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Quantum chemical studies on excited state intermolecular proton transfer of oxazine dyes

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Abstract

The excited state lifetimes of oxazine dyes nile blue and oxazine 720 show a significant solvent dependence. As an aid to the interpretation of the decay in acidic environments the ground electronic states and the first singlet excited states of oxazine monocations and dications have been studied by methods of quantum chemistry. Ab initio calculations carried out on the lower members on this series show a significant increase of the electron densities of the ring nitrogen on excitation. The calculated electron energies also suggest that the second proton attaches to the ring nitrogen in the excited states, in contrast to the ground states where (in the case of oxazine 720) the second proton attaches to the terminal nitrogen.

A kinetic scheme is proposed for the decay process in which in acidic environments the main deactivation path is the reaction of excited state monocations with protons, followed by internal conversion and subsequent deprotonation of the ground state dications. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Oxazine dyes; Quantum chemical calculations; Intermolecular relaxation

1. Introduction

Oxazine dyes (**I** and **II**) are an important group of chromophoric compounds, used as biological stains, as fluorescence standards and as laser dyes in tuneable dye lasers in the range 600–900 nm [1]. These compounds may exist as neutral molecules, monoca-

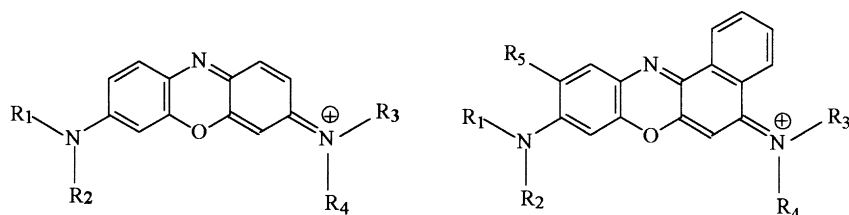
tions, dications or even trications, depending on the environment [2].

In lasers the monocationic forms are found to be particularly efficient laser dyes. The schemes below show one resonant structure for each of the monocationic forms of **I** and **II**, respectively. Among the derivatives listed in the schemes oxazine 118 (**Ia**), cresyl violet (**IIa**), nile blue (**IIb**) and oxazine 720 (oxazine 170) (**IIc**) are the most frequently used laser dyes.

Laser action takes place between the first excited

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**Ia:** R₁-R₄: H**IIa:** R₁-R₅: H**Ib:** R₁-R₂: C₂H₅; R₃-R₄: H**IIb:** R₁-R₂: C₂H₅; R₃-R₅: H**Ic:** R₁, R₃: C₂H₅; R₂, R₄: H**IIc:** R₁, R₃: H; R₂, R₄: C₂H₅; R₅: CH₃

singlet state S₁ and the ground state S₀, the laser efficiency being strongly influenced by the non-radiative intramolecular and intermolecular decay of the S₁ state. The longer the excited state lifetime, the better is the laser efficiency to be expected.

In recent papers [3,4] we have studied the dependence of the excited state lifetime of nile blue (**IIb**) and oxazine 720 (**IIc**) on the solvent, on the temperature and on the pH in aqueous solutions. Measurements were performed using the pump-probe method with synchronously pumped picosecond lasers. It was found that the lifetime depended very much on the polarity of the solvent, polar protic solvents in particular enhancing the decay of the excited state.

In aqueous solutions we found that the rate decay constant of the excited state (the reciprocal of the life-

time) was a linear function of the hydrogen ion concentration. The following equations, with their associated *r* correlation coefficients, could be fitted to the experimental data (at room temperature) [4].

$$\text{IIb, } k/10^9 \text{ s}^{-1} = 4.13[\text{H}^+] + 2.67, \quad r = 0.9992$$

$$\text{IIc, } k/10^9 \text{ s}^{-1} = 4.13[\text{H}^+] + 0.50, \quad r = 0.9996$$

It was concluded [3,4] that in acidic solution the intermolecular decay plays an important role in the shortening of the lifetimes. The two equations have the same slopes but different intercepts. The slopes reflect the intermolecular part, the intercepts are characteristic of the intramolecular part of the decay. The intramolecular relaxation is of different mechanism for these compounds, depending on the substituents [5]. In nile blue (**IIb**) the predominant radiationless

