

FLASH PHOTOLYSIS STUDY OF DIAMINOPYRIDINES

J. WOLLEBEN and A. C. TESTA

Department of Chemistry, St. John's University, Jamaica, NY 11439 (U.S.A.)

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Summary

The triplet-triplet absorption spectra of three diaminopyridines have been assigned from variable-temperature flash photolysis studies. In all cases the lowest triplet state is $\pi\pi^*$ with a phosphorescence lifetime of about 2 s at 77 K in ethyl ether-pentane-ethyl alcohol. Complete neglect of differential overlap-configuration interaction calculations were performed to supplement the interpretation of the fluorescence and phosphorescence data and to provide a satisfactory correlation of the observed and predicted behavior of these molecules.

1. Introduction

In a previous study from this laboratory we reported the excited state properties and flash photolysis behavior of 2-, 3- and 4-aminopyridines [1]. As an extension of our interest in nitrogen heterocyclics we have initiated a flash photolysis study of diaminopyridines (DAMPs) with the intent of characterizing their excited state properties, including propensities for fluorescence, triplet generation and triplet-triplet absorption, as well as any radicals that arise during photoexcitation. Complete neglect of differential overlap-configuration interaction (CNDO-CI) calculations on 2-aminopyridine have provided some insight into the ordering of electronic states and have allowed reasonable predictions to be made of its fluorescence properties resulting from (i) protonation [2] and (ii) substitution of a methyl group on the pyridine ring [3]. We have undertaken variable-temperature flash photolysis studies of 2,3-, 2,6- and 3,4-DAMP, in different solvents, and supplemented these results with CNDO-CI calculations, with the aim of developing an overview of their excited state behavior. We have already reported that in the case of 2,6-DAMP the lowest triplet state lies at unexpectedly higher energies, presumably as a result of perturbation of the orthogonality between n and π orbitals at the ring nitrogen [4].

2. Experimental details

2.1. Materials

The three DAMPs investigated (2,3-, 2,6- and 3,4-) were obtained from Aldrich Chemical Co. and recrystallized prior to use. Spectrograde solvents, methanol, ethyl alcohol, isopropyl alcohol, acetonitrile and ethyl ether-pentane-ethyl alcohol (in the ratio 5:5:2) (EPA), were used as supplied.

2.2. Apparatus and procedures

The xenon flash photolysis apparatus and procedures employed have already been described [1]. Solution concentrations were typically about 4×10^{-4} M. Phosphorescence measurements of the DAMPs at 77 K were made in EPA using 317 nm excitation. CNDO-CI calculations for the DAMPs were performed with the CNDUV99 program available from the Quantum Chemistry Program Exchange [5].

3. Results

3.1. Room temperature flash photolysis

The flash photolysis behavior of the DAMPs in degassed ethyl alcohol is summarized in Fig. 1, in which it is seen that millisecond transients are observed for all three isomers. The relatively long lifetime for these transients precludes them from being triplet-triplet absorption. It was observed that the 2,3 isomer was the most photochemically active and exhibited two

