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HYDROGEN BONDING OF AROMATIC AMINES IN HYDROXYLIC SOLVENTS. PART 1. ABSORPTION SPECTROSCOPY OF SUBSTITUTED ANILINES AND HYDROGEN BOND-INDUCED REHYBRIDIZATION OF TRIVALENT NITROGEN ATOMS*

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The longest wavelength absorption band of substituted anilines containing electron-accepting groups is characterized as an intramolecular charge-transfer (ICT) transition. Dual absorption peaks observed for the ICT transition of some *para*-substituted anilines in a strongly hydrogen-bonding solvent, hexafluoropropan-2-ol (HFP) can be attributed to two inequivalently hydrogen-bonded species with differently hybridized aniline nitrogens in HFP. The hydrogen bond-induced rehybridization causes appreciable changes in the ICT absorption spectra of highly polar aromatic amines. Rehybridization of aromatic amino nitrogens depends on the OH acidity in the solvent molecule and the basicity of the substituted anilines. The geometry of trivalent nitrogens in aryl amines is critically dependent upon the ionization potential of the amino group, the electron affinity of the electron-accepting substituent and the substitution site of the electron-withdrawing group with respect to the amino moiety.

INTRODUCTION

The electronic structure of conjugated systems consisting of an electron-donor and an electron-acceptor moiety have been extensively studied from the viewpoint of intramolecular charge-transfer (ICT) interactions.[1-7] The concept of ICT excitation, originally proposed by Nagakura, Tanaka and co-workers,[1,2] has been applied to the interpretation of absorption spectra for substituted benzenes and many related phenomena. For example, the photochemical reactivity of amino-substituted benzophenones can be rationalized in terms of ICT.[8] The formation of a twisted intramolecular charge-transfer (TICT) state has been widely postulated in the explanation of dual fluorescence of *p*-*N*,*N*-dimethylaminobenzonitrile and related species,[9,10] which can be regarded as one of the most important extensions of the ICT concept. Shake-up satellites of the ICT nature have been identified in nitro-N 1s core electron spectra observed for *p*-nitroanilines and derivatives.[11] The concept of ICT also plays an important role in designing luminescent substances (e.g. laser dyes[12]) and organic crystals for second harmonic generation.[13]

The stereochemistry of trivalent nitrogen atoms in the aromatic amines has been of great interest for a long time.[14-30] A variety of spectroscopic techniques have been applied to investigate the properties of aniline and derivatives: rotational,[25,26] vibrational,[22,27] electronic absorption,[14-21] fluorescence[29] and VUV photoelectron[30] spectroscopy. In addition, measurements of dipole moment,[31,32] polarizability[33] and x-ray diffraction of crystals[34] have been employed for structural analysis. These studies provide indirect or direct evidence for the non-planarity of aniline in the vapour,[25,26] liquid[22,27] and crystalline[34] phases. Aniline is a non-planar molecule whose dihedral angle between the plane of the amino group and the aromatic ring is

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* This paper is dedicated to Professor Jiro Tanaka on the occasion of his 63rd birthday.
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ca 40°. The energy barrier to inversion has been evaluated from analysis of the vibrational[28] and fluorescence[29] spectra. A number of papers have reported molecular orbital calculations for the molecular structure and the inversion barrier of aniline and derivatives.[35–42] The calculated results are in qualitative and sometimes quantitative agreement with the experimental observations.

The planarity of aniline is increased on the introduction of an electron-withdrawing substituent into the *para* position with regard to the amino group and is further increased by strengthening the electron-accepting ability of the *para* substituent.[22,24,33,35,36,38] Alkylation of the amino nitrogen is another way of increasing the planarity.[40,42] As determined by x-ray analysis, *p*-nitroaniline,[43] *p*-*N*-methylnitroaniline[13] and *p*-*N*,*N*-dimethylnitroaniline[44] are non-planar in the crystalline phase, although they are nearly planar. In all cases the amino moiety is rotated out of the aromatic plane. The twist angles are 10·6° for *p*-nitroaniline,[43] 2·0° for *p*-*N*-methylnitroaniline[13] and 7·3° for *p*-*N*,*N*-dimethylnitroaniline.[44] In contrast, the nitro group is almost completely coplanar with the phenyl ring.

It has been indicated that the nitrogen atom in *N*-methylindoline (*N*-methyl-2,3-dihydroindole) may be either hybridized like sp^2 (planar) or like sp^3 (pyramidal).[20] Maier and Turner[30] pointed out that the geometry around the N atom is pyramidal in the case of indoline. It has been suggested that two structurally inequivalent species exist at equilibrium in the ground state of 5-cyano-*N*-methylindoline (5CMI).[24] One of the two interpretations given in Ref. 24 is based on the hybridization of the amino nitrogen. The aromatic amines studied in this work are more or less closely related to 5CMI.

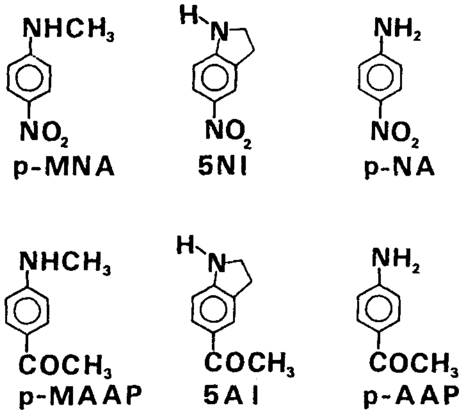
It is well known that the geometry of aromatic amines is determined by a variety of factors affecting the potential energy of the aryl amines.[21,35,36,38] The optimum configuration is a compromise between the intrinsic tendency of trivalent nitrogens to be pyramidal and the expected tendency in conjugated systems to assume a planar configuration in order to maximize the resonance interaction with the aromatic nucleus. Therefore, the amino moiety is pyramidal or coplanar with respect to the aromatic plane, depending on the nature of the ligands on the nitrogen atom and substituents bonded to the aromatic ring. Several papers have described the correlation between the physico-chemical properties of *p*-nitroanilines and hybridization of the amino nitrogen.[22,45–49]