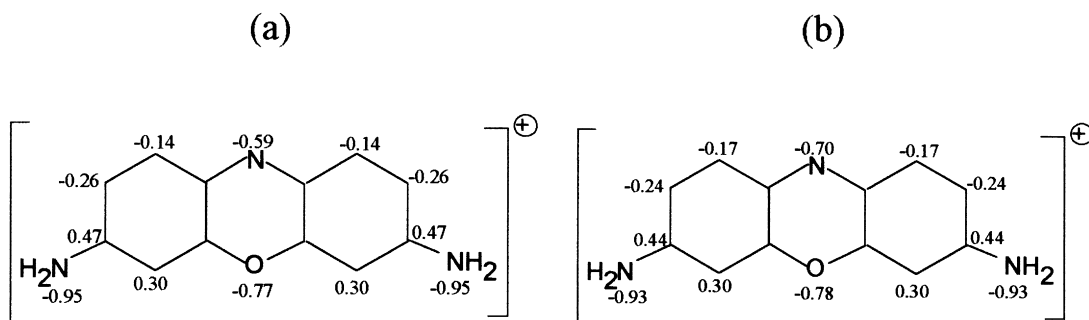


Fig. 1. (a) Ground state and excited state; (b) electron densities of **Ia**.

decay process involves the relaxations via internal rotation of the diethylamino groups, and accordingly a strong temperature dependence was found in the lifetime. In cresyl violet (**IIa**) and oxazine 720 (**IIc**) the excited state lifetimes do not show a significant temperature dependence, suggesting that the internal conversion mainly takes place through N–H vibrations.

The identical slopes of the equations above indicate that the intermolecular relaxation is of similar mechanism for the two compounds. In acidic solutions the predominant decay is the fast reaction of the excited state molecules with the protons, leading to excited state dications and depleting the S_1 state of the monocations.

The aim of the present work was to investigate the intermolecular relaxation of the excited electronic states of oxazines in acidic environments. For this reason we have studied the ground electronic state and the first singlet excited state of oxazine monocations and dications by methods of quantum chemistry. We have not found any ab initio calculations in the literature on these groups of molecules, but MNDO semi-empirical calculations on the monocations have been carried out by Blanchard [6]. The MNDO calculations show a significant increase of valence electron density of the heterocyclic nitrogen on excitation for both **I** and **II**. From the quantum chemist's point of view these molecules are quite large, so that we have selected oxazines **Ia–c** for the ab initio calculations, in the hope that the results can be used qualitatively for **IIa–c**.

2. Calculations

Ground state geometries of compounds **I–II** have been optimised within the framework of MNDO formalism [7]. This method is proved to give good results for molecular structure [8]. All internal coordinates have been taken into account in the optimisation of the geometry. For the smaller molecules (**Ia–c**) the spectroscopic properties (transition energies and oscillator strengths), dipole moments and the electron density distribution (both in the ground and excited states) have been calculated by the CIS method using a 3/21G* basis set. Obviously, using small basis with the CIS method no precise excitation energies can be

expected but the data calculated for similar molecules are comparable. The calculations were performed with the GAUSSIAN 94 [9] program package.

3. Results and discussion

The calculated ab initio electron densities on the atoms (except on the hydrogen atoms) of **Ia** in the ground state and in its first excited singlet state are shown in Fig. 1. It can be seen that the only significant change on excitation is the increase of the negative charge on the ring nitrogen from -0.59 to -0.70 . The same charge densities, -0.59 in the ground states and -0.70 in the excited states are found on the ring nitrogens of **Ib** and **Ic**. MNDO semi-empirical calculations also indicated an increase of the negative charge on the ring nitrogen for both **Ia** and **IIa–c** [6].

In acidic environment the cations **Ia–c** and **IIa–c** can take up a second proton in an equilibrium reaction. This kind of behaviour of **IIc** was extensively studied by Gvishi and coworkers [2,10,11]. They established from NMR measurements that in the ground state of **IIc** the second proton attaches to the terminal nitrogen rather than to the ring nitrogen. They also found an increase of about eight orders of magnitude in the equilibrium constant for the formation of the dication on excitation.

The change in charge densities and in the equilibrium constant on excitation suggest that in the excited state the second proton is more likely to attach to the ring nitrogen rather than to the terminal nitrogen. The calculated energies of the dications with three different positions of the second proton both in the ground state and in the excited state are shown in Table 1. For **Ia** and **Ic** these calculations show that the most stable form in the ground state is that in which the second proton attaches to the terminal nitrogen. In **Ib** the calculations show that the dication with the second proton attached to the ring nitrogen is likely to be the most stable form. In the first excited state of all three molecules the forms with the second proton attached to the ring nitrogen are found to be the most stable. In all cases the least favoured configuration is when the second proton attaches to the oxygen. These data support the assumption that a fast reaction may take place between the excited state monocations and the proton

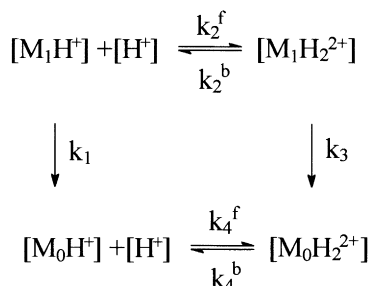
Table 1

Ground state and S₁ excited state electron energies (in atomic units) of **1a–c** with the second proton on the terminal nitrogen, ring nitrogen and oxygen, respectively

Second proton	1a		1b		1c	
	Ground state	excited state	Ground state	excited state	Ground state	excited state
Terminal nitrogen	–694,580	–694,426	–849,761	–849,626	–849,870	–849,721
Ring nitrogen	–694,573	–694,469	–849,820	–849,722	–849,851	–849,752
Oxygen	–694,477	–694,358	–849,767	–849,653	–849,714	–849,607

in an acidic environment, and it is most probable that the second proton attaches to the ring nitrogen.