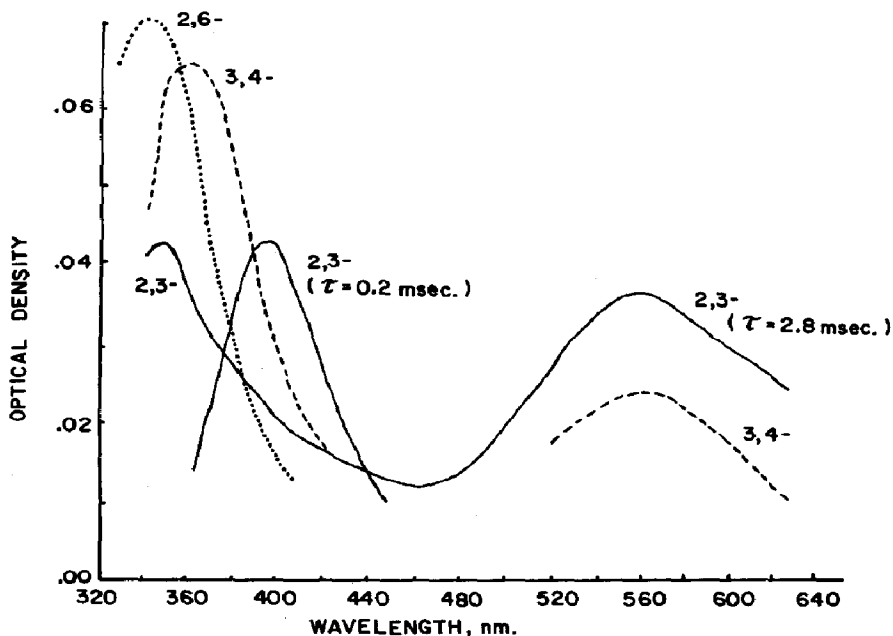


Fig. 1. Room temperature flash photolysis transients for 2,6-, 2,3- and 3,4-DAMP in degassed ethyl alcohol (80 J per flash).

transients. One of these has a lifetime of 0.2 ms, absorbing at about 400 nm, and the second transient has $\tau = 2.8$ ms, absorbing at 350 and 560 nm. The millisecond transient decay of the radicals for each of the three molecules follows second-order kinetics, with the exception of the short-lived 2,3-DAMP transient absorption, which exhibits first-order kinetics.

Transient absorptions for 2,6-DAMP were also measured in water ($\tau = 5$ ms) and in acetonitrile ($\tau = 15$ ms) with a peak at 410 nm. It is known that the absorption spectrum of the 2,6-dimethylpyridinium cation, reported by David *et al.* [6], appears at 400 nm, which suggests that 2,6-DAMP photoionizes in water and acetonitrile.

3.2. Variable-temperature flash photolysis

On cooling solutions of DAMPs in EPA and in isopropyl alcohol the transients seen at room temperature disappear and in their place new transients, which exhibit first-order decay kinetics, are observed at temperatures below -155 °C. In the low temperature flash photolysis of 2,6-DAMP in EPA a transient with peaks at 460 and 590 nm grows rapidly below -155 °C and reaches a maximum optical density at -165 °C. The same transient absorption is observed in isopropyl alcohol at temperatures below -90 °C. No transient absorption was observed on cooling ethyl ether solutions down to -115 °C. Figure 2 shows these spectra at -170 °C in EPA for the three isomers investigated. The same transient is observed in isopropyl alcohol below -90 °C. The activation energies for the triplet-triplet decays were determined to be 4.1 kcal mol $^{-1}$, 3.3 kcal mol $^{-1}$ and 2.7 kcal mol $^{-1}$ for 2,3-DAMP, 2,6-DAMP and 3,4-DAMP respectively. By comparing the absorption and emission decay constants, which are the same within experimental error,

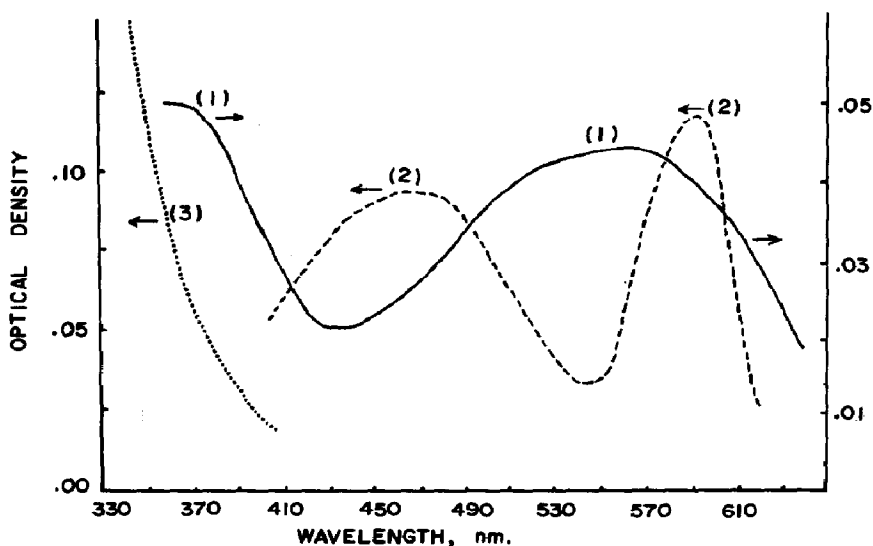


Fig. 2. Triplet-triplet absorption spectra of DAMPs (about 4×10^{-4} M) in EPA at -170 °C: spectrum 1, 2,3-DAMP (180 J); spectrum 2, 2,6-DAMP (80 J); spectrum 3, 3,4-DAMP (80 J).

we were able to assign these spectra to molecular triplet-triplet absorption. With 2,6-DAMP in EPA at 103 K the absorption decay constant was $44 \pm 6 \text{ s}^{-1}$, while the phosphorescence decay constant was $39.5 \pm 2.8 \text{ s}^{-1}$.

