

PHOTOIONIZATION AND TRIPLET-TRIPLET ABSORPTION OF 4-PYRROLIDINOPYRIDINE

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Summary

A variable-temperature flash photolysis study of 4-pyrrolidinopyridine coupled with phosphorescence and photolysis experiments at 77 K provides evidence that photoionization is a primary process involving an upper triplet state which reverses upon warming. Triplet-triplet absorption was observed at 77 K in ether-isopentane-ethanol with a wavelength maximum of 510 nm and a triplet state lifetime of 1.1 s and was confirmed by comparison with the molecular phosphorescence which has the same lifetime and a wavelength maximum of 380 nm. A second emission in the vicinity of 500 nm observed at 173 K in isopropyl alcohol, which was shorter lived than the molecular phosphorescence, is tentatively assigned as emission from the molecular cation. Evidence for cation emission and recombination with an electron was also obtained for 4-*N*-dimethylaminopyridine. The broadening of the UV absorption band at 257 nm for 4-pyrrolidinopyridine upon cooling in alcoholic and acidic media is attributed to the presence of two or more conformers or to complexation via hydrogen bonding or protonation with the solvent.

1. Introduction

The process of photodissociation and photoionization has remained a subject of continuing interest [1 - 7]. Although cations are expected to be short lived at room temperature owing to irreversible reactions, at low temperatures the absence of diffusion tends to stabilize these species. A recent review of the literature [3] indicates that generally the process is biphotonic and involves either an upper singlet or a triplet state. Although we have previously reported evidence for photodissociation modes in some aminoazines [8], we have been unable to observe photoionization. It is reasonable to expect that if an efficient electron donor substituent were used the probability of this process occurring would be enhanced. The

molecule 4-pyrrolidinopyridine appears to be a suitable case, since initial observations at 77 K showed that its emission decreased with continued irradiation. In view of this behavior we undertook an investigation of its flash photolysis and phosphorescence behavior. Because of its structural similarity, 4-*N*-dimethylaminopyridine was also investigated.

2. Experimental details

2.1. Materials

4-pyrrolidinopyridine obtained from the Aldrich Chemical Co. was vacuum sublimed at 322 K to yield colorless crystals. 4-*N*-dimethylaminopyridine was recrystallized prior to use. The solvents isopropyl alcohol, acetonitrile, isooctane and ether-isopentane-ethanol (EPA) (Spectrograde) were used as received.

2.2. Apparatus and procedures

The absorption spectra were obtained using a Cary model 14 spectrophotometer. Steady state irradiations at 77 K were performed using an unfiltered high pressure mercury arc since the reversible photochemical effects reported here were barely perceptible when monochromatic excitation at 254 or 285 nm was used. Flash photolysis measurements were made using the conventional 20 μ s xenon flash apparatus described previously [9].

3. Results

The UV excitation of 4-pyrrolidinopyridine in EPA at 77 K gives a phosphorescence emission centered at 380 nm; however, its intensity decreases with irradiation time as shown in Fig. 1. It should be noted that upon thawing and refreezing the phosphorescence appears to recover its initial value. Spectrum 1' in Fig. 1 is the phosphorescence spectrum measured using a 10 nm band interference filter centered at 285 nm, from which the 0-0 band of the lowest triplet is estimated to be at 28 500 cm^{-1} . After three successive photolyses followed by thawing and refreezing cycles the phosphorescence intensity returned to its initial value as is seen in Fig. 1, spectra 4, 6 and 7. No phosphorescence was observed in a methylcyclohexane glass. In order to assess the reversibility of this emission the UV absorption spectrum was also measured after photolysis at 77 K. The behavior of the absorption spectrum of 4-pyrrolidinopyridine in EPA following UV irradiation at 77 K is summarized in Fig. 2. Spectrum 2 shows the growth of a new band at 320 nm, while spectra 3 and 4 show the disappearance of this band after thawing and refreezing respectively.

