# Hydrogen Bonding, Protonation and Twisting in the Singlet Excited State of some 2-(4-Aminophenyl)pyrido-oxa-, -thia-, and -imidazoles



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The absorption and fluorescence characteristics of 2-(4-aminophenyl)pyrido[3,2-*d*]oxazole (**1**), of its thiazole **2** and imidazole **3** analogues, as well as of the corresponding pyrido[3,4-*d*]imidazole **4** have been examined. $S_1$ is a planar $\pi\pi^*$ ICT state, similarly to *p*-electron-withdrawing substituted anilines. In the protonated form, the chromophore is the heterocyclic moiety. With compounds **3** and **4** in alcohols, hydrogen bonding depending on proton donating and accepting properties of the medium determines the fluorescence. In this case, a red-shifted emission attributed to a twisted TICT state is also observed.

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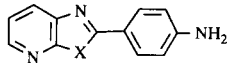
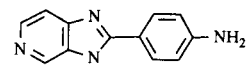
The fluorescence of heterocycles is a subject not only of academic but also of practical interest. As an example, benzoxazoles and benzothiazoles fluoresce strongly and are used as whitening agents [1,2] photoconducting materials [3], and laser dyes [4-6]. A further area of interest lies in the study of hydrogen transfer and prototropism with suitable substrates such as amino- [7] and aminophenylbenzazoles [8-11]. These equilibria usually are different in the singlet excited state than in the ground state, and may involve intramolecular [12] (besides intermolecular) interaction. With the aim of extending the knowledge in the field, we studied the fluorescence of some 2-(4-aminophenyl)pyrido-oxa-, -thia-, and -imidazoles we had recently synthetized [13,14]. As it appears from the following, the predicted trends were confirmed, but some unexpected equilibria were also revealed.



1 X=O
2 X=S
3 X=NH



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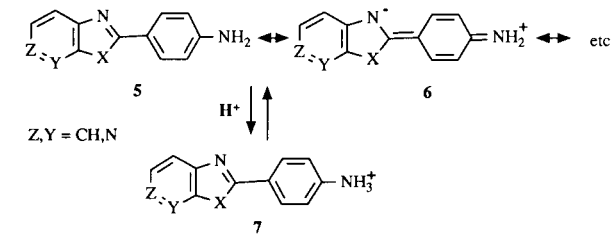
## Results and Discussion.

The compounds considered in this work were the 2-(4-aminophenyl) derivatives of pyrido[3,2-*d*]oxazole (**1**), pyrido[3,2-*d*]thiazole (**2**), pyrido[3,2-*d*]imidazole (**3**) and pyrido[3,4-*d*]imidazole (**4**). The characteristics of the lowest-energy absorption band and of the fluorescence band for these compounds in representative solvents are summarized in Tables 1 and 2. All compounds exhibit both an intensive (log $\epsilon > 4$) absorption and an efficient fluores-



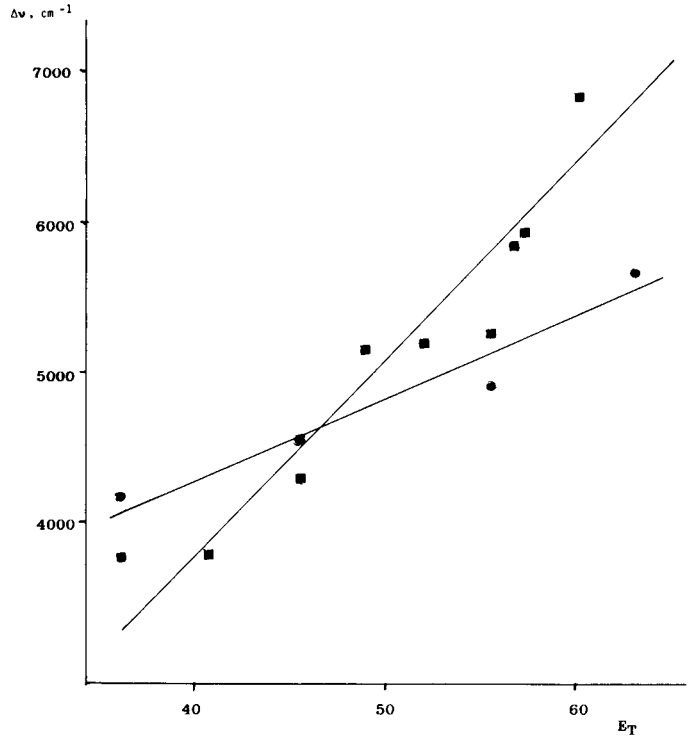




Figure 1. Stokes shift ($\Delta\nu$) *vs* solvent polarity ($E_T$) for heterocycles **3** (■) and **4** (●).

