

FLASH PHOTOLYSIS STUDY OF AMINOPYRIDINES

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Summary

A variable temperature flash photolysis study in different solvents indicates that the triplet-triplet (T-T) absorption of 2-aminopyridine, 2-N-dimethylaminopyridine and 4-aminopyridine can be observed at temperatures below -160°C in EPA. The absorption wavelength maxima for 2-aminopyridine (390 nm) and 4-aminopyridine (395 nm) are attributed to pyridine-type T-T absorption rather than to an intramolecular charge transfer T-T absorption. The absence of T-T absorption for 3-aminopyridine in the wavelength region 350 - 600 nm, despite its long phosphorescence lifetime of 3.6 s, suggests that an upper triplet state exists at an energy exceeding $60\,000\text{ cm}^{-1}$. The absence of triplet absorption in ethyl ether and 3-methylpentane for 2-aminopyridine and 4-aminopyridine supports the view that the triplet yield is enhanced in polar and hydrogen bonding solvents.

Introduction

In previous studies from this laboratory we reported the fluorescence and phosphorescence parameters of 2-aminopyridine (2-AMP), 3-aminopyridine (3-AMP) and 4-aminopyridine (4-AMP) [1 - 3]. With the aim of further elucidating the excited state properties of these molecules we initiated a flash photolysis study in order to consider the upper triplet states of these molecules. Despite the many reports in the literature concerned with substituted benzenes, naphthalenes and other polycyclic aromatics, the upper triplet states of simple aromatic heterocyclics have not been thoroughly investigated. Thus far we have shown that the fluorescence yields of the three isomeric molecules decrease in the order $2 > 3 > 4$, while the reverse order is observed for the phosphorescence behavior [1, 2]. The phosphorescence yields of 2-AMP, 3-AMP and 4-AMP in EPA at 77 K are 0.07, 0.38 and 0.54, respectively [2]. Although relaxation from electronically excited states of pyridine has not directly been observed, triplet-triplet (T-T) absorption has been reported for 4-N-dimethylaminopyridine [4]; however, its appear-

ance in the visible region ($\lambda_{\text{max}} = 500 \text{ nm}$) was attributed to an intramolecular charge transfer triplet-triplet absorption. Consequently, thus far no T-T absorption below 400 nm is known for any pyridine derivatives, which would be characteristic of the ring π, π^* system. In the case of benzene T-T absorption is known to occur at 240 nm [5] and a weaker band is also observed at 430 nm [6]. Cadogan and Albrecht [7] reported that the T-T absorption spectrum of aniline in EPA appears at 420 nm.

Owing to the solvent effect on the luminescence behavior of aminopyridines [1 - 3] flash experiments were undertaken in different solvents to try to evaluate whether or not the triplet yield is solvent dependent, unlike the situation which prevails in aromatic hydrocarbons.

Experimental

Materials

2-AMP, 3-AMP and 4-AMP, obtained from the Aldrich Chemical Co., were purified as described elsewhere [1]. 2-N-dimethylaminopyridine was distilled at 119 °C and 98 Torr prior to use. Spectrograde solvents, EPA, ethyl ether and isopropyl alcohol, were used as received. Chromatoquality 3-methylpentane was dried over MgSO_4 before using.

Apparatus

The flash apparatus (20 μs pulse) employed a 200 W tungsten-halogen lamp as the analyzing source which was focused by means of quartz lenses through the long axis of the flash photolysis cells onto the entrance slit of an Aminco grating monochromator. The output of an RCA 1P28 photomultiplier tube was fed via a cathode follower to a Tektronix 545B oscilloscope equipped with a 1A5 plug-in unit. In most experiments the flash energy was 80 J, however, in cases where the transient yields were low higher flash energies were employed. The sample was placed between two xenon flash lamps. Concentrations were generally $4 \times 10^{-4} \text{ M}$ and all samples were vacuum degassed at 10^{-4} Torr prior to flame sealing. For variable temperature studies the flash cell was mounted in an optical quartz Dewar and cooled by a flow of heated liquid nitrogen. The temperature inside the Dewar was monitored by an iron-constantan thermocouple whose voltage regulated a relay to control a heating coil which boiled liquid nitrogen. Since photoproducts are generated in room temperature experiments each solution was cooled to at least $-50 \text{ }^\circ\text{C}$ prior to flashing in an attempt to avoid photochemical decomposition. Using this procedure the solutions were found to be photochemically stable under repeated flashing.

