **69**, 2679 (1965).

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(12) (a) Z. Yoshida and E. Osawa, *J. Am. Chem. Soc.*, **88**, 4019 (1966); (b) R. West, "Proceedings of International Symposium on Molecular Structure and Spectroscopy," Tokyo, 1962, p D-117-1.

(13) Note that CCl_4 was used as reference (*i.e.*, inert) solvent for these for solubility reasons. As shown in the discussion section, CCl_4 is certainly not as "inert" as hydrocarbon solvents and the *K*'s in this section are systematically low and the Δ's systematically high when compared with similar data from cyclohexane or similar solvents.

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Table III. Hydrogen-Bonding Solutes in the Methylbenzenes (40 ± 1°)

Solute	Solvent[a]	K, l./mole	Δ, Hz	$\Delta G°$, kcal/mole	$-\Delta H°$, kcal/mole	$-\Delta S°$, eu
CH_2Cl_2	Benzene	0.12	84	1.32	1.7	9.7
	Toluene	0.15	81	1.17	2.0	10.0
	Mesitylene	0.17	82	1.12	2.1	10.4
	α-MN	0.22	104	0.95	1.4	7.4
	Dioxane	0.20	−28	1.0	1.3	7.4
$CHCl_3$	Benzene	0.13, 0.13[b,c]	89, 84[b,c]	1.26	1.7, 1.9[b,c]	9.6
	Toluene	0.17	92	1.09	2.2	10.5
	Mesitylene	0.21	106	0.96	2.4	10.6
	α-MN	0.22	117	0.94	1.6	8.2
	Dioxane	0.50	−39	0.43	2.2	8.4
$CHCl_2CN$	Benzene	0.31	110	0.73	1.7	7.8
	Toluene	0.38	112	0.61		
	Mesitylene	0.70	116	0.22	2.3	8.2
	PMB	1.5	126	−0.26		
	Dioxane	1.4	−47	−0.21	3.5	11.8
	α-MN	0.53	139	0.39	1.5	6.0
$CH(NO_2)_3$[b,d]	Benzene	0.87	96	0.08		
	Toluene	1.6	112	−0.27		
	Xylenes	2.8 ± 0.2	117 ± 4	−0.65		
	Mesitylene	4.2	121	−0.87		
	Durene	8.8	130	−1.32		
	PMB	25	121	−1.97		
	HMB	32	143	−2.10		
		e *f*	Δν	*e*	*e*	*e*
Phenol[b]	Benzene	0.27 0.33	49	0.79	1.5	7.6
	Toluene	0.32 0.39	58	0.69	2.1	9.3
	Mesitylene	0.41 0.57	78	0.54	2.7	11.0
	HMB	0.51 0.63	106	0.41	3.0	11.0
	Naphthalene	... 0.58	48			
	α-MN	... 0.69	55			

[a] The following abbreviations have been used: PMB = pentamethylbenzene, HMB = hexamethylbenzene, and α-MN = α-methylnaphthalene. [b] The original work was done in mole fraction units which we have converted to molar units as outlined in ref 1b. [c] Reference 8. [d] Reference 11. [e] Reference 12b. [f] Reference 12a.

Table IV. Charge-Transfer Solutes in the Methylbenzenes (40 ± 1°)[a]

Solute	Solvent	K, l./mole	Δ, Hz	$\Delta G°$, kcal/mole	$-\Delta H°$, kcal/mole	$-\Delta S°$, eu
DNB	Benzene	0.13 (0.12)[b,c]	110 (109)	1.28 (1.29)	1.3	8.4
	Mesitylene	0.21 (0.20)	103 (99)	0.96 (0.98)	1.4	7.5
	HMB	0.84 (0.50)	73 (116)	0.10.(0.43)	3.0	9.8
	α-MN	0.64	113	0.28	1.6	9.3
TNB	Benzene	0.28 (0.25)[b,d]	83 (86)	0.77 (0.86)	1.9 (2.0)	8.6 (9.1)
	Mesitylene	0.80 (0.72)	66 (66)	0.14 (0.21)	2.7 (2.1)	9.1 (7.6)
	HMB	3.1 (2.9)	66 (67)	−0.70 (−0.67)	3.4 (2.8)	8.5 (7.0)
	α-MN	3.4	102	−0.76	3.5	8.8

[a] CCl_4 as inert solvent. The following abbreviations have been used: DNB = 1,4-dinitrobenzene, HMB = hexamethylbenzene, TNB = 1,3,5-trinitrobenzene, and α-MN = α-methylnaphthalene. [b] We have converted the original data to molar units as outlined in ref 1b. [c] Reference 7. The K's were reported at 33.5° and were recalculated for 40° using the ΔH's from this work. [d] Reference 5.

Table V. Comparison of Nmr and Dielectric Work

Solute	Solvent	K, l./mole	Δ, Hz	$-\Delta G_{nmr}$ (40°),[a] kcal/mole	$-\Delta G_{diel}$ (20°), kcal/mole
CH_3CCl_3	Dioxane	0.09	−12	0.47	0.41
CH_2ClCH_2Cl		0.14	−21	0.62	0.47
CH_2ClCCl_3		0.18	−31	0.72	0.66
$CHCl_2CCl_3$		0.42	−56	1.13	0.85
CH_2Cl_2		0.22	−28	0.81	...
$CHCl_3$		0.51	−40	1.14	...
CH_3CCl_3	Benzene	0.06	77	0.32	0.14
CH_2ClCH_2Cl		0.10	77	0.51	0.28
CH_2ClCCl_3		0.11	79	0.48	0.31
$CHCl_2CCl_3$		0.11	65	0.51	0.39

[a] $\Delta G_{nmr} = RT \ln (1 + B_0K)$, where B_0 is the molar concentration of neat solvent. ΔG is the free energy change for the transfer of the solute from cyclohexane to dioxane or benzene.

Discussion

The fact that a set of concentration-dependent chemical shifts is describable by eq 2 sets certain limits on acceptable physical models. The most important restriction is a stoichiometric one. A good fit to eq 2 suggests that a monomer–dimer equilibrium is sufficient to describe the data. It has been shown that trimer and higher *n*-mer formation is detectable as a marked deviation from eq 2.[1a,18] Such deviations were not observed in any of the systems discussed here. We found no evidence of the presence of significant concentrations of "clusters."[10,19] We estimate that if 10% of the solute

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(18) But see G. D. Johnson and R. E. Bowen, *J. Am. Chem. Soc.*, 87, 1655 (1965), for the problem of detecting small amounts of trimer using the double reciprocal form of the Benesi–Hildebrand equation.

(19) T. Matsuo, *J. Phys. Chem.*, 72, 1819 (1968).

