# PHOTONICS OF 7-AZAINDOLINES

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## Summary

The quantum yields of photodissociation of 7-azaindolines (7-AIs) in non-polar solvents from the lower triplet state are about 0.2 - 0.3 and do not depend on the excitation wavelength. The quantum yields of intersystem crossing of 7-AIs are about 0.34 and the quantum yields of fluorescence for all 7-AIs are about 0.17 (in heptane) at room temperature and approach unity between −130 and −150 °C.

## 1. Introduction

It has been shown earlier that, in contrast with 1,2-dihydroquinolines [1], 1,2,3,4-tetrahydroquinolines [2] and derivatives of aniline [3] and indole [4], 7-azaindolines (7-AIs) dissociate photochemically from the lower triplet state [5]. Therefore, the quantum yields of photodissociation and fluorescence of 7-AIs do not depend on the excitation wavelength [6, 7]:
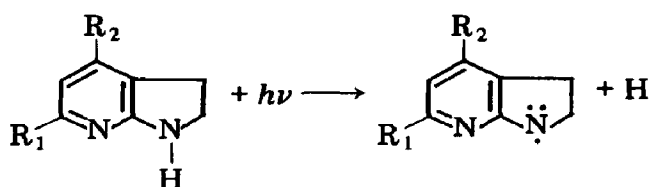


I: $R_1 \equiv H$, $R_2 \equiv CH_3$
II: $R_1 \equiv R_2 \equiv CH_3$
III: $R_1 \equiv R_2 \equiv Cl$

Effective photodissociation from the higher excited states which competes with internal conversion is inherent in all aromatic amines [1 - 7]. Therefore, the anomalous behaviour of 7-AIs should be attributed to the perturbation introduced by the replacement of the benzene nucleus with a pyridine nucleus. In the present study we deal with the spectroluminescence and photochemical properties of the perturbation and also the dependence of these properties on the structure and position of the lower electronic excited levels.

## 2. Experimental details

The syntheses of 7-AIs I - IV
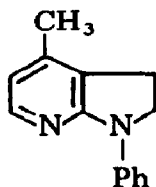


**IV**

the measurement of the absorption, fluorescence and phosphorescence spectra, the methods for determining the quantum yields of fluorescence and phosphorescence and also the fluorescence anisotropy spectra have been described elsewhere [6, 7]. The absorption spectra and decay kinetics of short-lived aminyl radicals were measured on a flash photolysis apparatus with a resolution time of 20 $\mu$s and an energy of 700 J [1]. The absorption spectra were recorded on a Specord UV–visible spectrophotometer and luminescence measurements were carried out on an Aminco–Bowman spectrofluorometer.

The quantum yield $\varphi_{ISC}$ of intersystem crossing of 7-AIs I - III was determined by triplet–triplet energy transfer from the 7-AIs and benzophenone (as a standard donor ($\varphi_{ISC} = 1$ [8])) to biacetyl under conditions of complete energy transfer. The concentration of the $T_1$ state of biacetyl was registered in terms of the intensity of the biacetyl phosphorescence in benzene. Secondary amines quench the $T_1$ state of biacetyl because the triplet state of biacetyl abstracts hydrogen from amines [9]. Assuming that $\varphi_{ISC}$ for IV and $\varphi_{ISC}$ for I - III are equal, we may take the $N$-phenyl-substituted 7-AI IV as a model compound to determine $\varphi_{ISC}$ as follows. The cell was filled with a solution of IV (optical density OD = 0.3 at $\lambda = 315$ nm) and biacetyl in benzene. The solution was deoxygenated by means of freeze–thaw cycles in vacuum and the spectrum of the sensitized phosphorescence of biacetyl ($\lambda_{ex} = 315$ nm, $\lambda_{phos} = 520$ nm) was recorded at 20 °C. This spectrum was similarly measured for a solution of benzophenone (OD = 0.35 at $\lambda = 315$ nm) and biacetyl in benzene. The concentration of biacetyl in both cases was $10^{-3}$ M. The lifetime of the $T_1$ state of benzophenone and the 7-AI is greater than 1 $\mu$s [9]. Hence we may assume that the energy of triplet excitation is completely transferred from benzophenone and the 7-AI to biacetyl. This is supported by the fact that an increase in the biacetyl concentration does not increase the yield of the sensitized phosphorescence.

