in γ-irradiated MTHF is consistent with an isolated trapped electron, while the one-photon photobleaching of e_t^- produced by TMPD photoionization in MTHF is consistent with the Coulomb well model. This difference sugggests that e_t^- produced by photoionization is trapped somewhat closer to a cation than e_t^- produced by γ irradiation. Further studies on this point would be of interest. This difference also suggests that the energy level structure illustrated in Figure 9 for e_t^- in γ-irradiated 3MH is at least a possible working model at present.

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Flash Photolysis Study of 4-*N*-Dimethylaminopyridine

A. C. Testa

Contribution from the Department of Chemistry, St. John's University, Jamaica, New York 11432, and the Max-Planck Institute for Spectroscopy, Göttingen, West Germany. *Received September 14, 1972*

Abstract: A flash photolysis study of 4-*N*-dimethylaminopyridine in different solvents has led to the assignment of three transient species, together with their corresponding absorption maxima: (a) neutral radical, $\text{Py-}\dot{\text{N}}\text{-CH}_3$ ($\lambda_{\max}$ 315 and 395 nm); (b) radical cation resulting from photoionization ($\lambda_{\max}$ 500 nm); and (c) triplet–triplet absorption ($\lambda_{\max}$ 500 nm). The radical–radical recombination is a second-order process occurring at room temperature with a value of $k/\epsilon_{395\text{ nm}} = 2.58 \pm 0.2 \times 10^5$ cm sec^{-1} in 2-propanol, $4.5 \pm 0.5 \times 10^5$ cm sec^{-1} in acetonitrile, and $1.8 \pm 0.4 \times 10^6$ cm sec^{-1} in ethyl ether. The triplet–triplet absorption is only observed at low temperatures ($< -55°$ in IPA, $< -90°$ in ethyl ether, and $< -150°$ in EPA). The lack of triplet–triplet absorption in 3-MP to temperatures of $-185°$ is probably due to significant variation of the triplet yield with solvent. A short-lived transient ($\tau \approx 50$ μsec) attributed to the radical cation with $\lambda_{\max}$ 500 nm was observed at room temperature only in acetonitrile. The energy of activation for the triplet decay rate constant in EPA was determined to be 3.5 kcal/mol.

Recent interest in the flash photolysis literature has been directed toward the elucidation of electronically excited states in aromatic heterocyclic molecules. The triplet–triplet absorption of acridine has been reported by several groups.[1-5] Qualitative observations of T–T absorption in pyrimidine, pyridazine, quinoxaline, and phenazine in hydrocarbon glassses at 77°K have also been performed.[6] With the use of steady-state cross illumination, Henry and Kasha[7] investigated T–T absorption of quinoxaline, phenoxazine, phenothiazine, and carbazole. Hadley[8] has used the flash photolysis technique to show that internal conversion from the singlet may be important in quinoxaline. Other flash photolysis studies of aromatic heterocyclics include phenoxazine,[9] thymine, uracil,[10,11] and orotic acid.[12] Although no triplet–triplet absorption has been observed in pyridine, we recently reported the T–T absorption of 4-*N*-dimethylaminopyridine in EPA at $-180°$, which exhibits a maximum at 500 nm.[13] This molecule is particularly interesting since we have previously demonstrated that its phosphorescence polarization changes sign on going from a polar solvent such as EPA to a nonpolar solvent such as 3-methylpentane.[14] Since this was the first reported T–T absorption for a pyridine derivative, it became of interest to study the flash photolysis behavior of 4-*N*-dimethylaminopyridine (4-DMAMP) in different solvents with the aim of better understanding the interaction between $^3n,\pi^*$ and $^3\pi,\pi^*$ states. Accordingly, this investigation was performed in isopropyl alcohol, EPA, acetonitrile, ethyl ether, methylcyclohexane, and 3-methylpentane with the temperature varied from room temperature down to 77°K, depending upon the solvent system selected.