The flash photolysis of vacuum-degassed 4-pyrrolidinopyridine in isopropyl alcohol at room temperature gives a 2 ms transient with a peak

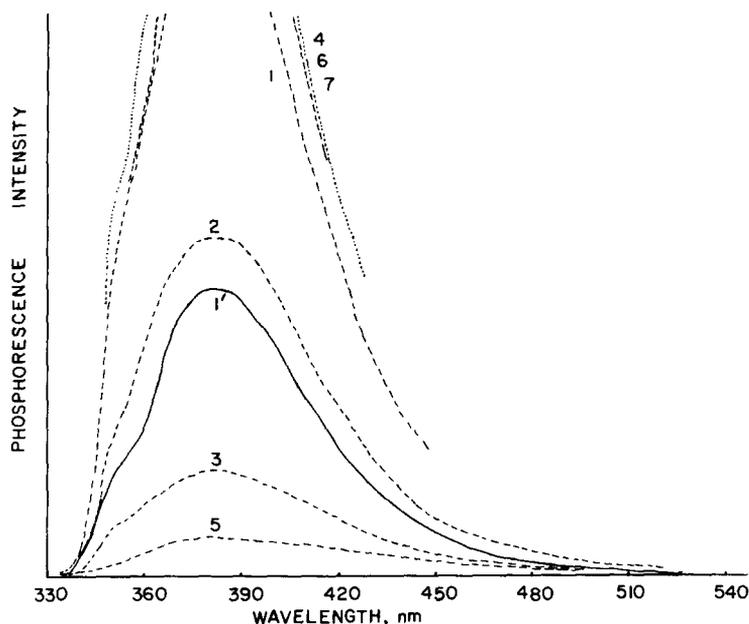


Fig. 1. Variation in the phosphorescence from 2×10^{-4} M 4-pyrrolidinopyridine in EPA at 77 K with photolysis (unfiltered lamp) and thawing-cooling cycles: spectrum 1, $t = 0$; spectrum 2, 1 min irradiation; spectrum 3, 4 min irradiation; spectrum 4, sample 3 after thawing and recooling to 77 K; spectrum 5, 5 min irradiation of sample 4; spectrum 6, sample 5 thawed and reooled; spectrum 7, after third irradiation, thawing and recooling cycle.

at 395 nm which is shown as spectrum 1 in Fig. 3. It was also observed that most of the 257 nm absorption band of 4-pyrrolidinopyridine disappeared after about 35 flashes. This transient also appears in acetonitrile; however, no transients were observed in hydrocarbon solvents. A photoproduct absorbing at 340 nm was formed as is seen in Fig. 4. It should be noted that the photoproduct generated by flashing at room temperature is not the same as that generated by steady state photolysis at 77 K, *i.e.* the product absorbing at 320 nm disappears upon thawing. The flash data also indicate that the extent of photoproduct formation at 340 nm is negligible at 173 K relative to that observed at room temperature. Since the signal is strongest in isopropyl alcohol, variable-temperature measurements were made in this solvent. Upon cooling, the 395 nm band disappeared, and no new absorbing transients were detectable down to 173 K; however, normal molecular phosphorescence with a peak at 380 nm was observable at 173 K, and a second emission in the vicinity of 500 nm was also seen, *i.e.* no absorbing transients were observed at 173 K but two emissions were detectable.

Variable-temperature flash photolysis measurements were also performed in EPA and indicated one absorbing transient at 510 nm with a lifetime of 1.1 s at 77 K, shown as spectrum 2 in Fig. 3, and one emission band

