Dissociation constants of 3-hydroxy-2-naphthylamine in the ground and excited singlet states

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Absorption spectra of 3-hydroxy-2-naphthylamine at various acid concentrations indicate the presence of five species, viz. the dication, monocation, neutral, monoanion and dianion, whereas the fluorescence spectra of the above compound under similar conditions yield six species, the zwitterion being the sixth, besides the above five. The excitation fluorescence spectrum has established that monocation is the ground state precursor for the zwitterion. Proton-induced fluorescence quenching is observed for the monocation. The dication is formed by the protonation of the amino group and the ring carbon atom, whereas the dianion is formed by the deprotonation of the hydroxyl group and \(-\mathrm{C} - \mathrm{H}\) bond in the \(S_0\) state but by the deprotonation of \(-\mathrm{OH}\) and \(-\mathrm{NH}_2\) groups in the \(S_1\) state. The prototropic equilibrium between neutral and monoanion species is not established in \(S_1\) state during the lifetimes of the conjugate acid-base pair.

Ellis and Rogers\(^1\) have assigned the absorption spectrum of 3-hydroxy-2-naphthylamine (2,3-NA) in the \(pH\) range of 4 to 8 to a neutral species and the fluorescence spectrum to a zwitterion. This conclusion was based on the fact that \(pK_a\) value for the deprotonation reaction of \(\alpha\)-naphthol in the \(S_1\) state is 2.8 (ref. 2) which is lower than that of the protonation reaction of the amino group in the \(S_0\) state, indicating thereby the formation of a phototautomer in the excited singlet state. In 2,3-NA, the amino and the hydroxyl groups are adjacent to each other and thus intramolecular H-bonding is expected between the two groups in the \(S_0\) state. The formation of phototautomer should be a monoprotonic process and thus should be independent of the nature of the solvents and acid concentration so long as the species is neutral. This kind of phenomenon and intramolecular H-bonding in the \(S_0\) state have been observed in many molecules\(^3\)\textendash\(^11\). The phototautomer is observed nearly in all the solvents. Actually the above kind of behaviour in 2,3-NA is only observed in the aqueous medium\(^1\). Further, it is also well established that the \(-\mathrm{NH}_2\) group becomes a very weak base in \(S_1\) state and the protonation constant in \(S_1\) state is \(-0.8\) (ref. 12). On these grounds, it seems that the assignment of the fluorescence spectrum by Ellis and Rogers\(^1\) to a zwitterion in the \(pH\) range of 4 to 8, in our view, is highly doubtful.

The present study has been carried out to remove this discrepancy. This study has been further supplemented by recording the spectral characteristics in different solvents. The \(pK_a\) values of the various prototropic reactions in \(S_0\) and \(S_1\) states have been determined and discussed.

Materials and Methods

3-Hydroxy-2-naphthylamine (2,3-NA) (Aldrich Chemicals) was of high purity grade and its purity was checked before use. Solvents employed were also of high purity and these were further purified before use. The instruments used and calculation procedures employed were the same as discussed in our recent papers\(^13\)\textendash\(^19\).

Results and Discussion

The absorption and fluorescence spectral data of 2,3-NA in different solvents and at various acid concentrations are compiled in Tables 1 and 2, while the spectra of various prototropic species of 2,3-NA are shown in Fig. 1. Data in Table 1 indicate that with change in solvent the long wavelength absorption band maximum is largely red shifted as compared to that of naphthalene\(^20\) whereas the middle band system is not much affected. The long wavelength band is slightly red shifted as the polarity of the solvents increases but undergoes blue shift with increase in H-bonding ability of the solvent. Whereas under similar environments, the fluorescence spectrum is continuously red shifted. The absorption spectra of neutral, monocation and monoanion in aqueous medium are similar to those observed by Ellis...
Table 1—Absorption maxima (nm) and molar extinction coefficient (dm³ mol⁻¹ cm⁻¹)* of 3-hydroxy-2-naphthylamine in different solvents and acidity at 298 K