The intensity of the biacetyl phosphorescence sensitized by 7-AIs is described by the formula

$$J^{AI} \propto \varphi_{ISC}^{AI} OD^{AI} \tag{1}$$

where $\varphi_{ISC}^{AI}$ is the quantum yield of the intersystem crossing of IV and $OD^{AI}$ is the optical density of IV at $\lambda = 315$ nm (the biacetyl absorption may be

neglected because of the small optical density of biacetyl at the given excitation wavelength).

The intensity of the phosphorescence of biacetyl sensitized by benzophenone may likewise be written as

$$J^{BP} \propto \varphi_{ISC}^{BP} OD^{BP} \tag{2}$$

where $\varphi_{ISC}^{BP}$ is the quantum yield of intersystem crossing of benzophenone and $OD^{BP}$ is the optical density of benzophenone at $\lambda = 315$ nm. Combining eqns. (1) and (2) gives

$$\varphi_{ISC}^{AI} = \frac{J^{AI} OD^{BP}}{J^{BP} OD^{AI}} \varphi_{ISC}^{BP} \tag{3}$$

The method yields $\varphi_{ISC}^{AI} = 0.34$ for **IV**.

## 3. Determination of extinction coefficients of aminyl radicals and quantum yields of 7-azaindoline dissociation

The extinction coefficient $\epsilon$ ($M^{-1}$ $cm^{-1}$) of the aminyl radicals produced from 7-AI photodissociation was measured by studying the flash photolysis of the benzophenone-sensitized formation of the aminyl radicals [10]. On flash photoexcitation of deoxygenated solutions of 7-AI **I** (concentration, $1 \times 10^{-2}$ M) and benzophenone (concentration, $0.8 \times 10^{-2}$ M) in benzene through a UFS-6 type of filter (only benzophenone is excited), the triplet state of benzophenone cleaves hydrogen from **I** and yields the ketyl radical of benzophenone and the aminyl radical of the 7-AI in equimolar concentrations. The extinction coefficient $\epsilon$ of the aminyl radical is an order of magnitude lower than that of the ketyl radical. Therefore, the absorption of the aminyl radical can be disregarded. The concentration of the ketyl and hence aminyl radicals produced can be determined from the known extinction coefficient of the benzophenone radical ($\epsilon = 3.22 \times 10^3$ $M^{-1}$ $cm^{-1}$ at 545 nm [10]). Oxygen quenches the ketyl radicals completely and only the aminyl radicals contribute to the optical absorption. The concentration of 7-AI is very much greater than that of oxygen. Therefore, the triplet state of benzophenone is quenched completely by interaction with 7-AI (quenching by oxygen can be neglected), and hence the concentration of the aminyl radicals produced is the same as for deoxygenated solutions.

When the radical concentration and the optical path of the cell are known, we can calculate the extinction coefficient of the aminyl radical. For the aminyl radical produced by the photolysis of 7-AI **I** in benzene at $\lambda = 440$ nm, $\epsilon = 450$ $M^{-1}$ $cm^{-1}$. It should be noted that the absorption spectra of the aminyl radicals recorded after cleavage of hydrogen by the triplet state and in photodissociation are almost the same.

The quantum yields of the photodissociation of 7-AIs **I** - **III** were related to the known quantum yields of 1,3,3-trimethyl-6-nitrospiro-2*H*-benzopyrane-2,2′-indoline. The extinction coefficient $\epsilon$ of the merocyanine calculated from $\varphi_B = 0.65$ (where $\varphi_B$ is the quantum yield of photocolouration of the spyropyran) is $4.4 \times 10^4$ $M^{-1}$ $cm^{-1}$ [11].

## 4. Discussion

Structurally, 7-AIs closely resemble *o*-aminopyridines, whose spectro-luminescence properties have been studied thoroughly [12 - 16]. Therefore, it seems expedient to investigate both types of compound simultaneously.