Results

The absence of T-T absorption at room temperature in all the molecules investigated necessitated a variable low temperature study in order to slow

down electronic relaxation. When 4×10^{-4} M 2-AMP in EPA was flashed no triplets were observed until a temperature of -155 °C was achieved. At this temperature a transient with an absorption maximum at 390 nm appears. Further cooling slowed down the rate of decay of the absorbing transient and at -160 °C the first order decay constant was 381 ± 39 s $^{-1}$. Since 2-AMP phosphoresces, the decay constant was also measured at 435 nm for the emission at the same temperature. A value of 393 ± 14 s $^{-1}$ was obtained which is in satisfactory agreement with the absorption decay constant, thereby confirming that the absorbing transient is indeed the triplet. The spectrum for the triplet is given in Fig. 1, which indicates a maximum at 390 nm. Triplet absorption was also observed in isopropyl alcohol at temperatures below -89 °C and at -110 °C the first order decay constant was measured to be $(5.5 \pm 1.2) \times 10^2$ s $^{-1}$. Triplet absorption was not observed in ethyl ether cooled to -110 °C nor in 3-methylpentane cooled to -188 °C.

When 2-N-dimethylaminopyridine in EPA at temperatures below -166 °C is flashed triplet absorption is observed with a maximum at 470 nm. At a temperature of -171 °C the unimolecular decay constant of the triplet was determined to be 285 ± 44 s $^{-1}$. Verification that the absorbing species was the triplet was again achieved by comparing the decay constant for phosphorescence at 420 nm with that of the absorption transient. T-T absorption was also observed in isopropyl alcohol and in 3-methylpentane, however, the intensity was much weaker in the latter case. In all three solvents the transient decay was found to be unimolecular.

Although 3-AMP phosphoresces, flash photolysis of this molecule in EPA does not give rise to any T-T absorption in the wavelength region above 300 nm. This observation is surprising since the absorption and emission characteristics of 2-AMP and 3-AMP are similar. At 77 K the exciting flash

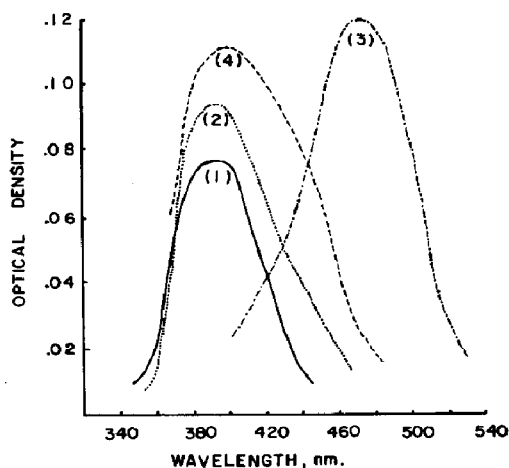


Fig. 1. T-T absorption spectra of aminopyridines: curve 1, 2-AMP in EPA, -166 °C; curve 2, 2-AMP in isopropyl alcohol, -110 °C; curve 3, 2-N-dimethylaminopyridine in EPA, -173 °C; curve 4, 4-AMP in EPA, -170 °C. Degassed solutions at concentrations of about 4×10^{-4} M, 80 J per flash.

produces an easily detectable phosphorescence in 3-AMP with a maximum at 450 nm and a lifetime of 3.6 s; consequently, the absence of T-T absorption in EPA cannot be attributed to a small triplet yield.

