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# The photochemistry of azines

Ya N Malkin, V A Kuz'min
Institute of Chemical Physics, USSR Academy of Sciences, Moscow

ABSTRACT. The features of the luminescence spectra and photochemistry of heterocyclic amines, such as derivatives of pyridine, quinoline, acridine, and diazines, in liquid and solid solutions are examined. The relationship between the composition of the lowest electronically excited states and the luminescence and photochemical properties is analysed. Particular attention is given to the nature of the photochemically active, electronically excited state.

The bibliography includes 106 references.

## Contents

| | | |
|---|---|---|
| I. | Introduction | 164 |
| II. | Features of the luminescence spectra | 164 |
| III. | Photochemical properties | 170 |

## I. Introduction

At the present time the theoretical treatment of the mechanisms of photolytic processes in complex organic molecules and the reactivity of excited states are based on the findings of photophysics obtained by studying the luminescence spectroscopic properties of these systems. Progress in the photophysics of complex molecules (the relationship between the spectroscopic properties and structure,[1–4] the effect of the medium, the theory of radiationless transfers[5–10]) has considerably outstripped the advances in theoretical photochemistry. This circumstance is to a considerable extent due to the absence of data on the multiplicity and nature of the orbitals of the photochemically active, electronically excited state; a very limited number of photochemical reactions have been characterised through a reliable value of the quantum yield. In the present review the data on the reactivity of six-membered azines have been correlated on the basis of theories on the fundamental photochemical processes.

## II. Features of the luminescence spectra

### 1. Pyridine, quinoline, and isoquinoline

The composition of the lowest electronically excited states and luminescence properties of six-membered *N*-heterocyclic compounds have been examined in monographs.[5,9] These compounds, including pyridine, quinoline, isoquinoline, and acridine, differ formally from aromatic hydrocarbons in that they have an $-N=$ atom instead of a methylene group. In this case the π-system remains unchanged and the absorption spectra of such compounds have much in common with the spectra of the hydrocarbon analogues of *N*-heterocycles since in both cases they result to a considerable extent from $\pi \rightarrow \pi^*$ transitions. These $\pi \rightarrow \pi^*$ transitions have the same polarisation as the transitions that give rise to the absorption and fluoroscence spectra of aromatic hydrocarbons.[5]

In the absorption spectra of pyridine the $\pi \rightarrow \pi^*$ bands ($\lambda_{max}$ = 255 and 195 nm, $\varepsilon_{max}$ = 1800 and 7500 litres $mol^{-1}$ $cm^{-1}$) are more intense than the corresponding bands for benzene. This is because the electronegative nitrogen atom disturbs the symmetry of the π orbitals, so that while there is a complete similarity of the $\pi \rightarrow \pi^*$ transitions in benzene and pyridine the latter are more probable[6] (Table 1).

**Table 1.** Spectroscopic properties of azines.[15,16]

| Compound | Molecular symmetry | Energy of $S(\pi, \pi^*)$ state, eV | Energy of $S(n, \pi^*)$ state, eV | $\varphi_{ISC}$ | $\varphi_{fl}$ |
|---|---|---|---|---|---|
| Pyridine | $C_{2v}$ | 4.75 | 4.27 | — | $6 \times 10^{-5}$ [a] |
| Quinoline | $D_{2h}'$ | 3.97 | 3.6 | 0.31 [b] | — |
| " | — | — | — | 0.50 [c] | |
| " | — | — | — | 0.065 [d] | — |
| Isoquinoline | $D_{2h}'$ | 3.92 | 3.6 | 0.24 [c] | — |
| 2,2'-Dipyridyl | — | — | — | — | $5 \times 10^{-3}$ [d] |
| " | — | — | — | — | $9 \times 10^{-3}$ [d] |
| Pyridazine [e] | $C_{2v}$ | 4.90 | 3.30 | — | — |
| Pyrimidine [e] | $C_{2v}$ | 5.00 | 3.85 | — | — |
| Pyrazine | $D_{2h}$ | 4.64 | 3.83 | — | — |
| S-Triazine | $D_{3h}$ | 5.45 | 3.84 | — | — |
| S-Tetrazine | $D_{2h}$ | 2.41 | 2.23 | — | — |
| 1,2,4-Triazine | $D_{2h}'$ | — | 2.75 | — | — |
| Quinoxaline | $C_{2v}$ | 3.84 | 3.30 | — | — |
| Cinnoline | $C_s$ | 3.84 | 3.30 | — | — |
| Phthalazine [e] | $C_{2v}$ | 4.09 | 3.20 | — | — |
| Acridine [e] | $C_{2v}$ | 3.30 | 3.30 | — | — |
| Phenazine [e] | $D_{2h}$ | 3.25 | 2.85 | – | — |

Note. $\varphi_{ISC}$ and $\varphi_{fl}$ are the quantum yields for intersystem crossing and fluorescence; [a] gas, normal conditions; [b] in benzene; [c] in a butanol : isopentane (3 : 7) mixture at 77 K; [d] in hexane; [e] the luminescence properties are given in more detail in Table 10; unmarked values are given for solutions in cyclohexane.

By studying the electronic spectra of pyridine, pyrazine, and pyrimidine in compressed gases and comparing the π-electron systems of heterocycles and benzene it was possible to deduce that the π-electron systems of pyridine in the $^1B_{2u}$ and $^1B_{1u}$ π,π*-states

(notation adopted by analogy with benzene) and also those of pyrazine and pyrimidine in the $^1B_{1u}$ state resemble the corresponding system in benzene. In the transition of diazines to an excited $^1B_{2u}$ state, their π-electron systems are considerably different from that of benzene.[11–13] At the same time the excitation of pyridine, which is accompanied by the appearance of a band due to a $^1B_{1u}$ transition, is considerably different from the analogous excitation of benzene (the $^1B$ band of benzene corresponds to the transition to a $^1E_{1u}$ state, so comparisons cannot be made between these molecules in this excited state). In addition, pyrazine completely resembles benzene in its excitation to a $^1B_{2u}$ state.[14]

Apart from π,π* bands, in the spectra of pyridine and quinoline derivatives there are bands due to $n \rightarrow \pi^*$ transitions, which are directed perpendicular to the plane of the molecule. The occurrence of these transitions only slightly alters the absorption spectra of the molecules but has a very marked effect on the luminescence properties, which differ considerably from the properties of their hydrocarbon analogues.[5]

Zelikina et al.[14] were the first to record directly structural $n,\pi^*$ bands in the spectra of solutions of pyridine, pyrazine, and pyrimidine in compressed krypton, xenon, and $CF_4$ (120–200 K). In the case of pyridine the $n \rightarrow \pi^*$ is superimposed on the long-wavelength section of a more intense $\pi \rightarrow \pi^*$ band. The vibronic structure of the $n,\pi^*$-band is completely eliminated even in hexane at room temperature,[14] i.e., intramolecular interactions can only be minimised in compressed gases. All these $n,\pi^*$ bands undergo a bathochromic shift when there is a change from rarefied vapour to solutions in Kr and He.[14–17]

The luminescence properties of azines are determined by the relative configuration of the lowest electronically excited states of $n,\pi$- and $\pi,\pi^*$-type (Fig. 1). Heterocycles luminesce very weakly, whereas the corresponding aromatic hydrocarbons exhibit marked fluorescence and phosphorescence.[5] Pyridine hardly fluoresces at all and does not phosphoresce, quinoline does not fluoresce in non-polar solvents but fluoresces in polar solvents ($\pi,\pi^*$-type fluorescence), while acridine exhibits weak fluorescence in all aliphatic solvents but in alcohols the fluorescence increases markedly (see Table 2). Only for quinoline and isoquinoline has $\pi,\pi^*$-type phosphorescence been recorded.

In one monograph[5] the features of the luminescence spectra of monoazines are examined in a somewhat simplified manner, only in relation to the structure and relative configuration of the lowest electronically excited states and without taking into account the interaction between them, even though this interaction has a decisive effect on radiationless deactivation processes.[9] Thus, it is assumed that for all monoazines $T(\pi,\pi^*)$ is the lowest state and in this case only $\pi,\pi^*$-phosphorescence can occur. As the size of the π-system increases, the energy of the $S(\pi,\pi^*)$ state decreases more rapidly than that of $S(n,\pi^*)$, so that even in quinoline in the vapour phase and in hydrocarbon solvents the energies of the $S(\pi,\pi^*)$ and $S(n,\pi^*)$ states coincide. In all these amines with a single nitrogen atom (apart from pyridine) the $n,\pi^*$ band is not at longer wavelength, and *N*-heterocycles in which the $\pi,\pi^*$ band in the absorption spectrum occurs at shorter wavelength than in acridine must exhibit $\pi,\pi^*$-phosphorescence (Fig. 1).

In acid media and polar solvents (especially when intramolecular hydrogen bonds are formed with the nitrogen atom of the heterocycle), those molecules in which the energy of the $T(n,\pi^*)$ state is higher than that of the $S(\pi,\pi^*)$ states (quinoline, azaphenanthrene, acridine, and benzacridine)[5] start to fluoresce (Table 2).

The fluorescence of pyridine, quinoline, isoquinoline, and acridine is exceptionally weak or absent altogether in aprotic solvents but quite considerable in protic solvents,[9,15] and it is assumed that even this weak fluorescence in aprotic solvents is due to impurities.[9] However, the decrease in quantum yield of fluorescence in aprotic solvents is not due to an increase in intersystem crossing; for

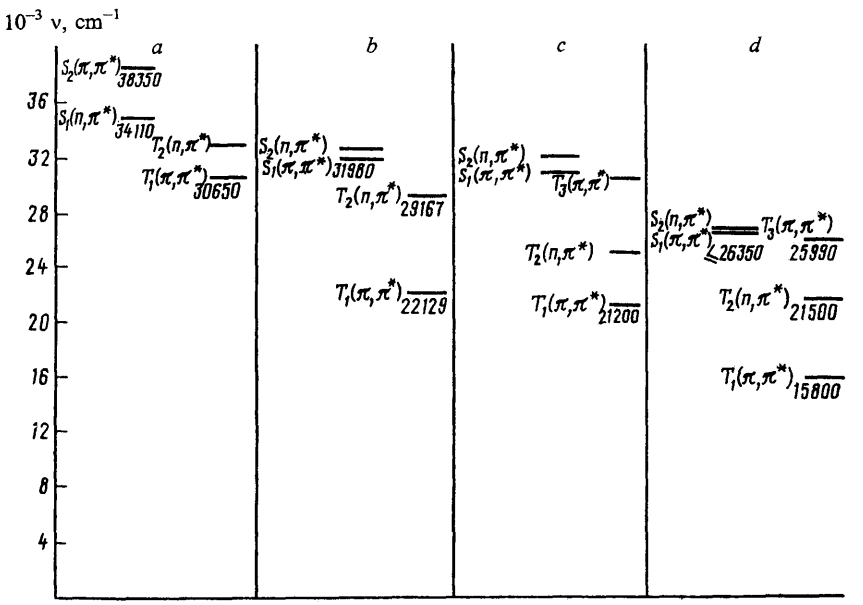



**Figure 1. Distribution of the lowest energy levels of monoazines in non-polar solvents:**[18–20] ***a*, pyridine; *b*, quinoline; *c*, isoquinoline; *d*, acridine.**

quinoline and isoquinoline the yields in the triplet state are equal to ~0.2 and 0.3 respectively.[9] Therefore the absence of fluorescence in these compounds in aprotic solvents is related to an acceleration of the $S_1 \rightarrow S_0$ internal conversion. This increase in internal conversion is due to a vibrational interaction between the closely situated $S(n,\pi^*)$ and $S(\pi,\pi^*)$ levels or, particularly in the case of quinoline and isoquinoline, to a perturbation (or even conversion) of the state as a result of movement along the coordinate corresponding to an extraplanar "scissor" vibration (in other words, as a result of a Jahn–Teller pseudoeffect). This perturbation (or inversion) must lead to a considerable increase not only in the rate of $S_1 \rightarrow S_0$ conversion but also $S_1 \rightarrow T_1$ intersystem crossing (experimentally this is exhibited by the lack of dependence of the quantum yield in the triplet states of quinoline and isoquinoline on the solvent[9]).