The observation of the low temperature transient for 2,3-DAMP in EPA at $-165 \text{ }^\circ\text{C}$, which exhibits first-order decay kinetics, necessitated a flash energy of 160 J, and the absorption and emission decay constants were shown to be the same within experimental error. With 3,4-DAMP in EPA at 92 K the transient absorption decay constant was $12.4 \pm 0.5 \text{ s}^{-1}$ while the emission decay constant was $10.3 \pm 1.3 \text{ s}^{-1}$. Noteworthy is that 3,4-DAMP has its triplet-triplet absorption below 350 nm, which suggests that it is a perturbed pyridine triplet-triplet absorption.

The phosphorescence spectra of these molecules were measured at 77 K in EPA and are shown in Fig. 3. The phosphorescence quantum yields and lifetimes of the DAMPs in EPA are summarized in Table 1, together with their room temperature fluorescence characteristics in ethyl alcohol. In non-polar solvents the fluorescence yield of the three DAMPs increases in the order 3,4- < 2,3- < 2,6-.

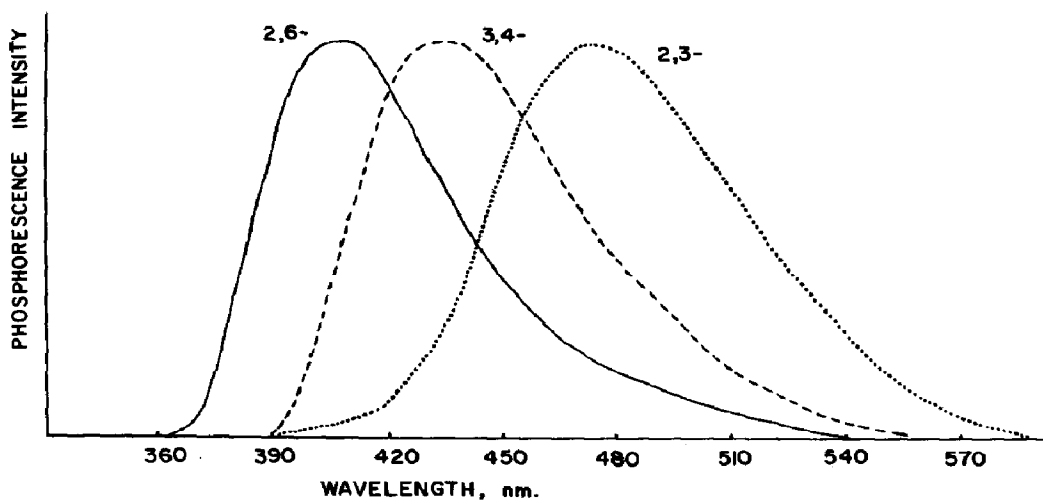


Fig. 3. Phosphorescence spectra of DAMPs in EPA at 77 K (317 nm excitation).

TABLE 1

Summary of fluorescence and phosphorescence data for 2,3-, 2,6- and 3,4-diaminopyridine

	Fluorescence data (25 °C; ethyl alcohol)			Phosphorescence data (77 K; EPA)		
	$\lambda_{\text{max}}^{\text{abs}}$ (nm)	$\lambda_{\text{max}}^{\text{fl}}$ (nm)	ϕ_{fl}	$\lambda_{\text{max}}^{\text{phos}}$ (nm)	ϕ_{phos}	τ_{p} (s)
2,3-DAMP	309	374	0.41	472	0.01	2.3
2,6-DAMP	309	355	0.17	405	0.03	2.5
3,4-DAMP	291	352	0.06	435	0.19	1.9

