A Study of Intramolecular Hydrogen Bonding in \( \alpha \)-Nitroaniline

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The presence of intramolecular hydrogen bond in \( \alpha \)-nitroaniline has been investigated by studying the IR spectrum of the compound in different proton accepting solvents. For the purpose of comparison, a similar study has been made on \( \rho \)-nitroaniline also. Frequency shifts of the asymmetric and symmetric \( N-H \) stretching bands show formation of associated species with the solvents. Analysis of the shift patterns shows the presence of hydrogen bond in \( \alpha \)-nitroaniline.

The presence of intramolecular hydrogen bonding in \( \alpha \)-nitroaniline has been a matter of greater controversy\(^1\)\textsuperscript{-6}. Pimental et al.\(^1\) pointed out that the differences in the \( N-H \) stretching frequencies of \( \alpha \)-nitroaniline in nitrobenzene are due to the presence of a weak hydrogen bond.

Medhi and Kastha\(^2\) studied the influence of proton acceptor solvents like ether, acetone, tetrahydrofuran and pyridine on the IR spectra of some \( \alpha \)-substituted anilines and concluded that the shifts in the \( N \) frequencies have no systematic dependence either on the dielectric constants or on the dipole moments of solvent molecules. According to them the smaller shifts in \( \alpha \)-nitroaniline compared to those in its \( \rho \)-isomer are due to steric effects. Krüger\(^3\), however, attributed the increase in the apparent HNH angle of \( \alpha \)-nitroaniline (121.7°) compared to that of aniline (110.9°) to intramolecular hydrogen bonding.

In view of the controversy about the presence of intramolecular hydrogen bond in \( \alpha \)-nitroaniline, it was thought worthwhile to re-examine the behaviour of \( \alpha \)-nitroaniline and to see whether solvent effect could be helpful in the diagnosis of intramolecular hydrogen bonding. The IR spectrum of the compound has been recorded in a wide range of proton accepting solvents of varying dielectric constants so as to get a clear picture of the solvent effect which might throw some light on the presence of intramolecular H-bond in \( \alpha \)-nitroaniline. For the purpose of comparison, \( \rho \)-nitroaniline, in which there is no intramolecular hydrogen bonding, has also been included in the present study.

The IR data are presented in Tables 1 and 2 and the spectra are presented in Figs 1-5.

Materials and Methods
The infrared spectra were recorded on a Perkin-Elmer 337 grating spectrophotometer (wave number linear) at a temperature of 28 ± 2°C, at a slow speed. Matched sodium chloride cells of 0.5 mm path length were used. The concentrations of the sol-
Table 2—Deviations of $v_{NH_2}$ values of $\alpha$- and $\beta$-Nitroanilines from Bellamy's Equation in Different Solvents

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Solvent</th>
<th>$\alpha$-Nitroaniline</th>
<th>$\beta$-Nitroaniline</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$v_{NH_2}$ ($cm^{-1}$)</td>
<td>$v_{NH_2}$ ($cm^{-1}$)</td>
<td>Deviation $v_{NH_2}$ ($cm^{-1}$)</td>
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<tr>
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<td>3400</td>
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<td>3375</td>
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<tr>
<td>3</td>
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<tr>
<td>4</td>
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<td>3345</td>
</tr>
<tr>
<td>5</td>
<td>TEA</td>
<td>3450</td>
<td>3300</td>
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</table>

Results and Discussion

Effect of halohydrocarbons

In carbon tetrachloride, the two $N - H$ stretching bands are found at 3500 and 3402 $cm^{-1}$ in the case of $\beta$-nitroaniline and at 3525 and 3400 $cm^{-1}$ in the case of $\alpha$-nitroaniline (Figs 1 and 2). The larger value of $v_{NH_2}$ in $\alpha$-nitroaniline ($125 cm^{-1}$) compared to that in $\beta$-nitroaniline ($98 cm^{-1}$) indicates the presence of a sufficiently strong intramolecular hydrogen bond in $\alpha$-nitroaniline. This is in agreement with Kruger's report that in $\alpha$-nitroaniline there is 56% hydrogen bonding.

