A NOTE ON THE HYDROGEN BONDING IN ISOMERIC AMINOPYRIDINES IN RELATION TO THEIR BASICITIES

K. C. MEDHI and G. S. KASTHA

Optics Department, Indian Association for the Cultivation of Science,
Calcutta-32

ABSTRACT. The infrared absorption spectra due to fundamental N H stretching vibrations of 2-, 3- and 4-aminopyridines in different environments have been studied and the frequencies of the symmetric and asymmetric N-H stretching vibrations of these compounds in very dilute solutions in CCl_4 have been compared with those of aniline in solution in the same solvent. It has been observed that the total solvent shifts in the N-H stretching vibrational frequencies of any of the aminopyridines in solutions in different solvents are linearly related to those of aniline in solutions in the corresponding solvents. The significance of the observed linearity and of the slopes of the straight line graphs in relation to the hydrogen bonding capacity and the basicities of the molecules of the aminopyridines has been discussed.

INTRODUCTION

From a study of the infrared absorption bands due to N–H stretching vibrations of aniline and some substituted anilines, it has been shown (Medhi and Kastha, 1963) that the ratios of the total solvent shifts, due to hydrogen bonding, in the frequencies of symmetric and asymmetric stretching vibrations of the N–H bonds in the NH_2 group in the molecule of any of these compounds in solutions in different solvents to those of aniline in solutions in the corresponding solvents are almost constant which is independent of the nature of the solvents. It was also shown that the constant values of these ratios, which are respectively greater or less than unity for compounds with electronegative or electropositive substituents, bear an almost linear relationship with the pK_a-values of the various phenyl amines and that they may be regarded as a measure of the proton donating power of these compounds with respect to aniline. In a subsequent paper (Kastha and Medhi, 1963) it was pointed out that in the series of phenyl amines investigated, under certain assumptions, the value of this constant for a particular compound is approximately equal to the ratio of the total charge on the nitrogen atom of the NH_2 group in aniline molecule to that on the N-atom in a molecule of the compound.

All these considerations apply to the case of aniline and its derivatives where the basic character of any of these compounds is due to the N-atom of the NH_2 group external to the benzene nucleus of its molecule. In order to see how far the conclusions mentioned in the previous paragraph are valid when the benzene

ring in the molecule of an amino-compound contains a nuclear N-atom in addition to the external NH_2 group the infrared absorption bands due to fundamental N–H stretching vibrations of the three isomeric aminopyridines in different states and also in dilute solutions in a large number of polar and non-polar solvents have been investigated. The results obtained have been discussed in the following paragraphs.

EXPERIMENTAL

The samples of 2-, 3- and 4-aminopyridines were supplied by Light and Company of England, and these were purified by repeated fractionation under reduced pressure. The sample of aniline used was of E. Merck's G. R. quality. The solvents were of chemically pure quality which were purified and dried by standard methods.

The infrared absorption spectra of all the compounds in the region of fundamental N–H stretching vibrations in different states and in very dilute solutions in the various solvents were recorded on a Perkin-Elmer Model 21 spectrophotometer with NaCl optics. The standard atmospheric water vapour band at 3740 cm^{-1} and the bands due to N–H stretching vibrations of aniline in very dilute solution in CCl_4 were used to check the calibration of the instrument from time to time.

RESULTS AND DISCUSSION

The frequencies of the absorption bands due to symmetric (v_s) and asymmetric (v_a) N–H stretching vibrations in the pure aminopyridines and also in their solutions in different solvents are given in Table I in which are also included for comparison the N–H stretching vibrational frequencies of aniline in solutions in the same solvents. These frequencies of aniline in solutions in carbon disulphide, benzene, acetonitrile, nitromethane and dioxane have been recorded in the present investigation, while the remaining ones are taken from data reported earlier (Medhi and Kastha, 1963). The total solvent shifts $(\Delta v_t = \Delta v_s + \Delta v_a)$ in the N–H stretching vibrational frequencies of the isomeric aminopyridines and aniline in different environments have been tabulated in Table II. The pK_a -value of aniline taken from Whetsel's paper (1961) and those of the aminopyridines determined experimentally by Albert *et al.* (1948) are included in both Tables I and II.

It is seen from Table I that the symmetric and asymmetric N–H stretching vibrational frequencies of 2-aminopyridine in solution in CCl_4 are almost identical with those of 4-aminopyridine in solution in the same solvent, while these frequencies of 3-aminopyridine in CCl_4 solution are smaller than those of either of the two compounds. Both the frequencies of 2- and 4-aminopyridines in CCl_4 solution are much higher than those of aniline in solution in the same solvent, but in the case of solution of 3-aminopyridine in CCl_4, these frequencies, though slightly higher, are very nearly the same as those of aniline. The higher values of these frequencies in the aminopyridines are to be expected, because the nuclear N-atom in the molecule of any of these compounds is more electron attracting than a corres-

ponding C–H group in the molecule of aniline. The consequent larger migration of charge from the NH_2 group to the ring would enhance the stretching vibrational frequencies of the N—H bonds.