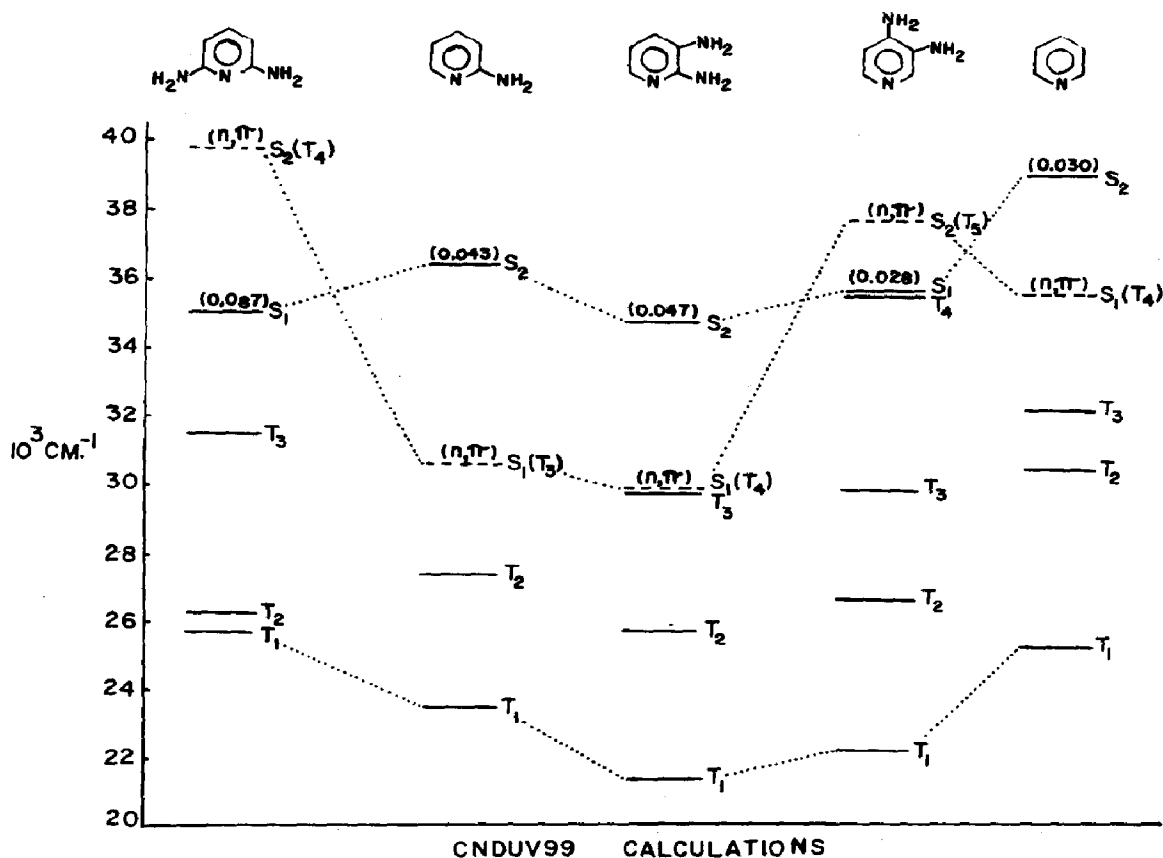


Fig. 4. Electronic state diagram constructed from CNDUV99 calculations for the three DAMPs investigated. The energy levels for pyridine and 2-aminopyridine are included for comparison between the molecules. The value indicated in parentheses is the predicted oscillator strength for the lowest $\pi\pi^*$ singlet.

3.3. CNDO-CI calculations of diaminopyridines

In Fig. 4 we have summarized the CNDUV99 molecular state diagrams for the three DAMPs, together with those for pyridine and 2-aminopyridine. The value in parentheses is the predicted oscillator strength for the lowest $\pi\pi^*$ transition, while dotted lines are used to indicate the $n\pi^*$ singlets, which in the CNDO-CI method result in zero oscillator strength and zero energy separation between $n\pi^*$ singlets and triplets.