When a pulse of photons of suitable wavelength is incident on an aqueous solution of the oxazine dyes in monocationic form, absorption of photons by the ground state chromophore leads to the creation of a non-equilibrium distribution of excited state species. The following reaction scheme is proposed for the subsequent decay of the excited state monocations after picosecond excitation in protic environments.



Here M_0H^+ and M_1H^+ denote the ground state and excited state monocations, respectively. $M_0H_2^{2+}$ and $M_1H_2^{2+}$ are for the ground state and excited state dications. k_2^f and k_4^f are second order, the rest are first-order rate constants. k_1 is the sum of the radiative and radiationless decay constants of the excited state monocations, k_3 being the corresponding term for the dications.

The time dependence for the decay of the concentration of the excited state monocations is given by the differential equation

$$\begin{aligned}
 \frac{d[M_1H^+]}{dt} = & -k_1[M_1H^+] - k_2^f[M_1H^+][H^+] \\
 & + k_2^b[M_1H_2^{2+}].
 \end{aligned} \quad (1)$$

The time dependence of the concentration of the excited state dications is

$$\begin{aligned}
 \frac{d[M_1H_2^{2+}]}{dt} = & k_2^f[M_1H^+][H^+] - k_2^b[M_1H_2^{2+}] \\
 & - k_3[M_1H_2^{2+}].
 \end{aligned} \quad (2)$$

It is assumed in this treatment that the rate of decay of $M_1H_2^{2+}$ is fast compared with its rate of formation, so that $d[M_1H_2^{2+}]/dt = 0$, yielding

$$[M_1H_2^{2+}] = \frac{k_2^f[M_1H^+][H^+]}{k_2^b + k_3}. \quad (3)$$

Substituting Eq. (3) into Eq. (1) we obtain

$$\frac{d[M_1H^+]}{[M_1H^+]} = -\left(k_1 + \frac{k_2^f k_3}{k_2^b + k_3} [H^+]\right) dt. \quad (4)$$

Hence in a solution of constant hydrogen ion concentration, this model predicts that the concentration of excited state monocations should change exponentially with time from its initially created concentration $[M_1H^+]_0$ according to:

$$[M_1H^+] = [M_1H^+]_0 e^{-kt}, \quad (5)$$

where

$$k = k_1 + \frac{k_2^f k_3}{k_2^b + k_3} [H^+]. \quad (6)$$

Since the pump-probe method monitors the decay of the excited state concentrations $[M_1H^+]$, it is possible to check the validity of this model. Certainly the form of the variation of k with hydrogen ion concentrations measured experimentally mirrors precisely the type of decay predicted from the model described above. Unfortunately, the available experimental data are insufficient for the determination of all the rate

constants in Eq. (6) separately. Further simplification is possible if k_2^b and k_3 are of different order of magnitude. If $k_2^b \ll k_3$, the former can be neglected in the denominator, and the slope equals k_2^f . On the other hand if $k_3 \ll k_2^b$, k_3 can be neglected in the denominator. The equilibrium constants for the protonation of **IIc**, determined by Gvishi and co-workers (in methanol solution) [2] suggest that the first assumption is valid in our case. From their data $k_2^f[\text{H}^+] \gg k_2^b$ since the equilibrium constant of the protonation reaction is strongly shifted towards the dications in the excited state. In our picosecond decay measurements we never experienced the accumulation of excited state dications, so according to Eq. (3) k_3 must be much greater than k_2^b .

4. Conclusions

From the picosecond decay measurements carried out previously on **IIb** and **IIc** [3,4] and from the quantum chemical calculations of this study we can conclude that in acidic environments the intermolecular deactivation of the excited states of these molecules is the reaction of the excited state monocations with the protons, followed by the fast internal conversion and subsequent deprotonation of the ground state dications. In hydrogen ion concentrations up to 1 mol dm^{-3} the first step is rate limiting, with a rate constant of $4.13 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. In higher proton concentrations the consecutive processes may become comparable, and the steady state assumption of excited dications may no longer be valid. The calculated charge distributions and electron energies support the assumption that the second proton

attaches to the ring nitrogens of the excited state monocations.

Acknowledgements

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