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ORIGINAL PAPER

Excited State Intramolecular Proton Transfer in O-Tosylaminobenzaldehyde

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Abstract Excited state intramolecular proton transfer (ESIPT) in o-tosylaminobenzaldehyde has been investigated. According to quantum-chemical calculations ESIPT in o-tosylaminobenzaldehyde is barrierless. Product of ESIPT undergoes efficient nonradiative deactivation caused by internal rotation of C(H)OH-group. The solvent orientational relaxation in anionic form of o-tosylaminobenzaldehyde was detected. The mechanism of anionic form fluorescence quenching at the addition of the base in a protic solvent is proposed. It consists in the intermolecular proton transfer from the protonated base to oxygen atom of aldehyde group followed by the internal rotation of C(H)OH-group.

Keywords Fluorescence · Proton transfer · Internal rotation · Relaxation

Introduction

Excited state intramolecular proton transfer (ESIPT) plays an important role in chemical and biological processes [1–4]. The ESIPT systems have six-or five-membered cycles with an intramolecular hydrogen bond between OH (or NH) and C=O (or N≤) groups. The structural and electronic configuration of the excited tautomer (ESIPT product) differs from the original one, and is characterized by an abnormally large Stokes shift of fluorescence. ESIPT systems are used as labels for studying the dynamics of solvation [5] and the dynamics of biochemical processes [6], as active media of photochemical lasers [7,8], ultraviolet stabilizers [9], metal ion sensors [10], data storage and optical switches [11]. They are also used as fluorescent probes to measure membrane potential in cell membranes [12].

At the excitation of aromatic systems with strong hydrogen bond having hydroxy group as a proton donor (OH-acids) ESIPT time is tens of femtoseconds [13–16]. It indicates a barrierless nature of the process. However, for aromatic systems with a weak hydrogen bond N–H···N and N–H···O=C (NH-acids) a barrier for the ESIPT and a corresponding increase in ESIPT time may exist. At the excitation of N-substituted 2-(2-aminophenyl)-4H-3,1-benzoxazin-4-ones ESIPT time depends on the electron-acceptor ability of substituent and ranges from 90 fs to 0.8 ps [17].

Information about the ESIPT mechanism in systems with N–H···O=C hydrogen bond is rather scant [18]. To establish the common regularities of ESIPT in compounds with such hydrogen bond the increase of the number of such systems is required. Derivatives of o-aminobenzaldehyde are promising from this point of view. Preliminary calculations of the ESIPT potential energy surface in o-aminobenzaldehyde have shown that this process is thermodynamically unfavorable. The electron-accepting tosylgroup was introduced into the molecule of o-aminobenzaldehyde to enhance the acidity of aminogroup. In the present paper ESIPT in o-tosylaminobenzaldehyde (**TAL**) and structural relaxation processes of ESIPT product are studied.

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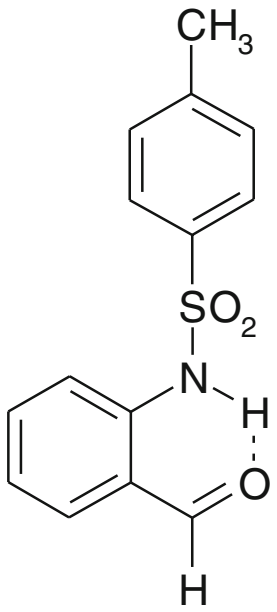
Experimental

Synthesis o-tosylaminobenzaldehyde was described previously [19,20].



TAL (TAL-al)

Methylcyclohexane (MCH), diethyl ether (ether), ethanol, butyronitrile were purified according to procedures [21]. The absorption spectra were recorded on a spectrophotometer "Shimadzu UV-3100", the fluorescence spectra - on spectrofluorimeter Perkin Elmer LS-55 and spectrofluorimeter "Elyumin-2 M", equipped with a cryostat for low temperature measurements. Fluorescence quantum yield was measured by comparing the areas under the corrected fluorescence spectra of studied compound and a solution of quinine bisulfate in 1 N sulfuric acid (φ_f=0.546) [22].

