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Association between Polar Molecules

Part 2.—Equilibrium and Thermodynamic Studies on the Dipole Association of Benzonitrile Derivatives with Hexamethylphosphoramide, Di-n-butyl Sulphone, Di-n-butyl Sulphoxide and Tetramethylurea in Non-polar Solvents

BY HIDEAKI FUJIWARA,* TATSUYA TAKAGI, YUTAKA YAMAZAKI AND YOSHIO SASAKI

Faculty of Pharmaceutical Sciences, Osaka University, 133-1 Yamadakami Suita, Osaka, 565 Japan

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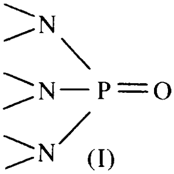
Dipole association between *p*-substituted benzonitriles and polar substances such as hexamethylphosphoramide(HMPA), di-n-butyl sulphone(DBSN), di-n-butyl sulphoxide(DBSX) and tetramethylurea (TMU) is investigated in non-polar solvent by means of n.m.r. spectroscopy assuming the formation of a 1 : 1 associate between the polar molecules. Association parameters (association constant and association shift) are derived and discussed in relation to the dipole moment and the substituent constant. The association constant is, as expected, dependent upon the dipole moment of HMPA, DBSN, DBSX and TMU, and also upon the substituent constants of the *p*-substituted benzonitriles. However, the correlation between this constant and the dipole moment of the benzonitriles is the reverse of that expected. Polarization in the Ph—X fragment in benzonitriles which opposes that in the C≡N bond is thought to cause this phenomenon.

The association shift, which is the change in shift on association, cannot be explained simply by the dipole moment of HMPA, DBSN, DBSX and TMU, and so the magnetic anisotropy of these compounds is considered to be responsible. However, when a comparison is made within each benzonitrile+polar substance system, the anisotropy effect seems to be cancelled out and a correlation is established with the substituent constants.

Thermodynamic parameters are also estimated for the association of HMPA with substituted benzonitriles and for association with substituted nitrobenzenes and several aliphatic nitro and nitrile compounds. These are in the range expected for the dipoles under consideration, and the model adopted to interpret the concentration and temperature dependences of the shift is proved to be sound.

In a previous report[1] we have investigated intermolecular interactions between *p*-substituted nitrobenzenes and hexamethylphosphoramide in non-polar solvents by analysing the n.m.r. concentration dependence. These interactions are thought to be dipolar and the results were discussed with regard to the dipole moment and the substituent constant. These approaches using n.m.r. as a diagnostic tool seem suitable for the elucidation of weak intermolecular interactions in solution. Although such approaches have been widely utilized for the study of hydrogen bonding and acidic-proton–aromatic-system interactions,[2] the reported results are very limited regarding dipole–dipole interactions.[1]

In the present study the interaction of *p*-substituted benzonitriles with several polar substances which contain well-known polar groups such as those shown below was investigated to show the effect of several types of polar group on dipole association.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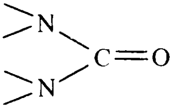
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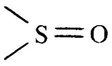
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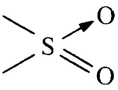

(IV)

For compounds of types (I)-(IV), hexamethylphosphoramide(HMPA), di-n-butyl sulphone(DBSN), di-n-butyl sulphoxide(DBSX) and tetramethylurea(TMU), respectively, were used. Compounds having n-butyl groups were selected for the sake of solubility.

RESULTS

We have analysed the n.m.r. concentration dependence by assuming the formation of a 1:1 associate between the interacting molecules. Because there exists a definite orientation force of an electrostatic nature between the two polar molecules and the concentration of these is very dilute in a non-polar solvent, the above assumption is considered justified. Job plots are consistent with this idea (fig. 1). This will also be confirmed if similar results (for the association constants) are reached when the equilibrium is observed from both sides for the two interacting molecules. However, such attempts were often disrupted by the poor solubility of the nitrobenzenes and benzonitriles in methylcyclohexane and by the very small changes in the ^{1}H shifts (< 1 Hz) in HMPA and TMU on addition of the polar molecules.

