

Short Communication

Evidence for perturbation of the pyridine non-bonding electron pair in 2,6-diaminopyridine

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In a previous study from this laboratory we discussed the phosphorescence of 2-, 3- and 4-aminopyridine (AMP) [1]. With regard to the diaminopyridines (DAMP) the possibility exists that steric effects in the vicinity of the ring nitrogen could destroy the planarity of the non-bonding electron pair of pyridine relative to its π electron system. In order to test this possibility we have investigated the phosphorescence of 2,6-DAMP and 2,3-DAMP and compared them with that of 2-AMP. Although the phosphorescence spectra of these three molecules are unstructured, we were particularly interested by the observation that the phosphorescence maximum of 2,6-DAMP (405 nm) appears at higher energies than those of 2-AMP (430 nm) and 2,3-DAMP (472 nm). It is noteworthy that the first absorption maximum is approximately the same for 2,6- and 2,3-DAMP and appears at 309 nm in ethyl alcohol. With the fluorescence spectra of these molecules already known [2], we have constructed in Fig. 1 an energy level diagram of the

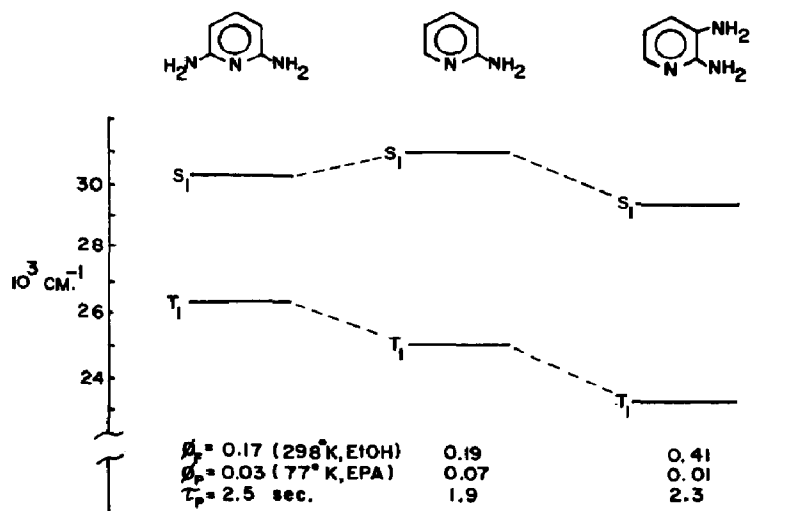


Fig. 1. Electronic state diagram (approximate 0-0 level representation) of the lowest excited singlet and triplet for 2,6-DAMP, 2,3-DAMP and 2-AMP constructed from fluorescence and phosphorescence measurements.

approximate 0–0 singlet and triplet levels of these molecules. Two features are evident in the diagram: (a) the energy of the lowest triplet for 2,6-DAMP lies highest and (b) the splitting between the lowest singlet and triplet states is the smallest for the 2,6-isomer. The phosphorescence lifetime of the molecules 2,6-DAMP, 2-AMP and 2,3-DAMP at 77 K were determined to be 2.5 s, 1.9 s and 2.3 s respectively, so that there is no difficulty in assigning the lowest triplet as π, π^* . The phosphorescence quantum yields measured at 77 K in ether–isopentane–ethanol (EPA) relative to the value of unity for benzophenone are also included in Fig. 1. It is evident that, although the singlet state energies are approximately the same for the three molecules, the lowest triplet in the 2,6-isomer is 3000 cm^{-1} higher in energy than the 2,3-isomer. We should like to suggest that in 2,6-DAMP non-planarity at the pyridine nitrogen destroys the orthogonality between the non-bonding electron pair and the π -electron system, forcing the lowest triplet to a higher energy. This shift is also supported by CNDUV99 calculations [3] which we have performed on these molecules. The n, π^* singlet is predicted to be at $40 \times 10^3 \text{ cm}^{-1}$ in 2,6-DAMP (S_2), at $30.1 \times 10^3 \text{ cm}^{-1}$ in 2,3-DAMP (S_1) and at $30.6 \times 10^3 \text{ cm}^{-1}$ in 2-AMP (S_1). For the triplet manifold CNDUV99 predicts the lowest triplet to be π, π^* and to lie at $25.75 \times 10^3 \text{ cm}^{-1}$, $23.58 \times 10^3 \text{ cm}^{-1}$ and $21.62 \times 10^3 \text{ cm}^{-1}$ for 2,6-DAMP, 2-AMP and 2,3-DAMP respectively.

We have in addition also observed that the phosphorescence maximum of 3,4-DAMP occurs at 435 nm, indicating a lower lying triplet than the 2,6-isomer even though the former has a higher singlet state. This behavior is consistent with the non-orthogonality of n, π^* and π, π^* transitions in 2,6-DAMP.

In aromatic nitrogen heterocyclics an efficient intersystem crossing occurs via $n, \pi^* - \pi, \pi^*$ interactions [4] which can be removed by destroying the orthogonality and interaction of these two transitions. Accordingly, the twofold decrease in the phosphorescence yield of 2,6-DAMP relative to 2-AMP is attributed to a higher lying $^1n, \pi^*$ state. The 2,6-isomer has the largest fluorescence yield of the aminopyridines, consistent with this effect. In 2,3-DAMP the large energy splitting between the lowest singlet and triplet could inhibit intersystem crossing while fluorescence is maintained at a rather high efficiency, as is observed experimentally in ethyl alcohol.

We believe that these observations provide an illustration of the importance of the preferred $n, \pi^* - \pi, \pi^*$ intersystem crossing process in aromatic nitrogen heterocyclics [4]. The effect is smaller in the singlet manifold since fluorescence reflects primarily the lowest π, π^* transition and its corresponding oscillator strength. CNDUV99 calculations on these molecules support the view that the lowest π, π^* transition and its corresponding oscillator strength provide a meaningful indicator of fluorescence behavior. It is evident that as the n, π^* transition shifts to a higher energy and interaction with π, π^* levels is diminished fluorescence should increase. In fact, 2,6-DAMP is the most efficient fluorescer of these molecules, *e.g.* in cyclohexane the values of ϕ_F are 0.16, 0.06 and 0.04 for 2,6-DAMP, 2,3-DAMP and 2-AMP

respectively. The 2,6-isomer is also the most efficient fluorescer of the aminopyridines in polar and hydrogen-bonding solvents.

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