HYDROGEN BONDING IN ANILINE AND SOME SUBSTITUTED ANILINES IN DIFFERENT ENVIRONMENTS

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ABSTRACT. A comparative study on the shifts in the frequencies of infrared absorption bands due to the symmetric and asymmetric N H stretching vibrations of aniline and some methoxy-and ethoxy anilines in the liquid state and in solutions in some polar solvents relative to those of the respective compounds in dilute CCl_4 solution has been made. The shifts observed with all the compounds in different environments have been attributed to the formation of intermolecular hydrogen bonds and it has been pointed out that the strength of the hydrogen bond depends on the electronic nature of the substituents and is affected by steric interactions between the molecules of the same type in the pure liquids and in the case of solutions of the ortho-compounds between the solvent and the solute molecules.

INTRODUCTION

Though inference about the formation of intermolecular hydrogen bonds, in solutions of aniline in polar solvents, between the solute molecules of aniline and molecules of the polar solvents, e.g., chloroform, tetrahydrofuran and dioxane was made by some workers (Krueger and Thompson, 1957; Whetsel, 1962), it was Bellamy, Hallam and Williams (1958) who pointed out that solvent-solute dipolar interactions are mainly responsible for the formation of such hydrogen bridges. Later, Cutmore and Hallam (1962) extended these investigations to some substituted aniline compounds and showed that the relative shifts may be related to the pK_a values of the amines provided that due considerations of other solvation interactions, such as structural effects are taken into account. But it seems that very little work on the influence of structure of the molecules of both the solute and solvent on the strength of intermolecular hydrogen bridges has been carried out. Recently, Medhi, *et al.* (1962) showed that hydrogen bonding in toluidines in the pure compounds and in solutions in polar solvents depends on the relative positions of the substituents and the Hammett σ-factor of the CH_3 group in the ring of the aniline molecule. In order to understand how the formation of hydrogen bonds in substituted anilines in different environments depends on the electronic nature and positions of the substituent groups and also on the characteristics of the polar solvents, the infrared spectra of some methoxy and ethoxy anilines in the pure state and in solutions in some polar solvents have been

investigated and the results have been compared with those obtained with ani-
·line under similar conditions.

EXPERIMENTAL

Pure samples of aniline, o-, m- and p-anisidine and o-and m-phenetidine
supplied by reputed firms of U.S.A. and England were fractionated and the
appropriate fractions were further distilled under reduced pressure. The solvents
were also carefully purified and dried. A Perkin-Elmer Model 21 spectrophoto-
meter provided with rock salt optics was used to record all the spectra due to the
pure compounds and their solutions with arrangements described in a previous
paper (Banerjee and Kastha, 1962). The absorption bands due to N-H stretching
vibrations of aniline in very dilute CCl_4 solution were recorded from time to time
to check the reliability of the recorded spectra.

RESULTS AND DISCUSSION

The symmetric (v_s) and asymmetric (v_a) N-H stretching vibrational frequen-
cies in cm^{-1} for the compounds are given in Table I Table II contains the values
of the shifts in cm^{-1} of the frequencies of symmetric and asymmetric vibrations
(denoted respectively by Δv_s and Δv_a) and their mean values for all the compounds
in different environments relative to the frequencies of the respective compounds
in 1% carbon tetrachloride solution. The values of Hammett σ-factors for some
of these compounds given by Krueger and Thompson (1957) are included in both
the Tables.

(a) *Aniline*

The two bands at 3402 and 3476 cm^{-1} of aniline in 1% CCl_4 solution shift
respectively to 3398 and 3460 cm^{-1} in 1% solution of the compound in chloroform
and with the increase in concentration of the chloroform solution the centres of
these two bands further shift to lower frequencies. Doublet structure of the two
bands in chloroform solution as reported by some workers (Krueger and
Thompson, 1957; Moritz, 1962, Whetsel, 1962) has not been detected, but the
band at 3460 cm^{-1} in 1% solution of aniline in chloroform is rather broad and
the strength of absorption in the region between the two bands is found to
increase markedly with increase in the concentration of aniline in the chloroform
solution. In contrast to the proton-donor solvent chloroform, the proton-acceptor
solvents acetone, ether, tetrahydrofuran and pyridine shift the N-H stretching
vibrational frequencies to lower frequencies by larger amounts. The shift is
largest in the case of pyridine solution and of the three other polar solvents,
each containing an oxygen atom with lone electron pairs, tetrahydrofuran pro-
duces larger shifts than either acetone or ether both of which shift the N-H
stretching frequencies by almost the same amount. The shifts in these frequencies
of aniline in the liquid state are intermediate between those in tetrahydrofuran
and in pyridine solutions,