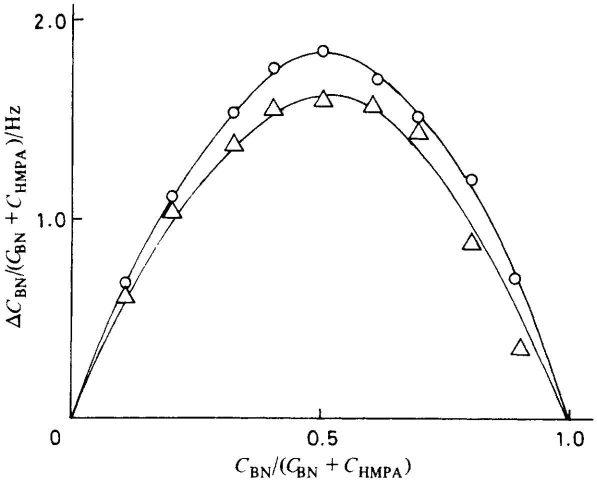


FIG. 1.—Job plots for the *p*-tolunitrile+HMPA system in methylcyclohexane. Similar results are found for other systems. $\Delta = \delta_{obsd} - \delta_A$; total concentration = 0.2 dm^3 mol^{-1}. ○, Experimental values for the *ortho* protons; △, experimental values for the *meta* protons.

Although only *meta* protons with regard to the NO_2 group gave rise to considerable concentration dependences in the previous nitrobenzene + HMPA system, both *ortho* and *meta* protons do so in the present case of benzonitrile + polar substance systems. Therefore, the association constant(K) and association shift(Δ_{AB}) are derivable for both protons. Sometimes a better agreement is reached between the K values from the *ortho* and *meta* protons if the infinite-dilution shift(δ_A^0) is used as the shift of A in the free state. An example is given in table 1 for the *p*-tolunitrile+HMPA and *p*-tolunitrile+DBSN systems. The table, which depicts a critical example, clearly shows that slight changes (only of the order of 10^{-3} ppm) modify the K values favourably. Calculations are given in table 2 for all systems studied here. Averages of the K values from the *ortho* and *meta* protons are used for further discussion.

TABLE 1.—COMPARISON OF K VALUES DETERMINED FROM DIFFERENT VALUES OF THE SHIFT IN A FREE STATE[a]

		calculation 1			calculation 2		
system[b]	site	δ'_A [c]	Δ_{AB} [d]	K	δ°_A [c]	Δ_{AB} [d]	K
I	*o*	584.2	24.9	2.0	584.3	25.3	1.9
I	*m*	560.8	33.9	1.4	560.1	32.4	1.7
II	*o*	584.2	12.4	2.6	584.3	12.6	2.2
II	*m*	560.8	16.2	1.3	560.1	13.6	2.2

[a] The shift and association constant (K) are expressed in units of Hz and $dm^3\ mol^{-1}$, respectively; [b] I, *p*-tolunitrile + HMPA, II, *p*-tolunitrile + DBSN system; [c] δ'_A, shift of A from TMS at its initial concentration ($0.03\ mol\ dm^{-3}$, calculation 1); δ°_A, shift of A from TMS at its infinite dilution (calculation 2); [d] $\Delta_{AB} = \delta_{AB} - \delta_A$ (association shift).