The absorption maxima and the intensities of both long wavelength bands of the absorption spectra of 7-AIs taken in various solvents closely resemble those of *o*-aminopyridines (Fig. 1). In ref. 13 the long wavelength absorption band of 2-aminopyridine is treated as that produced by the $\pi \rightarrow \pi^*$ ($^1A_1 - ^1B_2$) transition of pyridine slightly perturbed and bathochromically shifted under the effect of the amino group. However, as has been shown in ref. 17, the lower excited states of aromatic amines cannot be classified as pure $\pi,\pi^*$ since the $1,a_\pi$ states contribute considerably. The contribution of the $1,a_\pi$ states to the wavefunctions of the lower excited states generally does not exceed 20%. However, this together with the photochemical reaction may be responsible for the short lifetime of the $T_1$ states of the 2-aminopyridines and 7-AIs.
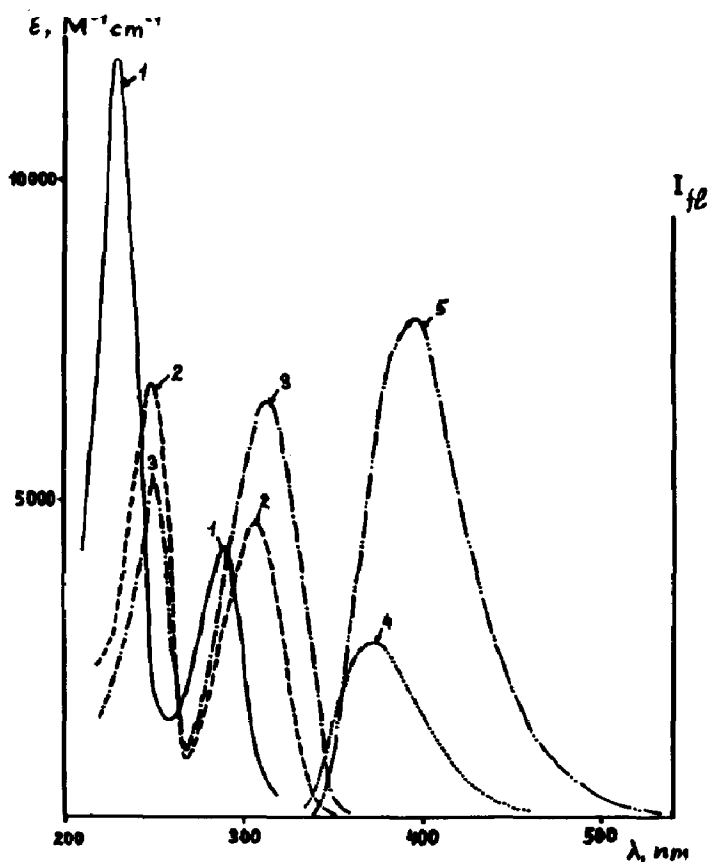


Fig. 1. Absorption spectra of 2-aminopyridine in heptane (spectrum 1), 7-AI I in propanol (spectrum 2) and 7-AI I in propanol with 0.1 M HCl (spectrum 3) and fluorescence spectra of 7-AI I in propanol (spectrum 4) and in propanol with 0.1 M HCl (spectrum 5).
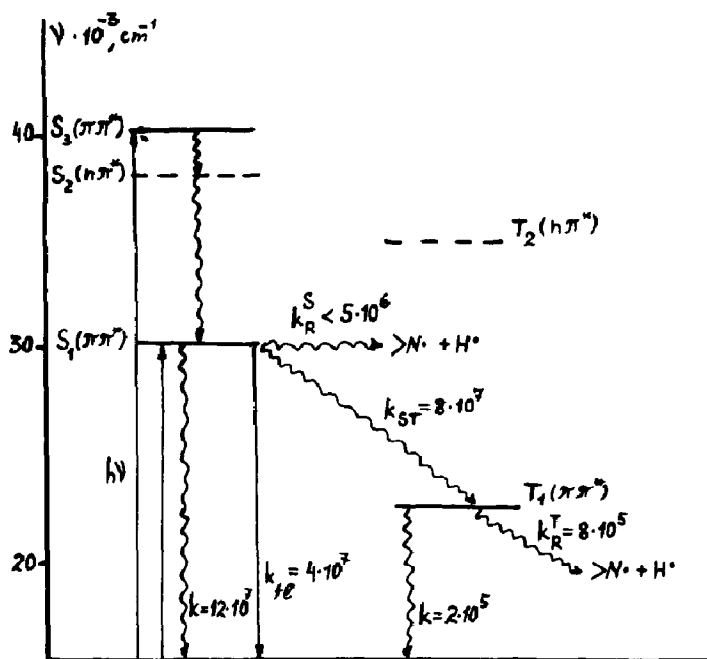
Fig. 2. Lower electronic excited levels of 7-AI I and 2-aminopyridine.