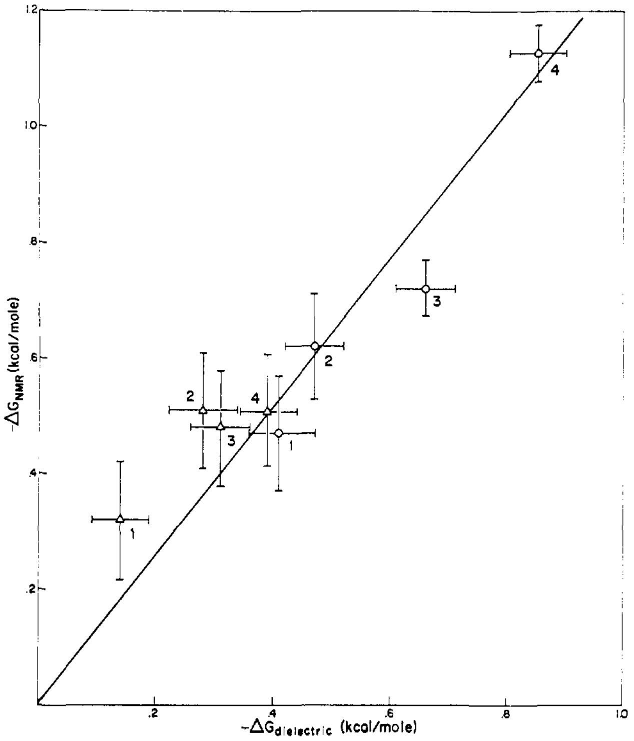

Figure 1. Comparison of free-energy changes measured by nmr and dielectric methods: O, dioxane; Δ, benzene; (1) CH_3CCl_3, (2) CH_2ClCH_2Cl, (3) CH_2ClCCl_3, (4) $CHCl_2CCl_3$.

were involved, good fits with eq 2 could not have been obtained. It is well known that eq 2 can only describe the average parameters (K, Δ, $\Delta H°$, etc.) for pairwise interactions.[1a,14] These interactions surely involve a large set of time-dependent geometries and energies. It must also be remembered that these thermodynamic properties are measured relative to (a) a reference state of a dilute solution of solute in hydrocarbon solvent and (b) the interaction of a nonpolar solute (TMS) with the solvents of interest.

The systems studied here have certain features in common. For example, the thermodynamic properties of the complexes for the different modes of interaction are similar ($\Delta H° = 0$ to -4.0 kcal/mole, $\Delta S° = -4$ to -12 eu, and $K = 0.03$ to 4.0 l./mole). In all cases these quantities are not too different from RT ($\sim$1 kcal/mole). The negative change in entropy in these systems is consistent with an associative mechanism. We have also noted that $\Delta H°$ is reasonably independent of temperature over a 100° range for those complexes from which data are available.

In a recent paper dielectric rotational lifetimes of order 10^{-11} sec were observed for weakly hydrogen-bonding or dipolar solutes in many of the solvents of interest to us.[16,17] These results suggest that the systems described in this paper, even if they involve well-characterized interactions, such as hydrogen bonding, have such short lifetimes that they are best considered as collison complexes.

A general equation for solvents shifts could be written as

$$\Delta = \Delta_E + \Delta_a + \Delta_s \tag{3}$$

where Δ_E is the electrostatic field contribution and contains terms for effects due to multipole fields, Δ_a is the magnetic anisotropy contribution, and Δ_s is a term arising from changes in the shielding of the protons because of hydrogen bonding or charge transfer.[2,20] For all complexes with aromatic solvents the dominant term is Δ_a. It is unlikely that a single term dominates the shifts observed in nonaromatic solvents. All the terms in eq 3 contain time-averaged, geometrical information, the aromatic systems being handled most easily. Calculations based on Bovey and Johnson's tables[21] suggest molecular separations of solvent and solute molecules of order 4–5 Å. We now proceed to a detailed description of the various interactions.

1. Electrostatic Interactions. The solvent shifts shown by polar solutes can be described by eq 2 even when it is clear that these solutes cannot engage in hydrogen bonding or charge transfer.[9,10] We have proposed that these solvent effects arise from the formation of weak 1:1 complexes.[1a] A qualitative picture of these interactions is available from classical electrostatics.

Free Energies of Formation. A simple model for calculating an electrostatic free energy of interaction between two polar molecules would assume two polarizable point dipoles separated by a distance r_{AB} and fixed in a rigid head-to-tail conformation. We assume a small dielectric constant of order unity. The equation for this interaction is[22]

$$\Delta G_{\text{electrostatic}} = -14.4\left[\frac{2\mu_A\mu_B}{r_{AB}^3} + \frac{\mu_A^2(\alpha_B)_{\parallel}}{r_{AB}^6} + \frac{\mu_B^2(\alpha_A)_{\parallel}}{r_{AB}^6}\right] \tag{4}$$

where the subscripts A and B refer to solute and solvent, respectively, ΔG is in kcal/mole, the dipole moments are in Debyes, r_{AB} is in Å, and $(\alpha_A)_{\parallel}$ and $(\alpha_B)_{\parallel}$ are in Å^3, these last being the elements of bond polarizability parallel to the dipole moments. Equation 4, corresponding to $\Delta G \gg RT$, serves as an upper limit for the electrostatic contribution to the free energy of formation. A simple calculation[22] is also available if $\Delta G \ll RT$ for which

$$\Delta G_{\text{electrostatic}} = \frac{-9.6}{RT}\frac{\mu_A^2\mu_B^2}{r_{AB}^6} - \frac{14.4\mu_A^2\alpha_B}{r_{AB}^6} - \frac{14.4\mu_B^2\alpha_A}{r_{AB}^6} \tag{5}$$

The symbols are the same as defined previously except that α_A and α_B are now some average of $\alpha_{\perp}$ and $\alpha_{\parallel}$ for each molecule. We might expect results intermediate between eq 4 and 5. We did experiments to investigate the forms of the first two terms of these equations. The third terms were not studied. If we assume that the radial separation and polarizabilities are approximately constant for the molecules of the type $(CH_3)_nMCl_{4-n}$, we can test the first term of these two equations by plotting the measured free energy against the appropriate power of $\mu_A\mu_B$ (Figure 2). Molecular properties for these calculations are listed in Table VI. Equation 5

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

(21) Tabulated in J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., "High Resolution Nuclear Magnetic Spectroscopy," Vol. 1, Pergamon Press, Oxford, 1966, p 595 ff.