Experimental Section

Materials. 4-*N*-Dimethylaminopyridine was obtained from EGA Chemie, West Germany, and purified by recrystallization. The solvents used in this investigation did not produce any absorbing transients upon flashing. Solutions of 4-*N*-dimethylaminopyridine were generally in the range 2×10^{-4} *M*.

Apparatus. All flash measurements were made with 10-cm path length cylindrical Suprasil cells (15-cm o.d.). Solutions were first vigorously degassed at 10^{-5} mm and then flame sealed under vacuum. An energy input of approximately 150 J/flash was employed using an apparatus described elsewhere.[15] A signal of 10-V was used to cover the range between 0 and 100% absorption, and kinetic

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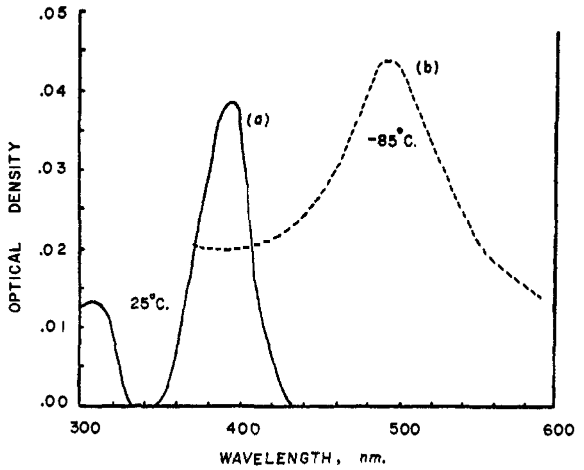
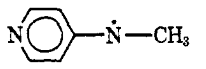


Figure 1. Transient absorption spectra obtained from flashing 4-*N*-dimethylaminopyridine in isopropyl alcohol at 25 (——) and at −85° (- - -).

analysis of transients was performed with a computer. Temperature variation studies were performed by heating liquid nitrogen with a resistance coil and passing the cold gas through a Suprasil dewar containing the sample cell. An iron–constantan thermocouple was used to monitor and regulate the temperature of the sample.

Results

Transient Spectra and Kinetics. (a) In 2-Propanol. Flashing of 2 × 10^{-4} *M* 4-DMAMP in degassed 2-propanol (IPA) gives rise to an absorbing transient with a lifetime of ~2 msec, which has its absorption maxima at 315 and 395 nm; see curve a in Figure 1. The decay is distinctly second order and has a value of k/ϵ_{395} = 2.58 ± 0.25 × 10^5 cm sec^{-1}. The process most likely arises from radical–radical recombination and, by analogy to the results with substituted anilines,[16] is most likely the neutral radical



The absorption spectrum of 4-DMAMP in IPA, before and after flashing, indicates a growth of photoproduct with a wavelength maximum at ~340 nm. It was observed that the photoproduct developed during the lifetime of the radical since the decaying transient did not immediately return to the base line in the region where the photoproduct absorbs. The uv absorption spectrum of a 8.6 × 10^{-5} *M* solution of 4-DMAMP in 2-propanol before and after many flashes is shown in Figure 2. The fact that no transient is observed when flashing in air-saturated solutions tends to favor involvement of the lowest triplet state. It has been demonstrated that the most typical processes occurring in the $^3\pi,\pi^*$ states of aromatic molecules are photodissociation and/or photoionization.[17,18]

Upon cooling the flash cell, contained in a Suprasil dewar, the second order, photochemically induced, radical process is inhibited and no transient is observed until a temperature of −55° is reached, when a new transient, decaying by a first-order process and possessing an absorption maximum near 500 nm, starts to grow in. At −85°, the absorbing transient obeys first-order kinetics with a rate constant 4.91 ± 0.3 × 10^3 sec^{-1}. The low-temperature transient observed in 2-propanol is given as curve b in Figure 1. Evidence that this spectrum is really due to triplet–triplet absorption will be presented later on in this report.