The scheme for the lower electronic excited levels of I (Fig. 2) has been constructed on the basis of measurements of the fluorescence and phosphorescence spectra of 7-AI I recorded in 3-methylpentane at 293 and 77 K and on the basis of quantum chemical calculations [15].

At low pH values in alcohols and water the intensity of the bands increases and the long wavelength absorption bands of the 7-AI and 2-aminopyridine shift bathochromically. This should be attributed to protonation of the 7-AI and 2-aminopyridine at the pyridine ring and formation of the cation (Fig. 1):
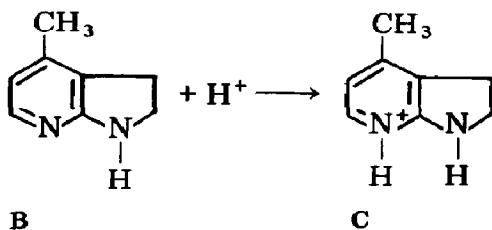


Protonation of the ring rather than of the amino group is proved by the bathochromic shift and an increase in the extinction coefficient of the long wavelength absorption band of the 7-AI (when protonation takes place at the amino group a hypsochromic shift is observed).

The oscillator strength and fluorescence lifetime of 7-AIs do not change considerably in going from heptane to alcohol (Table 1). This indicates that for 7-AIs in all solvents the lower singlet state is the $S_1(\pi l,\pi^*)$ state involving intramolecular charge transfer. In non-polar solvents the $S_1(\pi l,\pi^*)$ and

TABLE 1

Spectroluminescence properties of 7-azaindolines and 2-aminopyridine [12, 18]

| Solvent | Compound | $\lambda_{ab}^{max}$ (nm) | $\epsilon$ $(M^{-1} cm^{-1})$ | $\lambda_{fl}^{max}$ (nm) | $\varphi_{fl}$ | $\tau_{fl}$ (ns) | $k_{fl} = \varphi_{fl}/\tau_{fl}$ $(s^{-1})$ | $k_{fl}$ [a] $(s^{-1})$ |
|---|---|---|---|---|---|---|---|---|
| Heptane | 2-Aminopyridine | 290 | 4250 | 332 | 0.04 | 24.2 | $1.7 \times 10^6$ | — |
| | I | 303 | 4610 | 350 | 0.17 | 3.9 | $4.2 \times 10^7$ | $7.3 \times 10^7$ |
| | II | 308 | 7340 | 360 | 0.18 | 2.2 | $8.2 \times 10^7$ | $9.1 \times 10^7$ |
| | III | 308 | 6520 | 360 | 0.023 | 0.8 | $2.9 \times 10^7$ | $7.6 \times 10^7$ |
| | I + CH$_3$COOH (0.1 M) | 317 | — | 450 | 0.046 | — | — | — |
| n-Propanol | 2-Aminopyridine | 296 | 4400 | 352 | 0.18 | 5.1 | $3.5 \times 10^7$ | — |
| | I | 308 | 4610 | 375 | 0.32 | 4.6 | $6.9 \times 10^7$ | $5.6 \times 10^7$ |
| | II | 310 | 7780 | 375 | 0.25 | 3.7 | $6.8 \times 10^7$ | $9.1 \times 10^7$ |
| | III | 315 | 6790 | 385 | 0.0065 | — | — | $11.0 \times 10^7$ |
| | I + 0.1 M H$_2$SO$_4$ | 317 | — | 395 | 0.8 | — | — | — |
| Acetonitrile | 2-Aminopyridine | 293 | 4800 | 345 | 0.25 | 5.0 | $5.0 \times 10^7$ | — |
| | I | 305 | — | 368 | 0.23 | — | — | — |
| | II | 310 | — | 368 | 0.21 | — | — | — |
| | III | 312 | — | 370 | 0.0014 | — | — | — |

[a]Calculated from ref. 19.

$S_2(n,\pi^*)$ states are similar in energy and therefore markedly interact vibrationally. This reduces the emission owing to intense intersystem crossing.