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Table VI. Molecular Properties Used for Electrostatic Calculations

A. Dipole Moments[a]			
Compound	μ, D	Compound	μ, D
$MeCCl_3$	1.62	Me_3CCl	2.20
$MeSiCl_3$	1.90	Me_3SiCl	2.20
$MeGeCl_3$	2.63	Me_3SnCl	3.50
$MeSnCl_3$	3.62	CH_2Cl_2	1.47
Me_2CCl_2	2.20	CH_2Br_2	1.40
Me_2SiCl_2	1.89	CH_2I_2	1.11
Me_2GeCl_2	3.11	$MeNO_2$	3.15[b]
Me_2SnCl_2	4.22	MeCN	3.5[b]

B. Polarizabilities[c] and Magnetic Anisotropies[d]				
Bond	$\alpha_{\parallel} \times 10^{25}$, cm^3	$\alpha_{\perp} \times 10^{25}$, cm^3	$\alpha \times 10^{25}$, cm^3	$\Delta\chi \times 10^6$
C–H	7.9	5.8	6.5	1.50
C–F	...	...	(9.6)[e]	1.88
C–Cl	36.7	20.8	26.1	4.84
C–Br	50.4	28.8	36.0	6.90
C–I	...	...	(48)[e]	10.1
C_6H_6[f]	63.5	123.1	103.2	−54

[a] All dipole moments are from A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman & Co., San Francisco, Calif., 1963, unless otherwise indicated. [b] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955. [c] Reference 22c, p 950. [d] Calculated in ref 24, from data in C. Kittel, "Introduction to Solid State Physics," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1956, pp 206, 211. [e] Estimated from the van der Waals radii of the halogens. [f] The entire benzene ring can be considered as a functional group for these calculations.

seems to contain the better approximation, suggesting that the dipoles rotate relatively freely.

The second term in eq 4 and 5 can be examined using the methylbenzenes for which $\mu \cong 0$. From representative data we see that ΔG *vs.* $\mu_A{}^2$ is linear (Figure 2). As another check, K increases in the series CH_2X_2, X = Cl, Br, I, even while μ_B is decreasing (Table II). One cannot attach much importance to the quantitative features of models as simple as those proposed here. We note, however, that Figures 1b and 2 suggest that an average "radius of interaction," $\bar{r}_{AB}$, can be defined for molecules of similar size and shape. Using eq 5 and the observed free energies, these $\bar{r}_{AB}$'s range from 4.0 Å for the weakest interactions to 3.5 Å for the strongest. These numbers are consistent with interacting bond dipoles but are presumably lower limits for the actual center-to-center separations. Inasmuch as eq 5 serves as a low estimate of the electrostatic contribution to the free energy, it seems likely that the electrostatic terms are sufficient to explain interactions of the size actually observed. Note that the explicit temperature dependence of eq 5 predicts a negative ΔS, which is observed, but a ΔH of zero, which is not observed.

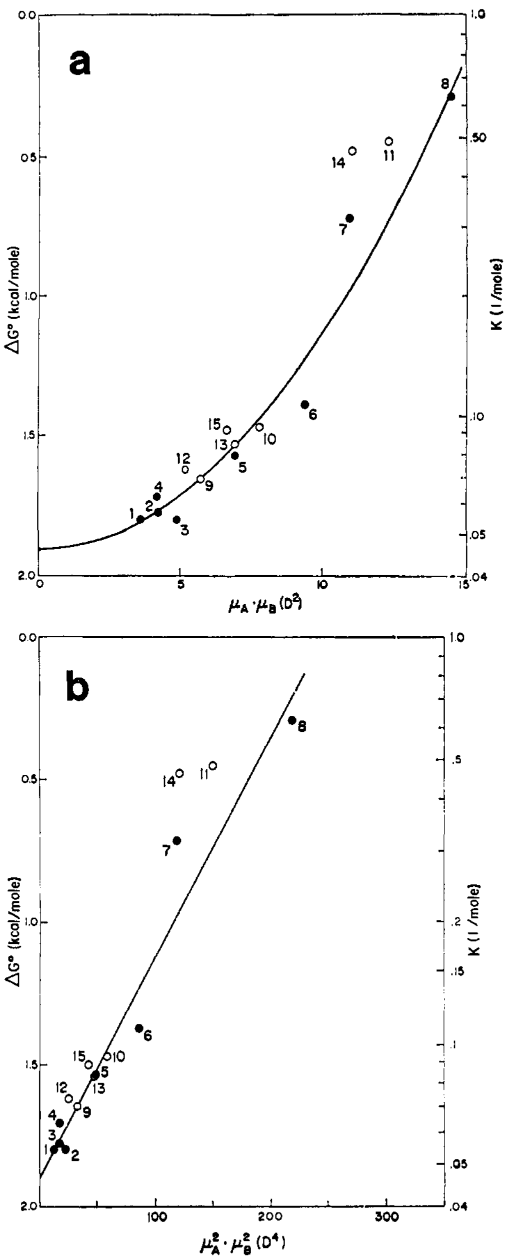

Figure 2. (a) Measured free energy of association for polar solutes in polar solvents plotted *vs.* $\mu_A \times \mu_B$. Solid circles denote systems in which both molecules are of the type Me_nMCl_{4-n}; open circles, systems in which at least one component is of another type. Systems: (1) $MeCCl_3$–Me_3CCl, (2) $MeSiCl_3$–Me_3CCl, (3) Me_2CCl_2–Me_3CCl, (4) Me_2SiCl_2–Me_3CCl, (5) Me_2GeCl_2–Me_3CCl, (6) Me_2SnCl_2–Me_3CCl, (7) Me_2GeCl_2–Me_3SnCl, (8) Me_2SnCl_2–Me_3SnCl, (9) MeCN–$MeCCl_3$, (10) MeCN–Me_3CCl, (11) MeCN–Me_3SnCl, (12) $MeNO_2$–$MeCCl_3$, (13) $MeNO_2$–Me_3CCl, (14) $MeNO_2$–Me_3SnCl, (15) Me_2SnCl_2–CH_2Cl_2. (b) Same data plotted *vs.* $\mu_A{}^2 \times \mu_B{}^2$. The line is a least-squares fit to points 1–8 (slope = −0.00777, intercept = +1.90)5.

Limiting Solvent Shifts. As noted earlier, for these systems there are two possible contributors to the limiting solvent shift, Δ_{AB}: an electric field term and a magnetic anisotropy term. We can estimate the relative importance of these terms in the following way. The change in screening constant of the solute proton is approximately related to the change in electric field at the proton by $\sigma_E = -2 \times 10^{-12}E$.[20,23] There is some debate about the magnitude of the coefficient in this equation. Several authors argue for a larger value (~4–5 × 10^{-12}) because the shifts calculated from the original expression are too small. We feel that the discrepancy is due to the neglect of the anisotropy term discussed below. To calculate the electric field we consider both dipole and induced dipole contributions. The magnetic anisotropy term is that derived by McConnell.[24] With a rigid head-to-tail geometry the limiting solvent shift in hertz at 60 MHz is given by

$$\Delta_{AB} = -60\left[\frac{4\mu_B}{r^3} + \frac{8\mu_A(\alpha_B)}{r^3 r_{AB}{}^3} + \frac{1.1 \times 10^6(\Delta\chi)}{r^3}\right] \quad (6)$$

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

(24) H. M. McConnell, *J. Chem. Phys.*, 27, 226 (1957).