TABLE 2.—ASSOCIATION PARAMETERS FOR THE *p*-SUBSTITUTED BENZONITRILE + POLAR SUBSTANCE SYSTEMS IN METHYLCYCLOHEXANE AT 34.1 °C[a]

benzonitriles			polar substances							
			HMPA		DBSN		DBSX		TMU	
p-substituent	μ_{BN} [b]	site	Δ_{AB}	K	Δ_{AB}	K	Δ_{AB}	K	Δ_{AB}	K
H	3.97	*o*	0.277	2.2	0.132	2.7	0.176	2.2	0.209	1.1
		p	0.288	2.5	0.143	2.5	0.183	1.6	0.160	1.4
CH_3	4.40	*o*	0.297	1.9	0.140	2.3	0.173	1.9	0.203	0.9
		m	0.363	1.7	0.152	2.2	0.199	1.7	0.269	0.9
$C(CH_3)_3$	4.64	*o*	0.310	1.7	0.140	2.3	0.206	1.3	0.221	0.8
		m	0.310	1.7	0.126	1.8	0.204	1.5	0.221	0.8
OCH_3	4.97	*o*	0.221	2.7	0.150	2.7	0.181	2.1	0.167	1.2
		m	0.426	3.0	0.172	2.8	0.271	2.1	0.297	1.3
$N(CH_3)_2$	6.60	*o*	0.127	1.7	0.112	1.9	0.093	1.6	0.077	1.0
		m	0.352	2.2	0.159	1.9	0.203	1.7	0.258	0.8
Cl	2.50	*o*	0.506	4.9	0.234	3.7	0.300	3.0	0.350	1.7
		m	0.297	4.6	0.199	3.5	0.260	2.9	0.330	1.6

[a] Δ_{AB} and K are in units of ppm and $dm^3\ mol^{-1}$, respectively. Errors are within ±1% for Δ_{AB} and ±5% for K. [b] μ_{BN}, dipole moments of benzonitriles from ref. (3), the value in benzene is adopted consistently.

TABLE 3.—TWO-PARAMETER TREATMENT OF $\ln K$ BY THE EQUATION $\ln K = p\sigma_i + q\sigma_\pi^+ + r$

polar substance	p	q	r	f [a]
HMPA	2.47	0.38	0.73	0.03
DBSN	1.31	0.59	0.90	0.04
DBSX	1.52	0.30	0.58	0.11
TMU	1.72	0.36	0.00	0.23[b]

[a] Fitting parameter f = (root mean square deviation)/(root mean square of the data). [b] Relatively large f value is due to smaller value of K in this case.

DISCUSSION

ASSOCIATION CONSTANT

Plots of the association constants for the systems containing DBSN, DBSX and TMU against those for the systems containing HMPA show a linear relationship between them. A least-squares fit of the data according to the relation $y = ax$ results in

$$K(\text{DBSN}) = 0.90\,K(\text{HMPA}) \quad \text{r.m.s.d.} = 0.52\ \text{dm}^3\ \text{mol}^{-1} \tag{1}$$

$$K(\text{DBSX}) = 0.73\,K(\text{HMPA}) \quad \text{r.m.s.d.} = 0.33\ \text{dm}^3\ \text{mol}^{-1} \tag{2}$$

$$K(\text{TMU}) = 0.41\,K(\text{HMPA}) \quad \text{r.m.s.d.} = 0.17\ \text{dm}^3\ \text{mol}^{-1}. \tag{3}$$

The proportionality constants in these equations vary with the ratio of dipole moments (μ) of the polar substances: $\mu_{\text{DBSN}}/\mu_{\text{HMPA}} = 0.81$, $\mu_{\text{DBSX}}/\mu_{\text{HMPA}} = 0.71$, and $\mu_{\text{TMU}}/\mu_{\text{HMPA}} = 0.63$ from the values for HMPA(5.54 D),[3] DBSN(4.46 D),[4] DBSX(3.93 D)[4] and TMU(3.47 D),[4] where the value of di-iso-butyl sulphoxide is cited for DBSX. This fact confirms that the dipolar term is dominant in the intermolecular interaction and also that the experimental determination of K is accurate enough to disclose simple relationships.