The protonation of the pyridine ring of 7-AIs in alcohols and water markedly increases the energy of the $n,\pi^*$ transitions compared with that of the $\pi l,\pi^*$ transitions because the proton interacts with the lone electron pair of the pyridine nitrogen. This results in rearrangement of the lower electronic excited states. As the calculations for 2-aminopyridine have shown [5], protonation increases the energy of the lower $n,\pi^*$ state by 2.51 eV. Thus, the lower $n,\pi^*$ state of 7-AIs cannot participate in the interaction with the $\pi l,\pi^*$ state as often takes place in 2-aminopyridines in non-polar solvents [12 - 15].

This sharply increases the quantum yield of the fluorescence of the 7-AI cations compared with that of the neutral compounds (Table 1). The quantum yield increases because the $S(n,\pi^*)$ state is "removed" and because conditions favourable for interconversion of the states are absent (Fig. 2).

We failed to register the dication of 7-AIs even in 10 M $H_2SO_4$ (it should be noted that the p$K$ of the dication of the model 2-aminopyridine is $-7.6$ [12], i.e. the second protonation proceeds with great difficulty). Sulphuric acid does not quench the fluorescence of the monocation. This indicates that the second protonation does not take place even in the excited state.

In alkaline media the OH$^-$ anion quenches the fluorescence of 7-AIs. When the KOH concentration exceeds 1 M the spectrum exhibits a new fluorescence band with $\lambda_{max}$ = 475 nm (Fig. 3). The excitation spectrum of the new band coincides with the fluorescence excitation spectrum of the neutral form.
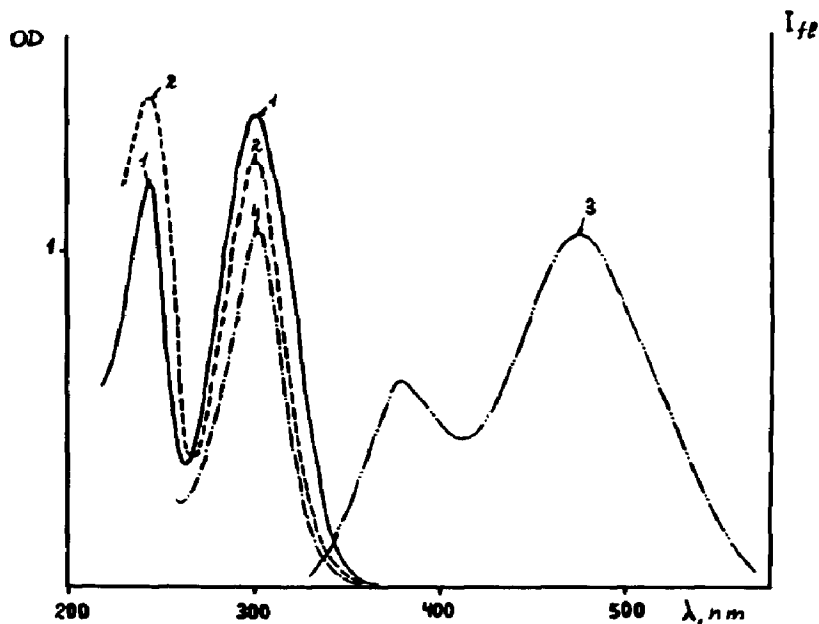


Fig. 3. Absorption spectra of 7-AI I in $H_2O$ (spectrum 1) and in $H_2O$ with 10 M KOH (spectrum 2) and fluorescence spectrum (spectrum 3) and fluorescence excitation spectrum (spectrum 4) of 7-AI I in $H_2O$ with 3 M KOH (spectrum 4).

The band with $\lambda_{max}$ = 475 nm (Fig. 3) should be attributed to the fluorescence of the 7-AI anion produced in the adiabatic photodissociation of the 7-AI in the excited state. This is associated with an increase in the acidity in the excited singlet state:

$$B^* + OH^- \longrightarrow \left( \begin{array}{c} CH_3 \\ \end{array} \right)^* + H_2O$$
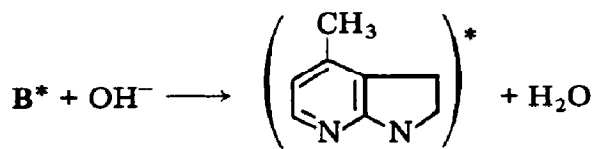
The fluorescence of 2-aminopyridine in an alkaline medium has been reported; the fluorescence of the anion, however, has not been registered [20].