Thus, a vibrational interaction between the singlet $n,\pi^*$ and $\pi,\pi^*$ states of virtually all monoazines results in an extremely rapid radiationless deactivation of the $S_1$ state. The rate of radiationless deactivation in the gas phase increases sharply on excitation of the extraplanar scissor vibration of the lowest excited state.[26,27]

The main contribution to internal conversion of the thermalised $S_1$ state is provided by the highest vibrational sublevels of the $S_1$ state. In a deuteriated compound this effect is even more important since the frequency of the scissor vibration decreases, resulting in a reverse isotope effect in internal conversion.

On going from aprotic solvents to protic ones the $\pi,\pi^*$ bands undergo a bathochromic shift while the $n,\pi^*$ bands experience a hypsochromic shift. Consequently, if the lowest singlet state in the heterocyclic amine is a $\pi,\pi^*$ state [or if the $S_1(n,\pi^*)$ levels are situated only just below it], the increase in the distance between the $S_1$ and $S_2$ levels results in a sharp decrease in the rate of internal conversion.[28]

Confirmation of the decisive role of a vibrational interaction between the $n,\pi^*$ and $\pi,\pi^*$ states in the luminescence of monazines (the "proximity effect")[9] is provided by the temperature dependence of the quantum yield of fluorescence. The quantum yield of fluorescence for isoquinoline in ethanol decreases markedly with an increase in temperature.[9,29] In this case the quantum yield of intersystem crossing (ISC) is virtually independent of temperature (~0.2 and ~0.3 at 298 and 77 K respectively). As the temperature increases the hydrogen bonds between isoquinoline and ethanol are weakened, resulting in a convergence of the $S(\pi,\pi^*)$ and $S(n,\pi^*)$ states and an intensification of the vibrational interaction, i.e., on heating the rates of $S_1 \rightarrow S_0$ and $S_1 \rightarrow T_1$ conversions increase simultaneously. As we shall see below, the "proximity effect" in one form or another determines the luminescence properties of all aromatic azines.

The kinetics of the decay of the triplet state of pyridine in the vapour phase are non-exponential. This is due to the existence of two closely situated triplet states that have different lifetimes. A model has been put forward in which it is assumed that there is a strong vibrational interaction between the almost degenerate $T(\pi,\pi^*)$ and $T(n,\pi^*)$ states of pyridine, which results in the appearance of a double minimum on the potential surface of the $T_1$ state[30,31] in the direction of the extraplanar "scissor" vibration. In this case the thermally relaxed $T_2$ state of pyridine is non-planar while the activated state is planar, and the rate constants for $T_1 \rightarrow S_0$ relaxation of these two states differ, amounting to less than $10^5$ and $5 \times 10^6$ $s^{-1}$ respectively.

A study of the hyperfine splitting at zero field of pyridine and its derivatives[32] has confirmed that the $T_1 \rightarrow S_0$ transition in pyridine is forbidden (this is evident from the small intensity of the O–O band). The occurrence of this transition is due to a vibrational interaction of the lowest triplet state with the closest $^3E(\pi,\pi^*)$ state and its spin-orbit interaction with $\sigma\pi^*$ and $\pi\sigma^*$ singlet states. In neutral molecules the vibrational interaction of the singlet $S(\pi,\pi^*)$ states with $T(n,\pi^*)$ states is apparently not strong enough to affect

**Table 2.** Luminescence spectral and photochemical properties of acridine and its derivatives.

| Compound | Solvent | $\varphi_{fl}$ | $\varphi_{ISC}$ | $\tau_{fl}$, ns | $E_a$, kJ mol$^{-1}$ | $\varphi_m^S$ | $\varphi_{rad}^S$ | $\varphi_m^T$ | $\varphi_{rad}^T$ | $\varphi_{tot}$ | Refs. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Acridine | Ethanol | 0.09 | — | — | 16.0 | 0.043 | 0.043 | 0 | 0.043 | 0.129 | [18, 19] |
| Acridine | Methanol | 0.09 | — | — | 18.2 | 0.027 | 0.032 | 0.006 | 0.063 | 0.128 | [18] |
| Acridine | Benzene | 0.00061 | 0 | — | 4.1 | — | — | — | — | — | [18, 20] |
| Acridine | Isopropanol | 0.12 | — | — | 14.0 | 0.03 | 0.058 | 0 | 0 | 0.088 | [18, 20–22] |
| Acridine | Toluene | 0.001 | 0.05 | — | — | — | — | — | — | 0.05 | [23] |
| Acridine | t-Butanol | — | 0.61 | — | — | — | — | — | — | 0.01 | [22] |
| Acridine | Anisole | 0.07 | — | — | — | — | — | — | — | 0.01 | [22, 24] |
| Acridine | Acetonitrile | 0.03 | 0.42 | 2.1 | 6.7 | — | — | — | — | 0.02 | [16, 21] |
| Acridine | n-Hexane | 0.0005 | 0.5 | — | 4.0 | — | — | — | — | — | [17, 21] |
| Acridine | Water/KOH (pH 12) | 0.37 | 0.5 | 11.0 | 22.7 | — | — | — | — | — | [25] |
| Perdeuteroacridine | Water/KOH (pH 12) | 0.31 | — | 11.5 | — | — | — | — | — | — | [25] |
| 9-Chloroacridine | Water/KOH (pH 12) | 0.26 | — | 6.5 | — | — | — | — | — | — | [25] |
| 9-Methylacridine | Water/KOH (pH 12) | 0.38 | — | 9.5 | — | — | — | — | — | — | [25] |
| 9-Propylacridine | Water/KOH (pH 12) | 0.43 | — | 10.4 | — | — | — | — | — | — | [25, 26] |
| 9-Aminoacridine | Water/KOH (pH 12) | 0.81 | — | 15.4 | — | — | — | — | — | — | [27] |
| 9-Methyl-3,4-benzo-acridine | Toluene | 0.08 | — | 3.0 | — | — | — | — | — | — | [25] |
| 1,2,7,8-Dibenzo-acridine | Toluene | 0.22 | — | 8.0 | — | — | — | — | — | — | [28] |
| 1,2,3,4,5,6,7,8-Tetra-benzoacridine | Toluene | 0.24 | — | 12.0 | — | — | — | — | — | — | [28] |

Note. $\tau_{fl}$ is the lifetime of fluorescence; $E_a$ is the energy of activation obtained from the temperature dependence of $\varphi_{fl}$; $\varphi_m^S$, $\varphi_{rad}^S$, $\varphi_m^T$, and $\varphi_{rad}^T$ are the quantum yields for photoreduction of acridine from singlet and triplet states by a molecular and radical mechanism respectively.

the vibrational structure of the hyperfine splitting parameters at zero field. Phosphorescence of the pyridinium cation occurs from the $^3A_1(\pi,\pi^*)$ state (originating from "removal" of the $n,\pi$ states) and has much in common with the phosphorescence of benzene. Thus, although the symmetry of pyridinium ($C_{2v}$) is lower than the symmetry of benzene, replacement of carbon by nitrogen leads to only a slight perturbation of the spin-orbit interaction in the benzene ring.

## 2. Acridine

The pattern of distribution for the lowest electronically excited states of acridine has been quite reliably established (Fig. 2). Previously the dependence of the quantum yield of the fluorescence of acridine on the solvent was interpreted as the result of a change in the nature of the $S_1$ state—$\pi,\pi^*$ in protic solvents and $n,\pi^*$ in aprotic solvents.[28,33] The lifetime of the $S_1$ state of acridine is equal to 50 ± 6 ps in hexane and 350 ps in ethanol.[34] However, after the detection of acridine fluorescence in a matrix of n-octane at 77 K and in benzene at room temperature,[35] it was accurately established that even in these solvents the lowest level corresponds to the $S_1(\pi,\pi^*)$ state.

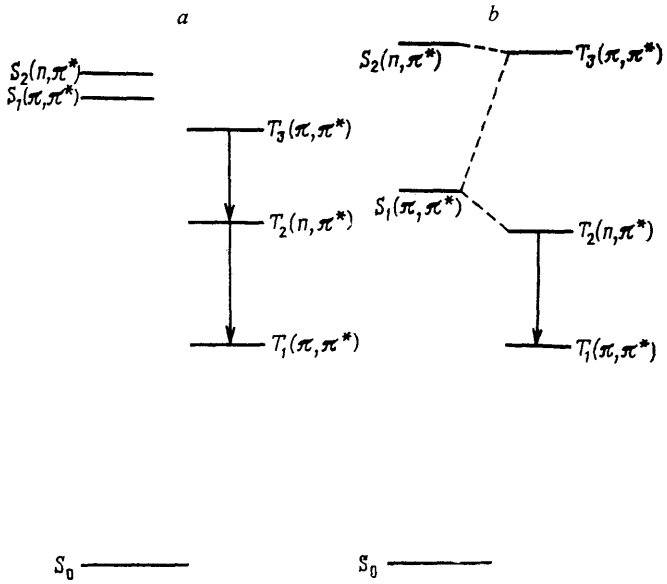



**Figure 2. Distribution of the lowest energy levels of the electronically excited states of acridine: *a*, in benzene; *b*, in water at pH > 7.**

Acridine undergoes photoreduction in solvents that can readily eliminate a hydrogen atom, and its lowest electronically excited state varies in different solvents (Fig. 2).[17] It was found that the $\varphi_{ISC}$ of acridine decreases as the temperature increases in reactive solvents (methyl methacrylate and polymethyl methacrylate) and does not depend on the temperature in benzene (in which there is no photoreduction). In the opinion of Kasama and Kikuchi,[17] in water ISC takes place from the $S_2(n,\pi^*)$ state, which is thermally populated as a result of the following sequence of processes: $S_1(\pi,\pi^*) \rightleftarrows (\Delta E)S_2(n,\pi^*) \rightarrow T_3(\pi,\pi^*) \rightarrow T_1(\pi,\pi^*)$ ($\Delta E$ is the difference in energy between the $S_1$ and $S_2$ states). In benzene $\Delta E$ is very small and ISC takes place very rapidly, while in water $\Delta E$ = 1900 cm$^{-1}$ and internal conversion can thus compete with ISC.[36] Schmidt et al.[36] determined the values of $\Delta E$ for acridine in different solvents; but it was mistakenly assumed by them that the lowest state of acridine is the $S_1(n,\pi^*)$ state (see Table 2).[37]

The fact that the sum of $\varphi_R$ + $\varphi_{ISC}$ + $\varphi_{PR}$† for acridine in solvents that are capable of eliminating a hydrogen atom is less than the sum of $\varphi_R$ + $\varphi_{ISC}$ in inert solvents, suggests that acridine is deactivated by removal of hydrogen and subsequent recombination.

