

THE FLUORESCENCE SPECTRA OF DIANIONS OF α - AND β -NAPHTHYLAMINES

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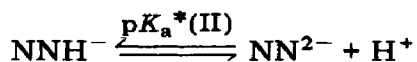
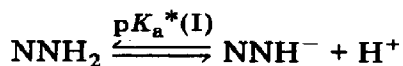
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Summary

The fluorescence spectra of the dianions of α - and β -naphthylamines were observed at high OH^- concentrations and the fluorescence quantum yields were calculated. The $\text{p}K_a^*$ values were determined for the respective equilibria.

It is well established that the arylamines [1] are stronger acids in the S_1 state than in the S_0 state and $\text{p}K_a^*$ for the deprotonation reaction has been calculated from the quenching of the fluorescence intensity of the neutral amines as a function of pH, as the imino anions ($\text{R}-\text{NH}^-$) formed in general are non-fluorescent. Moreover, these fluorometric titrations are carried out by exciting the neutral molecules at their absorption maxima because no isobestic points are observed since there is hardly any change in their absorption spectra, indicating that the ground state $\text{p}K_a$ values are greater than H_-15 or H_-16 .

We have studied the spectral behaviour of different carbocyclic and heterocyclic amines [2 - 6] in the H_0 -pH- H_- range from -9 to 16 . It is found that emission is not observed from different anions, indicating that these ions either are not formed at all or are non-fluorescent. 9-Phenanthrylamine [2] was the exception; the monoanion formed in the pH range from 11 to 14 was non-fluorescent but the dianion formed at $H_- > 14$ exhibited a blue-shifted fluorescence band compared with the neutral molecule. The fluorescence spectrum from the monoanion of β -naphthylamine in the pH range from 10 to 13 has been observed [7, 8]. We have extended this study up to H_-16 to establish whether the dianions of β -naphthylamine ($\beta\text{-NNH}_2$) and α -naphthylamine ($\alpha\text{-NNH}_2$) are fluorescent or not, since their existence has been speculated [9], as shown in the following equilibria:



α - and β -naphthylamines were obtained from Riedel de Haen and were purified by recrystallization from ethanol and sublimation under vacuum. Analytical grade NaOH (BDH) was used as such. Triply distilled water was used to prepare the aqueous solutions. The concentrations used were of the order of 1×10^{-4} M. Yagil's basicity scale [10] for NaOH-H₂O mixtures was used for the solutions above pH 13.

The absorption spectra were recorded with a Cary 17D spectrophotometer and the fluorescence measurements were made on a scanning spectrofluorometer fabricated in our laboratory [11]. The excitation and emission monochromators were calibrated using a calibration mercury lamp. The pH measurements were made on a Toshniwal pH meter model CI-44A. The quantum yields of the monoanion and dianions of the α - and β -naphthylamines were calculated relative to the quantum yields of their respective neutral molecules [12], and the wavelength used for the excitation was 325 ± 4 nm. In the fluorometric titrations, the relative fluorescence intensities were measured at the analytical wavelength as a function of pH or H_- ; a wavelength of 325 nm was used for excitation since no isosbestic point was observed.

The absorption spectra of the α - and β -naphthylamines studied in the pH- H_- range from 7 to -16 are identical with those of the neutral molecules, supporting the earlier conclusions [1] that the deprotonation of the amino group does not take place in the S₀ state. The results of the fluorescence studies up to pH 13 are similar to the earlier conclusions, *i.e.* the monoanion of α -naphthylamine is non-fluorescent [8] and that of β -naphthylamine gives a red-shifted band maximum at 520 nm [7, 8]. Both molecules gave broad and blue-shifted fluorescence maxima compared with both the neutral and the monoanionic species above pH 14. The fluorescence intensity of the species formed from α -naphthylamine (Fig. 1, band maximum at 412 nm) continued to increase even up to H_- 16 but that of β -naphthylamine (Fig. 2, band maximum at 395 nm) reached a saturation limit. Similar results were observed for 9-phenanthrylamine [2]. We assign the blue-shifted fluorescence band maxima in both cases to the formation of dianions of the α - and β -naphthylamines. The large blue shift observed in the fluorescence spectra of the dianions could be due to the loss in the aromatic character of the molecules and the new structures might be stabilized as a result of the different canonical structures available, and thus the negative charge becomes delocalized on the ring. Had the charge been localized on the nitrogen atom after deprotonation, a red shift should have been observed in the fluorescence spectra. The fluorescence quantum yields of the dianion of α -naphthylamine, the monoanion of β -naphthylamine and the dianion of β -naphthylamine are found to be 0.01, 0.03 and 0.10 respectively. The decrease in the fluorescence quantum yields could be due to the increase in the charge transfer interaction of the amino group with the carbocyclic ring, thus leading to internal conversion, but this cannot be said with certainty.

The Förster cycle method [13] to calculate pK_a^* values could not be used in these cases as (i) the ground state pK_a values cannot be calculated,