Hydrogen-bonding (HB) effects on the electronic spectra of aniline and derivatives have been studied by many workers.[31,46–56] On changing the solvent from methanol or ethanol to water, anomalous blue shifts of absorption maxima have been observed for aniline,[51,53,56] *N*,*N*-dimethylaniline,[50] *m*-aminoacetophenone,[56] *p*-aminoacetophenone[51,55] and *m*-nitroaniline.[56] This paper is mainly concerned with the anomalous behaviour of the ICT bands of highly polar anilines in a strongly hydrogen-bonding solvent, hexafluoropropan-2-ol (HFP).[57]

EXPERIMENTAL

The compounds studied included 15 *para*-disubstituted benzenes, *p*-D-C_6H_4-A, where D = NH_2, NCH_3 and $N(CH_3)_2$ and A = CN, COOH, $COCH_3$, COC_6H_5 and NO_2). Other related species are indoline-5-carboxylic acid (5CI), *p*-aminopropiophenone (D = NH_2 and A = COC_2H_5), 5-acetylindoline (5AI), 4-nitro-2-methylaniline (pNoT) and 5-nitroindoline (5NI). *Meta*-substituted aniline and related species examined were *m*-D-C_6H_4-A, where D = NH_2 and $N(CH_3)_2$ and A = COOH, $COCH_3$ and NO_2, and 6-nitroindoline. The structures of some sample molecules are shown in Chart 1.

Most of the chemicals studied were commercially available. *N*-Methylamino-substituted derivatives were synthesized by the photo-oxidative demethylation of the corresponding *N*,*N*-dimethylamino compounds.[58] 5AI was obtained by the photo-Fries rearrangement of *N*-acetylindoline in acetone.[59] 5CI was prepared via the haloform reaction of *N*-acetyl-5AI. Electronic absorption spectra were measured on a Hitachi U-3200 spectrophotometer. The concentration of the aromatic solute was changed from *ca* 2×10^{-5} to 10^{-3} M and that of cyclodextrin (CDx) was *ca* 10^{-2} M. α-Cyclodextrin was added to aqueous solutions of *p*-amino-substituted benzenes and β-CDx to other aqueous solutions. Vibrational spectra were recorded on a Shimadzu IR-460 spectrophotometer.


p-MNA 5NI p-NA

p-MAAP 5AI p-AAP

Chart 1

RESULTS AND DISCUSSION

Absorption properties of *para*-substituted anilines

Absorption spectral data for a series of *para*-substituted anilines are summarized in Tables 1–3. From Table 1 it can be seen that a red shift of the ICT band is observed with an increase in the ICT interaction (e.g. methylation of the amino group or substitution of the electron-accepting group with a higher electron affinity). *Para*-substituted anilines in propan-2-ol (IP) undergo gradual red shifts of the absorption maxima and intensification of the ICT bands on methylation of the amino group. However, the spectral behaviour in polyfluorinated alcohols [trifluoroethanol (TFE) and HFP] is complicated. From Table 1, a distinctly different behaviour for the amino and *N,N*-dialkylamino compounds can be seen. The absorption maxima of the ICT transition for the NH_2 derivatives are dependent on the solvents and decrease in the following order: IP > HFP–IP (1:1, v/v, mixture of HFP and IP) > TFE > HFP. On the other hand, those for the $N(CH_3)_2$ derivatives increase in the opposite order: IP < HFP–IP (1:1) < TFE < HFP. The spectral changes observed on changing the solvent from IP to HFP can be summarized as follows: (1) conspicuous blue shifts of absorption maxima with deformation of band shape for the NH_2 compounds with A = CN, COOH, $COCH_3$ COC_2H_5 or COC_6H_5; (2) appearance of an anomalously broadened peak or double peaks for *p*-nitroaniline, pNoT, the $NHCH_3$ compounds with A = COOH, $COCH_3$ or COC_6H_5 and indoline derivatives (5CI, 5AI and 5NI); and (3) large red shifts of the absorption maxima with a normal or slightly deformed band shape for the $N(CH_3)_2$ compounds (see Table 1 and Figures 1 and 2).

Absorption spectra of *p*-nitroaniline and related species in HFP are shown in Figure 2. *p*-Nitroaniline is an exception, since it is the only NH_2 compound whose absorption band is abnormally broadened. The absorption band of 5NI is similar to that of *p*-nitroaniline in that they are abnormally broadended or double peaked. On the other hand, the corresponding *N*-methylated or *N,N*-dimethylated nitroanilines

Table 1. Absorption maxima and molar extinction coefficients for *para*-substituted anilines $[p\text{-}(H_3C)_xNH_{2-x}C_6H_4A]$ and related compounds[a]