4. Discussion

From the variable-temperature flash data we have been able to assign the triplet-triplet absorption spectra of the three DAMPs studied. The 2,6 and 2,3 isomers show two absorption maxima that are separated by approximately 4180 cm^{-1} and 9500 cm^{-1} respectively, which implies absorption to different higher-lying triplet states. We believe that the shorter wavelength band in 3,4-DAMP is related to the π system of pyridine; however, the longer

wavelength maxima at 560 nm and 590 nm in 2,3-DAMP and 2,6-DAMP respectively suggest a charge transfer transition. Comparison of these triplet-triplet absorption spectra for 2,3- and 2,6-DAMP with those of aromatic amines indicates a similarity [7]. The shortest wavelength absorption maximum was observed with 3,4-DAMP, which does not exhibit the charge transfer bands at longer wavelengths. We have previously reported that for 3-aminopyridine the absence of triplet-triplet absorption in the region above 300 nm was probably due to a higher-lying $n\pi^*$ singlet and a larger $\pi\pi^*$ (S_1-T_1) energy splitting, which resembles the situation present in benzene. The CNDO-CI calculations for DAMPs also predict that the largest S_1-T_1 splitting occurs with 3,4-DAMP.

The results of the CNDO-CI calculations shown in Fig. 4 do provide some insights into the excited state behavior of DAMPs. Among the predictions, which are verified experimentally, is the correct ordering of the lowest $\pi\pi^*$ singlet and triplet and the phosphorescence energy of the three molecules investigated. The calculations also correctly predict that the oscillator strength f of the lowest $^1\pi\pi^*$ transition correlates with the fluorescence yield in a non-polar solvent such as cyclohexane ($\phi_F(2,6\text{-DAMP}, f = 0.087) > \phi_F(2,3\text{-DAMP}, f = 0.047) > \phi_F(3,4\text{-DAMP}, f = 0.028)$). In ethyl alcohol the enhanced fluorescence of 2,3-DAMP is due to inversion of states, resulting in S_1 becoming $\pi\pi$. Taken collectively, the molecular orbital (MO) calculations summarized in Fig. 4 reasonably account for the fluorescence propensity of the five molecules shown. In pyridine the lowest $^1\pi\pi^*$ (S_2) lies at higher energies and does not effectively couple to the allowed S_1 ($^1n\pi^*$) to induce any significant fluorescence. With regard to the three DAMPs the fluorescence yield correlates with the oscillator strength of the lowest-lying $\pi\pi^*$ transition, as we have already shown with the methyl derivatives of 2-aminopyridine [3].

The phosphorescence results indicate that the lowest triplet is $\pi\pi^*$ in all cases, since the phosphorescence lifetimes are of the order of seconds for the three molecules. The MO calculations are consistent with this view and also illustrate the unexpectedly high triplet energy of T_1 in 2,6-DAMP, despite the relative constancy in energy of the lowest $^1\pi\pi^*$ state for the three DAMPs.

The room temperature flash transient data are much more difficult to interpret as a result of the observation of different transients in different solvents; however, we would like to suggest that the 410 nm transient for 2,6-DAMP observed in water and in acetonitrile is the molecular cation, because of its similarity with that of the 2,6-dimethylpyridinium cation [6]. The transients observed in ethyl alcohol for the three molecules can only be tentatively assigned to the radical resulting from the amine N-H fission as has been seen in aromatic amines [8].

In summary, we have assigned the triplet-triplet absorption spectra of the DAMPs, characterized their phosphorescence behavior and demonstrated a reasonable correlation of observed excited state properties with predictions from CNDO-CI calculations.

References

- 1 J. Wolleben and A. C. Testa, *J. Photochem.*, **8** (1978) 125.
- 2 A. C. Testa and U. P. Wild, *J. Phys. Chem.*, **85** (1981) 2637.
- 3 A. C. Testa and U. P. Wild, *J. Phys. Chem.*, **83** (1979) 3044.
- 4 J. Wolleben and A. C. Testa, *J. Photochem.*, **19** (1982) 267.
- 5 H. Baumann, *QCPE*, **11** (1977) 333.
- 6 C. David, P. Janssen and G. Geuskens, *Spectrochim. Acta*, **27A** (1971) 367.
- 7 K. Cadogan and A. Albrecht, *J. Phys. Chem.*, **73** (1968) 1868.
- 8 E. Land and G. Porter, *Trans. Faraday Soc.*, **59** (1963) 2027.