With increasing solvent polarity, the absorption and fluorescence spectra of 7-AIs exhibit a bathochromic shift. The shift is anomalously high in solvents capable of forming hydrogen bonds (water, alcohol); therefore, in propanol the shift is greater than that in the considerably more polar acetonitrile (Table 1). The shift is produced by the hydrogen-bonded complex of the 7-AI and water or alcohol. The complex forms at the nitrogen of the pyridine ring:
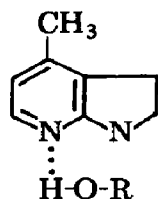
The enthalpy of complex formation for pyridine increases with increasing p$K$ of the alcohol ($\Delta H$ for ethanol and butanol is 2.27 kJ mol$^{-1}$ and 0.44 - 1.1 kJ mol$^{-1}$ respectively [18]). The complex easily decomposes in alkaline media; when alkali is added to aqueous solutions the absorption spectrum resembles that taken in non-polar heptane (Fig. 3).

To conclude, the lower excited state of 7-AIs in all solvents investigated is the mixed S($\pi$l,$\pi^*$) state (for terminology see ref. 17). In alcohols and water the gap between the S(n,$\pi^*$) state and the energetically similar S($\pi$l,$\pi^*$) state increases and the vibrational interaction is weakened. This increases the lifetime of the state. Hence, the fluorescence and phosphorescence of 7-AIs originate from the S$_1$($\pi$l,$\pi^*$) and T$_1$($\pi$l,$\pi^*$) states.

## 5. Photochemical properties

The flash photoexcitation of 7-AIs in hexane at room temperature under anaerobic conditions produces aminyl radicals (Fig. 4). The decay kinetics of the aminyl radicals obey a parabolic law. The decay probably represents recombination and disproportionation
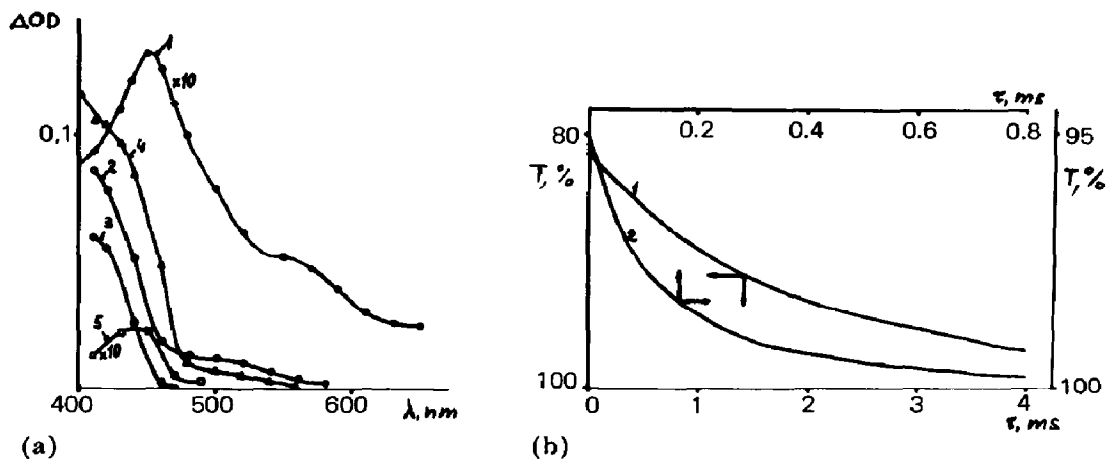
Fig. 4. (a) Absorption spectra of short-lived intermediate products formed $10^{-5}$ s after pulse photoexcitation of 7-AI I (concentration, $2 \times 10^{-4}$ M): spectrum 1, in heptane in the absence of oxygen; spectrum 2, in propanol in the absence of oxygen; spectrum 3, in propanol in the presence of oxygen; spectrum 4, in $H_2O$ in the absence of oxygen; spectrum 5, in $H_2O$ with 5 M KOH in the absence of oxygen. (b) Decay kinetics of short-lived intermediate products: curve 1, in propanol; curve 2, in heptane.

$$RN + RN \longrightarrow products$$

similar to the reaction of the aminyl radicals in the photolysis of dihydroquinolines reported earlier [19].