Compound	*x*	IP	HFP–IP	TFE	HFP	Shift
Benzonitrile (A = CN)	0	276·6 (2·13)	269·0 (1·99)	263·0 (1·75)	251·0 (1·73)	B
	1	284·2 (2·56)	281·6 (2·48)	280·6 (2·23)	276·4 (1·53)	B
	2	291·4 (2·65)	298·0 (2·93)	298·8 (2·89)	300·4 (2·39)	R
Benzoic acid (A = COOH)	0	288·8 (1·62)	279·2 (1·56)	269·2 (1·32)	261·0 (1·49)	B
	1	301·6 (2·24)	303·2 (2·14)	301·8 (1·77)	308·0 (1·04)	AN
					280·0 (1·18)	AN
	2	305·0 (2·24)	313·0 (1·93)	314·8 (2·21)	324·0 (1·31)	R
5CI		305·6 (1·57)		288·8 (1·14)	270·8 (1·05)	B
Acetophenone (A = $COCH_3$)	0	317·0 (2·03)	309·4 (1·57)	297·8 (1·41)	282·2 (1·45)	B
	1	329·6 (2·52)	330·2 (2·71)	331·8 (2·67)	337·2 (1·38)	AN
					301·5 (0·98)	AN
	2	332·0 (2·53)	341·2 (2·71)	344·6 (2·82)	355·2 (2·17)	R
5AI		336·6 (2·21)	334·6 (1·46)	313·8 (1·13)	303·4 (1·28)	AN
					Sh. 360 (0·30)	AN
Propiophenone (A = COC_2H_5)	0	316·4 (2·25)	305·0 (1·37)	294·2 (1·15)	277·8 (1·36)	B
Benzophenone (A = COC_6H_5)	0	335·2 (1·80)	327·4 (1·46)	318·0 (1·39)	296·6 (1·44)	B
	1	348·0 (2·09)	350·2 (2·21)	353·0 (2·02)	362·4 (1·57)	AN
	2	350·6 (2·27)	362·6 (2·52)	366·8 (2·38)	381·0 (2·53)	R
Nitrobenzene (A = NO_2)	0	376·2 (1·69)	370·0 (1·46)	367·4 (1·15)	362·6 (0·88)	AN
	1	386·0 (1·82)	394·0 (1·83)	396·6 (1·76)	409·6 (2·05)	R
	2	386·0 (1·94)	407·6 (2·18)	413·8 (2·28)	431·6 (2·32)	R
5NI		400·6 (1·60)	411·2 (1·54)	414·2 (1·33)	431·6 (1·02)	AN
					362·2 (0·65)	AN
pNoT		378·0 (1·55)			381·2 (0·95)	AN
					Sh. 350 (0·88)	AN

[a] Absorption maxima are given in nm. The numbers in parentheses are the molar extinction coefficients (10^4 l mol^{-1} cm^{-1}). The number of methyl groups on the anilino nitrogen is indicated by *x*, i.e. NH_2 (0), $NHCH_3$ (1) and $N(CH_3)_2$ (2). IP propanol-2-ol; HFP–IP = 1:1 (v/v) mixed solvent; HFP = hexafluoropropan-2-ol; 5CI = indoline-5-carboxylic acid; 5AI = 5-acetylindoline; 5NI = 5-nitroinodoline; pNoT = 2-methyl-4-nitroaniline. Sh. means a shoulder on a stronger band. Shift: spectral shift on going from IP to HFP. B (blue shift): the pyramidal form is dominant in HFP (See text). AN: anomalously broadened peak or double peaks in HFP. A comparable amount of each species co-exists at equilibrium in HFP. R (red shift): the planar form is dominant in HFP.

Table 2. Spectral data in water for *para*-substituted anilines, *p*-AC_6H_4D, and corresponding indoline derivatives[a]

A	D	max.	ε	FWHM	Shift
NH_2	CN	270·0	1·98	5240	B
$NHCH_3$	CN	283·8		4960	B
$N(CH_3)_2$	CN	296·9		4760	R
NH_2	COOH	276·7	1·40	6360	B
$NHCH_3$	COOH	295·8		6360	B
$N(CH_3)_2$	COOH	304·4		6550	R
NH_2	$COCH_3$	311·2	1·65	5840	B
$NHCH_3$	$COCH_3$	332·2		4920	R
$N(CH_3)_2$	$COCH_3$	345·8		4280	R
5AI		329·6	1·44	6010	B
NH_2	COC_6H_5	332·0		4230	R
$NHCH_3$	COC_6H_5	353·4		4810	R
$N(CH_3)_2$	COC_6H_5	368·4		4200	R
NH_2	NO_2	380·0	1·30	6160	R
$NHCH_3$	NO_2	407·2		4840	R
$N(CH_3)_2$	NO_2	423·8		4410	R
5NI		420·8	1·24	6080	R

[a] FWHM = full width at half maximum in (cm^{-1}); ε = molar extinction coefficient in ($10^4\ l\ mol^{-1}\ cm^{-1}$); Max. = absorption maxima (nm). Shift: spectral shifts observed on going from IP to water; B = blue shift and R = red shift.

exhibit normal band shapes. These findings can be correlated with the aniline basicity.[45] From the fact that *p*-nitroaniline (*p*-NA) is a stronger base than *p*-*N*-methylnitroaniline (*p*-MNA) and *p*-*N*,*N*-dimethylnitroaniline (*p*-DMANA),[45] *p*-NA is much more sensitive to a strong proton donor such as HFP. A simple single band observed for the *N*-methylated *p*-nitroanilines suggests that there is only one dominant species in HFP. Since *N*-methylated *p*-nitroanilines are almost planar in the crystalline phase,[13,44] they may take a nearly planar structure in alcoholic solvents. In contrast, it can be inferred that there are two different species at equilibrium for 5NI in HFP. The rotation about the C(aromatic ring)—N bond is impossible for the indoline derivative owing to the intramolecular bridge formation. Thus the anomalous dual peaks cannot be explained in terms of the presence of a planar species and a twisted form. Instead, it is plausible to assume a shallow pyramid and a nearly planar form.

Absorption spectra of *p*-amino-substituted acetophenones (NH_2, *p*-AAP; $NHCH_3$, *p*-MAAP; and $N(CH_3)_2$, *p*-DMAAP) are more or less closely related to that of 5-acetylindoline (5AI). Distinct double peaks are observed for both *p*-MAAP and 5AI. The long-wavelength component in the doublet is intensified in the order *p*-AAP < 5AI < *p*-MAAP < *p*-DMAAP. It is interesting that the spectral shape observed for 5AI is more similar to that of *p*-AAP than to that of *p*-MAAP. It can be concluded that 5AI also exists in two forms, one a shallow pyramid and the other a nearly planar structure.