Quantum chemical calculations were carried out by the Firefly v.7.1 software package [23] in the Research Computing Center M. V. Lomonosov Moscow State University ("Chebyshev" supercomputer). For conformational analysis in the ground state the geometry parameters of **TAL** were optimized on Hartree-Fock level with 6–31**++ basis at a fixed value of corresponding torsion angle. The total energy was determined with the same basis using second-order Møller-Plesset perturbation theory (MP2). The geometry parameters of **TAL** in S_1 excited state were optimized with the complete active space self-consistent field (CASSCF) method with 6–31**++ basis at a fixed value of N–H distance (for ESIPT PPE calculation) and corresponding torsion angle (for relaxation PPE calculation). The 8 electrons and 8 orbitals were included in the active space. Averaging over the states S_0, S_1 and S_2 with equal weights was used. The total energy was determined with the same basis with second order extended multi-configuration quasi-degenerate perturbation theory (XMCQDPT2) [24].

Results and Discussion

The absorption spectra of neutral and acidified solution **TAL** are located in the UV region (Table 1). Absorption spectra **TAL** have a small hypsochromic shift with increasing solvent polarity (7 nm by going from MCH to ethanol). This shift is caused by a change in direction of the dipole moment upon excitation due to charge transfer. The solvation shell optimal for the ground state becomes unfavorable for the excited molecule. The temperature has small effect on the position of absorption maximum, but heating an ethanol solution to 60° C leads to the appearance of a weak long-wavelength absorption at 400 nm.

The fluorescence quantum yield of **TAL** solutions at room temperature is low (Table 1). Fluorescence spectra of **TAL** solutions consist of one band with an abnormally large Stokes shift.

The fluorescence quantum yield of ethanol solution is twice as large as one in the butyronitrile. In addition, long-wavelength band with a maximum of 380 nm dominated in the fluorescence excitation spectrum of ethanol solution and is absent in the absorption spectrum at room temperature (Fig. 1).

The weak absorption in this region appears in ethanol by heating. These experimental facts point out that some kind of form **TAL** is present in small quantities in the ground state in ethanol solution. This form is characterized by the absorption maximum 380 nm and rather intensive fluorescence with maximum at 530 nm, with an anomalously large Stokes shift. This form may be an anion **TAL-A**, which is stabilized by the polarity and the H-bond formation ability of ethanol. Disappearance of the long-wavelength band in the fluorescence excitation spectrum (Fig. 1) and the reduction of fluorescence quantum yield by half (Table 1) with the acidification of **TAL** ethanol solution prove the presence of an anion.

To clarify the nature of fluorescence in nonpolar and aprotic solvents, as well as in acidified ethanol it is necessary to

Table 1 The maxima of the absorption $\left(\lambda_a^{max}\right)$ and fluorescence $\left(\lambda_f^{max}\right)$ spectra and fluorescence quantum yield (φ_f) of **TAL** at room temperature

Solvent	λ_a^{max}	λ_f^{max}	φ_f
	nm		%
methylcyclohexane	329	528	0.02
ether	324	528	0.02
butyronitrile	323	525	0.05
butyronitrile with Et_3N	391	501	42.9
ethanol	322	526	0.11
ethanol with H_2SO_4	322	521	0.05
ethanol with Et_3N	373	529	1.9

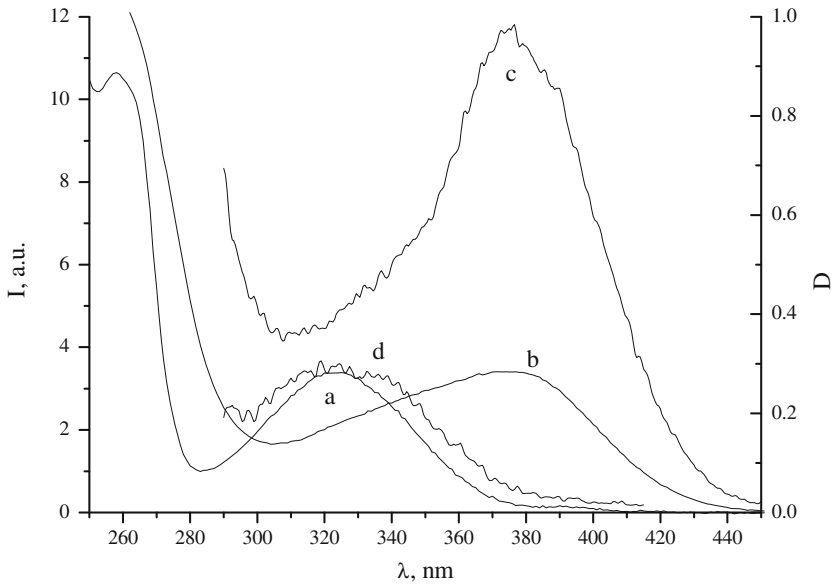


Fig. 1 The absorption spectra of **TAL** in ethanol (**a**), in ethanol with the addition of triethylamine (**b**) and fluorescence excitation spectra in ethanol (**c**) and acidified ethanol solution (**d**)