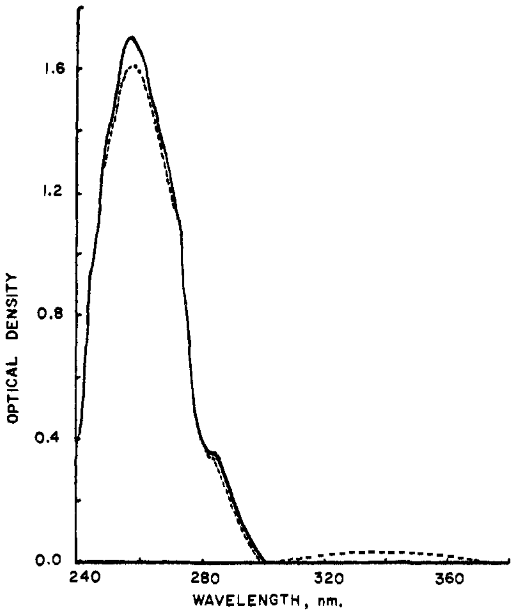
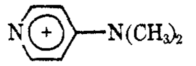


Figure 2. Uv absorption spectrum of 8.6 × 10^{-5} *M* 4-*N*-dimethylaminopyridine in isopropyl alcohol before (——) and after (- - - -) flashing.

(b) In Acetonitrile The flashing of 4-DMAMP in degassed acetonitrile at room temperature gives rise to the same transient (τ ~ 1.5 msec) as seen in isopropyl alcohol, with an absorption maximum near 315 and 395 nm and a second-order decay process with a value of k/ϵ_{395} = 4.5 ± 0.5 × 10^5 cm sec^{-1}. The radical transient is shown as spectrum a in Figure 3. In addition to the radical–radical recombination process in acetonitrile there appears a second, faster decaying transient, with a lifetime of ~50 μsec, resolved in time from the millisecond radical transient, which appears to be second order, but the detailed kinetic analysis was not made due to interference from the exciting flash. For this same reason, its intensity dependence was not investigated. This short-lived transient spectrum is shown as spectrum b in Figure 3. This transient seems to correlate with the cations of substituted anilines[16] and is most probably due to the molecular cation



(c) In Ethyl Ether. In this solvent flashing at room temperature, after degassing, gives rise to a second-order decay process similar to that seen in isopropyl alcohol and acetonitrile and attributed to the neutral radical obtained *via* photodissociation. The absorption maximum appears at 395 nm and the kinetic analysis gives a value of k/ϵ_{395} = 1.8 ± 0.4 × 10^6 cm sec^{-1}. Upon cooling the sample the dissociation event is inhibited and at −90° an absorbing species with a maximum at 500 nm starts to grow in, which has a decay rate that is essentially first order. The absorption spectrum of this transient agrees very closely with the transient observed at −85° in isopropyl alcohol. At

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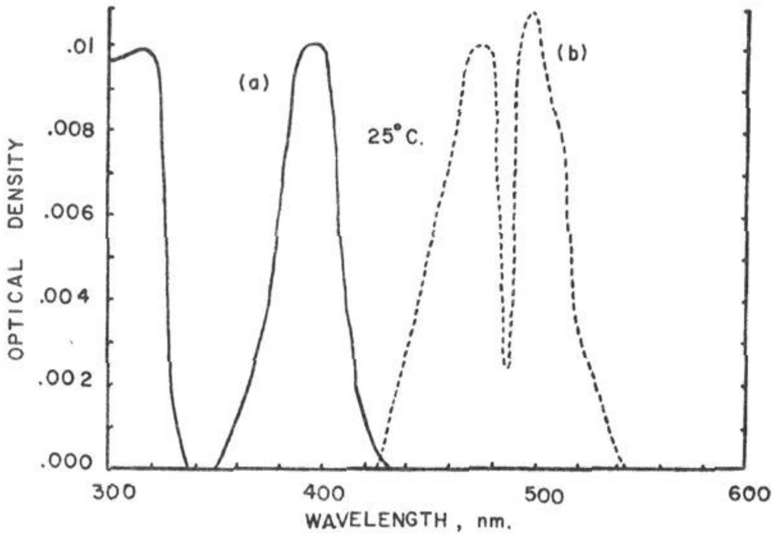

Figure 3. Transient absorption spectra obtained from flashing 4-*N*-dimethylaminopyridine in acetonitrile at 25°. Spectrum a is attributed to the neutral radical and spectrum b is attributed to the molecular cation.