Table 1

Absorption and Fluorescence Characteristics of Compounds **1** and **2**

| Fluorescence | Solvent | Absorption maxima, nm | Fluorescence maxima, nm | Fluorescence quantum yield |
|---|---|---|---|---|
| **1** | Cyclohexane | 327, 340 (sh) | 348 (sh), 364 | 0.9 |
| | MeOH | 343 | 409 | 0.9 |
| | $H_2O$, *p*H 7 [a] | 331 | 420 | 0.8 |
| | 0.5 [a] | 301 | 345 | 0.1 |
| | $H_2SO_4$ 50% | 329 | – | – |
| **2** | Cyclohexane | 335, 345 (sh) | 363 (sh), 381, 420 (sh), | 0.9 |
| | MeOH | 355 | 427 | 0.8 |
| | $H_2O$, *p*H 7 [a] | 342 | 440 | 0.35 |
| | 0.5 [a] | 313 | 365 [b] | 0.03 |
| | $H_2SO_4$ 50% | 336 | – | – |

[a] At intermediate *p*H both forms are present and selective excitation leads to appropriate emission. [b] Residual emission at 440 nm still present (not considered in the calculation of $\phi_F$).

Table 2

Absorption and Fluorescence Characteristics of Compounds **3** and **4**

| Fluorophore | Solvent | Absorption maxima, nm | Fluorescence maxima, nm | Fluorescence quantum yield |
|---|---|---|---|---|
| (**3**) | Dioxane | 328 | 374 | 0.47 |
| | $CH_2Cl_2$ | 327 | 373 | [a] |
| | MeCN | 329 | 383 | 1 |
| | MeOH | 334 | 405, 475 (sh) | 0.72 |
| | EtOH | 341 | 414, 480 (sh) | 0.62 |
| | *i*-PrOH | 339 | 411, 480 (sh) | 1 |
| | $EtOCH_2CH_2OH$ | 338 | 410, 470 (sh) | 0.68 |
| | $CF_3CH_2OH$ | 317 | 405, 517 | 0.02 |
| | $CH_2OHCH_2OH$ | 339 | 423, 500 (sh) | 0.24 |
| | $CH_2OHCHOHCH_2OH$ | 336 | 420 | 0.19 |
| | $H_2O$, *p*H 7 [b] | 327 | 430 | 0.06 |
| | *p*H 0,5 [b] | 319 | 370 | 0.02 |
| | $H_2SO_4$ 50% | 314 | – | – |
| (**4**) | Dioxane | 317 | 365 | 0.15 |
| | MeCN | 317 | 370 | 0.46 |
| | MeOH | 323 | 382, 470 (sh) | 0.35 |
| | $H_2O$, *p*H 7 [b] | 326 | 396 | 0.4 |
| | *p*H 0.5 [b] | 288 | – | – |
| | $H_2SO_4$ 50% | 291 | – | – |

[a] Photochemically unstable. [b] At intermediate *p*H both forms are present and selective excitation leads to the appropriate emission.

cence ($\phi > 0.5$) in organic solvents as well as in water at a neutral *p*H. The fluorescence in an apolar medium, such as cyclohexane, is more structured than the absorption band and shows a small Stokes shift. In the case of compound **1** the 0-0 vibrational maxima in the fluorescence and in the absorption spectra are almost superimposed. As for polar solvents, while affecting only marginally the absorption spectrum, they cause a conspicous red shift of the fluorescence spectrum, and Stokes shift of 6000-8000 $cm^{-1}$ are observed for all compounds in water. In Figure 1 the Stokes shift is plotted *vs* the solvent polarity parameter $E_T$ for compounds **3** and **4** and shows a reasonable linearity. This evidence demonstrates that $S_1$, is a $\pi\pi^*$ state with internal charge transfer (ICT) character. The ground state is best described by formula **5** but in the singlet excited state the zwitterionic formula **6** (and its mesomeric structures) becomes more important as the polarity of the medium increases.

In aqueous solution at a lower *p*H both-absorption and emission spectra are strongly blue shifted. Both emissions are observed in the *p*H range 1-4. Under these conditions **1-4** are partially protonated ($pk_a$ is *ca* 2.5 in all cases) and selective excitation of the protonated or the unprotonated form leads to the short, or respectively to the long, wavelength fluorescence. Thus, emission is faster than proton exchange. The fluorescence of the protonated form is reminescent of that of the parent heterocycles under similar conditions both as far as the wavelength and as far as the intensity ($\phi_f < 0.1$) are concerned. For example, similar data have been reported for benzimidazole in aqueous acids [7]. This is consistent with the representation that when the amino group is protonated the chromo-

phore involved in the transition is essentially the heterocyclic ring. In turn, this can be likened to an aniline (or phenol, or thiophenol) derivative carrying two electron withdrawing substituents in positions 2 and 6. Thus also in the protonated form **7**, $S_1$ is a $\pi\pi^*$ (ICT) state, though with different localization of the donor and acceptor moieties. Noteworthy, compound **4** having a different aza substitution does not show any fluorescence from the protonated state, possibly because the ICT state in less stabilized and a $n_N\pi^*$ state is sufficiently low for favoring an alternative decay pathway such as intersystem crossing to the triplet. Under strongly acidic conditions, where the dication is present, none of the present compounds emit. Same related benzothiazoles have been reported to emit also when diprotonated [11]. Apparently, the additional basic center present in these molecules (the pyridine nitrogen) is involved in further protic equilibria inhibiting emission.