TABLE 4.—VARIATION OF ^{31}P CHEMICAL SHIFT OF HMPA ON ADDITION OF CYANO COMPOUNDS[a]

compound added[b]	Δ^c/Hz
benzene	-1
benzonitrile	-11
p-tolunitrile	-6
p-anisonitrile	-8
p-chlorobenzonitrile	-13
propionitrile	-3

[a] Data from INDOR experiments on a Hitachi R-20B n.m.r. spectrometer (60 MHz for ^{1}H). [b] 0.3 mol dm^{-3} of the compound is added to a solution of 0.03 mol dm^{-3} HMPA in methylcyclohexane. [c] Δ, Variation of the shift on addition of the cyano compound. The minus sign denotes a down-field shift on addition.

In contrast, when association constants are plotted against μ_{BN} in each benzonitrile + polar substance system, a deceptively simple relation appears: K decreases with μ_{BN}. In the benzonitriles polarization in the CN group is delocalized to the relatively large phenyl ring, and the *p*-substituent modifies the charge distribution in the CN group as well as that in the phenyl group. This may make the simple dipolar representation of the molecule invalid for a microscopic interaction in this case. Plots of the K values against the substituent constants[5] σ_i and σ_π^+ show a correlation between the K and σ_i. The two-parameter treatment for $\ln K$ gives sufficiently low values of f (table 3), especially for higher K values, which indicates a dominance by the σ_i term. This σ_i dependence and the above inverse proportionality of μ_{BN} could be accounted for by considering polarization in the Ph—X fragment, where Ph is the phenyl ring. This polarization would cause a local dipole moment which opposes that in the CN group or a quadrupole moment over the whole molecule, which contributes to the increased value of K. The σ_i and μ_{BN} dependence does not necessarily mean that the main site of interaction in benzonitriles is the phenyl ring. In fact, the ^{31}P chemical shift of HMPA is seen to move down-field on addition of benzonitriles (table 4), supporting the absence of the P atom above the phenyl ring in an associate. Association around the CN group also seems likely because of the predominant excess charges on this group.

ASSOCIATION SHIFT

The association shift Δ_{AB} is determined from the shift of both *ortho* and *meta* protons with regard to the CN group (table 2). However, the substituent dependence is so small at the *meta* position that no discernible correlation is found for this, and so the discussion below concerns the *ortho* position. Plots of Δ_{AB} in the systems containing DBSN, DBSX and TMU against those in the system containing HMPA reveal the following relation, which is similar to eqn (1)-(3):

$$\Delta_{AB}(\text{TMU}) = 0.71\ \Delta_{AB}(\text{HMPA}) \quad \text{r.m.s.d.} = 0.01\ \text{ppm} \tag{4}$$

$$\Delta_{AB}(\text{DBSX}) = 0.63\ \Delta_{AB}(\text{HMPA}) \quad \text{r.m.s.d.} = 0.02\ \text{ppm} \tag{5}$$

$$\Delta_{AB}(\text{DBSX}) = 0.49\ \Delta_{AB}(\text{HMPA}) \quad \text{r.m.s.d.} = 0.03\ \text{ppm.} \tag{6}$$

The proportionality constant is in the reverse order to the ratio of dipole moments of the polar substances in contrast to the case of *K*. If the association shifts arise exclusively from the increased polarization of CN group which is induced by the electric-field effect of the partner molecule and which will lead to an electron-density decrease in the phenyl ring,[1] they must clearly be correlated with the dipole moment of the partner molecule. Since this is not the case here, another factor must be taken into account. Thus the magnetic anisotropy effect of the partner molecule may be regarded as having masked the electric-field effect because of the observation of the shift at the *ortho* position.

TABLE 5.—TWO-PARAMETER TREATMENT OF Δ_{AB} BY THE EQUATION $\Delta_{AB} = a\sigma_i + b\sigma_\pi^+ + c$

polar substance	*a*	*b*	*c*	*f*[a]
HMPA	0.46	0.52	0.34	0.11
DBSN	0.21	0.13	0.15	0.04
DBSX	0.18	0.26	0.22	0.08
TMU	0.10	0.29	0.23	0.03

[a] *f* = fitting parameter [see footnote (*a*) in table 3].