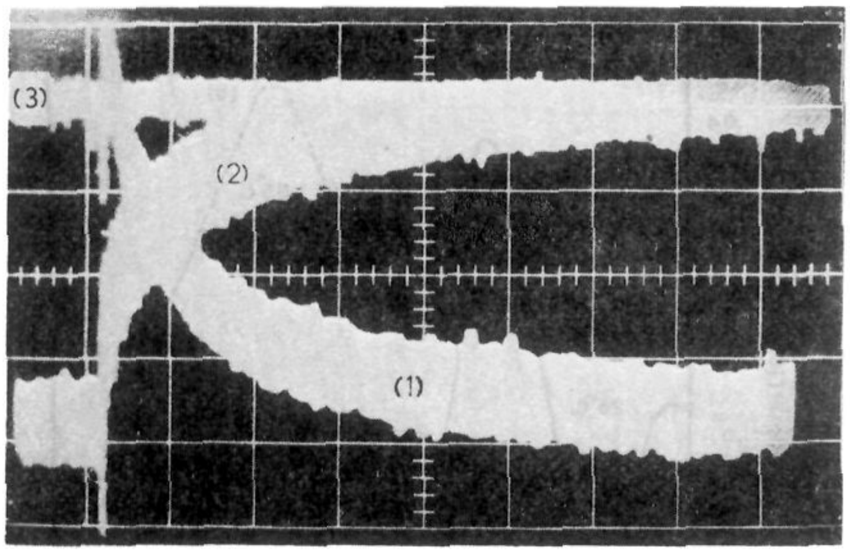

Figure 4. Oscilloscope traces of transient decay of absorbing and phosphorescing species of 1.9×10^{-4} *M* 4-*N*-dimethylaminopyridine in EPA, measured at −177°. (1) Absorbing transient recorded at 500 nm with the vertical axis at 0.20 V/cm and the horizontal time axis at 10 msec/cm. (2) Phosporescence decay at 370 nm with a vertical sensitivity of 0.50 V/cm and the same time sweep as 1. (3) The baseline for return of the phosphorescence emission (energy input 150 J in 20 μsec, 10 cm absorption path length).

−110°, this first-order decay rate constant has a value of $1.05 \pm 0.1 \times 10^4$ sec^{-1}.

(d) EPA Solutions. This solvent was selected for its utility over the broad temperature range from room temperature to −196°. Flashing at room temperature after vacuum degassing yielded no absorbing transient; however, upon cooling an absorbing transient becomes evident at −150°, which intensifies upon further cooling. This transient is the same as the one observed in isopropyl alcohol at −85° and in ethyl ether at −110° and very likely due to the lowest triplet state. At −177° the lifetime of the absorbing transient is 18 msec, and the decay kinetics of the absorbing and emitting species could be compared. The phosphorescence yield and lifetime of 4-*N*-dimethylaminopyridine in EPA at 77°K are 0.87 and 0.63 sec, respectively.[14] In Figure 4 are presented the resulting transient decays for absorption and emission rising from flash excitation of 4-DMAMP at −177°. It is evident that the decay of the absorbing species at 500 nm, curve 1, matches the decay of the emitting species at 370 nm, curve 2, and is therefore identified as a process involving the lowest triplet state. We have previously shown that the lowest triplet state in 4-*N*-dimethylaminopyridine is $^3\pi,\pi^*$.[14] The T–T absorption spectrum of 4-DMAMP is similar to the result given as spectrum b (Figure 1) in isopropyl alcohol and also observed in ethyl ether. In view of the wide temperature range over which EPA can be used for flash photolysis measurements, an Arrhenius plot was made to determine that the energy of activation for decay of the triplet state is 3.5 kcal/mol. The rate constants at different temperatures are given in Figure 5 and the magnitude of the determined value is attributed to the usual variation of solvent viscosity with temperature. An extrapolation of the data, assuming no photochemistry, indicates that the triplet lifetime should be ~10^{-8} sec at room temperature.