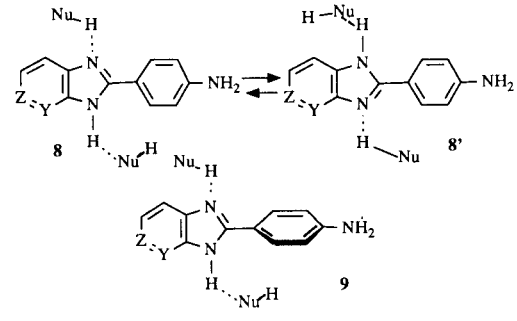
While this simple rationalization is sufficient for compounds **1** and **2**, the situation with the pyridoimidazoles **3** and **4** requires a more detailed discussion. The main peculiarities with respect to the other derivatives are (i) a weaker fluorescence in water and (ii) a double emission in alcohols. The latter phenomenon has been examined in detail (see Table 2). The fluorescence maximum appears to undergo a shift to the red with increasing proton acceptance of the solvent (*e.g.* MeOH < EtOH, *i*-PrOH, or $EtOCH_2CH_2OH$) besides the generally observed shift to the red with the solvent polarity (*e.g.* MeOH < $EtOCH_2CH_2OH$ < $CH_2OHCH_2OH$, $CF_3CH_2OH$). The fluorescence quantum yield, on the other hand, decreases strongly with the acidity of the solvent (alcohols > > $H_2O$ > $CF_3CH_2OH$). As for the second emission, this appears as a marked shoulder at the long-wavelength end of the main fluorescence band in all the alcohols we tested (but not in different solvents), with a separate maximum in trifluoroethanol and an intensity between 15 and 40% of the main emission. The ratio between the two bands does not depend on the irradiation wavelength. However, the intensity of the short-wavelength emission increases and that of the other one decreases on lowering the temperature (*e.g.* for **3** the ratio between the two emissions increases from 4.2 to 6.7 when the temperature is lowered from 20 to −35°).

Since this behavior is obtained only with the pyridoimidazoles **3** and **4** and not with their oxa and thia analogues, it must be related to the NH group.

The simplest model accounting for these observations calls for strong hydrogen bonds involving both the $sp^2$ nitrogen(s) and the NH group in these compounds (*e.g.* formula **8**). This accounts for the importance of both proticity and the proton acceptor capability of the medium. The expected increase in basicity of the $sp^2$ nitrogen in the excited state explains the inefficient emission in stronger proton donating solvents such as water or trifluoroethanol. Indeed, this is due to a fast prototropic equilibrium, *e.g.* between formula **8** and **8'**. This is well distinguished from actual protonation in acidic aqueous medium, recognized from the specific emission of the cation (see above) as well as for the double emission from different tautomers, which has been reported for some related 2-(2-aminophenyl) derivatives [12].

As for the long wavelength emission, this can be explained with the participation of a twisted intramolecular change transfer (TICT) state [15,16], *e.g.* formula **9**, as previously observed with electron withdrawing substituted anilines. The rotation **8** → **9** encounters a small barrier (see the temperature effect and the viscosity effect with glycerol), as reported also in previous cases [15]. The fact that the emitting twisted state is populated only with the imidazole derivatives and only in alcohols shows that stabilization of the heterocyclic ring through H-bonding, as in formula **8**, is required for making the barrier to rotation low enough. In the other cases emission take place from the planar state with an efficiency near to unitary.

In conclusion, this work identifies a new class of heterocyclic compounds possessing TICT states, a phenomenon of potential applicative significance on which research is active, and gives information about hydrogen bonding and protonation in the excited state of heterocycles.




## EXPERIMENTAL

The heterocycles **1-4** were prepared by reduction of the corresponding *p*-nitrophenyl derivatives as previously reported [13,14].

Absorption spectra were measured by means of a Cary 19 spectrophotometer. Corrected emission spectra were measured by means of a Perkin-Elmer LS50 spectrofluorimeter. Fluorescence quantum yields were determined by using quinine sulfate in 0.1*N* sulfuric acid as the standard ($\phi_F$ = 0.55). Buffered aqueous solutions were prepared by mixing the appropriate amounts of potassium hydroxide and phosphoric acid. To these a concentrated methanolic solution of the fluorophore was added, in such a way as to obtain a 0.5% (v/v) methanolic solution *ca* $10^{-6}M$ in the fluorophore.

Acknowledgment.

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