In contrast, if the Δ_{AB} are compared in each system of benzonitrile + polar substance, some characteristics are disclosed regarding the μ_{BN}, σ_i and σ_π^+. The two-parameter treatment for σ_i and σ_π^+ is given in table 5, and the resulting coefficients as well as the fitting parameter are shown to be comparable with the previous case.[1] In the present case, as mentioned above, the magnetic anisotropy effect of the partner molecule is considered to contribute to Δ_{AB}. Therefore, the satisfactory results of the two-parameter treatment support the assumption that the anisotropy effect is cancelled out when one considers the substituent effect on Δ_{AB} with the same partner molecule.

Both the ^{1}H and ^{31}P low-field shifts in the Δ_{AB} values (table 3 and 4) are consistent with the increase in intramolecular polarization caused by the association: increased electrical polarization in the polar molecule is enhanced by the neighbouring dipole of the partner molecule.

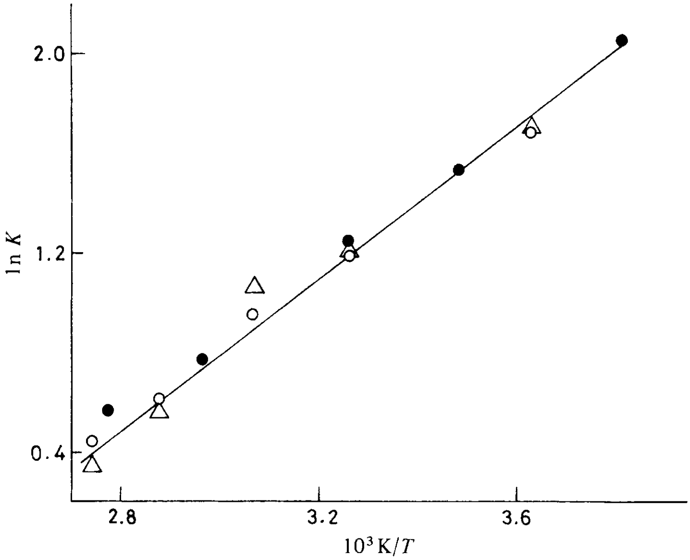


FIG. 2.—van't Hoff plots for the dipole association between *p*-methoxynitrobenzene and HMPA. Association constants are determined from the shift data of the *meta* protons with regard to the nitro group. ○, Run 1; △, run 2; ●, run 3.

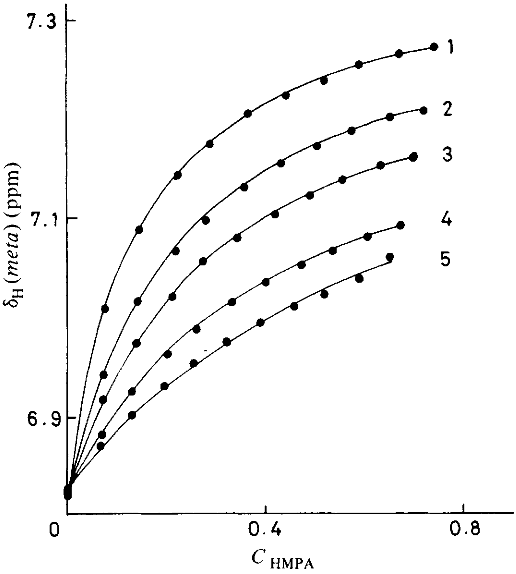


FIG. 3.—Concentration and temperature dependences of the ^{1}H shift of the *meta* protons in the *p*-methoxynitrobenzene+HMPA system in methylcyclohexane. Concentrations are *ca.* 0.03 mol dm^{-3} (constant) for nitrobenzene and *ca.* 0-0.7 mol dm^{-3} for HMPA. Temperature: 1, 262.4; 2, 287.4; 3, 307.2; 4, 337.3; 5, 360.8 K.