(e) Nonpolar Solvents (3-Methylpentane (3-MP) and Methylcyclohexane (MCH)). No transients were observed in these solvents upon flashing at room temperature, nor was any transient observed to −110° in methylcyclohexane and −185° in 3-methylpentane. The absence of any transient in the latter case is surprising since the phosphorescence lifetime of 4-*N*-dimethylaminopyridine in 3-MP at 77°K is 0.32 sec, and its T–T absorption should easily be observable if there is any significant intersystem crossing. The low phosphorescence yield ($\phi_p = 0.023$) in 3-MP, as well as the absence of T–T absorption at −185°, strongly suggests that the triplet yield is very small in the nonpolar solvents. A referee has suggested that the lack of T–T absorption in 3-MP at −185° may be due to the Shpol'skii effect; however, this is an unlikely possibility since there is no evidence to indicate that it is operative in the present system.

In Table I the flash kinetic data for 4-*N*-dimethylaminopyridine in different solvents are summarized. Although the photodissociation event was observed in three different solvents, only in acetonitrile, at room temperature, was evidence for the cation observed. In nonpolar solvents, such as 3-MP and MCH, no radical transients nor triplets were observed.

Table I. Summary of the Flash Kinetic Data for 4-*N*-Dimethylaminopyridine in Different Solvents

(1) Radical–radical recombination (395-nm band)		
		k/ϵ
(a) Isopropyl alcohol		$2.58 \pm 0.2 \times 10^5$ cm sec^{-1}
(b) Acetonitrile		$4.5 \pm 0.5 \times 10^5$ cm sec^{-1}
(c) Ethyl ether		$18 \pm 4 \times 10^5$ cm sec^{-1}
(2) Cation disappearance in acetonitrile (500-nm band)		
($\tau \approx 50$ μsec)		$k/\epsilon = 2.07 \pm 0.4 \times 10^7$ cm sec^{-1}
(3) Low-temperature triplet–triplet absorption (500-nm band)		
		k, sec^{-1}
(a) Isopropyl alcohol	−70°	$8.5 \pm 1 \times 10^3$
	−85°	$5.52 \pm 0.4 \times 10^3$
(b) Ethyl ether	−110°	$10.5 \pm 1 \times 10^3$
(c) EPA	−155°	$4.81 \pm 0.2 \times 10^3$
	−165°	$1.29 \pm 0.1 \times 10^3$
	−185°	$2.08 \pm 0.2 \times 10^1$

Discussion

It is clear from the results that the triplet–triplet absorption of 4-*N*-dimethylaminopyridine can only be observed at low temperatures under conditions in which the photodissociation event is inhibited. The absorbing transients in acetonitrile, namely, the neutral radical and the molecular cation, typify the photochemical events observed in simple aromatic molecules and provide evidence for the involvement of a $^3\pi,\pi^*$ state. Investigations concerning the competition between photoionization and photodissociation of aromatic compounds have been a subject of continuing interest.[17,18] In general, the photoionization is accomplished by a two-photon process, with the lowest triplet state as the intermediate. In the present study the neutral radical and molecular cation most likely arise from the lowest triplet state, but the latter species probably occurs *via* a two-photon process. Similar two-photon ionization processes involving the triplet have been reported in phenoxazine,[9] TMPD,[17,19,20] and certain acridines.[21]