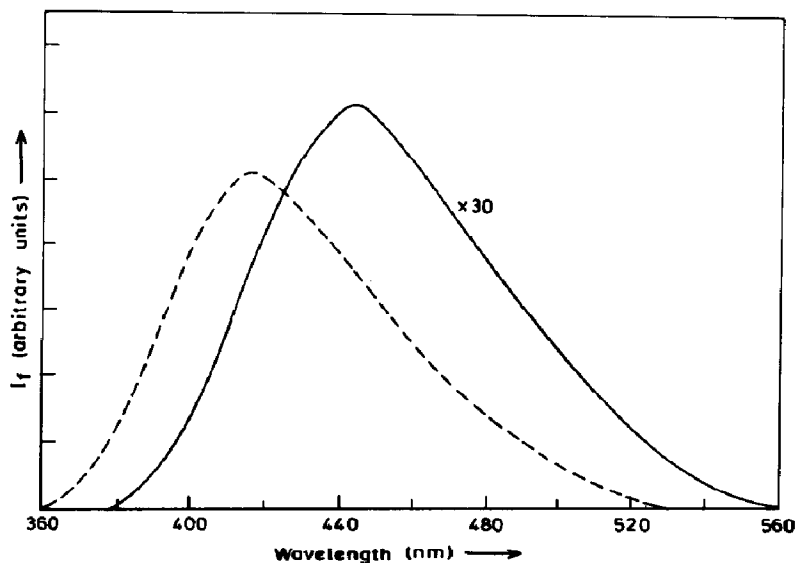


Fig. 1. Fluorescence spectra of α -naphthylamine (—) and the dianion (---) of α -naphthylamine at 298 K and H_{-16} .

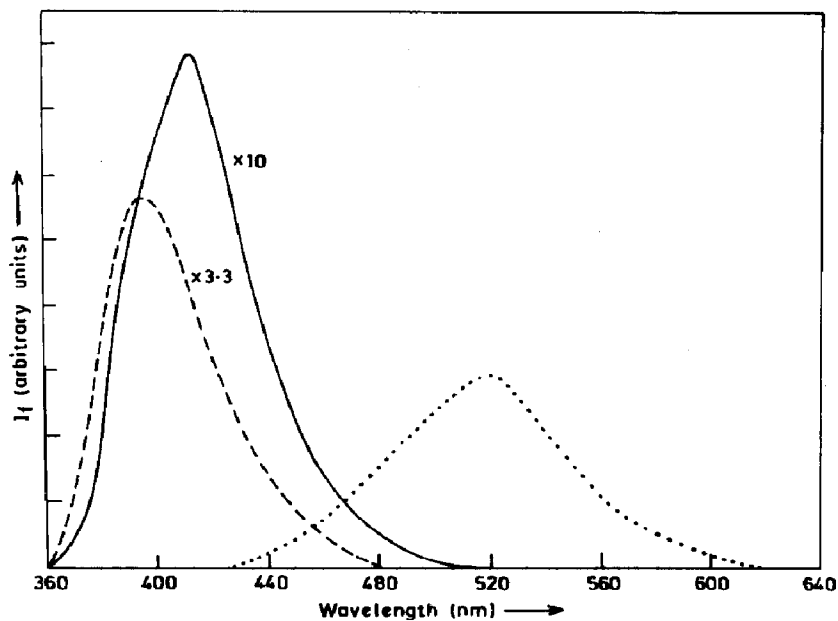


Fig. 2. Fluorescence spectra of β -naphthylamine (—) and the monoanion (.....) and dianion (---) of β -naphthylamine at 298 K.

(ii) the monoanion of α -naphthylamine is non-fluorescent and (iii) the formation of dianions is followed by changes in the structures of the molecules. ΔpK_a ($pK_a^* - pK_a$) for the neutral-monoanion equilibria of β -naphthylamine calculated by this method is found to be -10.83 , which seems to be very large. This could be due to a difference in solvent relaxation of the two

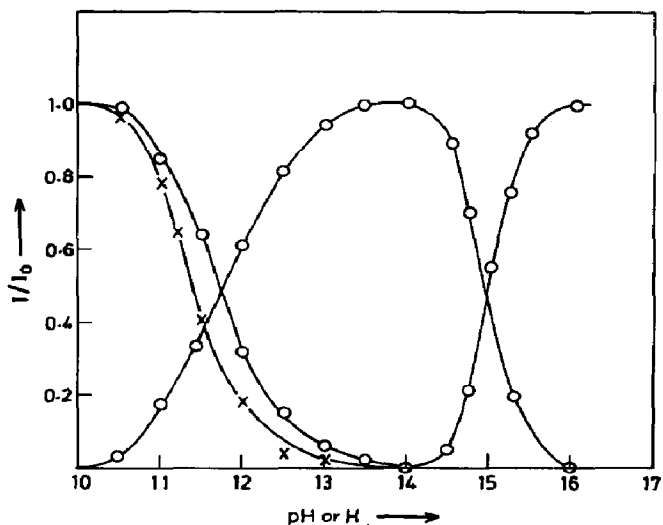


Fig. 3. Plot of the relative fluorescence intensities of the respective species of α -naphthylamine ($-x-$) and β -naphthylamine ($-o-$) vs. pH or H_- at 298 K.

species in the two states. The relative fluorescence intensities as a function of pH or H_- of the respective species are plotted in Fig. 3 and the values of the respective pK_a^* values are given in Table 1. The value of $pK_a^*(I)$ for β -naphthylamine agrees with the earlier results within the limits of error but that of α -naphthylamine is lower than the reported value [14]. The error could be due to inherent difficulties in the photopotentiometric technique [14] used to evaluate this constant, because this technique has not previously been used for this purpose. The value of $pK_a^*(II)$ for the monoanion-dianion equilibrium of β -naphthylamine is found to be 14.95 whereas, for α -naphthylamine, this value must be higher than $H_- 16$, as no saturation limit is reached for this species. There can be small errors involved in these calculations as the radiation used for excitation was not the wavelength of the isosbestic point. However, the intersection of the curves at the midpoint has shown that the values obtained are not very different from their actual values.

In conclusion, it may be pointed out that both protons of the amino group in α - and β -naphthylamines in the S_1 state can be removed, supporting the earlier conclusion that amino groups become stronger acids in the first excited singlet state.

TABLE 1

Excited singlet state acidity constants of α - and β -naphthylamines

Equilibrium	α -Naphthylamine	β -Naphthylamine
I	11.35	11.75
II	>16	14.95

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