compare the fluorescence excitation spectra with the absorption spectra of the original form **TAL-al** (Fig. 1). The similarity of these spectra indicates that the only form that absorbs light in this region is **TAL-al**, which is a complex with an intramolecular hydrogen bond. The absence of an open form (without an intramolecular hydrogen bond) is a consequence of large electron-accepting ability of tosyl group. The existence of o-tosylaminobenzaldehyde as a complex with an intramolecular hydrogen bond (**TAL-al**), i.e. configuration necessary for ESIPT, is confirmed by quantum chemical calculations of the potential energy dependence of **TAL** on the torsion angle C_1-C_2-C_3-O_4. Conformational analysis showed the existence of two energy minima corresponding to planar forms with angles 0° and 180° (Fig. 2).

The rotamer with an intramolecular hydrogen bond N–H···N (**TAL-al**) is more favorable energetically.

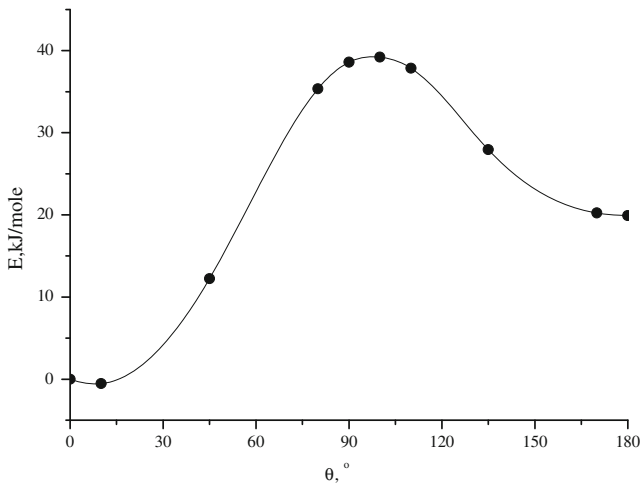
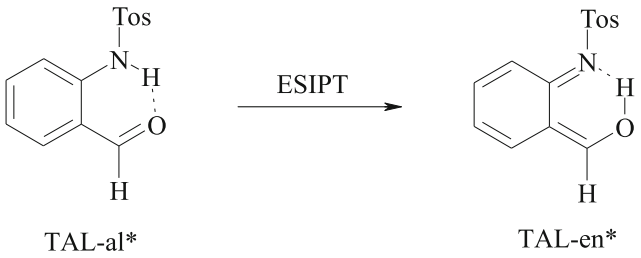


Fig. 2 The dependence of rotamer potential energy on torsion angle (θ) C_1-C_2-C_3-O_4 in the ground state

Abnormally large fluorescence Stokes shift of **TAL** indicates the existence of some process in excited state. The independence of value of this shift on the temperature, viscosity and polarity of the medium, points out that this process is ESIPT and fluorescence is related with the product (**TAL-en**).

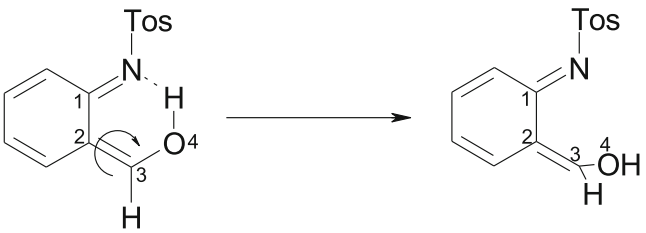


TAL-al* TAL-en*

According to quantum chemical calculations ESIPT in **TAL*** proceeds without the potential barrier (Fig. 3) with 100 % yield.

The low fluorescence quantum yield of tautomer **TAL-en** is the result of the efficient nonradiative deactivation. **TAL-en** fluorescence quantum yield increases with decreasing temperature (Fig. 4, Table 2).