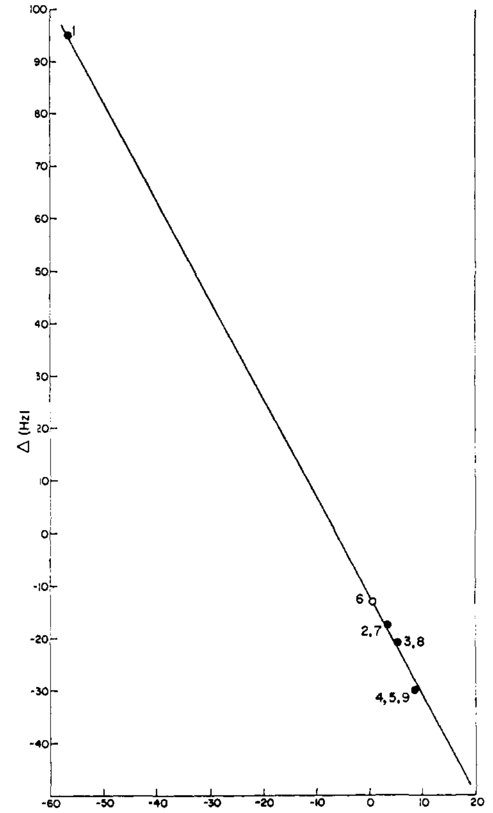

Figure 3. Limiting solvent shift *vs.* $\Delta\chi_{C-X}$ for nitromethane in some symmetric top solvents (solid circles). Also, to test the approximation discussed for the derivation of eq 6, a few other molecules are plotted (open circles). Solvents: (1) benzene, (2) Me_3CCl, (3) Me_3CBr, (4) Me_3CI, (5) MeI, (6) 1-fluorohexane, (7) all 1-chloroalkanes, (8) all 1-bromoalkanes, (9) 1-iodobutane. Data for points 5, 7, 8, and 9 are from ref 1a.

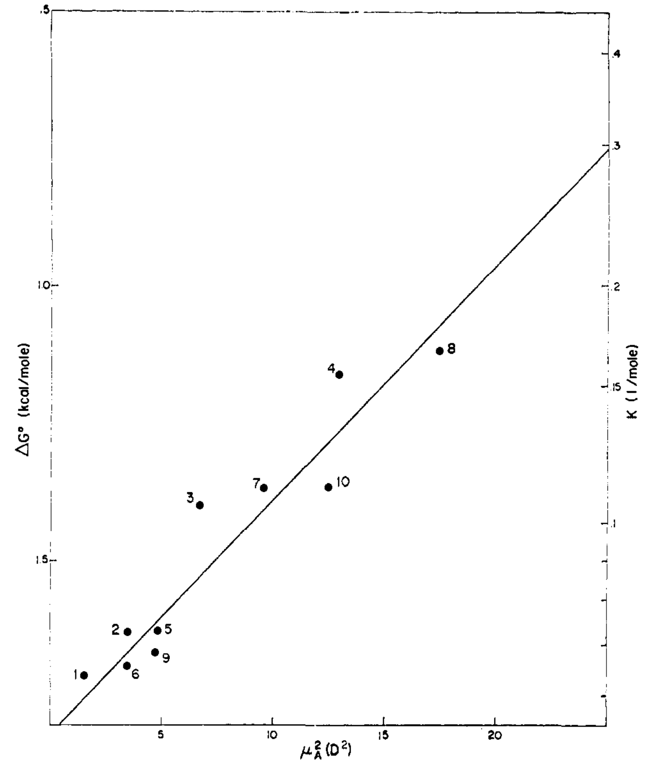

Figure 4. Measured free energy of association for polar solutes in toluene *vs.* $\mu_A{}^2$ (least-squares fit) (slope = −0.04271), intercept = +1.815: (1) $MeCCl_3$, (2) $MeSiCl_3$, (3) $MeGeCl_3$, (4) $MeSnCl_3$, (5) Me_2CCl_2, (6) Me_2SiCl_2, (7) Me_2GeCl_2, (8) Me_2SnCl_2, (9) Me_3SiCl, (10) Me_3SnCl. Points 3 and 4 have a larger uncertainty than usual because the reference frequency had to be estimated (the inert solvent obscures both signals).

where r (Å) is the distance between the center of the solvent bond moment and the solute proton, and $\Delta\chi = \Delta\chi_{CX} - \Delta\chi_{CH}$, where $\Delta\chi_i$'s are the susceptibilities of solvent and inert bond moment, respectively. Other terms are the same as previously. The anisotropy term was derived assuming that two of the components of the anisotropy are equal. It is probably overestimated in eq 6 because the use of an internal standard will reduce the net effect.

For reasonable values of the parameters in eq 6, it is clear that the polarizability term is always negligible. Furthermore, only the anisotropy term need be considered for aromatic solvents. The relative magnitudes of the dipole and anisotropy contributions can be comparable in nonaromatic solvents. A qualitative test of eq 6 is given in Figure 3 where the limiting shift for nitromethane in haloalkanes and in benzene is plotted against $\Delta\chi$. Evidence for the dipolar term comes from the value of $\Delta(-11$ Hz) at $\Delta\chi = 0$. This shift is ascribed to the 2.1-D dipole moment of the haloalkanes. One can also calculate an average intermolecular separation by comparing the measured Δ's to those calculated from eq 6. The data of Figure 4 yield an r of 3.4 ± 0.1 Å.[25]

The limiting shifts of polar solutes in aromatic solvents increase somewhat with increasing polarity (Figure 5), probably because of increasing strength of interaction. For small variation in r the linear dependence is expected.[26] Figure 5 also illustrates a pronounced geometry effect on the limiting shifts: mono-, di-, and trimethyl limiting shifts standing in the rough ratio 3:2:1. Brown and Stark presented evidence that the *observed shift* of these solutes in aromatic solvents was a function of solute dipole moment and geometry.[10] We see here (Figures 4 and 5) that the dipole moment affects only the equilibrium constant while the solute geometry alters the limiting shift.

Summary of Electrostatic Effects. The energies for these systems are approximately described by electrostatic considerations alone and are found to be nearly independent of solute geometry. For a given solute all the methylbenzenes have similar interaction energies, suggesting that the ring polarizabilities are nearly the same. Limiting chemical shifts can be described by electrostatic and magnetic anisotropy contributions, the latter of course dominating aromatic systems. Solute geometry is very important in the aromatic solvents, mono-, di-, and trimethyl limiting shifts standing in the rough ratio 3:2:1.

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[25] Note that r_{AB} and r are not the same. r is the distance from the center of the solvent bond moment (or bond anisotropy) to the proton being studied. r_{AB} calculated above from energy considerations is a bond moment-to-bond moment separation. Also r_{AB} was estimated from eq 5 which contains some rotational averaging, whereas r is from eq 6 which is derived from a rigid model.