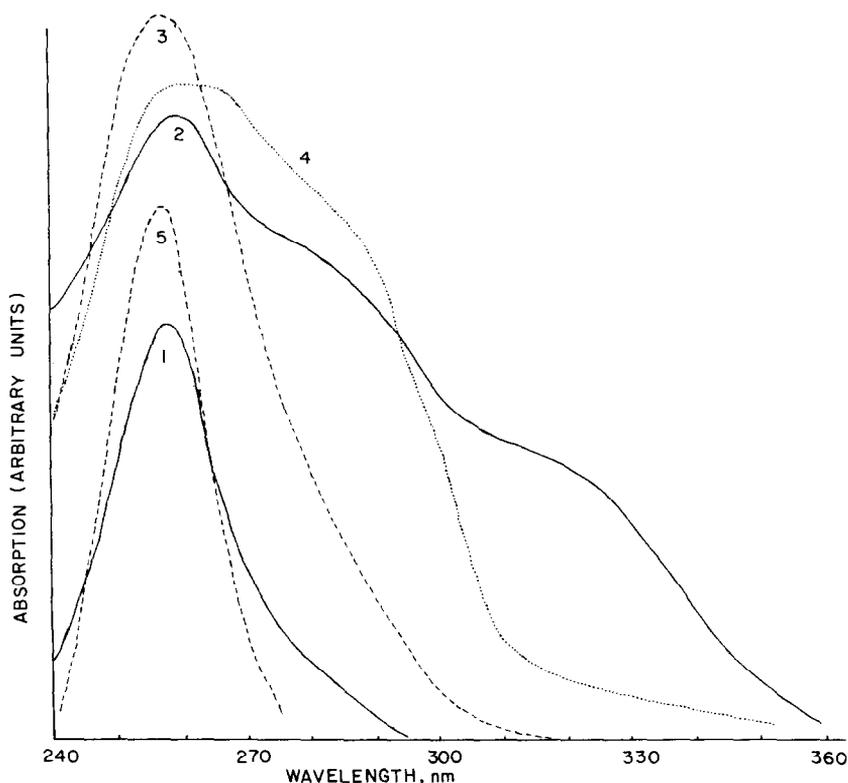


Fig. 2. Variation in the UV absorption band of 4-pyrrolidinopyridine before and after photolysis at 77 K: spectrum 1, 298 K, before photolysis; spectrum 2, 77 K, after 18 min photolysis; spectrum 3, 298 K, sample 2 after thawing; spectrum 4, 77 K, sample 3 refrozen; spectrum 5, 298 K, sample 4 after thawing.

at 380 nm with the same lifetime as the absorption band. No transients were observed in EPA from room temperature down to 96 K.

In order to compare the data for 4-pyrrolidinopyridine with those for a related molecule, we irradiated 4-*N*-dimethylaminopyridine at 77 K in EPA and found that its phosphorescence, centered at 390 nm, also decreased on irradiation using an unfiltered mercury lamp. Further, the initial phosphorescence intensity could be regenerated by thawing and refreezing. The variation in phosphorescence with irradiation time is shown in Fig. 5. Photolysis at 77 K in EPA generated a new absorption band with peaks at 322 and 332 nm, shown in Fig. 6, which disappeared upon thawing; this is very similar to the behavior exhibited by 4-pyrrolidinopyridine. The triplet-triplet absorption of 4-*N*-dimethylaminopyridine has previously been shown to appear at 500 nm [10] and is similar to that of 4-pyrrolidinopyridine reported in the present study.

An unexpected but noticeable effect which appears in the 257 nm absorption band of both 4-pyrrolidinopyridine and 4-*N*-dimethylaminopyridine