Absorption spectra of *p*-aminobenzoic acids are also related to those of *p*-aminoacetophenones. Indoline-5-carboxylic acid (5CI) in HFP exhibits a spectral behaviour similar to that of *p*-aminobenzoic acid. Distinct double peaks are observed for *p*-*N*-methylaminobenzoic acid in HFP. The short-wavelength component in the doublet for *p*-*N*-methylaminobenzoic acid is more intense than that for the corresponding *p*-*N*-methylaminoacetophenone. This difference can be attributed to the differing electron affinity of the *para* substituent.

Negligibly small spectral differences are noticeable

Table 3. Effects of CDx on the spectral behaviour of *p*-DC_6H_4A and 5-substituted indolines[a]

D/A	CDx	FWHM	Max.
NH_2/CN	α-	5140	273·8
$N(CH_3)_2/CN$	β-	4560	300·1
$NH_2/COOH$	α-	5970	281·9
$NHCH_3/COOH$	β-	5770	298·2
$N(CH_3)_2/COOH$	β-	5170	311·8
$NH_2/COCH_3$	α-	5790	312·6
5AI	β-	5700	331·8
NH_2/NO_2	α-	4650	398·0
5NI	β-	4770	428·2

[a] FWHM = full width at half maximum (cm^{-1}); Max. = absorption maxima (nm).

among the spectra observed in methanol, ethanol and propan-2-ol. The ICT band shapes in non-fluorinated alcohols are essentially the same, whereas those in the fluorinated alcohols largely depend on the number of trifluoromethyl groups. The absorption spectra change drastically on going from TFE to HFP in some cases.

It is noteworthy that anomalous dual peaks are clearly observed only in neat HFP. In the 1:1 mixture of IP and HFP, only a single absorption peak is observed for the $NHCH_3$ compounds which exhibit dual absorption bands in pure HFP. The absorption spectra in TFE are very close to those observed in the 1:1 mixture of IP

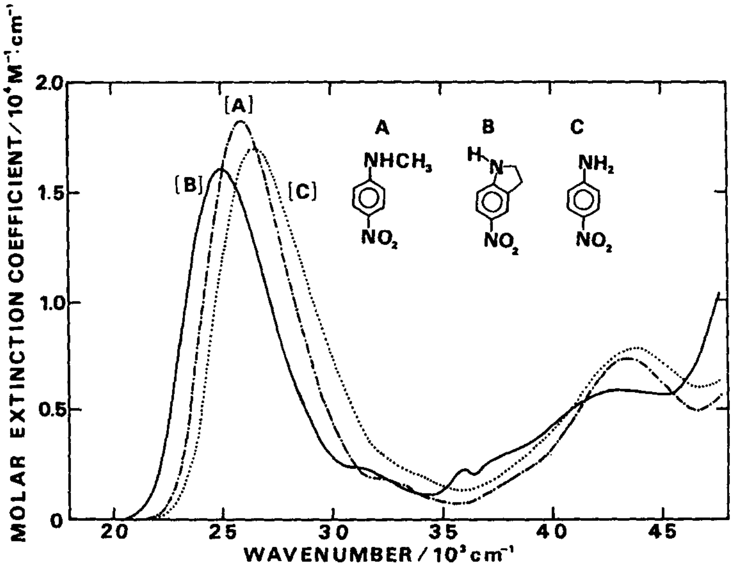


Figure 1. Absorption spectra in IP. (A) *p*-*N*-methylnitroaniline; (B) 5-nitroindoline; (C) *p*-nitroaniline

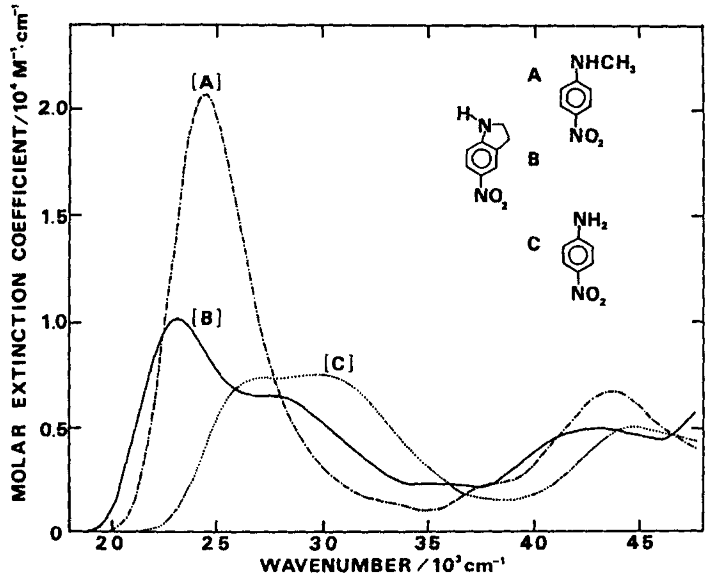


Figure 2. Absorption spectra in HFP. (A) *p*-*N*-methylnitroaniline; (B) 5-nitroindoline; (C) *p*-nitroaniline

and HFP. It is also noted that the integrated absorption intensity of the ICT band is approximately constant for all solvents regardless of the absorption band shapes.

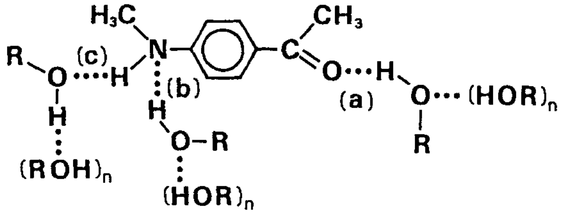
In order to understand the unusual dual peaks, the occurrence of the following should be clarified: (1) an intramolecular phenomenon (e.g. the presence of stable conformers), (2) a solute–solute interaction (e.g. dimer formation in the ground state) or (3) a solute–solvent interaction. Dimer formation in the ground state can be ruled out because the absorption spectra are independent of the solute concentration. Therefore, it is concluded that the doublet structure in the absorption spectra arises from structurally inequivalent species. Some specific solute–solvent interactions will be considered in terms of correlations between solvent properties and spectral behaviour in the following section.