THERMODYNAMIC PARAMETERS

Enthalpies (ΔH°) and entropies (ΔS°) of association can be determined from van't Hoff plots after measuring the temperature dependence of the association constants (fig. 2). These plots are obtained from the dependence of the shift on concentration as well as on temperature (fig. 3). It is seen in fig. 3 that the addition of HMPA drastically enhances the temperature dependence of the shift. This phenomenon is readily interpreted as being due to the enhancement or suppression of the association by temperature. The ΔH° values thus derived amount to 7-12 kJ mol^{-1} (table 6), and an enthalpy–entropy compensation relation holds approximately (fig. 4).

The dipole–dipole interaction energy is expressed as:[6]

$$E = -\frac{1}{3kT}\frac{\mu_A^2\mu_B^2}{r^6}. \qquad (6)$$

For the pair HMPA($\mu = 5.54$ D) and nitrobenzene($\mu = 3.93$ D) at 300 K, this energy amounts to -8 kJ mol^{-1} when $r = 5.5$ Å, and to -16 kJ mol^{-1} when $r = 5$ Å; these values are comparable with the enthalpies observed in the present study.

Furthermore, the enthalpies may be regarded as comparable with those reported for the dimers of acetone or acetonitrile, *i.e.* $-(16\text{-}22)$ kJ mol^{-1} in the gas phase;[7] the rather large value for the latter case might be ascribable to a difference in the dielectric constant of the media.

TABLE 6.—ENTHALPIES (ΔH°) AND ENTROPIES (ΔS°) FOR THE ASSOCIATION OF HMPA WITH VARIOUS NITRO AND NITRILE COMPOUNDS IN METHYLCYCLOHEXANE

compounds	$-\Delta H^\circ$/kJ mol^{-1}	$-\Delta S^\circ$/J K^{-1} mol^{-1}
(I) nitrobenzenes (*p*-substituent)		
$N(CH_3)_3$	7.2	16.0
OCH_3	11.9	28.7
CH_3	9.9	29.2
D	8.3	23.1
$OCOCH_3$	10.3	26.0
Cl	9.3	22.8
(II) benzonitriles (*p*-substituent)		
$N(CH_3)_3$	8.3	22.8
OCH_3	11.8	27.1
CH_3	9.5	26.6
$C(CH_3)_3$	9.6	28.7
Cl	8.1	20.4
(III) others		
acetonitrile	11.4	26.7
nitromethane	12.8	26.2
nitroethane	12.4	29.1

Although a definite correlation would be expected from eqn (6) between the ΔH° and μ values, no relations were observable between them. In contrast, a regular relation holds for plots of ΔH° against σ_π^+. These results are similar to the plots of ln K against μ or σ_π^+ in our previous report. Therefore, entropy terms are thought to take part in the association in a regular manner, causing the ΔH°–ΔS° relationship and the similar behaviour for both ln K and ΔH°. For a full understanding of the ΔH°

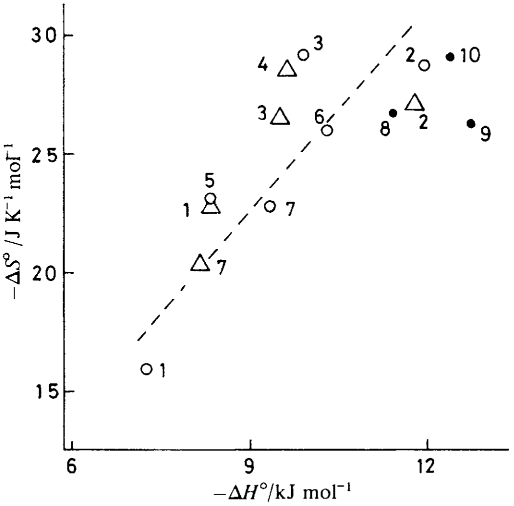


FIG. 4.—Enthalpy–entropy relationship for association between polar molecules. Solvent: methylcyclohexane. Polar substances: ○, *p*-substituted nitrobenzenes; △, *p*-substituted benzonitriles; ●, others (8, acetonitrile; 9, nitromethane; 10, nitroethane). *p*-Substituents; 1, $N(CH_3)_2$; 2, OCH_3; 3, CH_3; 4, $C(CH_3)_3$; 5, D; 6, $OCOCH_3$; 7, Cl.