Flash photolysis of 4-AMP in EPA gives rise to an absorption transient detectable at temperatures up to $-160\text{ }^{\circ}\text{C}$ which exhibits a maximum at 395 nm. The absorption decay constant is first order with $k = 24.9 \pm 5.9\text{ s}^{-1}$ at $178\text{ }^{\circ}\text{C}$ and compares favorably with the decay constant for the phosphorescence monitored at 355 nm which is $26.4 \pm 7.1\text{ s}^{-1}$. This agreement in decay constants for the absorbing and phosphorescing species confirms its origin as the triplet state of 4-AMP. No T-T absorption was observed in 3-methylpentane down to a temperature of $-180\text{ }^{\circ}\text{C}$, nor was it observed in ethyl ether cooled to $-110\text{ }^{\circ}\text{C}$.

A variable temperature study of the first order decay constants for the triplet of 2-AMP, 2-N-dimethylaminopyridine and 4-AMP yielded activation energies of 3.5, 4.2 and 4.3 kcal mol $^{-1}$, respectively.

Discussion

It is apparent from these studies that at room temperature triplet relaxation in aminopyridines is rapid compared with the 20 μs flash pulse. The observation of T-T absorption below 400 nm in 2-AMP and 4-AMP suggests that the transition is of the pyridine type, π, π^* . In contrast, with 2-N-dimethylaminopyridine the 470 nm peak for the T-T absorption may implicate an intramolecular charge transfer transition. Prior to this study, only the intramolecular charge transfer T-T absorption of 4-N-dimethylaminopyridine at 500 nm had been reported for a pyridine derivative [4].

The results are conspicuous in that we were unable to observe any T-T absorption for 3-AMP down to a wavelength of 350 nm, despite its long phosphorescence lifetime. Since this flash absorption behavior is similar to that of benzene, we constructed an energy level diagram of the aminopyridines investigated, along with similar diagrams for benzene and pyridine, for the purpose of finding an explanation for the absence of T-T absorption in 3-AMP. The energies of the lowest excited singlet (S_1), the lowest triplet (T_1) and the upper triplet (T_n) obtained from fluorescence in ethyl alcohol [1], phosphorescence in EPA at 77 K [2] and the present flash photolysis study, respectively, are summarized in Fig. 2. From the overall emission characteristics of these heterocyclics, we suggest that a ${}^3n, \pi^*$ state is present in the vicinity of $33\,000\text{ cm}^{-1}$, which could account for the larger phosphorescence yield of 4-AMP, $\phi_p = 0.54$ in EPA [2], and 4-N-dimethylaminopyridine, $\phi_p = 0.87$ in EPA, relative to 2-AMP and 3-AMP. The existence of a ${}^3n, \pi^*$ (3B_1) state at $33\,223\text{ cm}^{-1}$ in pyridine has recently been predicted using the INDO technique modified for the calculation of triplet states [9]. The near degeneracy of $T(n, \pi^*)$ and $S_1(\pi, \pi^*)$ in 4-AMP should favor intersystem crossing, whereas in 2-AMP and 3-AMP the $T(n, \pi^*)$ state lies above $S_1(\pi, \pi^*)$ and the triplet yields would be smaller. Unfortunately, the