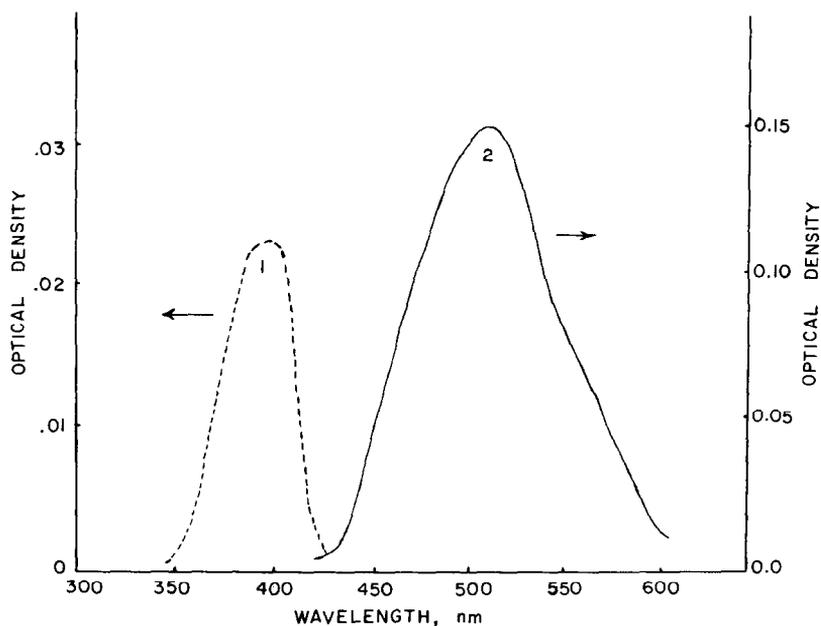


Fig. 3. Summary of transients observed in the flash photolysis of degassed 4-pyrrolidino-pyridine: spectrum 1, 1×10^{-4} M in isopropyl alcohol, room temperature radical transient ($\tau = 2$ ms); spectrum 2, 4×10^{-4} M in EPA, triplet-triplet absorption spectrum observed at 77 K ($\tau = 1.1$ s).

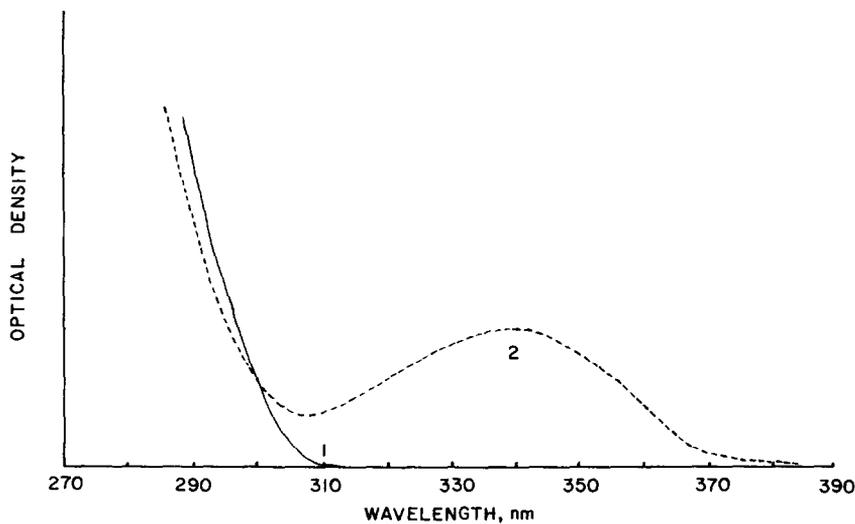


Fig. 4. UV absorption spectrum of the photoproduct obtained on flashing 1×10^{-4} M 4-pyrrolidinopyridine in isopropyl alcohol: spectrum 1, before flashing; spectrum 2, after flashing.