[26] Assume for aromatic solvents $u \cong (b/r^{12}) - (\mu_A{}^2\alpha/r^6)$. In the usual way $r_{min} = (2b/\mu_A{}^2\alpha)^{1/6}$. Substitute r_{min} in eq 6 and ignoring terms in μ_B for these nonpolar solutes

$$\Delta \cong -66 \times 10^6\left(\frac{\alpha}{2b}\right)^{1/2}\Delta\chi\mu_A$$

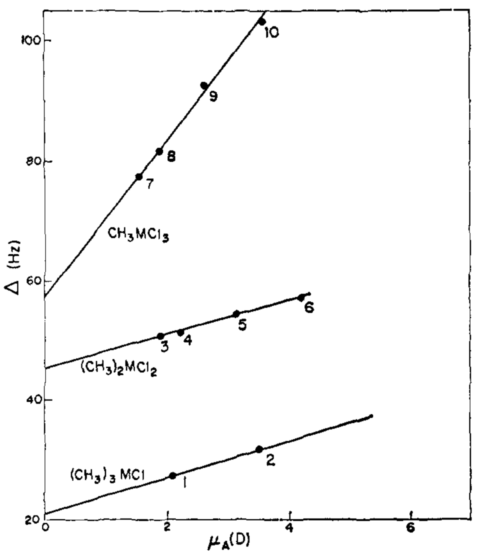

Figure 5. Limiting solvent shift *vs.* solute dipole moment for solutes of the type Me_nMCl_{4-n}. Solutes: (1) Me_3SiCl, (2) Me_3SnCl, (3) Me_2SiCl_2, (4) Me_2CCl_2, (5) Me_2GeCl_2, (6) Me_2SnCl_2, (7) $MeCCl_3$, (8) $MeSiCl_3$, (9) $MeGeCl_3$, (10) $MeSnCl_3$.

2. Hydrogen Bonding. We shall assume that CH_2Cl_2, $CHCl_3$, $CHCl_2CN$, and $CH(NO_2)_3$ hydrogen bond *via* the C–H bond to the π electrons of the methylbenzenes.[9,12a] The nmr results support this assumption. For a given solute in aromatic solvents the association constants increase in the same manner as do those for phenol.[12] In addition, the behavior of the limiting shifts in dioxane is characteristic of hydrogen bonding[2] (see below).

Free Energies. There is no simple, general theory to predict either the proton-donor ability[27] of the solutes or the proton-acceptor capacity of even the limited range of solvents studied here. If one is only interested in a related series of compounds, such as the methylbenzenes, a variety of correlations of molecular properties with ln (K_{eq}) has been proposed.[28] Our results are self-consistent in that proton-donor abilities are in the expected order: $C_6H_5OH > CHCl_2CN > CHCl_3 > CH_2Cl_2$, as are the proton-acceptor strengths: mesitylene > toluene > benzene with dioxane being a much better base than the aromatics.[29]

It has been proposed that hydrogen bonding proceeds by a charge-transfer mechanism[30] primarily because the K's for a given solute increase smoothly from benzene to hexamethylbenzene, in rough relation to the I_p of the base (see Table VII for I_p's). There are certain inconsistencies with this approach. First, nonaromatic solvents such as dioxane have much higher I_p's but are much better proton acceptors than the aromatic hydrocarbons. Second, based on I_p the naphthalenes would be expected to be comparable or superior to hexamethylbenzene in hydrogen-bonding ability, whereas ir frequency shifts indicate they are comparable to benzene or toluene (see Table III). Thus this correlation is most likely fortuitous and not direct evidence for CT behavior.

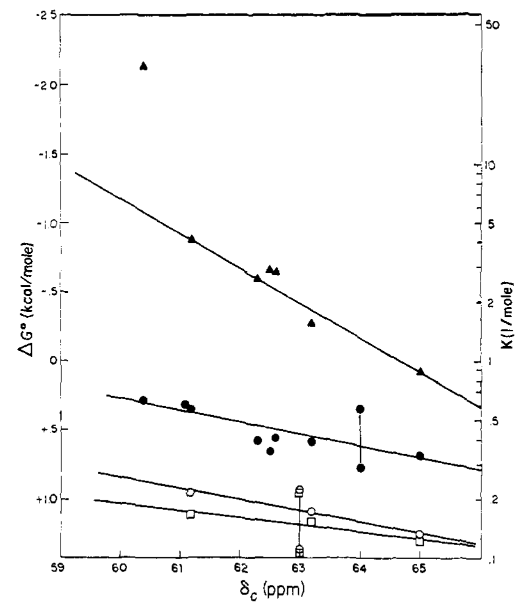

Figure 6. Measured free energy of association for hydrogen-bonding solutes in the methylbenzenes *vs.* average C-13 shift of aromatic ring (see Table VIII, footnote *b*); □, CH_2Cl_2; ○, $CHCl_3$; ▲, $CH(NO_2)_3$ (ref 11); ●, phenol (ref 12).

Alternatively, hydrogen bonding might proceed by a mechanism sensitive to the "basicity" or electron density of the proton acceptor. Nmr heteroatom coupling constants reflect solvent basicity[31] which is reasonable since J_{XH} is directly proportional to the electron density of the heteroatom.[32] Also Watts and Goldstein have observed changes in solute J_{CH} on hydrogen-bond formation.[33] We report here a correlation for ln K with $\delta_{C^{13}}$, the C^{13} chemical shift (Figure 6). δ_{C13} (Table VII) is related to reflect the electron density at a particular carbon atom,[34] and the average of the shifts of the six carbons could be proportional to the ground-state basicity of the ring. There is some scatter, but this plot covers a wide range of solutes and interaction strengths. The C^{13} chemical shifts and C^{13}–H coupling constants are consistent with the suggestion that α-methylnaphthalene is comparable to toluene in hydrogen-bond strength. The idea that hydrogen bonding proceeds by a mechanism sensitive to electron density rather than electron transfer is not new[35] and seems most consistent with our results. This use of C^{13} shifts is only applicable for carbon π electrons directly involved in the hydrogen bonding.

Limiting Shifts. The chemical shift for these solutes in aromatic bases should be determined by two of the terms of eq 3

$$\Delta \cong \Delta_{HB} + \Delta_a \qquad (7)$$

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(27) We will use the conventional proton-donor, proton-acceptor nomenclature for hydrogen bonding and electron-donor, electron-acceptor nomenclature for charge transfer.

(28) H. H. Perkampus, *Advan. Phys. Org. Chem.*, 4, 195 (1966).

(29) C_6H_5OH might be thought to be a much better proton donor than any CH bond. This is probably correct. The nmr results are surely augmented by the "dipolar" contributions discussed in the previous section. Thus 30–50% of the K_{obsd} for $CHCl_2CN$ ($\mu \sim 3.5$ D) is not due to hydrogen-bond formation. Not only is C_6H_5 OH much less polar, but ir methods which resolve "free" and "bonded" O–H stretch frequencies would not show "dipolar" effects in a direct way. For weak interactions one might generally expect $K_{nmr} > K_{ir}$ since the nmr averages over more effects.