A possible mechanism of deactivation **TAL-en*** is the rotation of C(H)OH-group.



TAL-en* TAL-en-r

This mechanism is confirmed by quantum-chemical conformational analysis of the dependence of the total energy of the molecule on the torsion angle C_1-C_2-C_3-O_4 (Fig. 5).

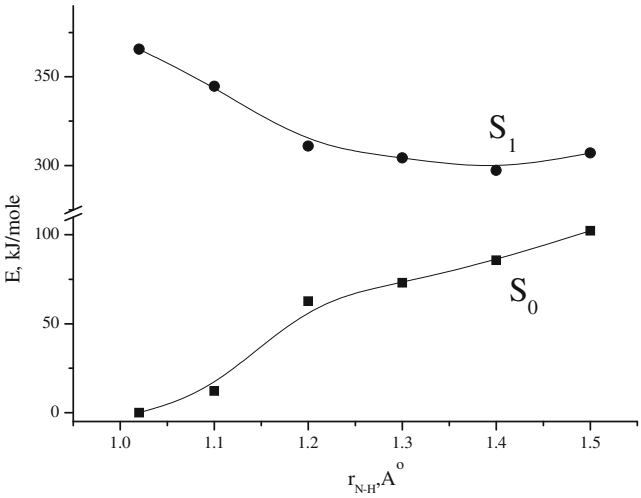


Fig. 3 The dependence of potential energy of **TAL** on N–H distance in the ground and excited states

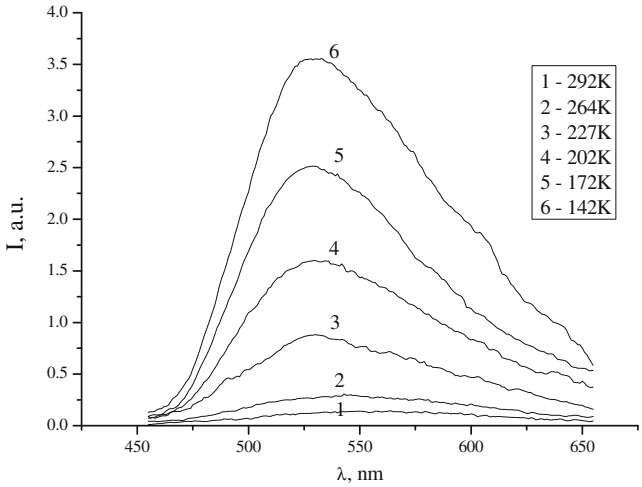
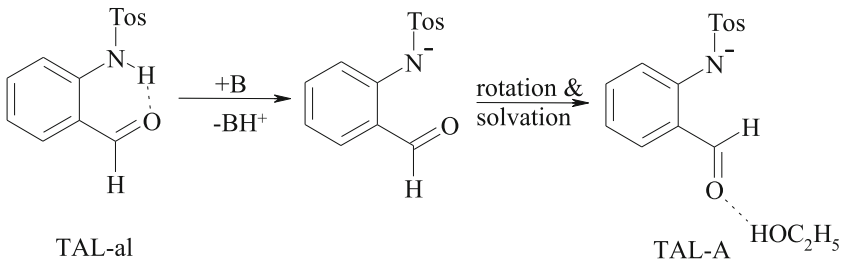


Fig. 4 Fluorescence spectra of **TAL-en** in ethanol at different temperatures

According to this analysis the rotation is barrierless and results in the rotamer in which the relaxed potential energy surface of S_1-state intersects S_0 and T_1. The probability of radiationless deactivation (internal conversion and intersystem crossing) of the excited molecule in this rotamer is high.

As it was noted before, rather high acidity of NH-group in **TAL** results in the formation of the anionic form **TAL-A** in ethanol in the ground state. The addition of organic base triethylamine (**B**) gives rise to intense long-wavelength absorption band of **TAL-A** (maximum 377 nm) (Figs. 1 and 6).

Rotation of the carbonyl fragment and the formation of hydrogen bonds with the solvent stabilize the anionic form.



Excitation of **TAL-A** leads to the fluorescence in the same region as **TAL-en** fluorescence (Fig. 6) with an abnormally large Stokes shift about 150 nm. Fluorescence quantum yield of the anion is higher than the corresponding value for **TAL-en** (Table 1).