Properties of solvent molecules and hydrogen-bonding (HB) effects on absorption spectra

The pK_a values increase in the order[60,61] HFP (9·3) < TFE (12·3) < IP (18) and the dielectric constants decrease in the order[62,63] TFE (26·7) > IP (19·92) > HFP (16·7). The first ionization energies increase in the order[64] IP < TFE < HFP. The increased ionization potential of the oxygen non-bonding electrons means weakening of the oxygen basicity. Because the self-association of alcohols in pure liquids is dependent on the basicity of the oxygen atom, the fluorinated alcohols are more unlikely to self-associate than the corresponding hydrocarbon alcohols.[65] The pK_a values indicate that HFP can serve as a strong proton donor, whereas HFP and TFE may not act as proton acceptors.[48]

The band width of ICT transitions is critically dependent on the number of trifluoromethyl groups in the solvent molecule or pK_a. This indicates that the abnormal behaviour is closely related to the HB ability of alcohols. The dielectric constants of methanol, ethanol, propan-2-ol, TFE and HFP do not show any significant correlation with the observed spectral shifts. The spectral features for highly polar aromatic amines in polyfluorinated alcohols can be mainly due to the HB interactions rather than to dipole–dipole interactions or the electronic polarization effect of solvents.

Since the electrostatic and charge-transfer interactions are of major importance in hydrogen-bond formation,[66–72] these interactions should be taken into account to explain the observed spectral features. It has been reported that there are three different types of HB for *p*-aminoacetophenone in alcoholic media.[55] These three modes of HB are described in Scheme 1. The configuration of the solvent molecules relative to the solute molecule should remain unchanged in the Franck–Condon excited state.[73] In this excited state the hydrogen bonds of types (a) and (c) are considered to be stabilized compared with the ground state and hence to cause a red shift, whereas the type (b) HB causes a blue shift because it is more destabilized than in the ground state.[53] The strongly hydrogen-bonding solvent HFP exerts a specific influence on the amino group through the type (b) HB, reducing its electron-donating ability (i.e. increasing the effective ionization potential of the amine moiety) and thereby reducing the magnitude of the ICT interaction within the solute molecule. In HFP type (c) HB may play no important role in comparison with type (a) or (b) HB. By analogy with the results obtained for the indoline derivatives, the double peaks observed for *p*-*N*-methylaminoacetophenone in HFP are explained in terms of the equilibrium between the less coplanar form and the nearly planar structure with regard to the amino moiety and the phenyl ring. The former corresponds to the blue-shifted component in the doublet and the latter to the red-shifted component.



Scheme 1

Hydrogen bonding at the carbonyl moiety may be identified by measuring the vibrational spectrum of *p*-MAAP in the C=O stretching frequency region. Broadening and intensification of the carbonyl band around 1600 cm^{-1} was observed on going from IP to HFP. Intensification in the lower frequency side suggests the formation of a hydrogen bond involving the C=O group. Similar spectral changes were also detected in the case of 5AI on going from IP to HFP. However, the observed spectral changes are much more drastic for 5AI than for *p*-MAAP. This indicates that the hydrogen bonding with HFP is stronger in 5AI than in *p*-MAAP.

On going from IP to HFP, *p*-*N*-methylnitroaniline (*p*-MNA) undergoes a red shift, whereas *p*-MAAP exhibits double peaks in HFP. This spectral difference can be explained in terms of the hydrogen bonding ability of the electron-accepting group (NO_2 or C=O) and the amino moiety. Although HB between the nitro group and OH moiety has been detected in alcohol solutions,[47] this HB interaction is generally smaller than the interaction between a carbonyl substituent and OH group because of low hydrogen-accepting ability of the nitro group.[66b] The conjugation between the anilino group and the acceptor substituent is stronger in *p*-MNA than in *p*-MAAP. Consequently, *p*-MNA is a weaker base than *p*-MAAP. Both the amino and the electron–acceptor group of *p*-MNA are weaker in hydrogen-bonding ability than those of *p*-MAAP.

Scheme 1 is only a simplified description because the hydrogen bonds are formed among the solute molecule and a cluster of solvent molecules. The type (b) HB may be strengthened by the cooperative interaction among the alcohol molecules in the hydrogen-bonding chain.[47,53] In connection with this scheme, it should be noted that HFP is a rather exotic solvent. The nature of mixed solvents consisting of IP and HFP is mainly governed by the IP content (see later).

It is possible to estimate the magnitude of energies associated with the 1:1 complex formation involving a strong OH···N hydrogen bond. Enthalpy changes due to the hydrogen-bond formation between HFP and nitrogen lone-pair donors are evaluated to be 9·7 ± 1·5 kcal/mol^{-1} (1 kcal = 4·184 kJ) (an average obtained from seven values reported in Ref. 74). This value is about twice as large as the enthalpy change commonly observed for OH···N hydrogen bonds.[75] The energy of the internal hydrogen bond of OH···F in TFE is evaluated to be 3·3 kcal mol^{-1}.[76] Therefore, as far as the 1:1 complex is concerned, the enthalpy change is estimated to be *ca.* 6 kcal mol^{-1} for the formation of an HFP···N lone pair hydrogen bond. On the other hand, the energy change due to the rehybridization of nitrogen from pyramidal to planar is 1·5–1·6 kcal mol^{-1} for aniline[28,29] and the resonance energy of aniline is considered to be about 6 kcal mol^{-1}.[17] Therefore, the destabilization associated with the structural change may be smaller than 8 kcal mol^{-1} in view of the minor change from the shallow pyramid to the planar form. Taking these values into account, it is reasonable to assume that the energy change associated with the rehybridization on the formation of a strong hydrogen bond is of the order of 1 kcal mol^{-1}, which is comparable to the thermal energy at room temperature. In other words, it is reasonable to assume two structurally inequivalent hydrogen-bonded species in the ground state of the *para*-substituted anilines in HFP.