It is indeed surprising that in only a few substituted benzenes has triplet–triplet absorption been reported. The triplet–triplet absorption of 4-DMAMP represents the first substituted pyridine in which this absorption has been observed. Although many substituted benzenes show photoionization and/or bond rupture, the triplet–triplet absorption spectrum for dimethylaniline exhibits maxima at 340 and 480 nm,[22] for *N*,*N*,*N'*,*N'*-tetramethylphenylenediamine at 565 and 600 nm,[19,23] while the T–T absorption of benzene has been reported to be at 240 nm,[24] with an additional weaker absorption appearing at 430 nm.[25] The T–T absorption of 4-DMAMP observed at −180° in EPA is best described as an intramolecular charge transfer T–T absorption, according to the theoretical model of Kimura.[26] For the purpose of comparison to other aromatic amines, the flash photolysis of *N*-dimethyl-β-naphthylamine in cyclohexane yields a triplet–triplet absorption with λ_{max} 475 nm, while the molecular cation appears at 535 nm.[27]

The lack of any observable T–T absorption in a nonpolar solvent is rather surprising, especially since the phosphorescence lifetime in 3-MP at 77°K is 0.32 sec. Previous phosphorescence polarization measurements have demonstrated close-lying $^3\pi,\pi^*$ and $^3n,\pi^*$ states, which can be inverted by solvent variation, and thereby strongly affect intersystem crossing; *i.e.*, the triplet yield of 4-*N*-dimethylaminopyridine in 3-MP is significantly decreased relative to its value in EPA. This proposed variation of triplet yield with solvent can be extremely important in determining the properties of electronically excited states in biologically important molecules. We believe that this investigation provides an impetus for fruitful investigations of the flash photolysis of other substituted pyridines.

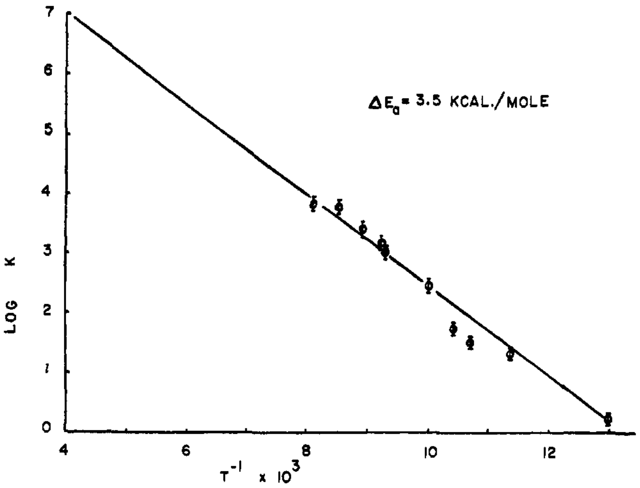

Figure 5. Arrhenius plot of the rate constant for deactivation of the triplet in EPA as a function of the reciprocal absolute temperature.

There is one rather unexpected result from the present study for which an explanation is not immediately forthcoming. While we were able to observe radical–radical recombination at room temperature in 2-propanol and T–T absorption at low temperatures, no transients were observed in EtOH and MeOH. It is generally conceded that the ability to form radicals is about the same in MeOH, EtOH, and IPA, and that the excitation events should be the same. Data on the specific conductance of alcohols indicates that 2-propanol is a better conductor than MeOH, EtOH, or 1-propanol. The following specific conductances at 25°, in units of ohm^{-1}, have been reported: MeOH = 1.5×10^{-9}, EtOH = 1.35×10^{-9}, 1-propanol = 9.17×10^{-9}, and 2-propanol = 5.17×10^{-7}.[28] The fact that the conductance of 2-propanol is significantly larger than the values for methanol and ethanol may possibly explain the absence of radical transients in MeOH and EtOH. One other significant difference regarding the alcohols is that the rate constants for electron transfer from the α-alcohol radical, $R_1R_2\dot{C}OH$, to nitrobenzene for methanol, ethanol, 1-propanol, and 2-propanol are in the ratio 1 :33 :35 :160.[29] The fact that the 2-propanol radical is a better electron donor than the corresponding radical in methanol and ethanol may indicate that it is involved in the flash experiments.

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