In the radiationaless deactivation of the $S_1$ state of acridine an important role is played by the $T_3(\pi,\pi^*)$ state,[32] whose energy is equal to 26050 cm$^{-1}$ in all solvents[38] and does not depend on the polarity of the latter.[17,37]

The magnitude of the energy gap between the electronically excited state of acridine depends also on the presence of substituents in the molecule and the annelation of the benzene rings (Table 2).[17] In all the acridine derivatives there are two routes for ISC to occur, with the rate of the process in one of them dependent on temperature and in the other not dependent on temperature. For all the acridines (except for 9-aminoacridine) the rate of the process: $S_1(\pi,\pi^*) \rightleftarrows (\Delta E)S_2(n,\pi^*) \rightarrow T_3(\pi,\pi^*)$ is dependent on temperature and the process: $S_1(\pi,\pi^*) \rightarrow T_2(n,\pi^*)$ is independent of temperature.[39]

In the case of 9-aminoacridine the energy gap is large, $\Delta E(T_3-S_1)$ = 4360 cm$^{-1}$, so participation of the $T_3$ state in the deactivation of the $S_1(\pi,\pi^*)$ state can be ignored (Table 2). The electron-donating $NH_2$ group gives rise to a hypsochromic shift of the $n,\pi^*$ bands and a bathochromic shift of the $\pi,\pi^*$ bands in the absorption spectrum, so the $T_2(n,\pi^*)$ level of 9-aminoacridine is higher than $S_1(\pi,\pi^*)$ and the dependence on temperature is solely determined by the possible transition $S_1(\pi,\pi^*) \rightarrow T_2(n,\pi^*)$.

Up to the present time there is still much that is unclear in the photophysics of acridine. Thus, the energy of activation of the fluorescence process of acridine in hexane and ethanol does not depend on the nature of the solvent, which cannot be explained by limiting the study to just the "proximity effect."[42]

## 3. Diazines

The lowest excited states of pyrazine, pyrimidine, and pyridazine are of an $n,\pi^*$-type.[5] The gas-phase absorption spectra exhibit a well resolved vibrational structure in the region of the $n,\pi^*$ transition (Fig. 3).

The lowest $T_1$ state of pyrazine and pyrimidine is the $T_1(n,\pi^*)$ state. When methyl substituents are introduced in the molecule, the $T(\pi,\pi^*)$ band experiences a bathochromic shift but the $T(n,\pi^*)$ band undergoes a hypsochromic shift, so the $T(\pi,\pi^*)-T(n,\pi^*)$ energy gap in methylated diazines is much less than in the initial unsubstituted compounds.[9] As the width of the gap decreases the quantum yield and lifetime of $n,\pi^*$-phosphorescence decrease considerably.[9] The change in the value of $\varphi_R$ for these compounds on methylation is solely due to the increase in probability of the radiationless transition $T_1(n,\pi^*) \rightarrow S_0$ (Table 3).

The dependence of the quantum yield of fluorescence on the excitation energy for pyrazine and pyrimidine vapour (Figs. 4 and 5) suggests[39] that while the rate constant $k_{ISC}$ in the region of the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ absorption bands is constant, the rate

† $\varphi_R$ is the quantum yield of photoreduction.[40,41]

constant for internal conversion $k_{IC}$ ($S_1 \rightarrow S_0$) increases sharply (to $10^{11}$ $s^{-1}$) for light with energy above 34 000 $cm^{-1}$. Thus, in the case of pyrazine, as for pyridine, at frequencies above 34 000 $cm^{-1}$ a route for rapid radiationless deactivation occurs (having the same origins).

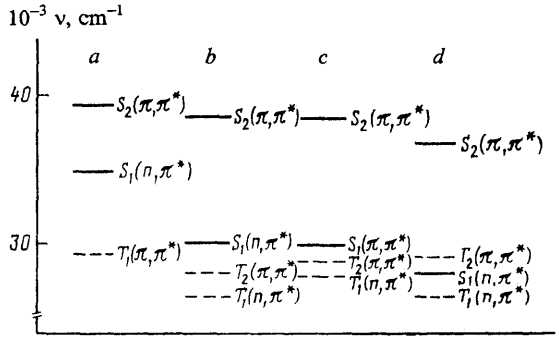



**Figure 3.** Distribution of the lowest energy levels of diazines: *a*, pyridine; *b*, pyrazine; *c*, pyrimidine; *d*, pyridazine.

**Table 3.** Quantum yields for intersystem crossing, fluorescence, and radiationless deactivation in the gas phase at a pressure of 1.0 mm Hg azine + 100 mmHg $SF_6$ (from the results of Yamazaki et al.).[38,40]

| Compound | Transition | $\nu_{0-0}$, $cm^{-1}$ | $\varphi_{fl}$ | $\varphi_{ISC}$ | $k_{IC} \times 10^{-11}$, $s^{-1}$ |
|---|---|---|---|---|---|
| Pyridine | $S_1(n,\pi^*) \leftarrow S_0$ | 34 769 | $5.9 \cdot 10^{-5}$ | 0.30 | 0.17 |
| | $S_2(\pi,\pi^*) \leftarrow S_0$ | 38 350 | $2.4 \cdot 10^{-6}$ | 0.0067 | 7.68 |
| Pyrazine | $S_1(n,\pi^*) \leftarrow S_0$ | 30 875 | $1.3 \cdot 10^{-3}$ | 1.0 | 0.001 |
| | $S_2(\pi,\pi^*) \leftarrow S_0$ | 37 840 | $0.9 \cdot 10^{-4}$ | 0.13 | 5.25 |
| Pyrimidine | $S_1(n,\pi^*) \leftarrow S_0$ | 31 072 | $15 \cdot 10^{-3}$ | 1.0 | 0.001 |
| | $S_2(\pi,\pi^*) \leftarrow S_0$ | 40 310 | $0.4 \cdot 10^{-4}$ | 0.08 | 2.63 |

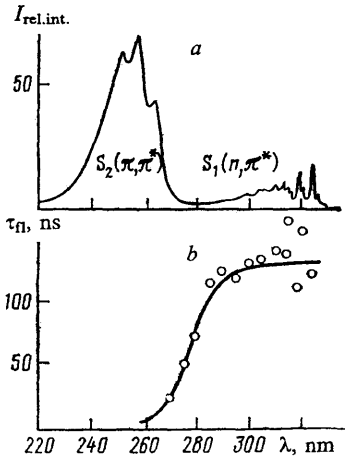



**Figure 4.** Absorption spectrum of pyrazine (*a*) and dependence of the lifetime of fluorescence (*b*) on the wavelength of excitation at a pyrazine pressure of 1 mmHg in the presence of $SF_6$.[39,40]

In contrast to pyrazine, $k_{ISC}$ for pyrimidine increases with an increase in excitation energy near the $S_1$ band, which leads to an even more marked decrease in $\tau_{fl}$ and $\varphi_{fl}$ (Figs. 4 and 5). The mechanism of this type of deactivation is possibly due to the acceleration of internal conversion as a result of photoisomerisation[43] (a similar mechanism has been proposed for benzene).

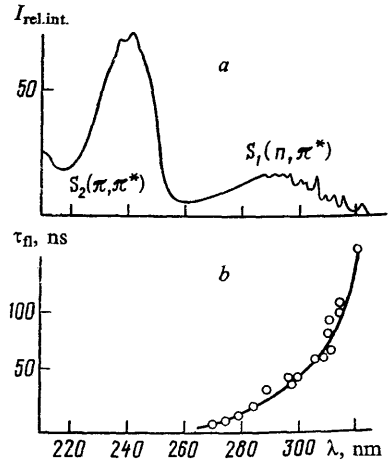



**Figure 5.** Absorption spectrum of pyrimidine (*a*) and dependence of the lifetime of fluorescence (*b*) on the wavelength of excitation[39,40].

The $T_1$ state of pyridine has been identified from the results of energy transfer studies;[44-47] only subsequently was the phosphorescence of pyridine itself detected.[44,45] The energy of this state has been estimated as 30 650 ± 800 $cm^{-1}$,[48] and the lifetime for phosphorescence of pyridine vapour is several microseconds. The phosphorescence of pyridine derivatives—lutidines, cyanopyridines, and aminopyridines—in a condensed state is discussed by Motten and Kwiram.[32,49]

## 4. Phenazine

Phenazine may be regarded as pyrazine with annelated benzene rings. The absorption and emission spectra of phenazine have been studied in detail in solution and monocrystals at 77 and 4.2 K.[10,50] The relative configuration of the lowest electronically excited states $S_1(n,\pi^*)$, $S_2(\pi,\pi^*)$, and $T_1(\pi,\pi^*)$ has been established (Fig. 6).[51-53]

Fluorescence occurs for phenazine itself. It is of $\pi,\pi^*$-type in alcohols and $n,\pi^*$-type in hexane (Tables 4 and 5).

Struve et al.[42] used picosecond laser photolysis to record the $T-T$ absorption spectrum of phenazine in isooctane and methanol and demonstrate the existence of two different routes for population of the lowest $T_1(\pi,\pi^*)$ state of phenazine by excitation of the singlet $S_3(^1L_b)$ state: $S_3 \rightarrow S(n,\pi^*) \rightarrow T_1(\pi,\pi^*)$ and $S_3 \rightarrow T_2(n,\pi^*) \rightarrow T_1(\pi,\pi^*)$.