In dichloromethane the two bands of $\alpha$- and $\beta$-nitroanilines suffer little or no change.

In chloroform solution, $\alpha$- and $\beta$-nitroanilines exhibit sharp singlets for the symmetric and asymmetric vibrations in contrast to clear doublets shown by $\alpha$- and $\beta$-anisidines and $\alpha$- and $\beta$-chloroanilines (Fig. 3). This shows lack of association between the $NH_2$ group and CHCl$_3$ molecules which may be due to the powerful electron withdrawing effect of the NO$_2$ group. In contrast, $-OCH_3$ and $-Cl$ groups are electron releasing groups and increase the electron density on nitrogen of the $NH_2$ group in anisidines and chloroanilines.

In dioxane the two bands of $\beta$-nitroanilines are found at 3430 and 3355 $cm^{-1}$ and in $\alpha$-nitroaniline these are found at 3475 and 3345 $cm^{-1}$. In order to find out the identity of these bands, the compounds were studied in binary solvent mixtures. For instance, the spectrum of $\alpha$-nitroaniline was recorded in CH$_2$Cl$_2$ containing different concentrations of di-
Fig. 3(a)—NH₂ bands of α- and p-anisidines in chloroform [α, α-anisidine; b, p-anisidine].

Fig. 3(b)—NH₂ bands of α- and p-chloroanilines in chloroform [α, p-chloroaniline; b, α-chloroaniline].

Fig. 4—NH₂ bands of α-nitroaniline in acetonitrile + dichloromethane [a, 0.05 ml acetonitrile + 0.95 ml CH₂Cl₂; b, 0.1 ml acetonitrile + 0.9 ml CH₂Cl₂; c, 0.2 ml acetonitrile + 0.8 ml CH₂Cl₂; d, 0.3 ml acetonitrile + 0.7 ml CH₂Cl₂; e, 0.4 ml acetonitrile + 0.6 ml CH₂Cl₂].

Fig. 5—NH₂ bands of α-nitroaniline in acetonitrile + dichloromethane [a, 0.05 ml acetonitrile + 0.95 ml CH₂Cl₂; b, 0.1 ml acetonitrile + 0.9 ml CH₂Cl₂; c, 0.2 ml acetonitrile + 0.8 ml CH₂Cl₂; d, 0.3 ml acetonitrile + 0.7 ml CH₂Cl₂; e, 0.4 ml acetonitrile + 0.6 ml CH₂Cl₂].

oxan. When the spectrum of the compound was recorded in dichloromethane containing very small quantity of dioxane, besides the two original bands found in CH₂Cl₂ (at 3520 and 3400 cm⁻¹), two new bands were found at 3475 and 3345 cm⁻¹. On gradually increasing the concentration of dioxane, the intensities of the two N–H bands in CH₂Cl₂ (3520 and 3400 cm⁻¹) started gradually decreasing and those of the new bands (3475 and 3345 cm⁻¹) started gradually increasing. This process continued till the original bands disappeared and the new bands persisted. This clearly shows that on adding dioxane to CH₂Cl₂, in addition to the two N–H bands of α-nitroaniline (in CH₂Cl₂) two association bands are exhibited whose intensities increase with the increasing concentration of the dioxane with the simultaneous decrease in the intensities of the bands due to CH₂Cl₂. In dioxane it was also found that the symmetric band was broader than the asymmetric band. This is attributed to the overlapping or merging of the two bands (− one due to the original symmetric band and the other due to association with the solvent molecules). Thus, binary solvent mixture study gives evidence for the formation of association bands with dioxane. In ether, the frequencies of the bands are slightly higher than those in dioxane. The bands of both the isomers are broader than those in
CCl₄. In anisole and diphenyl ether the two bands of p-nitroaniline are found at 3480 and 3390 cm⁻¹ and 3490 and 3395 cm⁻¹ respectively. In both the cases the shifts are small and binary solvent mixture study does not reveal the formation of new bands. But the N–H bands are considerably broad indicating the merger of the associated and unassociated bands. In o-nitroaniline also similar observations were made.