(30) Z. Yoshida and E. Osawa, *J. Am. Chem. Soc.*, 87, 1467 (1965).

(31) Reference 2, p 336.

(32) N. Muller, *J. Chem. Phys.*, 36, 359 (1962).

(33) V. S. Watts and J. H. Goldstein, *J. Phys. Chem.*, 70, 3887 (1966).

(34) H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, 468 (1961).

(35) G. C. Pimentel and A. L. McClellan, "The Hydrogen-Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

Table VII. Some Properties of the Methylbenzenes

Compound	I_p, eV[a]	δ_c, ppm[b]	$J_{^{13}CH}$, Hz[b]
Benzene	9.24	65.0	159
Toluene	8.82	63.2	156
o-Xylene	8.56	62.5	154
m-Xylene	8.56	62.6	160
p-Xylene	8.44	62.3	150
Mesitylene	8.39	61.2	154
Durene	8.02	61.1	142
Pentamethylbenzene	7.92	(59.6)	...
Hexamethylbenzene	7.85	60.4	...
Naphthalene	8.12	64.0	158
α-Methylnaphthalene	7.96[c]	(63.0)[d]	...
Biphenyl		63.3	162
Tetramethylethylene	8.30[e]	...	...
p-Dioxane	9.52[f]		142[g]

[a] A. Terenin and F. Vilessov, *Advan. Photochem.*, **2**, 419 (1964). [b] Rather than using either the C-13 shift of methyl carbon or the hydrogen carbon of a methylbenzene, we have calculated an average shift from $\delta_C = a\delta_{C-CH_3} + b\delta_{C-H}$, where a is the fraction of methyl positions, b is the fraction of nonmethyl positions, and δ_E and δ_{C-H} are the respective shifts for each: P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 1838 (1961). [c] K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957). [d] In the paper cited in ref 6, Lauterbur lists the C^{13} chemical shifts for various carbons. The appropriate values have been summed up for α-methylnaphthalene. [e] H. Huroda, M. Kobayashi, M. Kinoshita, and S. Takemoto, *J. Chem. Phys.*, **36**, 457 (1962). [f] F. H. Field and T. L. Franklin, "Electron Impact Phenomenon and the Properties of Gaseous Ions," Academic Press, New York, N. Y., 1957. [g] Reference 32.

where Δ_{HB} is a downfield shift associated with the formation of a hydrogen bonding and Δ_a is the shift arising from the magnetic anisotropy of the donor. Other small solvent effects have been ignored.[1a] As the strength of interaction increases, the donor and acceptor molecules are on the average drawn closer together; and although there is no *a priori* way to predict the trend in Δ, all of our results show an increasing trend in the limiting shift as K increases. Thus the anisotropy term increases more rapidly than Δ_{HB} decreases.

The complex interpretations of both the energetics and the limiting shifts for hydrogen-bond formation in aromatic solvents make it clear that the data for any one of these systems contains little information as to whether hydrogen bonding is actually the dominant mode of interaction. As a preliminary experiment to determine the hydrogen-bonding ability of a proton donor, we propose that the shift in neat dioxane serves as a useful, semiquantitative guide. Neat shifts greater than ~15 Hz (referenced to cyclohexane as an inert solvent) appear to be reliable evidence that the solute is capable of forming a reasonably strong hydrogen bond (Table VIII). This test confirms the lack of proton-donor ability of methyl groups in such compounds as CH_3NO_2, CH_3CN, CH_3CCl_3, etc.[9]

Table VIII. Shifts for the Chloroethanes in Neat Dioxane

Chloroethanes	δ_{neat}, Hz	Chloromethanes	δ_{neat}, Hz
CH_3CCl_3	−6.04	CH_2Cl_2	−19.72
CH_2ClCH_2Cl	−12.76	$CHCl_3$	−33.79
CH_3CHCl_2	−20.24	$CHCl_2CN$	−45.76
CH_2ClCCl_3	−20.70	CH_3NO_2	−11.6
$CHCl_2CH_2Cl$	−29.10 (-$CHCl_2$) −15.56 (-CH_2Cl)		
$CHCl_2CHCl_2$	−46.00		
$CHCl_2CCl_3$	−46.49		

3. Charge Transfer. Aromatic molecules are very popular for charge-transfer investigations, particularly as electron donors.[27] The choice of an aromatic donor appears obligatory for successful nmr work (see below). The complexes which we have investigated have both aromatic acceptors and donors. The thermodynamic results are in good agreement with other nmr measurements[3b,7] and in fair agreement with earlier ultraviolet studies.[36,37] In most of these cases ln K, as expected, is proportional to I_p.[38]

The sign, magnitude, and origin of nmr shifts for charge-transfer complexes have been a topic of some interest in the recent literature.[3a,15] The basic point of concern is the decreasing trend in Δ with increasing K. The chemical shift for such a complex is given by the following form of eq 3

$$\Delta = \Delta_{CT} + \Delta_a \tag{8}$$

where Δ_{CT} is the shift due to charge transfer *per se* and Δ_a is again an anisotropy contribution from the aromatic donor. The following effects can be considered to explain this trend: (1) a perturbation on Δ due to solvent competition,[4] (2) a diamagnetic contribution to Δ_{CT} due to the transfer of charge from donor to acceptor,[3a] (3) a paramagnetic contribution to Δ_{CT} due to a new low-lying excited state,[3a] and (4) a change in the large Δ_a term in going from donor to donor.[3a] We consider these in turn below.

To study charge-transfer complexes, one must frequently select solvents which are not "ideal." The effects of competition between donor and solvent for the acceptor have been treated in a number of papers.[4] We propose the following scheme for solvent competition

$$\mathrm{A} + \mathrm{B} \overset{K_1}{\rightleftharpoons} \mathrm{AB},\ \mathrm{A} + \mathrm{S} \overset{K_2}{\rightleftharpoons} \mathrm{AS} \tag{9}$$

which, if $S_0, B_0 \gg A_0$, yields

$$K_{obsd} = \frac{K_1 - K_2\rho}{1 + K_2S_0} \tag{10}$$

$$\Delta_{obsd} = \frac{K_1(1 + K_2S_0)\Delta_1 - K_2(K_1S_0 + \rho)\Delta_2}{(1 + K_2S_0)(K_1 - K_2\rho)} \tag{11}$$

where ρ is the ratio of the molar volumes of B and S, and S_0 is the neat concentration of S. The interaction of the solvent can be measured relative to a more inert solvent such as heptane. Accordingly we have determined K_2 and Δ_2 for DNB and TNB interacting with CCl_4 and then evaluated K_1 and Δ_1 for each system (Table IX). An experimental check on eq 10 and 11 was made by measuring K_1 and Δ_1 for TNB in benzene and mesitylene using heptane as the inert solvent. Although the correction for solvent participation acts to diminish the trend in Δ, we still find larger shifts in benzene than in hexamethylbenzene.