Methylation of the amino group counteracts the HB effect of HFP, which causes a blue shift. In fact, on going from *p*-*N*-methylaminoacetopheone to *p*-*N*,*N*-dimethylaminoacetophenone, the long-wavelength component is intensified and the short-wavelength peak is weakened to become a tailing. This phenomenon can be interpreted in terms of the increase in the population of the nearly planar hydrogen-bonded species and the decrease in the population of the slightly pyramidal hydrogen-bonded species. The increase in population of the planar hydrogen-bonded species may be related to the increased dipole moment in the ground state caused by further *N*-methylation. The literature values of the dipole moment in the ground state are 4·45 D for *p*-aminoacetophenone and 5·09 D for *p*-*N*,*N*-dimethylaminoacetophenone.[77] The augmentation of the dipole moment enhances the electron density at the carbonyl oxygen and thereby strengthens the type (a) HB. Spectral changes observed for *p*-aminobenzoic acids and *p*-aminobenzophenones are similar to those observed for *p*-aminoacetophenones and can be explained in the same manner as described above. The spectral behaviour of other species listed in Table 2 can also be interpreted in terms of the equilibrium between the pyramidal and the planar forms.

As far as the anomaly observed for the indoline derivatives is concerned, the nonplanarity caused by the rotation about C(phenyl ring)-N bond is negligible. On the other hand in the case of non-rigidized anilines, after a small angle twisting the N atom may achieve further stabilization by becoming more pyramidal in strongly hydrogen-bonding media. A similar hydrogen-bond induced twisting of the amino group has been suggested by Dearden and Forbes[51b] on the basis of steric effects.

Comparison of the absorption spectral properties of *para* isomers with those of *meta* isomers

It is interesting to note the spectral difference between

Table 4. Absorption maxima (nm) for the *meta* isomer, *m*-$\mathrm{DC_6H_4A}$, and 6-nitroindoline (6NI)[a]

D	A	Max. ($\mathrm{H_2O}$)	Shift	Max. (IP)	Max. (HFP)
$\mathrm{NH_2}$	COOH	305·8	B	319·8	299·2
$\mathrm{N(CH_3)_2}$	COOH	311·0	B	339·0	(no CT band)
$\mathrm{NH_2}$	$\mathrm{COCH_3}$	327·0	B	341·4	310·0
$\mathrm{N(CH_3)_2}$	$\mathrm{COCH_3}$	340·0	B	361·6	310·4
$\mathrm{NH_2}$	$\mathrm{NO_2}$	358·4	B	374·6	331·6
$\mathrm{N(CH_3)_2}$	$\mathrm{NO_2}$	387·6	B	398·8	*ca* 350[b] *ca* 450[b]
6NI		377·0	B	394·0	346·8

[a] 6NI = 6-nitroindoline; Max. = absorption maxima (nm). Shift: spectral shift observed on changing the solvent from IP to water; B = (blue shift).

[b] Two shoulders overlapped to the stronger band on the shorter wavelength side.

the *para* and the *meta* isomers. It is generally concluded that the *meta* isomer is less polar than the corresponding *para* series from the theoretical consideration that the mutual conjugation is very much larger in the *para* series than in the *meta* isomer.[16] The decrease in the ICT interaction corresponds to the increase in the amine basicity. Therefore, it is expected that the *meta* isomer undergoes a blue shift on going from IP to water or HFP. The observed results summarized in Table 4 are in accordance with this expectation.

The spectral properties observed for *m*- and *p*-*N*,*N*-dimethylaminoacetophenone can be compared with the molecular orbital calculations obtained by a simple composite-molecule method.[6] The contribution of charge-transfer configurations in the ground state is larger for the *para* isomer than for the *meta* isomer.[6] The theoretical calculations are consistent with the present findings, especially with the blue shift for less polar species.

m-*N*,*N*-Dimethylnitroaniline (*m*-DMANA) is not planar in the crystalline state, the amino group being rotated from the phenyl ring by 8·5°.[78] It exhibits double absorption peaks in HFP, whereas a simple single band is observed for *N*,*N*-dimethylated *p*-nitroaniline (*p*-DMANA). This different behaviour can be ascribed to the base strength of substituted anilines containing electron-accepting groups. It is well known that *m*-nitroaniline is a stronger base than the corresponding *para* isomer.[79] The spectral anomaly is observed for bases stronger than *p*-DMANA, namely for *p*-nitroaniline and *m*-DMANA.

The ICT band intensity of *m*-*N*,*N*-dimethylaminobenzoic acid (*m*-DMABA) is considerably diminished in pure HFP owing to protonation of the amino moiety, because the absorption spectrum of *m*-DMABA in HFP is very close to that of benzoic acid in the same solvent. It is noteworthy that the corresponding *para* isomer exhibits a slightly deformed absorption band with a red-shifted maximum in HFP. *p*-*N*,*N*-Dimethylaminobenzoic acid (*p*-DMABA) is a weaker base than *m*-DMABA. HFP acts as an acid toward *m*-DMABA, whereas it acts as a highly polar alcohol toward *p*-DMABA. This considerably different basicity may be due to differing hybridization on the amino nitrogens. Protonation of the amino moiety in *m*-DMABA clearly shows that the complete rehybridization takes place from the shallow pyramid to the sp^3 hybridized configuration. This finding also supports our view on the HB effects on electronic spectra. In addition, the normal ICT band with an absorption maximum at 342·2 nm was observed for *m*-DMABA in the HFP–IP (1:1) mixed solvent. Dilution of pure HFP by IP prevents the protonation of the anilino nitrogen in *m*-DMABA.