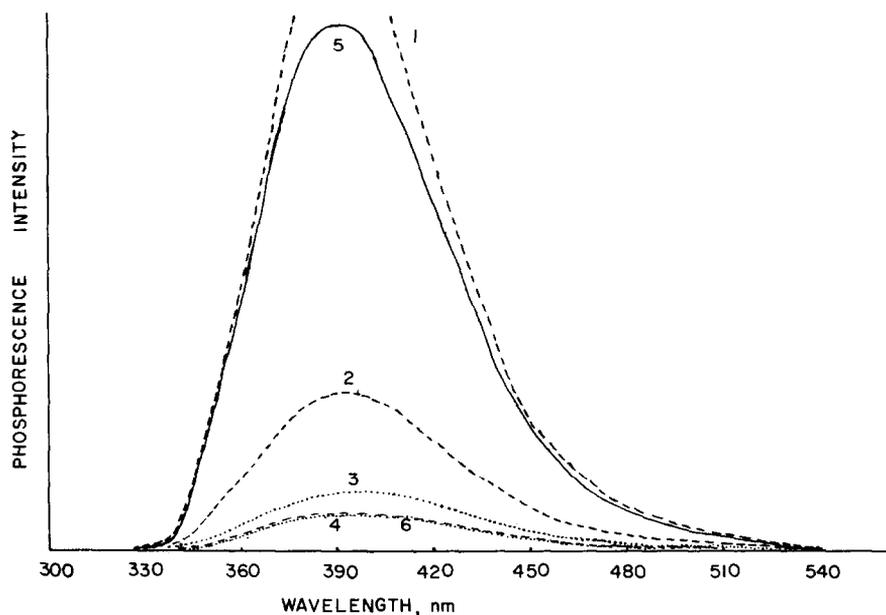


Fig. 5. Variation in the phosphorescence from 4-*N*-dimethylaminopyridine at 77 K in EPA with unfiltered UV irradiation and thawing-cooling cycles: spectrum 1, initial scan; spectrum 2, after 1 min irradiation; spectrum 3, after 6 min irradiation; spectrum 4, after 11 min irradiation; spectrum 5, sample 4 after thawing and refreezing; spectrum 6, after 10 min irradiation of sample 5.

is its broadening from a narrow band at room temperature to a partially resolved double peak at 77 K (see Fig. 2, spectra 4 and 5, and Fig. 6, spectra 3 and 4). We have also observed this partially resolved double peak in the UV spectrum of 4-pyrrolidinopyridine in methanol.

4. Discussion

It is evident from the phosphorescence behavior of 4-pyrrolidinopyridine in EPA that a reversible process, which involves its disappearance with irradiation at 77 K and its return upon thawing and refreezing, is occurring. Concomitantly, a new absorption band generated at 77 K, which appears at 320 nm, also disappears upon thawing. We conclude that these two events are related and involve the molecular cation generated by photoionization. In view of the relatively large triplet yield of 4-aminopyridine derivatives [11] it is reasonable to suggest that this process involves the lowest π,π^* triplet state which has insufficient energy and requires a second photon for ionization. Our results indicate a linear dependence of the extent of photoionization on the light intensity; however, this is probably