To determine Δ_{CT} independent of aromatic anisotropy terms, we have measured the shifts for TNB in three nonaromatic donors and the shift of mesitylene in ICl (Table X). For the two nonaromatic n donors we find no shifts although there is a color change indicative of charge transfer. For the nonaromatic π donor, tetramethylethylene (TME), we find an upfield shift of 3.2

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(36) G. Briegleb and J. Czekalla, *Z. Elektrochem.*, **59**, 184 (1955).

(37) G. Briegleb, "Molekulverbindungen und Koordinationverbindungen in Einzeldarstellungen. Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin-Wilmersdorf, Germany, 1961.

(38) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

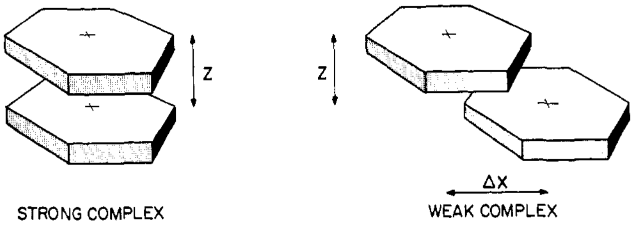

Figure 7. Suggested arrangement of donor and acceptor in CT complexes (see text).

Hz in addition to a color change. This upfield shift is consistent with the increasing electron density at the acceptor, but is far too small an effect to dominate Δ in aromatic acceptors. It was not unexpected that the chemical shift of mesitylene was shifted downfield when mixed with ICl, although again the effect was very small. Thus, there is no evidence for a general paramagnetic term of the type considered by Hanna.[3a]

Table IX. Solvent Competition in Charge Transfer[a] (40 ± 1°)

Solute	Solvent	K_2, l./mole	Δ_2, Hz
DNB	CCl_4	0.03	−28
TNB	CCl_4	0.09	−8.0

		K_{obsd}, l./mol	Δ_{obsd}, Hz	K_1, l./mole	Δ_1, Hz
DNB	Benzene	0.13	110	0.21	81
	Mesitylene	0.21	103	0.30	92
	Hexamethylbenzene	0.84	73	1.2	67
TNB	Benzene	0.28	83	0.65 (0.48)[b]	65 (70)[b]
	Mesitylene	0.80	66	1.6 (1.6)[b]	58 (56)[b]
	Hexamethylbenzene	3.1	66	6.1	58

[a] See text for significance of K_1, Δ_1, K_2, Δ_2, K_{obsd}, and Δ_{obsd}. [b] Determined experimentally using heptane as the inert solvent.

Table X. Nonaromatic Charge-Transfer Systems (40 ± 1°)

Acceptor	Donor	δ_{obsd}, Hz
TNB[a]	Hexamethylphosphoric triamide	0.0
TNB[a]	Tri-*n*-butylamine	0.0
TNB[a]	Tetramethylethylene	+3.2
ICl	Mesitylene[b]	−3.0

[a] ν_{ref}(TNB/heptane) = 555.2 Hz. [b] ν_{ref}(MES/cyclohexane–chloroform) = 325.0 Hz.

Since no large shifts are observed in TNB–TME and ICl–mesitylene systems, we must look to the anisotropy term to explain the decreasing trend. There is no evidence of any decrease in "ring current" in the methylbenzenes. If anything the dipolar data indicate a small increase in shielding abilities as methylation increases. However, the anisotropy term is known to be very sensitive to geometry,[38] and thus changes in average complex geometry could reduce the shielding from the donors. We propose, as has been suggested previously,[39a,c] a horizontal displacement of the donor and acceptor relative to each other such that as K increases, this lateral displacement decreases (Figure 7). The intermolecular separation probably decreases as well. Bovey and Johnson's tables indicate that for coaxial aromatic molecules, the anisotropic shift is very small and that as the two molecules are moved with respect to each other, the shift increases to a maximum when they have been moved somewhat more than one-half the molecular diameter[40] (Figure 8). The magnitude of this effect depends on the detailed molecular orientations. Note that the time-averaged motion generates a torus, with the weaker complexes having tori of larger radii. This model is consistent with two pieces of nmr experimental evidence: the trends in Δ within the methylbenzene series and the larger shifts for DNB compared with TNB in a common donor. We suggest that in all these cases the weaker interactions have more staggered geometries and hence greater shifts (if the radial separation does not change markedly). The predicted shifts for very strong or very weak complexes are interesting. For very strong complexes, where acceptor and donor approach coaxial geometry, one expects very small shifts (~0 Hz). For very weak complexes there should actually be a reversal of the trend (*i.e.*, increasing Δ from benzene to hexamethylbenzene) because the over-all separation of the partners assumes greater importance.[41,42]

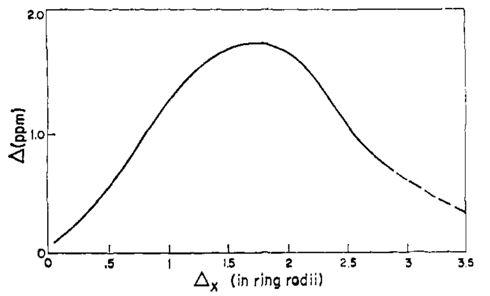

Figure 8. Typical plot of limiting chemical shift *vs.* horizontal displacement of donor and acceptor relative to each other for CT complexes (see text).

Comparison of Weak Interactions

Although the molecular mechanisms of the interactions studied differ widely, the inspection of Tables I–IV indicates that the thermodynamic properties alone cannot be used to distinguish the mode of association for weak complexes. Somewhat more information is obtained when both ΔG and Δ are considered for the interaction of a single solute with the series of methylbenzenes. Dipolar interactions show essentially the same free energy of interaction along the series, and the magnitude of ΔG can be roughly predicted from the dipole moment of the solute (Figure 4). Solutes which can hydrogen bond or charge transfer fall distinctly above the line (see Figure 9). Such solutes also show significant increases in K in the more methylated solvents, particularly for charge transfer. The increase of Δ for hydrogen-bonding solutes and the decrease of Δ for charge-transfer solutes can serve as an empirical distinction between the two interactions, but its reliability

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(39) (a) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952); (b) S. Iwata, J. Tanaka, and S. Nasakura, *ibid.*, **88**, 894 (1966); (c) H. H. Perkampus and U. Krüger, *Z. Physik. Chem.* (Frankfurt), **55**, 202 (1967).

(40) In ref 39, p 823, Mulliken shows that only this geometry fulfills the proper symmetry condition which leads to charge transfer.

(41) Parenthetically we speculate that this model might also account for a similar decreasing trend in UV-VIS extinction coefficients for charge-transfer complexes. ϵ is proportional to μ_{EN}, the transition moment which is given by eq 20 of ref 42. If the radial separation of the donor and acceptor decreases as the strength of the complex increases, and if this change in the radial term dominates changes in the overlap integral, then one predicts a decrease in ϵ as K increases. Some numerical support for this approach is presented by Mulliken[39a] (but also see Orgel and Mulliken[14] and Iwata, *et al.*[39b]).