In acetone the two bands of p-nitroaniline and o-nitroaniline are found at 3445 and 3365 cm⁻¹ and at 3495 and 3375 cm⁻¹ respectively. Binary solvent mixture study revealed that these bands are due to association. By adding a very small quantity of acetone to a solution of dichloromethane, formation of association bands could be observed clearly. By increasing the concentration of acetone the intensities of the association bands increased with simultaneous decrease in the intensities of the original bands. Finally, the original bands disappeared and association bands persisted in pure acetone as was observed in dioxane. This clearly shows that in acetone also intramolecular hydrogen bond is broken and both the N–H modes are affected by the association with solvent molecules. In acetone, just like that in dioxane, the symmetric band is broader than the asymmetric band showing that in the former the original band is overlapping with the association band. In acetonitrile also binary solvent mixture study revealed formation of associated species (Fig. 4).

In acetonitrile the N–H band of p-nitro- and o-nitro-anilines were found at 3455, 3366 and 3495, 3375 cm⁻¹ respectively. The bands of o-nitroaniline in this medium are slightly broader than those in CCl₄. The symmetric band is broader than the asymmetric band. The shifts in the asymmetric bands of both the isomers are larger than those in the symmetric bands. Binary solvent mixture study has shown that the shifts are due to association (Fig. 5).

In binary solvent mixture of triethylamine and CH₂Cl₂, four bands were observed for both the isomers. Two of them (a & c) are same as the original bands and the other two (b & d) are association bands (Table 1). In both the isomers frequency shifts are very large for the symmetric band.

In pyridine-CH₂Cl₂ mixtures both the isomers exhibited four bands as observed in triethylamine-CH₂Cl₂ mixtures. The new bands are due to association. The shifts in the symmetric bands of both the isomers are quite large compared to the shifts in the asymmetric band.

Spectra of o- and p-nitroanilines in different solvents indicate that there is no regular order in the frequency shifts of the asymmetric and symmetric N–H stretching bands; but the total shifts in the o-isomer are smaller than those in the p-isomer and a random survey of the deviations using Bellamy’s equation⁸ in the case of the two isomers in different solvents (Table 2) revealed some interesting results. In the case of p-nitroaniline the deviation from Bellamy’s equation in carbon tetrachloride, a non-interfering solvent, is very small or negligible showing the absence of any intramolecular hydrogen bond. The deviation remained small in other proton accepting solvent also (except in triethylamine) showing that the molecule forms 1:2 complexes with the solvents. But in the case of o-nitroaniline the deviation from Bellamy’s equation is very large in CCl₄ giving a clear indication of the presence of intramolecular hydrogen bond. The magnitude of deviation is more or less same in proton accepting solvents (except in TEA) showing that the intramolecular H-bonding in o-nitroaniline is not strong enough to resist the action of these solvents, and after breaking of the chelation in these solvents the molecule forms 1:2 complexes with the solvent molecules just like the p-isomer. The similarity of the deviations of p- and o-nitroanilines in triethylamine shows that in the case of the latter isomer the intramolecular hydrogen bond is completely broken and hence it behaves exactly like the p-isomer. Both the isomers show very large deviations from Bellamy’s equation which indicates that the stoichiometry of the complex is 1:1 in this solvent.

Thus, on the basis of studies in solvents having a wide range of proton accepting abilities, it could be concluded that there is a moderately strong intramolecular hydrogen bond in o-nitroaniline. The bond remains intact in halohydrocarbons, is slightly affected in anisole and diphenyl ether, but is completely broken in dioxane, ether, acetone, acetonaphone, acetonitrile, dimethylformamide, triethylamine and pyridine.

References