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Substituent Effect on the N-H Stretching Absorptions of 2-(Substituted anilino)pyridines

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Synopsis. The N–H stretching frequencies of the title compounds were determined precisely. These amines have two absorption bands in the N–H stretching region owing to the existence of the rotational isomers. Their frequencies were plotted against the Hammett σ-constants of the substituents, giving a negative ρ-value. The results gave support to the planar (sp^2) conformation of the *exo*-cyclic nitrogen atom.

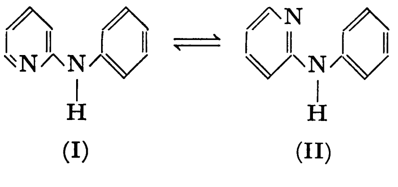
The substituent effect on the N–H stretching (ν_{NH}) frequencies have been reported for anilines,[1,2] *N*-methylanilines,[1] anilides,[3] and diphenylamines.[4] In these investigations, the frequencies were plotted against the Hammett σ or similar substituent parameters standing for their electronic effect. The results are rather contradictory giving ρ-values of different signs depending on the substituent (R) on the nitrogen atom (Table 1).

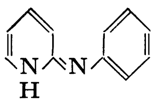
Table 1. Substituent(X) effect on the ν_{NH} frequencies of various *N*-substituted(R) anilines XC_6H_4NHR

R	Sign of ρ	Ref.
H	+	1, 2
CH_3	+	1
$COCH_3$	−	3
C_6H_5	borderline	4
2-C_5H_4N	−	this work
Cf. XC_6H_4OH	−	5

In our previous report, the contradiction was interpreted by assuming the participation of the two competing factors of the opposite direction. The electron attracting nature of a substituent would decrease the electron density on the amino nitrogen atom, causing the increase in the s-character of its N–H bonding orbital. The increase in the s-character, in turn, shortens and strengthens the N–H bond, giving rise to a high frequency shift of the ν_{NH} absorption. Alternatively, the decrease in electron density of the amino nitrogen atom weakens the N–H bond when the change in the hybridization is absent.

On the other hand, 2-anilinopyridines have been shown to have two absorption bands in the ν_{NH} region. They were assigned to the two planar rotational isomers I and II.[6] An alternative assignment of these two bands to the amino and the imino tautomers (I and III, respectively) were excluded by the spectroscopic evidences.[7,8]


(I) (II)


(III)

In this report, the hybridization of the *exo*-cyclic nitrogen atom will be discussed from the substituent effect on the ν_{NH} bands of 2-anilinopyridines.

Experimental

Infrared spectra were recorded with a Hitachi 225 infrared spectrophotometer. The frequencies were calibrated by the absorption bands of gaseous water at 3447.09 and 3442.41 cm^{-1} in order to keep the accuracy of the location of the band maxima within 0.2 cm^{-1}. The anilinopyridines were prepared by the usual procedures.

Results and Discussion

The frequencies and the intensities of the ν_{NH} bands are given in Table 2. The absorption bands were tentatively assigned to the rotamers I and II, respectively, according to the conclusion in our previous report.[6] The ν_{NH} frequencies, as well as the intensity ratios of the two bands, were plotted against the Hammett σ-constants.[9] In case when the substituent is mesomerically electron-attracting (+M), the σ^--constant is used instead. The ν_{NH} frequencies of both rotamers tend to decrease as the increase of σ-values, showing negative ρ-values. A negative ρ-value has been observed with a series of substituted benzamides,[3] of which nitrogen atoms have been proved to be sp^2-hybridized from other evidences. The results suggest that the *exo*-cyclic nitrogen atom in 2-anilinopyridine is sp^2 hybridized. Since the 2-pyridyl group in these

Table 2. The ν_{NH} absorptions of 2-(substituted anilino)pyridines

Substituent	ν_I / cm^{-1}	ε_I / l mol^{-1} cm^{-1}	ν_{II} / cm^{-1}	ε_{II} / l mol^{-1} cm^{-1}
4-NO_2	3412.4	97	3441.3	144
3-NO_2	3416.0	69	3445.3	97
4-$COOCH_3$	3416.1	89	3443.5	70
3-Br	3416.8	95	3446.1	73
3-Cl	3417.6	85	3446.2	67
4-Br	3417.7	91	3446.9	72
4-Cl	3417.8	86	3446.7	66
3-OCH_3	3418.6	90	3447.1	41
H	3418.9	92	3446.0	47
3-CH_3	3418.6	92	3447.2	40
4-CH_3	3419.6	102	3447.7	44
4-OCH_3	3419.1	94	3448.0	34

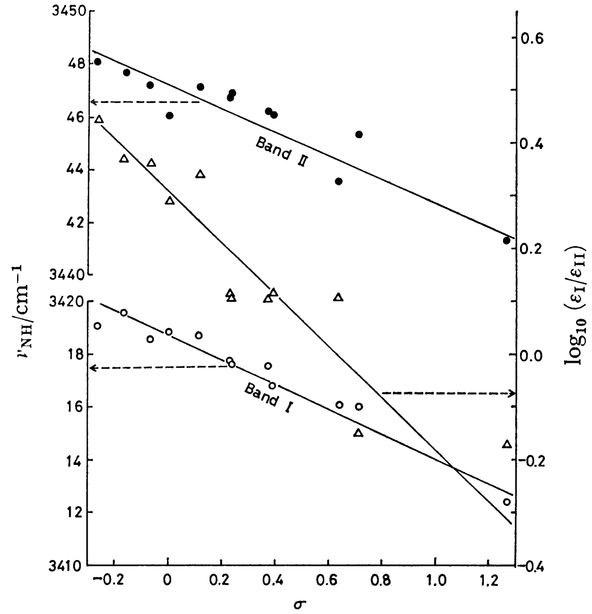


Fig. 1. The ν_{NH} and $\log_{10}(\varepsilon_I/\varepsilon_{II})$ *vs.* σ plot for 2-(substituted anilino)pyridines.

amines is more electronegative than the phenyl groups in diphenylamines which shows the borderline ρ-alue,$^{4)}$ the negative ρ-values are reasonable.

The $\varepsilon_I/\varepsilon_{II}$ ratios are also correlated with the σ-constants, the rotamer I (giving rise to the lower ν_{NH} band) becoming less favorable than the rotamer II when the substituent is electron-attracting. The results can be explained as follows. In the rotamer I, a weak attractive interaction$^{10)}$ keeps the N–H···N system nearly coplanar. As a result, the anilinopyridine molecule is twisted around the C_{Ph}–N bond because of the steric hindrance between 3- and 2′ (or 6′)-hydrogen atoms. On the other hand, the *exo*-cyclic nitrogen atom and the phenyl group can be coplanar in the rotamer II. In the latter case, the phenyl group with an electron-attracting substituent is stabilized by conjugating with the planarly attached amino group. Hence, the rotamer II is more favorable than the rotamer I when the substituent is electron-attracting.

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10) The low ν_{NH} frequency in the rotamer I suggests the participation of a weak hydrogen bond-like interaction, the N–H bond being weakened considerably by this interaction. However, the predominant force might be of dipolar nature.