(42) R. S. Mulliken, *J. Am. Chem. Soc.*, 72, 600 (1950).

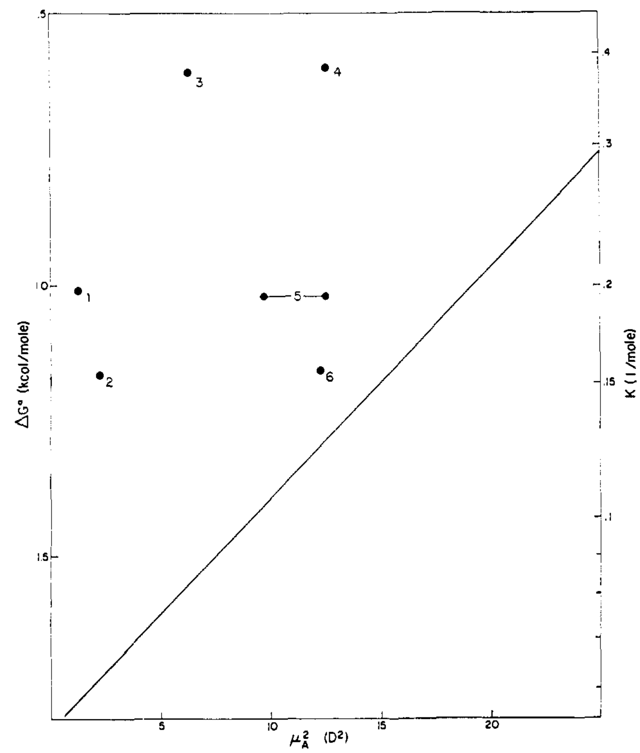

Figure 9. Measured free energy of association for polar solutes in toluene showing deviations due to hydrogen bonding and charge transfer: (1) $CHCl_3$, (2) CH_2Cl_2, (3) $CHCl_2CN$, (4) TNB, (5) CH_3NO_2, (6) CH_3CN.

has not been determined for solutes of radically different geometries.

Two solvents appear to offer a reliable way to detect the relative importance of the hydrogen bonding and charge-transfer abilities of a given solute. As mentioned above, dioxane produces large solvent shifts for those protons which can actually act as proton donors. We do not mean to imply that other types of interactions are missing in dioxane. It is simply that hydrogen-bond formation produces the major perturbation on the shift. Using the proposal that limiting shifts greater than ~20 Hz or neat shifts greater than ~15 Hz indicate hydrogen bonding, we would conclude that CH_3CCl_3 and CH_2ClCH_2Cl cannot hydrogen bond, whereas CH_2Cl_2, CH_2ClCCl_3, and $CHCl_2CH_3$ probably form weak but detectable hydrogen bonds (Table VIII). Even though the methylbenzenes are weaker proton acceptors than dioxane, it appears likely that CH_2Cl_2, $CH_2ClCHCl_2$, and $CHCl_2CH_3$ definitely interact more strongly with benzene than would be predicted from their dipole moments, whereas the K for CH_3CCl_3 falls on the line in Figure 4. CH_2ClCH_2Cl appears anomalous both to the nmr and the dielectric measurements, perhaps reflecting its variable conformation. The lack of shifts of TNB in dioxane[43] confirms that ring hydrogens cannot form hydrogen bonds.[9]

α-Methylnaphthalene has been shown to be a good electron donor in charge-transfer systems, whereas it is a relatively poor base for hydrogen bonding (see above). Thus we propose that the ratio of equilibrium constants of a given solute in α-methylnaphthalene and benzene be used to tell these two types of interactions apart. $K_{\alpha MN}/K_{benzene} > 3$ would indicate an important charge-transfer contribution (Table XI). Thus nitromethane which might have been expected to have considerable charge-transfer ability shows a somewhat larger ΔG than expected from its dipole moment, but it does not show particularly strong interactions with α-methylnaphthalene, leading to the conclusion that nitromethane interacts primarily as a strong dipole, although some weak charge-transfer ability is not ruled out.[44]

Table XI. $K_{\alpha MN}/K_{benzene}$ for Some Charge-Transfer and Hydrogen-Bonding Systems

Acceptor	$K_{\alpha MN}/K_{benzene}$
1,3,5-Trinitrobenzene	12
1,4-Dinitrobenzene	5
$CHCl_2CN$	2
Phenol	2
$CHCl_3$	2
CH_3NO_2	2

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Appendix I. Table of Reference Frequencies for Various Solutes

Solute	Solvent	Concn of solute, vol %	ν_{ref}, Hz (±0.05)
$CHCl_3$	Heptane	1.1	426.23
		2.1	426.59
CH_2Cl_2		1.1	307.15
$CHCl_2CN$		1.1	352.10
CH_3CCl_3	Cyclohexane	1.0	157.49
		2.0	157.60
CH_2ClCCl_3		1.0	248.40
		2.0	248.59
$CHCl_2CCl_3$		1.0	356.87
		2.0	356.96
$CHCl_2CHCl_2$		1.0	345.03
CH_3CHCl_2		1.0 ($-CHCl_2$)	343.47
$CHCl_2CH_2Cl$		1.0 ($-CHCl_2$)	333.98
		($-CH_2Cl$)	227.47
CH_2ClCH_2Cl		1.0	212.63
TNB	CCl_4	0.22[a]	559.28
DNB		0.16[a]	502.77
TNB	Heptane	0.15[a]	555.43
DNB		0.15[a]	497.74
CH_3CN	Cyclohexane	1.0	104.43
CH_3NO_2		1.0	245.05
$(CH_3)_3CCl$	Cyclopentane	2.0	92.94
$(CH_3)_3CBr$	Cyclohexane	1.0	103.46
$(CH_3)_3SiCl$		1.0	22.05
$(CH_3)_3SnCl$		1.2[a]	31.76
$(CH_3)_2CCl_2$		1.0	125.91
$(CH_3)_2SiCl_2$		1.0	42.26
$(CH_3)_2GeCl_2$		1.0	63.25
$(CH_3)_2SnCl_2$		1.4[a]	58.20
CH_3SiCl_3		1.0	60.68
CH_3GeCl_3		1.0	87.95[b]
CH_3SnCl_3		1.5[a]	80.30[b]
CH_3I		1.0	120.27

[a] These solutes are solids and their concentration is reported as weight per cent. [b] These values were estimated by calculation as a third parameter in the least-squares fit of the concentration data. This was necessary since all available inert solvents masked these peaks.

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(43) F. P. Gasparro, unpublished results.

(44) NOTE ADDED IN PROOF. Two papers with somewhat similar treatments of solute–solvent interactions have been recently published: R. L. Schmidt, R. S. Butler, and J. H. Goldstein, *J. Phys. Chem.*, 73, 1117 (1969); J. Homer and M. C. Cooke, *J. Chem. Soc., A*, 773, 777 9).69(1