The introduction of F and Cl atoms into the β-position of phenazine leads to a successive increase in quantum yield of fluorescence. A subsequent change to Br and I reduces $\varphi_{fl}$, with a bathochromic shift of the fluorescence spectrum occurring. When a halogen is introduced into the α-position there is no fluorescence flashing and the fluorescence spectrum does not change (Table 4).[41]

In the opinion of Osipov et al.[52] $\pi p_z$-conjugation between the π-electron system and the halogen can result in this type of bathochromic shift of the π,π*-levels, so that inversion of the π,π* and lowest $n,\pi^*$ level occurs. In the series F, Cl, Br, I the conditions for conjugation deteriorate since the 2-, 3-, 4- and 5-$p_z$ electrons are involved.

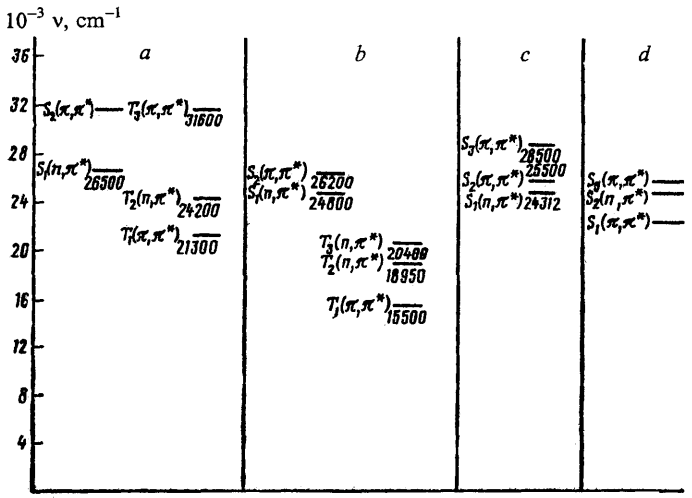



**Figure 6.** Distribution of the lowest energy levels of "anomalous" diazines.[92,96]

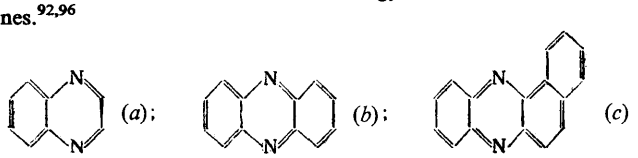



**Table 4.** Luminescence properties of phenazine derivatives in toluene at 20 °C.[41]

| Compound | $\varphi_n$ | $\tau_n$, ns |
|---|---|---|
| Phenazine | $7 \cdot 10^{-4}$ | 0.06 |
| 1,2-Benzphenazine | 0.012 | 0.2 |
| 1,2,3,4-Dibenzphenazine | 0.10 | 0.18 |
| 1,2,3,4,5,6,7,8-Tetrabenzphenazine | 0.16 | 1 |
| 1-Fluorophenazine | — | <2 |
| 1-Clhlorophenazine | — | <2 |
| 2-Fluorophenazine | — | 2 |
| 2-Chlorophenazine | — | 3.5 |
| 2-Bromophenazine | — | 5 |
| 2-Iodophenazine | — | 5 |

An unusual effect involving the increase in quantum yield and lifetime of fluorescence of phenazine itself has been detected when toluene is replaced by methyl iodide as the solvent at 77 K.[52] This is apparently due to the formation of weak charge-transfer complexes between phenazine and methyl iodide in which the *n*-electrons of phenazine are partially bonded.

Annelation of the benzene rings causes a reduction in energy of the $S_2(\pi,\pi^*)$ state of phenazine, which leads to an increase in quantum yield and lifetime of fluorescence (Table 4). In this case inversion of the $S_1(n,\pi^*)$ and $S_2(\pi,\pi^*)$ levels does not occur, namely, for all the phenazines the $S_1(n,\pi^*)$ state is the lowest. However, the proximity of these levels suggests that there is a considerable temperature-dependent vibrational interaction between them. The temperature causes excitation of the vibrations linking the closely situated states and thus determining the features of the luminescence spectra of the molecules. Osipov et al.[41] attribute the two-component fluorescence of benzphenazine and dibenzphenazine to emission from the $S_2(\pi,\pi^*)$ and $S_1(n,\pi^*)$ states, i.e., for these molecules emission from the $S_2(\pi,\pi^*)$ state is more effective than from $S_1(n,\pi^*)$. Phenazine becomes a stronger base in its $S_1$ and $T_1$ states than in the ground state. Its mono- and di-protonated forms have been recorded (Table 5, see also Table 10 for comparison).

**Table 5.** Luminescence properties of phenazine (A), its monocation ($AH^+$), and dication ($AH_2^{2+}$).[53]

| Compound | $\lambda_{max}$ | $\lambda_{0-0}$ | $E_{T_1}$, cm⁻¹ | $pK_{S_0}$ | $pK_{T_1}$ | $pK_{S_1}$ |
|---|---|---|---|---|---|---|
| A | 21 000 | 23 500 | 15 475 | 1.24 | 4.0 | 6.0 |
| $AH^+$ | 19 000 | 21 250 | 14 175 | 1.21 | 4.0 | 6.0 |
| $AH_2^{2+}$ | 15 200 | 17 300 | 9 300 | −4.30 | 5.7 | 4.1 |

Note. $pK_{S_0}$, $pK_{S_1}$, $pK_{T_1}$ are the p*K* values in the ground, $S_1$ and $T_1$ states.

## 5. Aminopyridines

A class of pyridine derivatives such as aminopyridines has been studied in detail as have 7-azaindolines, which are very similar to them in structure.[54–63] A study of the features of the luminescence spectra and quantum-chemical calculations of the composition of the lowest electronically excited states of aminopyridines[55–58] showed that the amino group does not significantly perturb the energy levels of pyridine (Fig. 7). As in the case of pyridines, the features of the luminescence spectra of aminopyridine are determined to a considerable extent by the vibrational interaction between closely lying singlet $n,\pi^*$ and $\pi,\pi^*$ levels.[64,65] The effect of the amino group is to cause the distance between the lowest $S(n,\pi^*)$ and $S(\pi,\pi^*)$ levels to become even smaller, and in non-polar solvents inversion even occurs so that $S_1(\pi,\pi^*)$ becomes the lowest level.

According to calculations,[66] the $S_1(n,\pi^*)$ level of 2-aminopyridines is situated 0.72 eV below the $S_2(\pi,\pi^*)$ level. However, an analysis of the effect of the solvent on the luminescence properties of 2-aminopyridine and also a study of the vibrational and rotational structure of its spectra[57] show that even in non-polar solvents the lowest state is the excited $S_1(\pi,\pi^*)$ state, and the band at 298.0 nm corresponds to the $^1A_1 \leftarrow {}^1B_2$ transition in pyridine somewhat shifted by the effect of the amino group.

In non-polar solvents the distance between the levels increases and the efficiency of radiationless deactivation decreases, resulting in an increase in the yield of fluorescence, and there is a correlation between the strength of the oscillator of the $\pi \rightarrow \pi^*$ band and the quantum yield of fluorescence[55] (Table 6).

2-, 3-, and 4-Aminopyridines do not phosphoresce in non-polar solvents but phosphorescence occurs in polar solvents. According to Wolleben and Testa[57] this phenomenon is due to the increase in the rate of $S_1 \rightarrow T_1$ intersystem crossing, since in polar solvents the relative position of the $T(n,\pi^*)$ and $T(\pi,\pi^*)$ levels changes (Fig. 8).

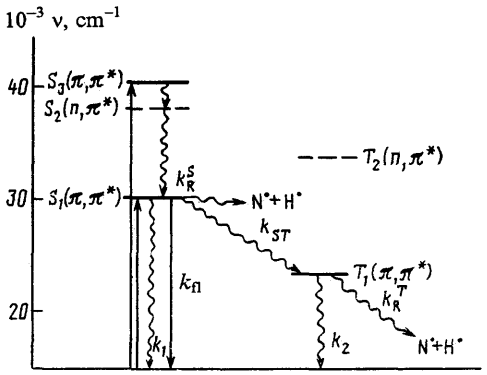



**Figure 7.** Distribution of the lowest energy levels of 5-methyl-7-azaindoline and rate constants for the fundamental processes taking place in it from the results of Dvornikov et al.:[59-62] $k_1 = 1.2 \times 10^8\ s^{-1}$; $k_2 = 2 \times 10^5\ s^{-1}$; $k_R^T = 8 \times 10^5\ s^{-1}$; $k_{fl} = 4 \times 10^7\ s^{-1}$; $k_{ISC} = 8 \times 10^7\ s^{-1}$; $k_R^S < 5 \times 10^6\ s^{-1}$; $k_R^S$ and $k_R^T$ are the rate constants of dissociation from the lowest singlet and triplet states respectively.

**Table 6.** Features of the luminescence spectra of 7-azaindolines and 2-aminopyridine.[55,57,59,60]

| Compound | Solvent | $\lambda_{abs}^{max}$, nm | ε, $mol^{-1}$ $cm^{-1}$ | $\lambda_{fl}^{max}$, nm | $\varphi_{fl}$ | $\tau_{fl}$, ns | $k_{fl} \times 10^{-7}$, $s^{-1}$ |
|---|---|---|---|---|---|---|---|
| 2-Aminopyridine | Heptane | 290 | 4250 | 332 | 0.04 | 24.2 | 6.2 |
| 5-Methyl-7-azaindoline | " | 303 | 4610 | 350 | 0.17 | 3.9 | 7.3 |
| 4,6-Dimethyl-7-azaindoline | " | 308 | 7340 | 360 | 0.18 | 2.2 | 9.1 |
| 4,6-Dichloro-7-azaindoline | " | 308 | 6520 | 360 | 0.023 | 0.8 | 7.6 |
| 5-Methyl-7-azaindoline | Heptane + $CH_3COOH$ | 317 | — | 450 | 0.046 | — | — |
| 2-Aminopyridine | Propanol | 296 | 4400 | 352 | 0.18 | 5.1 | — |
| 5-Methyl-7-azaindoline | " | 308 | 4610 | 375 | 0.32 | 4.6 | 5.6 |
| 4,6-Dimethyl-7-azaindoline | " | 310 | 7780 | 375 | 0.25 | 3.7 | 9.1 |
| 4,6-Dichloro-7-azaindoline | " | 315 | 6790 | 385 | 0.0065 | — | 11.0 |
| 2-Aminopyridine | Acetonitrile | 293 | 4800 | 345 | 0.45 | 5.0 | — |
| 5-Methyl-7-azaindoline | " | 305 | — | 368 | 0.23 | — | — |
| 4,6-Dimethyl-7-azaindoline | " | 310 | — | 368 | 0.21 | — | — |
| 4,6-Dichloro-7-azaindoline | " | 312 | — | 370 | 0.0014 | — | — |