The almost equality in the frequencies of N—H stretching vibrations in the molecules of 2-and 4-aminopyridines suggests that the values of the excess charge on the N–atoms in the 2-position and in the 4-position of the benzene ring with respect to the NH_2 group are almost equal while the higher values of these frequencies in comparison to those of aniline would indicate that magnitude of this excess charge is appreciable in both the molecules.

TABLE I

N–H stretching frequencies ν_s and ν_a in cm^{-1}

Compound and pK_a Solvent	2-amino pyridine 6.86	3-amino pyridine 5.98	4-amino pyridine 9.17	Aniline 4.68
Carbon	3420	3405	3422	3402
tetrachloride	3508	3480	3508	3476
Benzene	3413	3395		3393
	3495	3465		3466
Carbon	3409			3394
disulphide	3402			3470
Chloroform	3417	3406	3424	3398
	3509	3481	3521	3460
Acetonitrile	3400	3387	3409	3380
	3483	3456	3489	3457
Nitromethane	3410	3400	3419	3393
	3502	3467	3506	3465
Acetone	3390	3389	3385	3380
	3472	3441	3462	3450
Ether	3380	3376	3379	3376
	3461	3448	3418	3448
Dioxane	3373	3380	3384	3380
	3464	3442	3452	3451
Tetra hydrofuran	3370	3377	3383	3364
	3453	3437	3442	3438
Pyridine	3340	3352	3369	3340
	3460	3450	3459	3430
Pure liquid	3330	3340		3360
	3455	3430		3420
Pure solid	3310	3315	3319	
	3452	3391	3445	

TABLE II

Total solvent shift in N–H stretching frequencies

$$\Delta\nu_t = \Delta\nu_s + \Delta\nu_a \text{ in cm}^{-1}$$

Compound and pK_α Solvent	2-amino pyridine 6.86	3-amino pyridine 5.98	4-amino pyridine 9.17	Aniline 4.68
Benzene	20	25	—	19
Carbon disulphide	27	— —	—	14
Chloroform	2	—2	—6	20
Acetonitrile	45	42	32	41
Nitromethane	16	18	5	20
Acetone	66	55	83	48
Ether	84	61	103	54
Dioxane	91	63	94	47
Tetrahydrofuran	105	71	105	76
Pyridine	128	83	102	108
Pure liquid	143	115	—	98
Pure solid	166	179	166	—

Similar arguments in the case of 3-aminopyridine would show that the excess π-electron density on the nuclear N-atom is very small. These conclusions are in agreement with the calculations of Longuet-Higgin's (1950) who showed that the values of excess π-electron density on the nuclear N-atoms in 2- and 4-amino-pyridines are equal while that in the case of 3-aminopyridine is zero,

It is seen from Table I that in tho case of all the isomeric aminopyridines the frequencies of both the N–H stretching vibrations in different environments are less than those observed for each of the compounds in solution in CCl_4. In order to find out whether the total solvent shifts ($\Delta \nu_t$) of the three isomeric aminopyridines in solutions in different solvents show any correspondence with those of aniline in solutions in the same series of solvents (Table II), as observed previously in the case of other substituted anilines (Medhi and Kastha, 1963), the values of $\Delta \nu_t$ for each of the compounds have been plotted against the corresponding $\Delta \nu_t$ values of aniline in Figs. 1a, b and c.

It can be seen from the figures that the plots for all the three isomeric aminopyridines are straight lines with different slopes for different compounds. In the case of 4-aminopyridine, however, the points are widely scattered about the mean straight line and the value of the slope is not so certain as in the case of the other two compounds.

From this almost linear relation it may be concluded that the mechanism of hydrogen bond formation in the case of all the aminopyridines in different environments is similar to that occuring in the case of aniline under the same conditions.

The linear relation that has been shown to exist between the slopes of the straight lines for the various phenyl amines and their pK_a-values (Medhi and
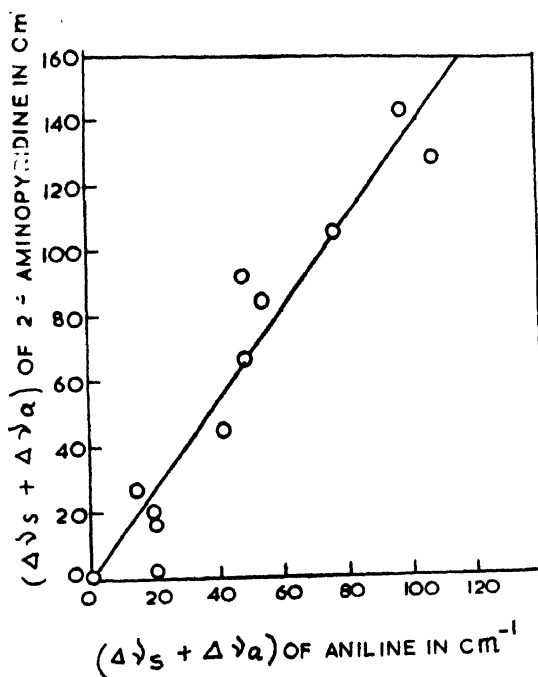