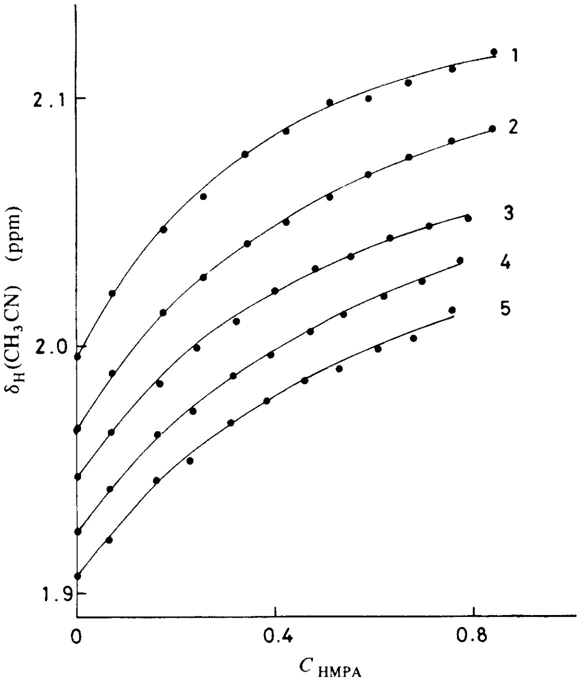


FIG. 5.—Concentration and temperature dependences of the ^{1}H shift of the acetonitrile protons in the acetonitrile+HMPA system in CCl_4. Temperature: 1, 255.3; 2, 280.3; 3, 306.4; 4, 328.3; 5, 344.3 K.

value, a quantitative estimation of the association energy would be necessary which takes into account the multipole interaction as well as that for dispersion. These studies are now underway using molecular-orbital calculations.

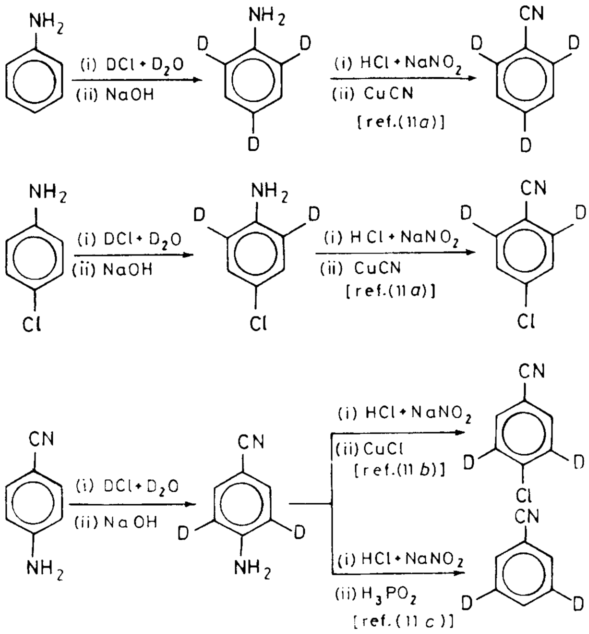
In this report a saturated hydrocarbon is used as solvent. We have found in a thermodynamic study that CCl_4 is not suited as an inert solvent for the present study. That is, the shift of the nitrile compounds does show a significant dependence on temperature even if the interacting partner molecule is excluded from the solution (fig. 5). Such a phenomenon is observable in other systems although reduced to *ca.* $\frac{1}{2}$. These facts suggest that the intermolecular interactions between the polar substances and CCl_4 is considerable. A charge-transfer interaction might be responsible for this.[8] Therefore, for a full interpretation of the data for CCl_4, some investigation of solvation effects caused by the solvent is needed. This will be the subject of a future study.