The relative position of the lowest $n,\pi^*$ and $\pi,\pi^*$ levels of 2-aminopyridine is highly dependent on the presence and nature of the substituent in the aromatic ring. The introduction of a methyl group into 2-aminopyridine (for example, the formation of 3-methyl-2-aminopyridine) leads to inversion of the lowest singlet $n,\pi^*$ and $\pi,\pi^*$ levels and to a reduction in width of the energy gap between them. Therefore the fluorescence of 3-methyl-2-aminopyridine occurs in non-polar solvents with the participation of the almost degenerate $S_1(\pi,\pi^*)$ and $S_2(n,\pi^*)$ states. At 77 K there is emission from $S_2$ while at room temperature it occurs from both states. The quantum yield of fluorescence is determined to a considerable extent by the strength of the oscillator of the long-wavelength $\pi,\pi^*$ transition, with which the $n,\pi^*$ transition is combined.[66] Calculations using the CNDO method showed[56] that as soon as the $S_1(\pi,\pi^*)$ state becomes the lowest state for 2-aminopyridine derivatives, this immediately leads to an increase in quantum yields of fluorescence in non-polar solvents. (Fig. 8).[67]

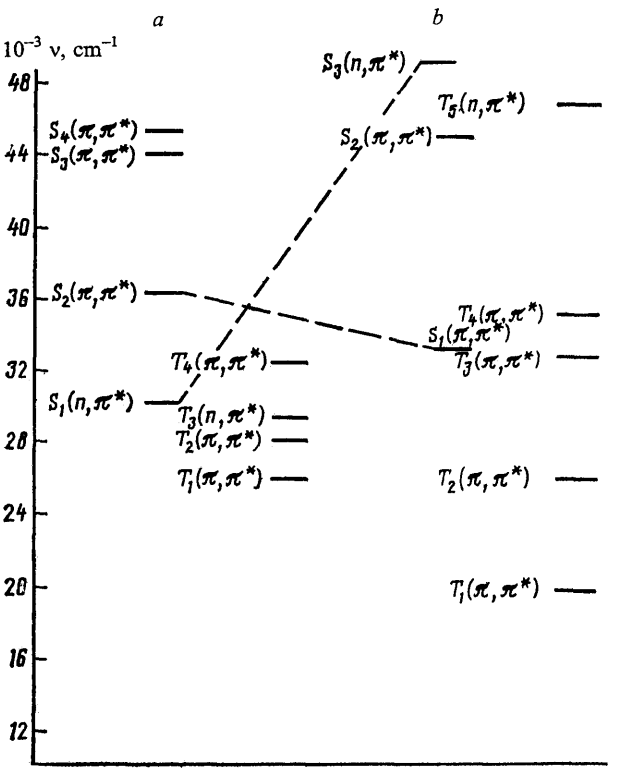



**Figure 8.** Distribution of the lowest energy levels of 2-aminopyridine (*a*) and its cation (protonated on the pyridine ring) (*b*).

## III. Photochemical properties

### 1. Pyridine, quinoline, acridine

As already mentioned above, pyridine is isoelectronic with benzene, but in pyridine there is a system of nitrogen $n,\pi^*$ states which does not occur in aromatic compounds. Hence the photochemical reactions of pyridine can be divided into those which are similar to the photochemical conversions of benzene and those which are determined by the presence of the unshared electron pair of nitrogen.

Amongst processes of the first type are photoisomerisation (formation of benzvalene, Dewar pyridine), photosubstitution, and also photodissociation of halide-substituted pyridines. Processes of the second type are represented by hydrogen abstraction reactions

(photoreduction), processes related to the acid-base dissociation of pyridines in an excited state, and processes involving cleavage of ring bonds.

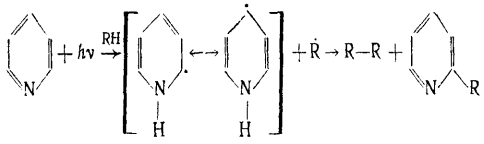
In the case of pyridine the photolytic processes that are typical of nitrogen-containing compounds occur via $n,\pi^*$ excited states (as a rule the lowest in energy), while "benzene-type" reactions require excitation of the π-system.

**a) Acid-base properties of pyridine.** According to CNDO calculations, the basicity of heterocyclic aromatic compounds in which the heteroatom is the basic site is considerably higher in the $S_1$ state that in the $S_0$ state.[62] The basicity of pyridine derivatives in the $S_1$ state is in fact higher than that in the $S_0$ state by a factor of 3–4, but the basicity of quinolines increases less (Table 7). Moreover, in protonation of the pyridine ring there is a marked increase in energy of the $n,\pi^*$ transitions compared to the $\pi,\pi^*$ transitions, since the proton interacts with the unshared electron pair on nitrogen. According to calculations,[56] when 2-aminopyridine is protonated the energy of the $S_1(n,\pi^*)$ state increases by 2.51 eV, as a result of which the vibrational interaction between the $S_1(n,\pi^*)$ and $S_2(\pi,\pi^*)$ states disappears and there is a sharp increase in the quantum yield of fluorescence in the cations. The increase in the basicity of bromine-substituted pyridine on going from the ground state to the $S_1$ and $T_1$ states is more related to the strong electron-donating properties of bromine as a result of the stronger conjugation of the $p,\pi$ orbital of bromine with the π orbital of pyridine in these states[62] (Table 7).

**Table 7.** Acid-base properties of derivatives of pyridine and quinoline in aqueous and aqueous alcohol solutions.[62–64]

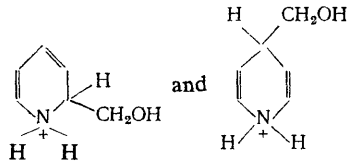
| Compound | $\lambda_{max}$, $cm^{-1}$ | $pK_{S_0}$ | $pK_{S_1}$ | $pK_{T_1}$ |
|---|---|---|---|---|
| Pyridine | 38 200 | 5.42 | 4.79 | — |
| 2-Bromopyridine | 37 800 | — | 2.66 | — |
| 3-Bromopyridine | 37 450 | 3.0 | 4.72 | — |
| Quinoline | 31 950 | 5.01 | 13.83 | 6.69 |
| 3-Bromoquinoline | 31 050 | 3.07 | 13.14 | 5.38 |
| 6-Bromoquinoline | 31 200 | 3.13 | 13.84 | 6.07 |
| Isoquinoline | 31 300 | 5.31 | 7.62 | 3.63 |
| 4-Bromoisoquinoline | 30 900 | 3.32 | 6.05 | 3.49 |

On irradiation, pyridine is capable of removing a hydrogen atom even from cyclohexane. Irradiation of pyridine at 253.7 nm in cyclohexane (RH) results in the formation of dicyclochexyl (R–R), 2-, and 4-cyclohexylpyridines, and 2,5-dicyclohexylpyridine in the ratio 20 : 10 : 10 : 1.[16]

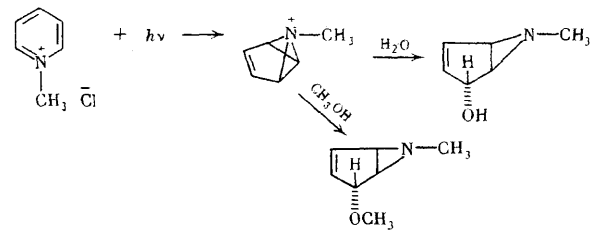


[According to our estimates the quantum yield in such a system does not exceed $2.3 \times 10^{-4}$, reaction takes place from the $S_1(n,\pi^*)$ state]. The resulting pyridine radicals can combine in the solvent cage to form dihydro-substituted compounds, recombination of which in turn leads to the formation of 2- and 4-substituted pyridines. In the presence of oxygen the yield of dicyclohexyl decreases by a factor of 10 and new products—cyclohexanol and cyclohexanone—are formed.

In a condensed state a large number of reactions involving introduction of substituents into the pyridine ring take place via the removal of a hydrogen atom by pyridine in an excited state. Thus, photoalkylation of pyridines in acid solution involves the removal of hydrogen by the nitrogen atom of a pyridine salt and the formation of the intermediates[26]

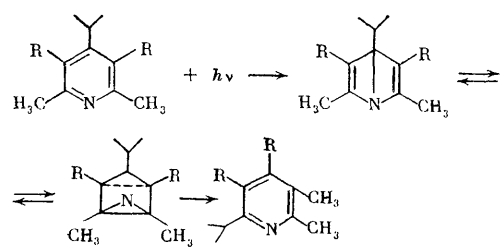


As a result of the recombination of these intermediates 2- and 4-methylpyridines, and 1-(2-pyridyl)-2-(4-pyridyl)ethane are formed. Another possible method for the photoconversion of pyridine in water and methanol is isomerisation with addition of the solvent.[16]



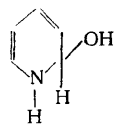
Pyridyl radicals could only be directly detected in an argon matrix. It was established that these radicals are photochemically active. On absorption of a second quantum they undergo ring-opening.[65]

The photoreduction of 3,5-dicarboxypyridines also takes place via the removal of hydrogen. Products from the photoreduction and addition of methanol (1,2- and 1,4-dihydropyridines with a hydroxymethyl group at the 2- and 4-positions) are formed in methanol. Removal of hydrogen by 3,5-dicarboxypyridines occurs in the $S_2(n,\pi^*)$ state and the resulting α-hydroxyalkyl radicals disproportionate. Malkin et al.[64] suggest that this reaction takes place via the $S_2$ state, since there is no correlation between the rate constants of fluorescence quenching and the photochemical reaction. In the excited $S_2(n,\pi^*)$ state of 3,5-dicarboxypyridines removal of hydrogen from the solvent as well as isomerisation to form the intermediate "Dewar pyridine" and prismane are possible. In this case photoreduction generally occurs more rapidly because of the large concentration of alcohol. However, the photoreduction of 4-isopropyl-3,5-dicarboxypyridine, whose isopropyl group gives rise to steric hindrance, does not occur, and instead of this isomerisation takes place



where R = COOH.

Pyridine decomposes very effectively on irradiation in aqueous solution;[65-67] the final product of photolysis are $CO_2$, ammonia, and water. The photolysis mechanism has so far not been precisely established, but it has been suggested[66-69] that on photoexcitation of the hydrogen-bonded complex that is formed between pyridine and water, radical addition of water takes place in the $S_1(n,\pi^*)$ state of pyridine at the 2- and 6-position to form the intermediate



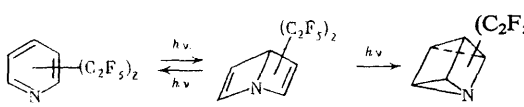
which then decomposes to give the relatively stable 5-amino-2,4-pentadienal, which has been detected as an intermediate.[65,66,70,71] However, in the opinion of Wilzbach and Raush[66] 5-amino-2,4-pentadienal is formed in water by hydrolysis of "Dewar pyridine" (2-azabicyclo[2.2.0]hexa-2,5-diene). Thus, in all of the solvents pyridine initially gives "Dewar pyridine", which is either reduced to 2-azabicyclohex-5-ene or hydrolysed to the aldehyde.[66] Photolysis of pyridine is accelerated when the pH is lowered and suppressed in an alkaline medium.[65] In general the pyridine ring is much less stable towards light than the aromatic ring of aniline, which is confirmation of the important role of *n*-electrons during photolysis.