<table>
<thead>
<tr>
<th>Cyclohexane</th>
<th>Dioxane (pH=7)</th>
<th>Methanol (pH=7)</th>
<th>Water (pH=12)</th>
<th>Monoanion (pH=7)</th>
<th>Dianion (pH=12)</th>
<th>Monocation (pH=17)</th>
<th>Dication (pH=19)</th>
</tr>
</thead>
<tbody>
<tr>
<td>274</td>
<td>277 (3.79)</td>
<td>276 (3.68)</td>
<td>274</td>
<td>—</td>
<td>263</td>
<td>273 (3.65)</td>
<td>279 (3.69)</td>
</tr>
<tr>
<td>285</td>
<td>287 (3.81)</td>
<td>286 (3.69)</td>
<td>285</td>
<td>290(sh)</td>
<td>290</td>
<td>284 (3.56)</td>
<td>290 (3.56)</td>
</tr>
<tr>
<td>295</td>
<td>298 (3.65)</td>
<td>296 (3.56)</td>
<td>295</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>323</td>
<td>325 (3.71)</td>
<td>323 (3.55)</td>
<td>314</td>
<td>325 (3.60)</td>
<td>335</td>
<td>310 (3.60)</td>
<td>316 (3.29)</td>
</tr>
<tr>
<td>330</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>337</td>
<td>338 (3.82)</td>
<td>337 (3.74)</td>
<td>331</td>
<td>344 (3.64)</td>
<td>348</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
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<td>—</td>
</tr>
</tbody>
</table>

* log εₘₐₓ values are given in parentheses

In naphthalene molecule²⁰, 312 nm band is long axis polarised (Lₐ) and the 275 nm band is short axis polarised (Lₕ). In these molecules, both the groups are present along the axis which would affect primarily the long axis polarised transitions as compared to the short axis polarised ones. From the above arguments and also from the data in Tables 1 and 2 it is clear that the lowest energy state of 2,3-NA is Lₚ. The spectral characteristics of this molecule in different solvents are consistent with the behaviour of the molecules containing these groups²¹,²², i.e. proton acceptor in S₀ state and the proton donor in the S₁ state.

Another point worth noting is that the long wavelength absorption band of 2,3-NA is more close to that of 2-naphthol²³,²⁴ (2-NOH), both in shape and band maxima (335, 330, 300 nm) rather than to that of 2-naphthylamine (2-AN, 340 nm)²⁰, which exhibits a broad band. Since the lone pair of electrons on the amino group pos-

and Rogers¹. The fluorescence band maximum of the monocation also agrees with that of Ellis and Rogers¹.
Table 2 – Fluorescence maxima (nm) and fluorescence quantum yields of 3-hydroxy-2-naphthylamine in different solvents and acidity at 298 K.

<table>
<thead>
<tr>
<th>Solvents/species</th>
<th>λ_{bm}</th>
<th>φ_f</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane</td>
<td>345,356</td>
<td>0.12</td>
</tr>
<tr>
<td>Dioxane</td>
<td>364</td>
<td>0.21</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>367</td>
<td>0.16</td>
</tr>
<tr>
<td>Methanol</td>
<td>372</td>
<td>0.17</td>
</tr>
<tr>
<td>Water (Neutral) (pH = 7)</td>
<td>382</td>
<td>0.41</td>
</tr>
<tr>
<td>Zwitterion (pH = 2)</td>
<td>415</td>
<td></td>
</tr>
<tr>
<td>Monocation (pH = 0)</td>
<td>347</td>
<td>0.08</td>
</tr>
<tr>
<td>Dication (H_+ 9)</td>
<td>370</td>
<td></td>
</tr>
<tr>
<td>Monoanion (pH = 12)</td>
<td>389</td>
<td>0.10</td>
</tr>
<tr>
<td>Dianion (H_- 17)</td>
<td>475</td>
<td></td>
</tr>
</tbody>
</table>

The data in Table 2 indicate that one more prototropic species of 2,3-NA is formed in the S_1 state as compared to that in the S_0 state. Under extreme basic conditions i.e. H_- > 15, unlike ground state, 475 nm fluorescence band is assigned to dianion formed by the deprotonation of the –OH group and –NH_2 group. This can be explained as follows. In 2-AN, though the monoanion in S_0 state is formed by the deprotonation of the –C–H bond (pK_a ~ 16)\textsuperscript{27}, the species in the pH range 11-14, in the S_1 state is a monoanion (λ_{max} at 352 nm)\textsuperscript{25}, formed by the deprotonation of the –NH_2 group. This is because the amino group becomes relatively stronger acid on excitation (pK_a^* = 11.75). Another kind of monoanion, as suggested by Chattopadhyay and Chowdhury\textsuperscript{27}, is formed at H_- > 15, having λ_{max} at 395 nm and pK_a^* = 14.95. The pK_a^* value for the monoanion-
dianion equilibrium of 2,3-NA, determined with the help of fluorimetric titration (Fig. 2) is also close to this value (15.4). The higher value of \( pK_a \) for the deprotonation of amino group, as compared to that of 2-AN (11.75), is due to the presence of negative charge ortho to the amino group leading to increase in charge density at the amino group.