Fig. 1. Plot of total solvent shifts ($\Delta \nu_s + \Delta \nu_a$) in cm⁻¹ of the compounds against those of aniline (a) 2-Aminopyridine. (b) 3-Aminopyridine. (c) 4-Aminopyridine.
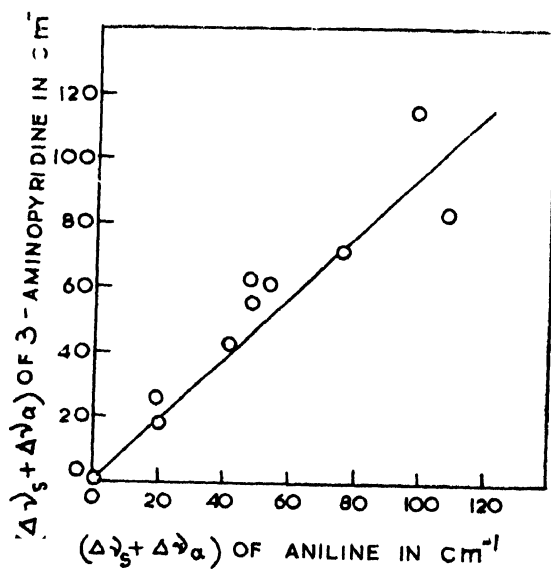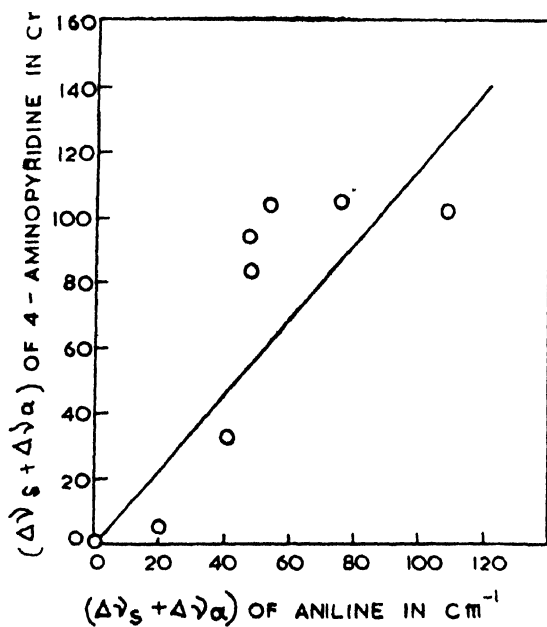
Fig. 1. (b)

Fig. 1. (c)

Kastha, 1963) has been used in the case of the aminopyridines to obtain the pK_a-values of these compounds by interpolation from the slopes of the straight lines in Figs. 1a, b and c. These values are given in Table III. The experimental

values of pK_a for these compounds (Albert *et al.*, 1948) are also included in the Table for comparison

TABLE III

Compound	Interpolated pK_a-value	Experimental pK_a-value
2-aminopyridine	1.1	6.86
3-aminopyridine	4.8	5.98
4-aminopyridine	3.0	9.17

The interpolated pK_a-values are found to be smaller than the experimental pK_a-values. This may indicate that the two different values of basicity have their origins in different mechanisms In the aminopyridines and similar N-hetero-cyclic amines the basicities of the compounds arise from the nuclear N-atoms in their molecules (Longuet-Higgins, 1950). However, in the case of aniline and its derivatives the N-atom in the NH_2 group of the molecules is responsible for their basicities. In the molecules of the phenyl amines the charge on the N-atom of the NH_2 group directly determines both the pK_a-value and the capacity for formation of hydrogen bonds (c.f. Kastha and Medhi, 1963). But in the case of the aminopyridines the excess π-electron density on the nuclear N-atom in the molecules of the compounds is responsible for their pK_a-values while the strength of the hydrogen bridges formed by the molecules of these compounds in different environments is governed by the charge on the N-atom of the amino-group. These facts may explain the difference between the interpolated pK_a-values and the experimental pK_a-values in the case of the aminopyridines.

REFERENCES

Albert, A., Goldacre, R. and Phillips, J., 1948, *J. Chem. Soc.*, 2240.

Kastha, G. S. and Medhi, K. C., 1963, *Ind. J. Phys.*, **37**, 568.

Longuet-Higgins, H. C., 1950, *J. Chem. Phys.*, **18**, 274.

Medhi, K. C. and Kastha, G. S., 1963, *Ind. J. Phys.*, **37**, 139 ; 275.

Whetsel, K. B., 1961, *Spectrochim. Acta*, **17**, 614.