**b) Photoisomerisation.** The most characteristic photolytic reaction of pyridine itself and its derivatives is photoisomerisation to form "Dewar pyridine" and benzvalene.[39] Reverse rearomatisation of these unstable isomers leads to the formation of various substituted pyridines. Isomerisation occurs both in the gas phase and in solution.[72] The product from the photolytic irradiation of pyridine in butanol at −15 °C is "Dewar pyridine", whose lifetime is almost 2 min.[72]

When pyridine is irradiated with light in an argon matrix at 8 K there is the initial formation of "Dewar pyridine", which is subsequently reduced to HCN and cyclobutene and then decomposes right through to acetylene.[72] Similar reactions of pyridine to HCN and acetylene also occur in the gas phase.

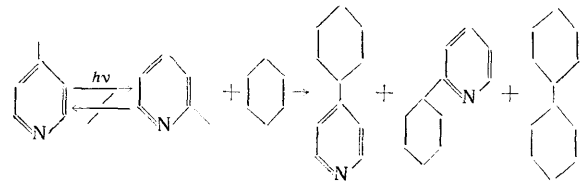
It is assumed[39] that the reversible photoisomerisation of pyridine to benzvalene occurs on excitation to the $S_2(\pi,\pi^*)$ state and it is this reaction that is responsible for the efficient radiationless deactivation of the higher excited states of pyridine in the gas phase.

As in the case of benzene, replacement of hydrogen in pyridine by a perfluoroalkyl group contributes towards the isolation of the respective "Dewar pyridines" and azaprismane in high yield:[72]



In contrast to perfluorobenzene, perfluoropyridine is light-stable. Photolytic irradiation of perchloropyridine results in cleavage of the C(3)−Cl bond, and the resulting radicals react with the solvent.[71,72]

Photolytic irradiation of 2-methylpyridine (2-picoline) in the gas phase gives 3- and 4-picolines. Irradiation of the different picoline and lutidine (dimethylpyridine) isomers results in the formation of other isomers, apparently via the formation of azaprismanes.[39,40] When 2- and 4-picolines and 3,4-lutidines are irradiated in cyclohexane, isomerisation and substitution occur,[39,73] while in the case of 2,3-, 2,4-, and 2,5-lutidines only substitution takes place:[73,74]



**c) Photosubstitution.** Halogen derivatives of pyridine undergo effective substitution of the halogen in water to form pyridines, the quantum yield being independent of the pH of solution. The reaction mechanism involves the heterolytic cleavage of the C−halogen bond ($S_N1$-type reaction) and reaction of the carbocation with water.

In the gas phase and also in heptane and methanol 2- and 3-bromopyridines when exposed to light form pyridine, while in water hydroxypyridine is formed.[71,75] In this case photosubstitution takes place via the $S_1$ state, in which pyridine is involved in a donor-acceptor reaction with water or other nucleophiles, resulting in substitution and induced deactivation. Substitution by hydrogen in non-aqueous solution is caused by homolytic dissociation of the C−halogen bond and removal of an H atom from the solvent by the respective radical.

The photoreduction of iodopyridine by sodium during matrix isolation leads to the formation of the respective pyridyl radicals[64] as a result of dissociative electron capture:

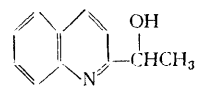
$$Na + PyX \xrightarrow{h\nu(\lambda > 500\ nm)} Na^+ + [PyX^-]^\cdot \rightarrow Py + X^\cdot.$$

2-, 3-, and 4-pyridyl radicals have been detected. Pyridyl radicals can undergo further photochemical reactions related to cleavage of a CN bond in the aromatic ring; this frequently occurs in the direct photolysis of alkylpyridines.[64,70] The pyridyl radicals detected are σ-radicals, and the orbital which is occupied by the electron is to the extent of 70% a *p* orbital of the bond undergoing cleavage.[70]

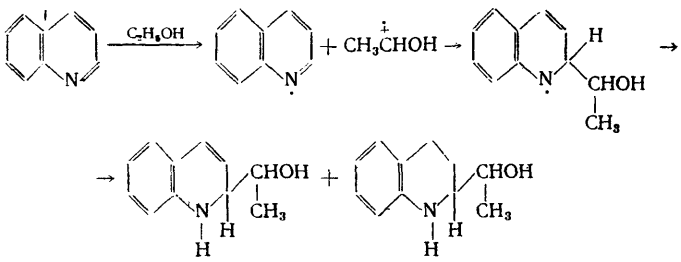
In acid media (HCl in ethanol) quinolines undergo photoalkylation to form 2- and 4-ethylquinolines. In the opinion of Stermitz et al.[76] protonated quinoline in an excited state removes a hydrogen at the β-position of ethanol so that a hydrogen atom adds on to the amine nitrogen atom. The resulting radicals react with quinoline at the 2- and 4-positions and elimination of water and rearomatisation subsequently occur, leading to the formation of alkylation products with a quantum yield of 0.02.[76] In acid solutions of isopropanol the photoalkylation of quinoline does not occur. Under these conditions the reduced forms of quinoline dimers are formed in low yield.

Photolytic irradiation of isoquinoline in ethanol in the presence of HCl leads to the formation of 1-ethylquinoline, while in isopropanol (as in the case of quinoline) photoalkylation does not occur.

Photolytic irradiation of quinoline in ethanol in the absence of acid leads to the formation of 2-(1-hydroxyethyl)quinoline:



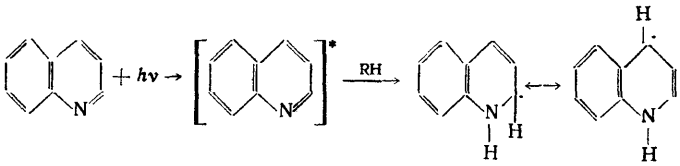
as well as traces of the 1,2,3,4-tetrahydroquinoline:



It is still not clear why substitution only occurs at the 2-position in the absence of acid.[76]

The photoalkylation of quinoline and isoquinoline in benzene also occurs in the presence of organic acids in an atmosphere of nitrogen. As in alcohols photoalkylation of quinoline occurs at the 2- and 4-positions while in isoquinoline it occurs at the 1-position. The mechanism of photoalkylation involves removal of a proton from the acid by quinoline in an excited state and formation of an exciplex. Decarboxylation of the exciplex leads to the formation of an ion pair, recombination of which gives products of reductive alkylation.[76,77]

When quinoline is irradiated in cyclohexane, 2-cyclohexylquinoline and 4-cyclohexylquinoline are formed, while in diethyl ether 2- and 4-(1-ethoxy)quinolines are formed.[67,78] Only 1-(1-ethoxy)isoquinoline is formed from isoquinoline in ether. The proposed mechanism involves the formation of unstable radicals:



Photolytic irradiation of 2-cyanoquinoline in alcohols results in photosubstitution of the CN group by OR; the same process occurs in acid solutions but with a lower quantum yield (as mentioned above, quinoline undergoes photoalkylation).[79] Sensitisation experiments show that photosubstitution occurs in the $T_1(\pi,\pi^*)$ state.

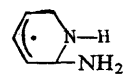
Examples of electrophilic photosubstitution of pyridine and quinoline are almost unknown, possibly because electrophilic reagents are often efficient quenchers of excited states. Moreover, it is difficult to produce a high concentration of an electrophilic reagent that is needed to carry out the reaction with a short-lived triplet state.

**2. Aminopyridines and 7-azaindolines**

The acid-base properties of aminopyridines and 7-azaindolines are virtually the same; the former and the latter are initially protonated on the pyridine ring ($pK_a$ 5.8–7.1),[70,74,76] but a second protonation on the amino group occurs with difficulty. The absorption spectrum of the dication of 3-aminopyridine undergoes a hypsochromic shift relative to the monocation and neutral form (3800 $cm^{-1}$ in water) while the fluorescence spectrum of the dication matches the fluorescence spectrum of the monocation. This is because adiabatic dissociation occurs in the $S_1$ state of the dication and fluorescence of the monoprotonated cation is observed.[66] This is a reflection of the general trend towards weakening of the basic properties of these heterocyclic amines in an excited state, as a result of which their cations dissociate adiabatically while neutral amines acquire the ability to fluoresce.[61,67] At the same time the acidity of the amino groups of all aromatic amines in an excited state increases, so both aminopyridines and 7-azaindolines undergo adiabatic dissociation by an acidic mechanism in the $S_1$ state on quenching of fluorescence with the $OH^-$ ion.[60]

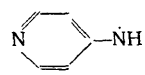
Protonation of the pyridine ring of 7-azaindolines in alcohols and water leads to a marked increase in the energy of $n \rightarrow \pi^*$ transitions compared with $^1\pi \rightarrow \pi^*$ transitions, since the proton interacts with the unshared electron pair of nitrogen in the pyridine ring. As was mentioned above, this is manifested in a sharp increase in the quantum yield of fluorescence of 7-azaindoline cations compared with the neutral compound (see Table 6). The increase in yield is due to "removal" of the $S(n,\pi^*)$ state and the absence of any possibility for intersystem crossing of the cations (Fig. 8).

When aminopyridines are irradiated, radicals of two types can be formed. It was proposed[58] that radicals that are formed by photolytic irradiation of 2-aminopyridine in cyclohexane should be regarded as of pyridyl type:

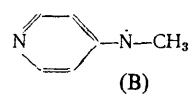


It is assumed that formation of the radical occurs in the $S_2(n,\pi^*)$ state of 2-aminopyridine by removal of a hydrogen atom from the solvent and that the NH bond is not cleaved (this conclusion was based on the absence of intermediates in the photolysis of 2-aminopyridine in methanol, ethanol, and acetonitrile).[58,68]

At the same time in the photolysis of 4-aminopyridine in isopropanol it is suggested[68] that there is cleavage of an NH bond and formation of an aminyl radical, whose absorption spectrum has a maximum at 440 nm:



It is thought that the NH bond of 4-*N*-methylaminopyridine is cleaved in isopropanol so that an aminyl radical is formed



(B)

The process takes place via an unidentified short-lived intermediate state. During photolysis in acetonitrile, the radical cation of 2-aminopyridine, whose absorption spectrum has a maximum at 500 nm, is formed in addition to (B).[57,58]

When the temperature is lowered the quantum yield for photodissociation of the NH bond decreases in all solvents and the triplet-triplet absorption of aminopyridines becomes appreciable[59,60] (this is the only case known to date of $T-T$ absorption in pyridine derivatives).