The blue shift observed in the fluorescence spectrum of 2,3-NA at pH~12 is due to monocation, formed by the protonation of the -NH\textsuperscript{−} group rather than the -O\textsuperscript{−} group of dianion. This is because -OH group is a stronger acid than the -NH\textsubscript{2} group. At pH~8, the fluorescence maximum at 382 nm is assigned to neutral species rather than to zwitterion, similar to that assigned by Ellis and Rogers\(^1\). On the other hand, 415 nm fluorescence band in the pH range of 4 to 0 is assigned to zwitterion. This is based on the following results: (i) The fluorescence band maximum (382 nm) of 2,3-NA resembles those observed in non-aqueous solvents. (ii) The fluorescence band maximum at 415 nm is nearly equal to that of \( \beta \)-naphtholate\(^24\) ion (420 nm), indicating that protonation of amino group will mop up the lone pair of the amino group, thereby preventing perturbation of the \( \pi \) cloud of the \( \beta \)-naphtholate ion. (iii) The excitation spectrum recorded at 415 nm (assigned to the zwitterion) resembles the absorption spectrum of monocation (present at pH<4 in \( S_0 \) state) rather than the neutral species of 2,3-NA. This indicates that the ground state precursor for the zwitterion is a monocation rather than the neutral species. The formation of monocation (347 nm) is consistent with the results of Ellis and Rogers\(^1\). With further increase in acid concentration, the fluorescence intensity of monocation is quenched, without the appearance of any other new species. This behaviour is assigned to the proton-induced fluorescence quenching of monocation of 2,3-NA and this behaviour exactly resembles that of 2-naphthol, where the proton-induced fluorescence quenching\(^2\) is observed below pH 1. A further red shift of the fluorescence band (370 nm) starts appearing below \( H_0 = 5 \). This also resembles the prototropic reaction of 2-naphthol\(^29\) at such high acid concentration and thus can be assigned to the dication formed by the protonation of the ring carbon atom. This reaction is further supported by the fact that the ground state \( pK_a \) value is obtained from the fluorimetric titrations (see later). Similar behaviour is also observed in the case of prototropic reactions of aromatic hydrocarbons\(^14,31,32\).

**Acidity constant**

The ground state \( pK_a \) values for the various prototropic reactions of 2,3-NA have been determined spectrophotometrically and these values are listed in Fig. 3. The \( pK_a \) values agree closely with those reported in literature\(^1\), within the limits of error. The \( pK_a \) value for the reaction dication-monomocation is lower than that of ring protonation of naphthalene (\( pK_a = 4\))\(^26\). This is due to the presence of positive charge on the molecule.

The \( pK_a \) values in \( S_1 \) state have been determined with the help of fluorimetric titrations (Fig. 2) and are also listed in Fig. 3. Forster cycle method\(^33\) could not be used to calculate the \( pK_a \) values in the \( S_1 \) state because either the prototropic reaction was different or the species involved were not the same in the \( S_0 \) and \( S_1 \) states, except for the dication-monomocation equilibrium. \( I/I_0 \) for zwitterion could not be plotted accurately in Fig. 2 because of the presence of three species, i.e. monocation, neutral and zwitterion. Approximate fluorimetric curve for zwitterion was plotted by neglecting the fluorescence intensity due to monocation as it was quite small during the formation part of zwitterion. Ground state \( pK_a \) value obtained from the fluorimetric titration curve for the neutral-monoanion indicates that the lifetimes of the conjugate acid-base species are small and thus the prototropic equilibrium is not established in the \( S_1 \) state during the lifetimes of these species. This is further supplemented by the fact that unlike fluorimetric titration curve of 2-naphthol\(^2\), no stretched sigmoid curve is obtained for 2,3-NA. No proton-induced fluorescence quenching of neutral amine is observed prior to the protonation of -NH\textsubscript{2} group. This may be due to the formation of zwitterion before the monocation is formed in the \( S_1 \) state. -NH\textsuperscript{3+} ion and the carbon centre become more acidic and more basic in their respective excited singlet states. These results are in agreement with those available in the literature\(^31,32\).

**Conclusions**

The following conclusions can be drawn from the above study: (i) The -OH and -NH\textsubscript{2} groups are twisted with respect to naphthalene moiety in \( S_0 \) state and the angle of twist decreases on excitation. (ii) The long wavelength transition in all the species is \( ^1A \rightarrow ^1L_b \). (iii) The ground state precursor for the zwitterion, formed in \( S_1 \) state is the monocation rather than the neutral molecule.

**Acknowledgement**

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References
33 Forster Th, Z Elektrochem, 54 (1950) 531.