Spectral comparison of 5-substituted indolines and *para*-substituted *N*-methylanilines

The photoelectron spectra of *N*-alkylated anilines and indoline are very similar.[30] The first ionization energies are almost the same: 7·65 eV for *N*-methylaniline and 7·67 eV for indoline.[30] Therefore, it is expected that there may be similarity in absorption properties for the *para*-substituted *N*-methylanilines and the corresponding indolines. This is the case for the spectra in IP solutions. However, the absorption behaviour of the 5-substituted indolines (5CI, 5AI and 5NI) in HFP is more closely related to that of the *para*-substituted aniline than that of the corresponding *N*-methylanilines (*p*-*N*-methylaminobenzoic acid, *p*-*N*-methylaminoacetophenone and *p*-*N*-methylnitroaniline). The indoline derivatives exhibit dual absorption peaks on going from IP to HFP. The observed absorption changes from IP to HFP are larger for the indolines than for the *N*-methylanilines. This can be explained in terms of the pK_a difference between the two series. The pK_a values for indoline and *N*-methylaniline are 4·97 and 4·39, respectively.[80] Replacement of *p*-H by an appropriate electron-withdrawing group makes the aromatic amines less basic. The decrease in basicity is mainly due to electronic effects (extended delocalization) and partly to the rehybridization of the nitrogen atoms in the 5-substituted indolines and the *N*-methylanilines. The steric constraint is greater in the former than in the latter.

Table 5. pK_a values of anilinium ions[a]

A/D	*p*-NH_2	*p*-$NHCH_3$	*p*-$N(CH_3)_2$	*m*-NH_2	*m*-$N(CH_3)_2$
CN	1·71 [81]		1·78 [82]	2·73 [81]	2·97 [82]
	1·74 [82]			2·75 [82]	
COOH	2·36 [83]			3·08 [83]	
	2·54 [84]			3·17 [84]	
$COCH_3$	2·19 [81]			3·56 [81]	
	2·29 [84]				
NO_2	0·96 [81]	0·55 [45]	0·61 [82]	2·45 [81]	2·63 [82]
	0·97 [45]		0·65 [45]	2·47 [82]	

[a] Numbers in brackets are literature references.

Therefore, the pK_a difference is enhanced on introduction of an electron-accepting substituent. This is consistent with the conclusion derived from the analysis of the NH stretching vibrational frequency.[23] Butt and Topsom[23] pointed out that hybridization at the nitrogen atom in 5-substituted indolines is different from that in the corresponding *para*-substituted *N*-methylanilines from the correlation between the NH stretching frequency and the Hammett substituent constant. The data on basicity may support the interpretation based on the inequivalent hybridization.

Absorption spectra in aqueous media

Spectral data observed for aqueous solutions are listed in Tables 2–4. A decrease in molar extinction coefficients has frequently been observed for *para*-substituted anilines in water[51] (compare the data in Tables 1 and 2). The large band widths in aqueous media are attributable to an ensemble of solute-solvent adducts. The decreased absorption coefficient is intimately associated with the increase in the band width (full width at half maximum) for the ICT transitions, thereby resulting in approximate constancy of the integrated absorption intensity. Addition of cyclodextrins to the aqueous solutions causes a decrease in the band width. This results from the decreased population of fully hydrogen-bonded species in water.

A similar decrease in the molar extinction coefficient has been reported for *N*-(*p*-nitrophenyl)aziridine in water.[46] In addition, a 3 nm hypsochromic shift of the absorption maximum has been observed for the aziridine in TFE relative to that in cyclohexane.[46] These observations may be characteristic of the aniline nitrogen, which is nearly sp^3 hybridized. The present findings for *para*-substituted anilines in water and the polyfluorinated alcohols are similar to those observed for *N*-(*p*-nitrophenyl)methylenimines.[46] Therefore, it can be generally concluded that when the aromatic amino nitrogen takes a pyramidal structure, a hypsochromic shift is expected together with a decrease in the extinction coefficient on going from the hydrocarbon alcohols to the polyfluorinated alcohols or water. Although the spectral band widths are increased in aqueous solutions, distinct double peaks have not so far been observed. This different behaviour from that in HFP is attributable to a lower acidity of the water OH group in comparison with the HFP hydroxyl group. It should be noted that, apart from this difference, the spectral shift observed on going from IP to water is similar to that on going from IP to HFP, namely the blue shift observed for the *para*-substituted anilines is switched to a red shift on further methylation of the nitrogen atom, e.g. on methylation of *p*-AAP to *p*-MAAP.

For the NH_2 and $NHCH_3$ compounds the NH stretching vibrational frequency can be used as a measure for pK_a values of the corresponding conjugate acids.[22] In addition, it has been pointed out that there is a good correlation between the NH stretching force constant and the s character in the hybridization state of the amino nitrogen atom.[22] This study has elucidated that the molecular planarity is one of the critical factors determining the spectral behaviour in HFP. In other words, the spectral behaviour may be correlated with the amine basicity (pK_as of the corresponding anilinium ions) or hydrogen-bonding ability. Some pK_a values taken from the literature are given in Table 5. Table 5 shows that the *meta* isomer is more basic than the corresponding *para* isomer. Since enhanced basicity corresponds to an increased s character in the amino nitrogen, the *para* isomer is more planar than the *meta* isomer. This means that the planar nitrogen is weaker in hydrogen-accepting ability. Red shifts in water are observed for the less basic *para*-substituted anilines (e.g. *p*-nitroaniline), whereas blue shifts in water are observed for the *meta*-substituted anilines (e.g. *m*-nitroaniline). This suggests that the blue shift is caused by stronger HB effects which give rise to a larger pyramidalization and that the observed red shifts are attributable to the solvent effects due to the high dielectric constant of water, which overrides the hydrogen-bonding effects.