It was shown by pulsed photolysis that the photolytic irradiation of 2-aminopyridine and 7-azaindoline in all solvents leads to cleavage of an NH bond and formation of aminyl radicals, which then dimerise (Table 8).[59,60] The removal of a hydrogen atom from the solvent by aminopyridine in the $S_2(n,\pi^*)$ state as proposed by Wolleben and Testa[58] is unlikely and contradicts the results of Dvornikov et al.[59–62]

The luminescence spectroscopic and photochemical properties of aminopyridines and 7-azaindolines are very similar and this provides the basis for the assumption that on photolysis of 2-aminopyridines

cleavage of an NH bond occurs and aminyl radicals are formed from the $T_1$ state. The similarity of the spectra of the resulting radicals to the spectra of other aminyl radicals may serve as confirmation of this.[57,63]

The lifetime of the $T_1$ state of 7-azaindoline in heptane at room temperature is 1 μs and such a short lifetime is also characteristic of the $T_1$ state of *o*-aminopyridines.[61–63] The $T-T$ absorption spectrum could only be recorded at −155 °C, the rate constant for deactivation of the $T_1$ state being 381 $s^{-1}$.[55,56]

The quantum yield of fluorescence of 7-azaindolines does not depend on the wavelength of excitation,[67] which is also confirmation that photodissociation occurs from the $T_1$ state of 7-azaindolines (and not from higher excited states as in the case of amines and indoles).

**Table 8.** Extinction coefficients of aminyl radicals and quantum yields for photodissociation of the N–H bond of 7-azaindolines in benzene.[59–61]

| Compound | $\varepsilon_{rad}$, $mol^{-1}$ $cm^{-1}$ | $\varphi_{rad}$ |
|---|---|---|
| 4,6-Dimethyl-AI* | 480 | 0.36 |
| 4,6-Dichloro-AI | 480 | 0.22 |
| 4-Methyl-AI | 457 | 0.24 |

*AI = 7-azaindoline.

## 3. Acridine

The most characteristic photolytic reaction of acridines is their reduction to acridanes, which occurs with varying efficiency in all solvents. The reduction takes place via both the $T_1(\pi,\pi^*)$ and $T_2(n,\pi^*)$ states.[80] The quantum yields of the photoreduction of acridine in different solvents are given in Table 2.

The photoreduction of acridine in non-polar solvents always takes place partly by a molecular mechanism and partly by a radical mechanism.[79–82] The radical mechanism involves the removal of a hydrogen atom by acridine in an excited state from the solvent to form acridine radicals, the destruction of which leads to the formation of acridane and dihydroacridane.[81,82] The molecular mechanism involves the successive or parallel reduction of acridine at two positions [N and C(9)], but is it not clear whether photoreduction occurs as a result of a one step process or via the formation of a short-lived intermediate.[81] A study of the photoreduction of acridines in binary mixtures showed[81] that the molecular and radical mechanisms occur independently of each other from different excited states of acridine.

In aqueous solution the photoexcitation of acridine results in its photoionisation, which occurs by a mechanism involving two quanta of energy. It follows from experiments on the effect of KI on the yield of solvated electrons that photoionisation mainly occurs via the $S_1$ state of acridine.[82] The reaction of a hydrated electron $e^-$ with a neutral molecule of acridine results in the formation of a neutral *C*-centred radical while the acridine radical cation (formed at the same time as $e^-$) is deprotonated to give an *N*-centred radical (Fig. 9).

The photochemistry of acridane (9,10-dihydroacridine) is closely related to the photochemistry of acridine. The photolytic irradiation of acridane and acridine in ethanol at 93 K and room temperature results in the formation of a radical cation (maxima in the absorption spectra at 638 and 358 nm), an *N*-radical (364 and 351 nm), and a *C*-radical (520 nm).[84] All these species are formed by a two-quantum mechanism from the $T_1$ state of acridane.[84]

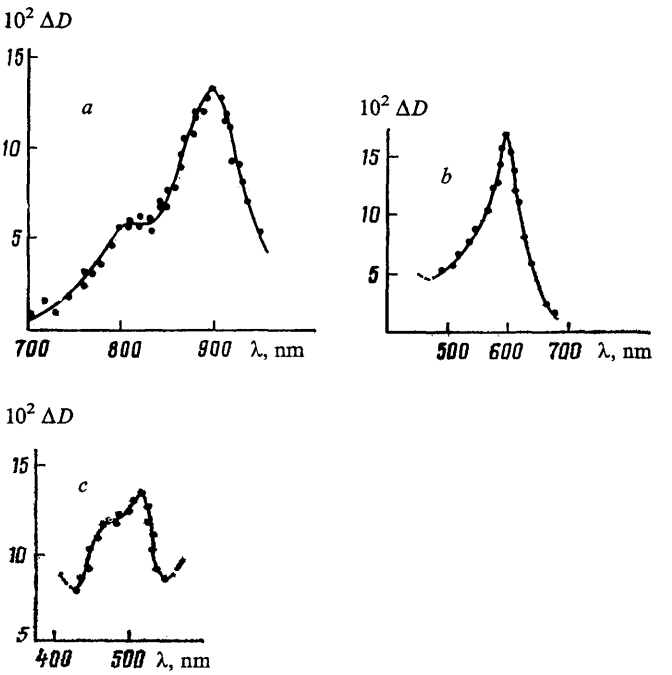
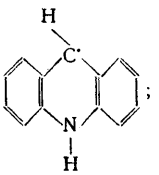
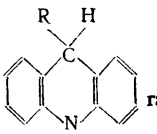
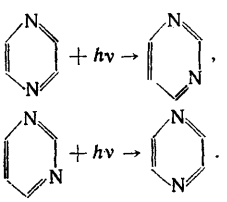



**Figure 9.** Absorption spectra of short-lived intermediates in the photolysis of acridine in ethanol: *a*, the acridine radical cation; *b*, the  radical; *c*, the  radical.

## 4. Diazines

Diazines undergo photoisomerisation in the vapour phase:[85]



The quantum yield for formation of an isomer increases with an increase in energy of excitation—by a factor of 100 for light at 253.7 nm ($S_2$ band) compared with light at 313 nm ($S_1$ band) (Table 9). Isomer formation competes with the deactivation of

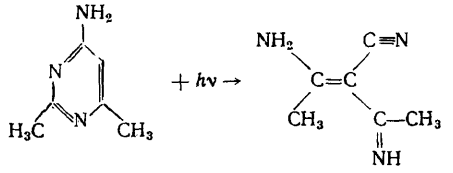
vibrationally excited molecules through collisions. The isomerisation of pyrimidine and pyrazine can be sensitised with mercury[85] but not with benzene, i. e., for photoisomerisation to occur a sufficiently high lying triplet state is required (Table 9).

**Table 9.** Quantum yields for photoisomerisation of diazines.[85]

| Initial compound | Compound formed | $\varphi_1^*$ | $\varphi_2^{**}$ |
|---|---|---|---|
| Pyrimidine | Pyrazine | $(1.7\pm0.1)\cdot10^{-3}$ | $(3.8\pm0.4)\cdot10^{-2}$ |
| 4,6-Dimethylpyrimidine | 2,5-Dimethylpyrazine | $(4.6\pm0.4)\cdot10^{-3}$ | $(3.6\pm0.4)\cdot10^{-2}$ |
| 5-Methylpyrimidine | 2-Methylpyrazine | $(7\pm0.7)\cdot10^{-3}$ | $(5.2\pm0.5)\cdot10^{-2}$ |
| Pyrazine | Pyrimidine | $(7\pm0.7)\cdot10^{-3}$ | $(2.8\pm0.2)\cdot10^{-2}$ |
| 2,5-Dimethylpyrazine | 2,5-Dimethylpyrimidine | $(3\pm0.3)\cdot10^{-3}$ | $(1.4\pm0.15)\cdot10^{-2}$ |
| " | 4,6-Dimethylpyrimidine | $(1.5\pm0.15)\cdot10^{-3}$ | $(7\pm0.7)\cdot10^{-3}$ |

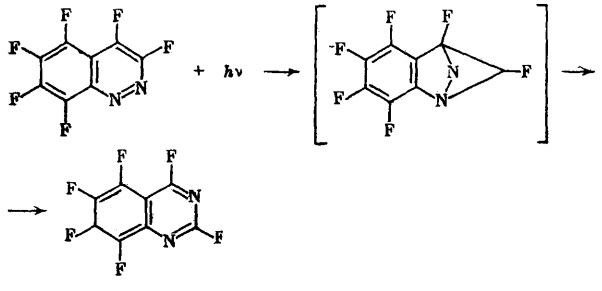
* $\varphi_1$ is the quantum yield for direct photolysis with light of wavelength 254 nm. ** $\varphi_2$ is the quantum yield for photolysis sensitised with mercury.

Perfluoropyridazine and perfluoropyrimidine are stable on irradiation at $\lambda$ = 253.7 nm.[72] Ring-opening of 2,6-dimethyl-4-aminopyrimidine in aqueous alkaline solutions occurs via the formation of a "Dewar" intermediate:



The reaction product is a stable nitrile. Pyridazine undergoes photoisomerisation in the vapour phase to a mixture of pyrimidine and pyrazine, while perfluoropyridazine is converted to perfluoropyrazine, which in turn can isomerise to perfluoropyrimidine.[86] Similar reactions also occur for other fluoropyridazines and perchloropyridazine, which is converted at 77K via its $S(n,\pi^*)$ state.[72,86]

Diazines with condensed benzene rings do not undergo photoisomerisation. The only known exception to this is perfluorocinnoline, which photoisomerises to perfluoroquinazoline:



It was shown using kinetic EPR spectroscopy that pyrazine, 2,3-pyridipyrazine, and 9,10-diazaphenanthrene can remove a hydrogen atom from isopropanol when they are in the $T_1(n,\pi^*)$ state, while quinoxaline, phthalazine, phenazine, and acridine can remove an H atom when they are in the $T(\pi,\pi^*)$ state.[78]

## 5. Diazines with anomalous photochemical properties

As a result of the vibrational interaction between the closely situated $S_1(n,\pi^*)$ and $S_2(\pi,\pi^*)$ levels in azines and diazines, efficient internal conversion occurs as a rule, and these compounds do not fluoresce. When hydrogen bonds are formed, the energy of the $n,\pi^*$ state increases and the quantum yield of fluorescence increases. In the majority of cases the addition of a proton also increases the intensity of fluorescence of *N*-heterocyclic compounds.[87–89]

Compounds containing a pyrazine ring (known as anomalous diazines) stand out from amongst the large number of diazines.[90] The anomalous nature of their behaviour lies in the large increase in their basicity in the $S_1$ and $T_1$ states. Moreover, in contrast to the other mono- and di-azines, the quantum yield of fluorescence and phosphorescence of the mono- and di-cations of anomalous diazines is very low (Table 10).