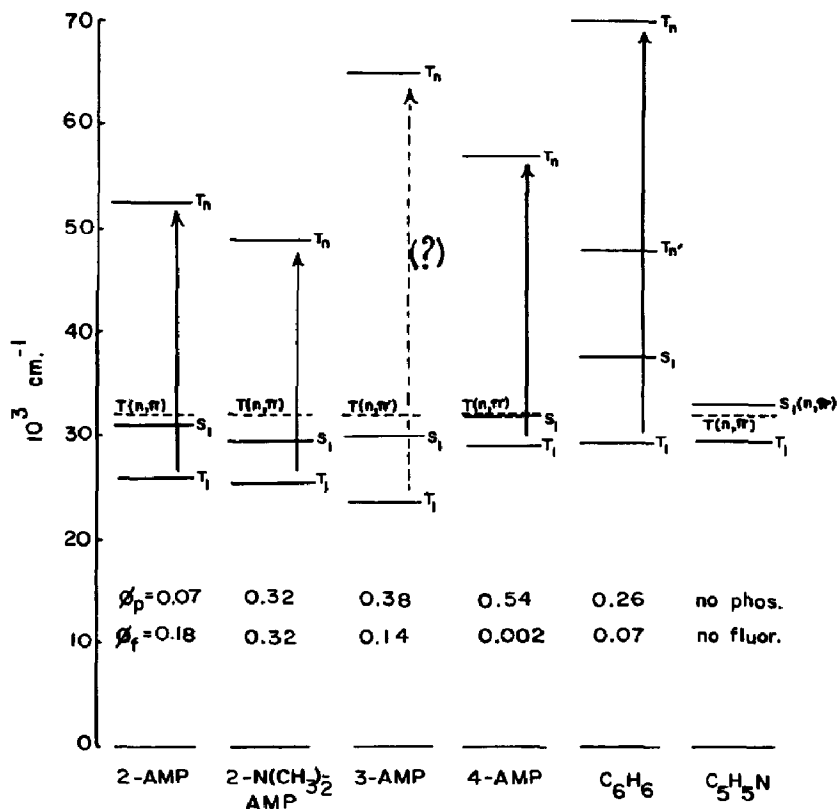


Fig. 2. Electronic state diagram (approximate 0-0 level representation) of aminopyridines constructed from fluorescence data in ethyl alcohol [1, 3], phosphorescence data in EPA [2] and the present flash photolysis study. The horizontal broken lines represent the suggested location of the $^3n, \pi^*$ level which can account for the variation of triplet population and phosphorescence in these molecules. The energy levels for benzene and pyridine are included for comparison purposes.

intensity of the triplet absorptions in Fig. 2 cannot be readily related to the triplet yield since photon input, the absorption spectra and extinction coefficients are different for each molecule. In 3-AMP there is the largest S_1-T_1 energy splitting of the four aminopyridines investigated, which resembles the situation present in benzene. In Fig. 2. it is also seen that the $^3n, \pi^*$ level of 3-AMP is well above that of the lowest singlet, so that its importance in intersystem crossing is minimized, thus making the emission characteristics of 3-AMP and benzene very similar. Consequently, we feel confident that the energy levels of 3-AMP resemble those of benzene more than they do those of pyridine and that the T-T absorption maximum of 3-AMP should appear in the vicinity of 250 nm as it does in benzene.

In the case of pyridine the placing of the $^3n, \pi^*$ level above the lowest $^3\pi, \pi^*$ state accounts for an inefficient intersystem crossing between states of the same symmetry, and in view of the absence of luminescence, it follows that internal conversion of S_1 to S_0 is important in pyridine.

The absence of T-T absorption for 2-AMP and 4-AMP in ethyl ether and 3-methylpentane can be attributed to a low triplet yield, a short triplet lifetime or a combination of both. In view of the solvent effect on the fluorescence [1] and phosphorescence [2] of these molecules, we consider the primary cause to be a solvent dependent triplet yield, *i.e.* ϕ_T increases with solvent polarity and hydrogen bonding ability.

Conclusion

The results presented in this study outline the conditions needed to observe triplets in related aromatic azines and should stimulate further studies directed towards a better understanding of electronic relaxation in heterocyclic molecules. It appears that the position of the lowest $^3n, \pi^*$ state dramatically controls the luminescence and excited state behavior of the aminopyridines.

References

- 1 A. Weisstuch and A. C. Testa, *J. Phys. Chem.*, 72 (1968) 1982.
- 2 S. Hotchandani and A. C. Testa, *J. Chem. Phys.*, 59 (1973) 596.
- 3 S. Babiak and A. C. Testa, *J. Phys. Chem.*, 80 (1976) 1882.
- 4 A. C. Testa, *J. Am. Chem. Soc.*, 95 (1973) 3128.
- 5 T. S. Godfrey and G. Porter, *Trans. Faraday Soc.*, 62 (1966) 7.
- 6 R. Astier and Y. H. Meyer, *Chem. Phys. Lett.*, 3 (1969) 399.
- 7 K. Cadogan and A. Albrecht, *J. Phys. Chem.*, 73 (1968) 1868.
- 8 S. Hotchandani and A. C. Testa, *J. Chem. Phys.*, 54 (1971) 4508.
- 9 J. R. Ridley and M. C. Zerner, *Theor. Chim. Acta*, 42 (1976) 223.