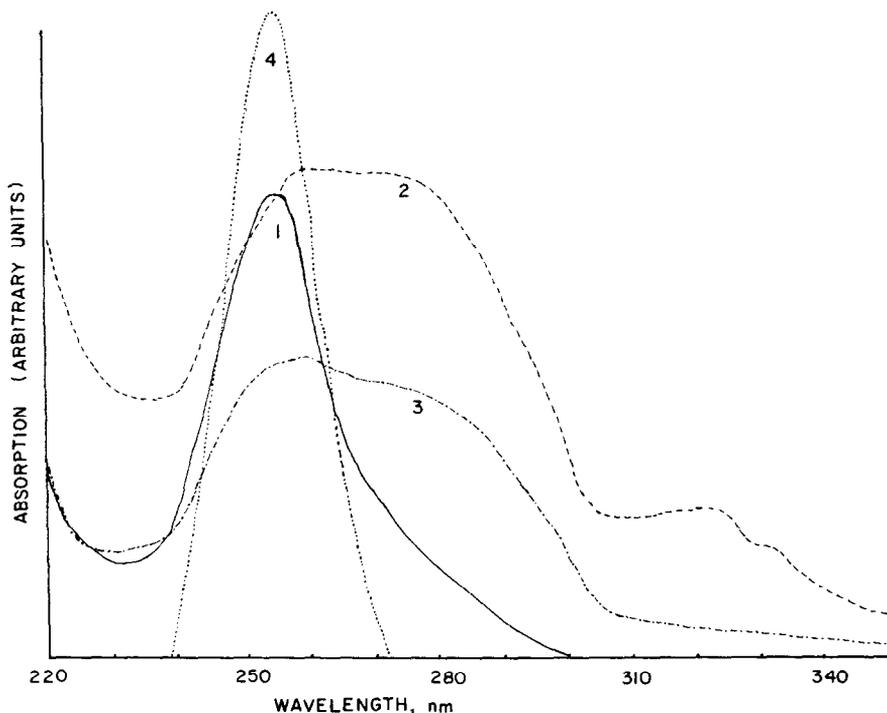


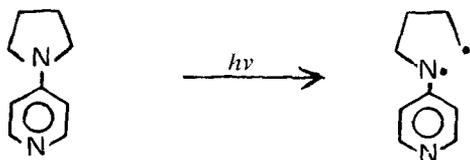
Fig. 6. Variation in the UV absorption spectrum (qualitative) of 4-*N*-dimethylaminopyridine in EPA: spectrum 1, 298 K, before photolysis; spectrum 2, 77 K, after 10 min irradiation; spectrum 3, 77 K, sample 2 after thawing and refreezing; spectrum 4, 298 K, sample 3 after thawing.

due to the long triplet lifetime (1.1 s) at 77 K which increases the probability of absorbing a second photon. 4-*N*-dimethylaminopyridine undergoes a similar reversible process when it is irradiated at 77 K and then warmed, providing additional evidence that both molecules undergo photoionization in a two-photon event involving the lowest π, π^* triplet state. Accordingly, the absorption band at 320 nm observed at 77 K for both molecules is that of the molecular cation. By comparison the molecular cation of *N*-dimethylaniline formed via an upper triplet state through a two-photon event exhibits absorption peaks at 327 and 336 nm [7]. The disappearance of the cation absorption upon thawing is due to the recombination of the cation and the electron as is summarized in the following scheme:



The variable-temperature flash photolysis data for 4-pyrrolidinopyridine in EPA allow us to identify its triplet-triplet absorption band at 510 nm with a lifetime of 1.1 s at 77 K, while its phosphorescence maximum appearing at 380 nm has the same lifetime at 77 K.

The room temperature transient appearing at 395 nm for 4-pyrrolidinopyridine in isopropyl alcohol, which has a lifetime of 2.0 ms and is removed by cooling, is probably due to a radical resulting from bond fission which can react with the solvent:



This photodissociation mode has been reported in aromatic amines [12]. Since our flash results in isopropyl alcohol at 173 K did not yield the triplet-triplet absorption at 510 nm that we observed in EPA at 77 K, we believe that it can be attributed to (1) an emission in this region ($\tau = 8$ ms at 173 K), which we have tentatively assigned to the molecular cation, and (2) the requirement of a lower temperature to slow down relaxation. The normal molecular phosphorescence at 380 nm has a lifetime of about 18 ms at 173 K in this solvent.

The broadened and partially resolved double-band appearance of the 257 nm UV absorption of 4-pyrrolidinopyridine upon cooling was unexpected. An attractive possibility is that it indicates the presence of two conformers upon freezing or that the band remaining at 257 nm arises from the unassociated molecule while the shoulder at 280 nm may be due to a complexed form of the molecule resulting from hydrogen bonding or protonation. Support for this interpretation is the presence of the 280 nm shoulder (absent in non-polar solvents) when 4-pyrrolidinopyridine is dissolved in methanol or in 50% isopropyl alcohol-water solutions 0.1 M in HCl.

In summary, we have demonstrated the reversible photoionization of 4-pyrrolidinopyridine and 4-*N*-dimethylaminopyridine and have identified a maximum at 510 nm for the triplet-triplet absorption of the former. An absorption observed at 320 nm for both molecules at 77 K is assigned to the molecular cation. Finally, the apparent broadening of the UV absorption band at 257 nm upon cooling for each of the two molecules suggests that two or more conformers or a complex with the solvent may be present at 77 K. However, an assessment of the importance of this effect at low temperatures in related molecules will have to await additional investigations.

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