**Table 10.** Features of the luminescence spectra of diazines.[89–98]

| Compound | $\varphi_n$ | $\varphi_{ISC}$ | Protonation I | | | Protonation II | | | Refs. |
|---|---|---|---|---|---|---|---|---|---|
| | | | $pK_{S_0}$ | $pK_{S_1}$ | $pK_{T_1}$ | $pK_{S_0}$ | $pK_{S_1}$ | $pK_{T_1}$ | |
| Pyrazine | 0.0013 | 1.0 | 1.0 | — | 11.5 | −6.6 | — | 11.1 | [39] |
| " | 0.00009 | 0.13 | — | — | — | — | — | — | [89] |
| " | 0.0004 | 0.33 | — | — | — | — | — | — | [98] |
| Pyrimidine | 0.0029 | 1.0 | — | — | — | — | — | — | [39] |
| " | 0.015 | 0.08 | — | — | — | — | — | — | [91] |
| " | — | 0.12 | — | — | — | — | — | — | [95] |
| Pyridazine | 0.0002 | 0.24 | 2.29 | — | — | −7.78 | — | — | [94] |
| " | — | 1.0 | — | — | — | — | — | — | [98] |
| " | — | 0.20 | — | — | — | — | — | — | [91] |
| Quinoxaline | 0.003 | 0.99 | 0.6 | 4.9 | 5.0 | −5.5 | 2.2 | — | [92] |
| " | — | 0.27 | — | — | — | — | — | — | [96] |
| " | — | 0.18 | — | — | — | — | — | — | [97] |
| Quinazoline | 0.0004 | 0.70 | — | — | — | — | — | — | [96] |
| Phthalzine | — | 0.48 | — | — | — | — | — | — | [94] |
| " | — | 0.43 | — | — | — | — | — | — | [96] |
| " | — | 0.95 | — | — | — | — | — | — | [97] |
| Phenazine | 0.006 | 0.76 | 1.21 | 6.0 | 4.0 | −4.3 | 4.1 | 5.7 | [52] |
| 1,4-Diazapahenanthrene | — | — | 0.9 | — | 6.4 | — | — | — | [92] |
| Benzophenazine | 0.0008 | — | 1.05 | 1.5 | 4.5 | — | — | — | [93] |
| " | 0.02 | — | — | — | — | — | — | — | [93] |
| 1,4-Diazatriphenylene | — | — | — | −0.4 | 6.3 | — | — | — | [93] |

Thus, for example, pyrazine itself is protonated in frozen solutions of $H_2SO_4$, and phosphorescence of its neutral (A) and mono- and di-protonated forms ($AH^+$ and $AH_2^{2+}$ respectively) occurs with maxima at 26 700, 21 600, and 24 100 $cm^{-1}$. In the opinion of Shinada[88] and Grabowska and Pakula,[89] while in free pyrazine phosphorescence occurs from the $T_1(n,\pi^*)$ state, in $AH^+$ and $AH_2^{2+}$ it takes place from the $T_1(\pi,\pi^*)(^3L_b)$ state. The electron density on the nitrogen atom of pyrazine increases with $\pi,\pi^*$-excitation and decreases with $n,\pi^*$-excitation (compared to the ground state). Thus, pyrazine, which is an extremely weak base in the ground state, increases its basicity in the $T_1$ state.[89]

In the opinion of Grabowska and Pakula,[89] all of the anomalies of pyrazine derivatives are related to the fact that the pyrazine ring in an excited state adopts a bent conformation, and the hybridisation of the N atom changes from $sp^2$ to $sp^3$. The basicity of 1,2-benz-

phenazine, like an anomalous diazine, increases substantially on excitation. Relaxation of the excited state of the 1,2-benzphenazine monocation results in the occurrence of this type of bent structure, in which the $S(\pi,\pi^*)$ state is very effectively mixed with the $S(n,\pi^*)$ and $S(\sigma,\pi^*)$ states (much more effectively than in a planar molecule). On excitation the cation of 1,2-benzphenazine is folded like a butterfly about the N—N axis, with quantum calculations showing that protonation occurs on the N(10) atom.[99] This bent structure containing two $sp^3$-hybridised N atoms is only formed by a pyrazine ring and not by a pyrimidine ring (this follows from an examination of molecular models[90]). On excitation there is a substantial increase in electron density in the pyrazine ring. In the $S_1$ state of doubly protonated 1,2-benzphenazine it is as if an additional electron has appeared, and in the case of 1,4-diazatriphenylene as if there is an increase of 1,4 electrons,[92] which results in an increase in basicity (Table 10).

A consequence of this increase in basicity is the fluorescence quenching of benzphenazine by a proton at the almost diffusion-controlled rate of $3 \times 10^9$ litres mol$^{-1}$ s$^{-1}$ to form a non-fluorescing dication.[100] An extremely rare phenonenon characterises the benzphenazine monocation—a dependence of the emissive deactivation constant of the $S_1$ state on temperature. This also reflects the change in geometry of the molecule on excitation.[100]

In other diazines that do not contain a pyrazine ring (5,12-diazatriphenylene, 1,7-diazaphenanthrene) and in all monoazines there is no such increase in electron density on excitation.

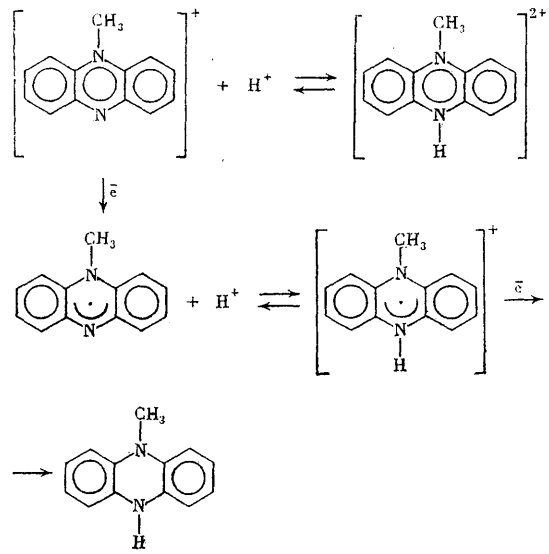
For the other (non anomalous) bicyclic diazines an absence of fluorescence from the free molecules ($\varphi_f \approx 10^{-3}$) is typical (Table 10), namely, in all these molecules only internal conversion competes with intersystem crossing. It was demonstrated using the method of optically detected magnetic resonance that for quinoxaline the lowest state is $T_1(\pi,\pi^*)$ and the intersystem degradation $T_1(\pi,\pi^*) \rightsquigarrow S_0$ occurs as a result of a strong vibrational interaction with the ground state involving the $z$-orbital component of spin-orbit coupling.[54] In contrast to all the remaining bicyclic diazines, the lowest triplet state of phthalazine is a mixed $T(n,\pi^*)-T(\pi,\pi^*)$ state and not a pure $\pi,\pi^*$ state.[101,102]

Phthalazine is reduced in isopropanol to form 1,2-dihydrophthalazine and its dimer 1*H*,1′*H*,2*H*,2′*H*-1,1-diphthalazine.[103] Photoreduction occurs through the removal of an H atom from isopropanol by phthalazine in the $S_1$ state to form 1,2-dihydrophthalazine with a quantum yield of 0.013. At the same time phthalazine undergoes dimerisation in the $T_2$ state with a quantum yield of 0.040. The photoalkylation of phthalazine occurs in alcohols on treatment with acids.[103]

## 6. Phenazine

During photolysis in the absence of oxygen, phenazine (in the same way as acridine) undergoes photoreduction to dihydrophenazine. In the presence of oxygen there is complete recovery of the initial phenazine. The quantum yield of the overall reduction of phenazine in toluene is $10^{-3}$ and in tetrahydrofuran the yield is $6 \times 10^{-2}$. A molecular complex between phenazine and dihydrophenazine which is in equilibrium with the initial reactants has been detected.[104] From an analysis of the dependence of the quantum yield of photoreduction on the concentration of tetrahydrofuran it was possible to conclude that the two lowest $T_1(\pi,\pi^*)$ and $T_2(n,\pi^*)$ states of phenazine participate in this process.[104,105] The decrease in quantum yield of photoreduction in the presence of eosin, which is accompanied by a triplet-triplet absorption of phenazine, indicates that photoreduction occurs at least partly via the $T_1(\pi,\pi^*)$ state. This is also confirmed by the sensitisation of photoreduction with diacetyl and the quenching of this process with oxygen. The rate constants for removal of an H atom from tetrahydrofuran by phenazine in the $T_2(n,\pi^*)$ and $T_1(\pi,\pi^*)$ states are equal to $1.5 \times 10^7$ and $4 \times 10^3$ litres mol$^{-1}$ s$^{-1}$ respectively. The quantum yields for photoreduction of phenazine in methanol, ethanol, and isopropanol on exposure to light at 365 nm are 0.023, 0.037 and 0.050 respectively.[104]

It was established by EPR spectroscopy and spectrophotometry that during photoalkylation of phenazine the methylphenazinium cation undergoes photoreduction in isopropanol on irradiation at 405 nm to form the stable methylphenazinyl radical and its radical cation. This radical exhibits a characteristic fluorescence with a maximum at 14 200 cm$^{-1}$ and lifetime of 5.1 ns. In addition, the methylphenazinium cation undergoes dealkylation to free phenazine and the radical cation is later reduced to dihydrophenazine.[106] The ratio of the processes involving dealkylation and reduction to the radical depends on the steric properties of the alcohols (solvents). Dealkylation does not occur in isopropanol, while in methanol and ethanol the efficiency of both processes is comparable. The p$K$ values of alkylated phenazines and their radicals have been determined:[106]



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The presence of an unshared electron pair that does not participate in conjugation in six-membered azines leads to a fundamental difference between the features of the luminescence spectra and photochemistry of azines and those of the aromatic amines examined by us previously.[83] For heterolytic amines photoreduction and cleavage of bonds in the ring are typical. In almost all azines there is a vibrational interaction to a given extent, resulting in a mixing of the closely situated $n,\pi^*$ and $\pi,\pi^*$ states (the proximity effect), which generally increases the probability of radiationless deactivation of the excited states. Therefore the formation of hydrogen bonds and protonation, which assists the destabilisation of the $n,\pi^*$ states and "removes" this type of vibrational interaction, always substantially alter the luminescence properties, leading as a rule to an increase in the quantum yield of fluorescence.

Heterocyclic amines, like aromatic amines have quite a low ionisation potential and participate in photoionisation and photooxidation, but on the other hand they have a set of properties characteristic of aromatic compounds (the capacity for photosubstitution, photoisomerisation, etc.). The ability of the NH bond to undergo dissociation is also common to all classes of amines.

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