Proton transfer and hydrogen bonding in binary and ternary systems

It was found that protonation takes place at the amino group of *N,N*-dimethylaniline ($pK_a = 5{\cdot}07$[82]) in HFP because its absorption spectrum contains a vibrational structure similar to that observed in the lowest energy transition of benzene or toluene. This is an example of extremely strong hydrogen bonds. In this case protonation is impeded on dilution of HFP by IP. In the 1:1 mixed solvent, the absorption maxima of DMA are more blue shifted than in methanol: 242·4 and 284 nm (shoulder) in HFP–IP (1:1) and 251·0 and 298·0 nm in methanol.[21,50] Ion-pair formation similar to the present observation has been reported for 2,4,6-trinitrophenol (H-donor) and aniline in dioxane.[85] The pK_a value for 2,4,6-trinitrophenol is 0·4,[79] whereas that of HFP is 9·3.[60] This shows that the proton transfer is very much facilitated in a more polar solvent.

It has been a standard procedure to investigate the hydrogen bonding between an H-donor and an H-acceptor in an inert solvent.[31] The equilibrium constant for 1:1 complex formation can be obtained by analysis of spectral changes induced by HB. In contrast, binary systems were studied in this work. The concentration of an H-donor is a maximum because the pure liquid is used as the H-donor and the solvent. The highest solute concentration for *p*-NA is 5×10^{-4} M and the concentration of pure liquid HFP is 9·5 M. Therefore, in this case one solute molecule is surrounded by at least 10^4

solvent molecules. The nature of HFP–IP mixed solvents is very sensitive to the IP mole fraction, because HFP is a strong H-donor and a very weak H-acceptor and mutual association takes place very efficiently on addition of a small amount of IP, which results in destruction of the liquid structure proper of pure HFP. Hence both the solute–solvent binary system and the standard ternary system can be used for elucidating the liquid structure of hydrogen-bonding solvents by probing the spectral properties of H-donor or H-acceptor solute molecules.

Relevance to TICT phenomena

The TICT model has been proposed for the dual emission of *p*-*N*,*N*-dimethylaminobenzonitrile and related species. Neither *p*-aminobenzonitrile nor *p*-*N*-methylaminobenzonitrile exhibits this kind of dual emission.[86] Although the TICT model can be applied to a wide variety of organic molecules,[9,10] the HB-induced rehybridization may be observed for any type of aromatic amines. The degree of rehybridization depends on the hydrogen-bonding ability of the solute and the solvent.

There have been no reports on light absorption due to the transition from the ground state to the TICT state.[9] The present observation of dual peaks cannot be interpreted by the TICT model. The model of different hybridization may be applied to the explanation of the dual fluorescence of 5-substituted indoline.[86,87] Since the indoline derivatives can be regarded as rigidized anilines, they have been used as reference compounds which may not form the TICT state. Pure sp^2 hybridization is very unlikely for the indoline nitrogen, because the compounds are not completely planar. The HB-induced rehybridization may be of some importance in determining the stable structure in the ground state and the relaxation pathway from the Franck–Condon excited state of the indoline derivatives in hydroxylic solvents.

From the estimated equilibrium constant (less than 0·03) at 298 K for 5-cyano-*N*-methylindoline (5CMI),[24] we can evaluate the energy difference between the dominant species and the high-energy form. The energy difference is calculated to be more than 2·1 kcal mol^{-1}. This value is comparable to the energy change associated with the formation of N(lone pair)···HO(HFP) hydrogen bond. From this assessment, double peaks or anomalously broadened peaks are expected to appear in the absorption spectrum of 5CMI in HFP.

CONCLUSION

Aromatic amines dissolved in HFP show characteristic absorbtion bands depending on the basicity. The behaviour of substituted anilines in HFP can be divided into the following four categories: (1) anilinium ion formation for *m*-DMABA and DMA; (2) conspicuously blue-shifted species for *p*-AAP; (3) co-existence of the pyramidal and the planar species for *p*-MAAP and *p*-NA; and (4) considerably red-shifted species for *p*-DMANA. Changes from (1) to (4) are observed on decreasing the base strength. The observed results can be characterized as an acid–base equilibrium and strong and weak hydrogen bonding. In addition, very weak HB can be formed by weak H-donors such as CH groups[88] or weak bases such as π-electron systems.[89] A more rigorous classification of HB should be made on the basis of a physical quantity such as the van der Waals radius. The criteria for classifying hydrogen bonds as weak or strong have been summarized in Ref. 72. The present qualitative description may serve as a first-order crude approximation.

HB-induced rehybridization of aromatic amino nitrogens is a general phenomenon in strongly hydrogen-bonding media. It can account for the spectral properties of a wide variety of aromatic amines. The analysis employed in this study postulates a correlation between the spectral behaviour and the molecular structure or the amine basicity. If this approach is generally valid, it should be possible to investigate the geometry of nitrogen atoms for aromatic amines by means of absorption spectroscopy in water or HFP.

It is of interest that the molecular structure of aniline in the crystalline state[34] is very close to that in the gas phase,[29] although NH···N hydrogen bonding is present in the former and absent in the latter. Similar structures have been observed for *p*-nitroaniline in the gas,[90] liquid[22,33] and crystalline states.[43] In spite of the fact that the N(amino)H···O_2N(nitro) hydrogen bonding in the crystal is not strong, it is one of important factors which determine the molecular packing of nitroaniline compounds in the crystalline state.[13] If appreciable crystal field effects are absent, the molecular structure in the crystal state may be close to that in the solution phase. However, if a strong HB interaction is present between the solute and the solvent, the geometry in the solution may be far from similar to that in the crystalline phase. The extreme case is a complete proton transfer from the H-donor to the H-acceptor.

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Supplementary Material. Figures 3–6 illustrate absorption spectra for *para*-substituted anilines and 5-substituted indolines in IP and HFP, and are available from the author.

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