The rate constant of recombination of the 7-AI aminyl radicals is independent of the 7-AI concentration between $1.1 \times 10^{-3}$ and $0.4 \times 10^{-4}$ M, i.e. the aminyl radicals are incapable of adding to the initial compound as in the case of 1,2-dihydroquinolines.

Oxygen quenches the photodissociation of 7-AIs completely. This proves the triplet nature of the photochemically active electronic excited state (as a result of the effect of oxygen on the yield of the aminyl radicals the lifetime of the $T_1$ state of 7-AI I in heptane is 1 $\mu$s). Oxygen has no further effect on the decay kinetics of the aminyl radicals, i.e. the rate constant of the interaction between oxygen and aminyl radicals from 7-AIs does not exceed $3 \times 10^{-4}$ mol$^{-1}$ s$^{-1}$ (Fig. 4).

The $T_1$ state of the o-aminopyridines also has a short lifetime [13]; the triplet–triplet absorption spectrum can only be registered below −155 °C and the rate constant for the deactivation is found to be $3.8 \times 10^2$ s$^{-1}$.

The sensitization of photodissociation in the presence of donors of triplet energy, benzene and toluene, confirms the triplet nature of the photochemically active state of 7-AIs. The photoexcitation of 7-AI I in heptane in the presence of benzene increases the yield of the reaction. The lower triplet state of both 7-AIs and 2-aminopyridine is the $T(\pi l, \pi^*)$ state.

The quantum yields of the aminyl radicals produced from 7-AIs (Table 2) determined in this study are very much greater than the quantum yields of the photodecomposition of the initial 7-AIs [6]. The product of the 7-AI photodecomposition has an absorption spectrum resembling that of the

TABLE 2

Extinction coefficients of aminyl radicals and quantum yields of photodissociation, intersystem crossing and phosphorescence of 7-azaindolines

| 7-AI | $\epsilon_{rad}^{max}$ ($M^{-1}$ $cm^{-1}$) | $\varphi_{rad}$ [a] | $\varphi_{ISC}$ [b] | $\varphi_{phos}$ [c] |
|------|------|------|------|------|
| I | 457 | 0.24 | — | 0.01 |
| II | — | 0.36 | — | 0.064 |
| III | — | 0.22 | — | 0.052 |
| IV | — | — | 0.34 | — |

[a] In heptane.
[b] In benzene.
[c] In 3-methylpentane.

initial compound and is probably a dimer of the aminyl radicals. It decomposes on exposure to light and yields the aminyl radicals.

The quantum yields of the photodissociation of 7-AIs I - III in heptane are similar to those of the intersystem crossing. Hence the probability of the photodissociation from the $T_1$ state of 7-AIs approaches unity.

A highly effective photochemical decomposition of the triplet state also follows from the fact that the lifetime of the triplet state of the $N$-phenyl derivative of IV (the C—N bond does not cleave) is $10^{-4}$ s. Assuming that the lifetime of the $T_1$ state is reduced because of the photochemical reaction, we may determine the rate constant for photodissociation from the $T_1$ state of I to be equal to $10^6$ $s^{-1}$.

The photodissociation proceeds from the lower triplet state and not from the higher excited states as was observed for 1,2-dihydroquinolines, 1,2,3,4-tetrahydroquinolines, indoles and anilines. This is confirmed by the facts that the quantum yield of the fluorescence of 7-AIs is independent of the excitation wavelength [6, 7] and that the 7-AIs have no deactivation channel associated with the deactivation of the higher excited levels.

A decrease in temperature of the solution increases the quantum yield of the fluorescence for all 7-AIs I - III. From −130 to −150 °C the quantum yield approaches unity (Fig. 5). Thus, the quantum yield of the intersystem crossing (and hence the reaction) should be close to zero. Indeed, the quantum yields of 7-AI phosphorescence are rather small (Table 2). Even prolonged photoirradiation of the 7-AI specimens in vitreous matrices of 3-methylpentane and $n$-propanol at 77 K does not produce aminyl radicals (they should be stable at that temperature). Tetrahydroquinolines, however, photoirradiated under similar conditions easily form the aminyl radicals which can be registered by means of electron spin resonance spectroscopy and spectrophotometry [1, 2].