Not only the frequencies of N-H stretching vibrations of aniline are changed but also the width and the strength of these absorption bands are affected by the polar solvents. The band 3476 cm^{-1} of aniline dissolved in pyridine becomes broad and is weakened in such a way that its presence in 1% solution is almost undiscernible and in solutions of higher concentrations it appears only as a hump. In the case of solutions in acetone, ether and tetrahydrofuran the ratio of the strength of the band due to symmetric vibration to its asymmetric counterpart is greater than that in CCl$_4$ solution. In the pure liquid and in solution in chloroform this ratio remains almost the same as in the solution in carbon tetrachloride.

The changes observed in solutions of aniline in polar solvents evidently arise from the formation of intermolecular hydrogen bridges between the hydrogen atoms of the NH$_2$ group of aniline molecule and the N-atom of pyridine or the oxygen atom of acetone, ether and tetrahydrofuran. The hydrogen bond in the pure liquid involves the hydrogen atom of the N-H bond of an aniline molecule and the N-atom of NH$_2$ group in a neighbouring molecule. The large shifts observed in the case of the pure liquid and in solution of pyridine indicate the formation of fairly strong N—H...N bonds.
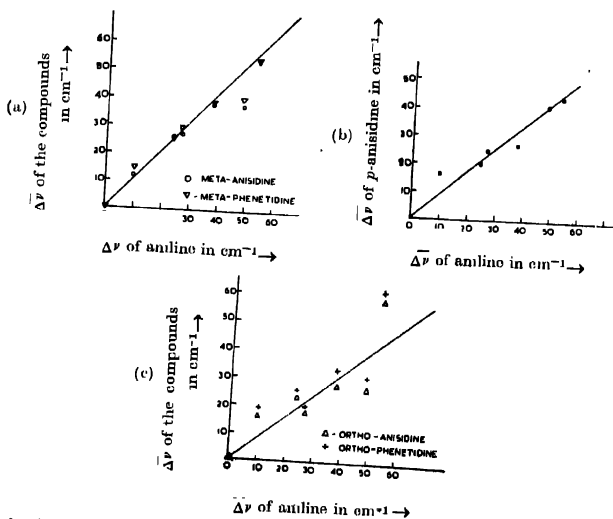

Fig. 1. Plot of mean solvent shifts ($\bar{\Delta\nu}$) in cm^{-1} of (a) *m*-anisidine and *m*-phenetidine, (b) *p*-anisidine, (c) *o*-anisidine and *o*-phenetidine, against those of aniline

(b) *Substituted anilines*

The N—H stretching vibrational frequencies of the ortho- and meta-isomers of anisidine and phenetidine in 1% CCl$_4$ solution are higher than those of aniline

in the same solution while in the case of para-anisidine these frequencies are lower than those of aniline. The observed variations in the frequency of N-H vibrations of these compounds in solutions of CCl_4 and other solvents with the Hammett σ-factor of the substituent methoxy and ethoxy groups are similar to those reported by Krueger and Thompson (1957) The nature of the solvent shifts (Δv_s and Δv_a) for all the substituted anilines in different solvents in general is the same as that observed with aniline under similar condition and this is clearly seen from the graphs in Fig. 1., where the mean values of the shifts Δv_s and Δv_a for each of the compounds have been plotted against the corresponding quantities for aniline. It is seen from the graphs that for all the compounds the mean solvent shifts are linearly related to those of aniline. The slope of the straight line is slightly greater than unity for the meta-compounds and for the ortho-compounds and para-anisidine the slopes are much less than unity. The unit slope of the straight line for meta-anisidine and meta-phenetidine indicates that the causes producing the solvent shifts in aniline and in the meta-compounds are almost similar, but the value less than unity of the slope for ortho-anisidine, ortho-phenetidine and para-anisidine points to the fact that the causes producing the solvent shifts are not operative in these compounds as effectively as in aniline. The proximity of the OMe and the OEt groups to the NH_2 group in the ortho-compounds and the negative value of Hammett σ-factor for p-anisidine may