EXPERIMENTAL

p-tert-butyl- and *p*-*NN*-dimethylamino-benzonitriles were synthesised from *p*-tert-butylbenzoic acid[9] and *p*-chlorobenzonitrile,[10] respectively. Other benzonitriles were of commercial grade. Solid benzonitriles were recrystallized several times and stored over silica gel after drying under vacuum. Liquid ones were distilled over CaH_2 under reduced pressure and stored over molecular sieve 4A. HMPA, DBSN, DBSX and TMU were distilled similarly using BaO as a desiccant and stored over molecular sieve.

N.m.r. spectral measurements were made as in a previous report[1] using methylcyclohexane as solvent. Although the shifts were measured relative to the internal TMS standard, the same results were obtained in the present work when one of the solvent methyl peaks was adopted as the standard.

^{31}P n.m.r. shifts were measured by the ^1H-{^{31}P} INDOR method on a Hitachi R-20 B n.m.r. spectrometer operating at 60 MHz, using a synthesizer (Anritsu MG514C) and an r.f. power



SCHEME 1.—Synthesis of the deuterated benzonitriles.

amplifier (Hitachi R-209 PA); the shifts were determined relative to the internal TMS standard. The temperature used was 34 °C.

Variable-temperature experiments were carried out according to a conventional procedure; the probe temperature was measured with a thermocouple(CC) immersed in methylcyclohexane. The temperature range used was typically *ca.* 0-90 °C. Temperature fluctuations during the shift measurement for over 10 samples were within ± 0.5 °C (in < 2 h). The temperature was varied *ca.* 5 times for each series of the sample preparation, and such measurements were repeated more than twice to test the reproducibility of the experiment. Errors in the measurement of ΔH° and ΔS° were estimated to be ± 0.4 kJ mol^{-1} (5%) and ± 1.2 J K^{-1} mol^{-1} (5%), respectively.

Since *ortho* and *meta* protons in *p*-substituted benzonitriles usually give AA′BB′ spectra, the accurate determination of the absolute shift of both protons is not straightforward. However, the spectral pattern does not vary so much on the addition of the polar substance that the relative variation of the shift (and hence K and A_{AB}) can be determined accurately by the measurement of two intense peaks in both the AA′ and BB′ regions. Exceptionally *p*-chlorobenzonitrile showed spectra of $J/\Delta\delta \simeq 1$ besides the large change in spectral pattern on addition of the polar substance. Accordingly, [*o*,*o*′-$^2H_2$]- and [*m*,*m*′-$^2H_2$]-*p*-chlorobenzonitriles were prepared, and K and Δ_{AB} were determined separately. [*m*,*m*′-$^2H_2$]- and [*o*,*o*′, *p*-$^2H_3$]-benzonitriles were also synthesised to obtain the association parameters for the benzonitriles. The synthesis of these deuterated compounds is shown in scheme 1. A typical run of the acid catalysed H–D exchange reaction of anilines is as follows: 5 g aniline, 20 cm^3 D_2O and 3 cm^3 37% DCl were sealed in an ampoule at *ca.* 10^{-5} Torr using a vacuum line. After heating at 140-150 °C for 40 h check was made of the extent of the deuterium exchange by n.m.r. (*ca.* 90 atom % usually); the aniline was then freed from its deuterochloride by 5% NaOH and extracted 3 times by 50 cm^3 ether. A crude product of the deuterated aniline was obtained (above 95% yield) which was used for the next diazotization reaction, followed by an appropriate treatment to give final products. The acid-catalysed H–D exchange reaction in the evacuated state was found to be very successful because of the lack of any subsidiary oxidation reactions.

The determination of K and Δ_{AB} was made in the same way as in the previous report using a NEAC S-900 computer at the Computation Centre, Osaka University.

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