Thus, at 77 K the main deactivation pathway of the $S_1$ states of the 7-AIs is fluorescence. As the temperature increases intersystem (and internal) crossing is enhanced.
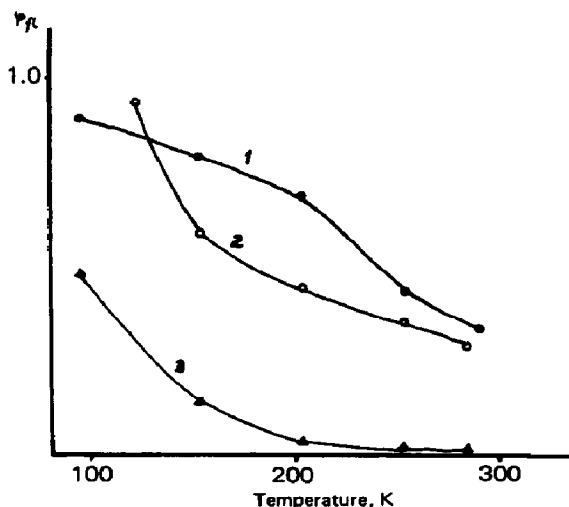
Fig. 5. Dependence of the fluorescence quantum yields of 7-AI on temperature in 3-methylpentane: curve 1, I; curve 2, II; curve 3, III.

The photoexcitation of alcoholic solutions of 7-AIs yields intermediate products with absorption spectra hypsochromically shifted with respect to those of the radicals in heptane (Fig. 4). The radicals form both in the absence and in the presence of oxygen. The yield, however, is higher when no oxygen is available.

As follows from Section 1, 7-AIs exist in alcohols and water as hydrogen-bonded complexes. The photodissociation of the complex gives the aminyl radicals hydrogen-bonded to alcohol at the pyridine ring. (As shown in ref. 21 the absorption spectra of the aminyl radicals produced from aniline do not change considerably in going from hexane to alcohol and water; therefore, the formation of the hydrogen bond with the aminyl nitrogen should not change the spectrum.)

The formation of the hydrogen-bonded complexes and their role in photodissociation are confirmed by the facts that in aqueous alkaline solutions (where the hydrogen-bonded complexes should decompose in the presence of the $OH^-$ ions) the radicals do not form in the presence of oxygen and that in the absence of oxygen their yield is negligibly small because the $OH^-$ ions quench the excited triplet states.

Thus, in alkaline and neutral media in water and alcohols (pH > 4) 7-AIs exist as the non-dissociated form B. Its photoexcitation leads to photodissociation yielding the aminyl radical.

The rate constants of some stages of deactivation of the electronic excitation energy may be estimated in heptane. The quantum yield of the photodissociation from the triplet state for compound I is as follows:

$$\varphi_p = \varphi_T \varphi_p{}^T = 0.24$$

$$\varphi_p{}^T = \frac{K_p{}^T}{K_p{}^T + K^T}$$

$$\varphi_T = \frac{K_T}{K_{f1} + K_T + K_{IC}}$$

where $K_p{}^T$, $K^T$, $K_{f1}$, $K_T$ and $K_{IC}$ are the rate constants of the reaction from the triplet state, of intersystem degradation $T_1 \rightsquigarrow S_0$, of fluorescence, of intersystem crossing and of internal conversion. Assuming that $\varphi_T \approx 0.3$ and $(K_p{}^T + K^T)^{-1} = \tau_T = 1$ $\mu$s, we obtain $K_p{}^T \approx 8 \times 10^5$ s$^{-1}$.

The flash photolysis set-up used in the present study records the change in the optical density to within about 0.01. Therefore, the quantum yield $\varphi_p{}^S$ of the photodissociation from the singlet state is 0.02 or less. Since $\varphi_p{}^S = K_p{}^S \tau_S$ (where $\tau_S$ is the lifetime of the singlet state of I in heptane), we have $K_p{}^S < 5 \times 10^6$ s$^{-1}$.

Such a small rate constant of the photodissociation from the singlet state indicates [22] that the homolytic dissociation of the R—H bonds notably proceeds only from the triplet state.

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