TABLE 1

N-H stretching frequencies in cm^{-1}

Compound and Hammett σ	Pure		Solution in						Type of vibration
	Liquid	Solid	CCl_4	$HCCl_3$	$(CH_3)_2CO$	$(C_2H_5)_2O$	$(CH_2)_{10}$	C_5H_5N	
Aniline	3360		3402	3398	3380	3376	3364	3340	ν_s
$\sigma = 0.0$	3420		3476	3460	3450	3448	3438	3430	ν_a
Meta-anisidine	3372		3404	3400	3381	3380	3368	3340	ν_s
$\sigma = +0.115$	3437		3480	3460	3452	3450	3440	3436	ν_a
Meta-Phenetidine	3367		3403	3391	3380	3373	3362	3341	ν_s
$\sigma = +0.150$	3434		3478	3461	3451	3450	3442	3432	ν_a
Para-Anisidine	3353	3307	3395	3380	3375	3366	3362	3342	ν_s
$\sigma = -0.268$	3420	3386	3460	3443	3440	3440	3439	3425	ν_a
Ortho-Anisidine	3380		3405	3393	3384	3380	3370	3328	ν_s
	3452		3480	3460	3455	3470	3460	3440	ν_a
Ortho-Phenetidine	3370		3403	3390	3376	3377	3363	3323	ν_s
	3454		3483	3458	3459	3469	3457	3440	ν_a

TABLE II

Solvent shifts in cm^{-1}

Mean values are given in brackets

Solution in	Aniline $\sigma = 0.0$		m-Anisidine $\sigma = +0.115$		m-Phoneti-dine $\sigma = +0.150$		p-Anisidine $\sigma = -0.268$		o-Anisidine		o-Pheneti-dine	
	$\Delta \nu_s$	$\Delta \nu_a$	$\Delta \nu_s$	$\Delta \nu_a$	$\Delta \nu_s$	$\Delta \nu_a$	$\Delta \nu_s$	$\Delta \nu_a$	$\Delta \nu_s$	$\Delta \nu_a$	$\Delta \nu_s$	$\Delta \nu_a$
CHCl$_3$	4	16	4	20	12	17	15	17	12	20	13	25
	(10)		(12)		(14.5)		(16)		(16)		(19)	
(CH$_3$)$_2$CO	22	26	23	28	23	27	20	20	21	25	27	24
	(24)		(25.5)		(25)		(20)		(23)		(25.5)	
(C$_2$H$_5$)$_2$O	26	28	24	30	30	28	20	20	25	10	26	14
	(27)		(27)		(29)		(24.5)		(17.5)		(20)	
(CH$_2$)$_4$O	38	38	36	40	41	36	33	21	35	20	40	26
	(38)		(38)		(38.5)		(27)		(27.5)		(33)	
	62	46	64	44	62	46	53	35	77	40	80	43
	(54)		(54)		(54)		(44)		(58.5)		(61.5)	
Liquid	42	56	32	43	36	44	42	40			33	29
	(49)		(37.5)		(40)		(41)		(26.5)		(31)	

be responsible for such shielding effect. Like the solvent shift, the changes in the width and intensity of the bands of the compounds in different environments also follow the same pattern as in the case of aniline.

A careful examination of Table II reveals that the solvent shifts for meta-anisidine and meta-phenetidine are slightly greater than the corresponding shifts for para-anisidine. The slightly positive value of the Hammett σ factor of meta-anisidine and meta-phenetidine makes the H-atoms in the NH$_2$ group slightly more positive and consequently the intermolecular N-H...N and N-H...O bridges are stronger in these cases than in the case of para-anisidine where the Hammett σ-factor is negative. The proximity of the methoxy and the ethoxy group to the NH$_2$ group in the ortho-compounds and consequent steric interaction complicate the simple interpretation. However, the largest solvent shift observed with these compounds in pyridine solution definitely indicates stronger N—H...N bonds and hence larger positive charge on the H-atoms of the NH$_2$ group of the compounds as compared to aniline, meta-anisidine and meta-phenetidine. Not only the influence of the steric effect of the solute molecules but also that of solvent molecules on the strength of the intermolecular N—H...O hydrogen bonds is to be considered. A comparison of the mean solvent shifts for the ortho-compounds in solutions of acetone, ether and tetrahydrofuran shows that the shifts in acetone and tetrahydrofuran are larger than the mean shift in ether solution.

This seems to indicate that the interaction of the steric hindrances of the OMe group or the OEt group in the ortho-compounds with the C_2H_5 group of other molecule makes the N-H...O bonds weaker in comparison to that in the solution in acetone or tetrahydrofuran.

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