At the addition of triethylamine to butyronitrile solution the formation of **TAL-A** occurs to a lesser degree

Table 2 Fluorescence quantum yield of **TAL-en** in ethanol at different temperatures

T, K	φ, %
292	0.05
264	0.12
227	0.31
202	0.58
172	0.86
142	1.26

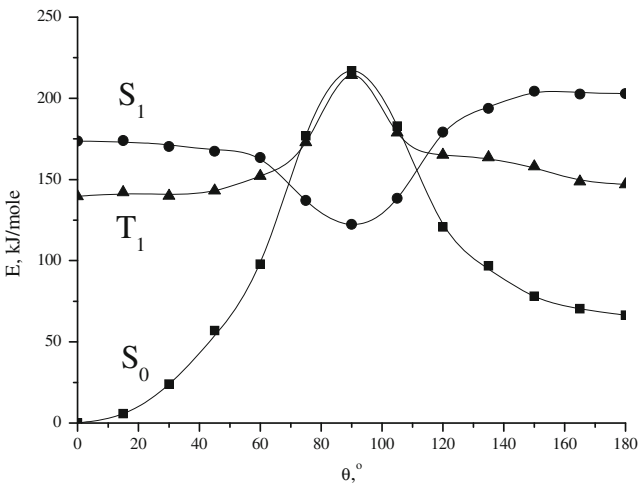


Fig. 5 The dependence of the potential energy of S_0, S_1 and T_1 states of **TAL-en** on the torsion angle C_1-C_2-C_3-O_4 (θ)

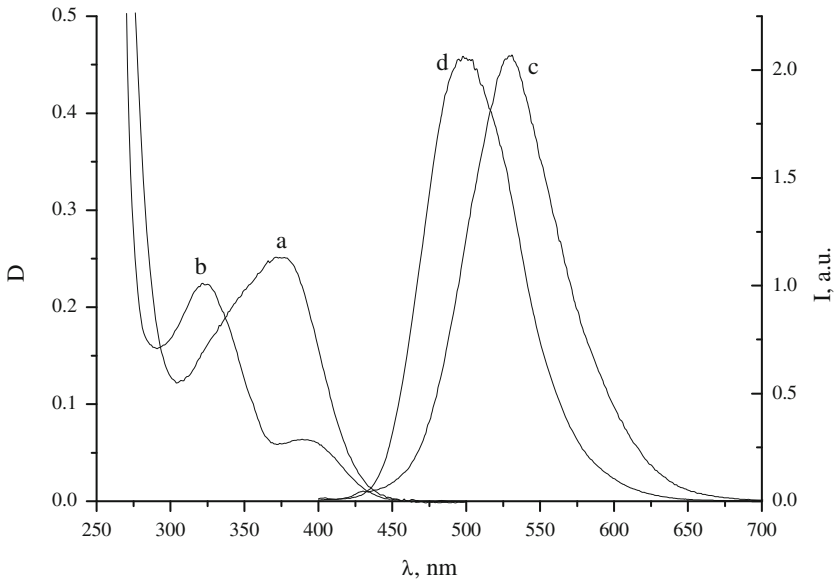


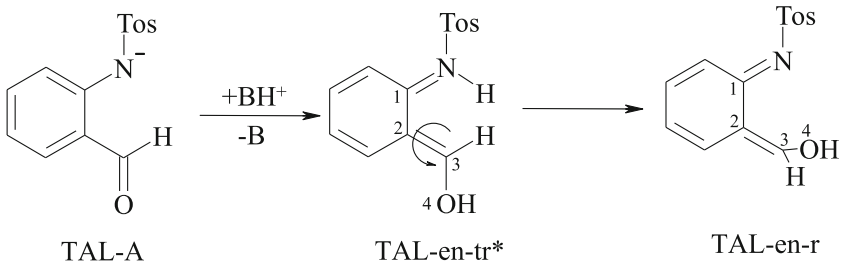
Fig. 6 Absorption (**a**,**b**) and normalized fluorescence spectra (**c**,**d**) of **TAL** in ethanol (**a**,**c**) and butyronitrile (**b**,**d**) in the presence of triethylamine

due to the lack of **TAL-A** stabilization by intermolecular hydrogen bonds. The fluorescence spectrum of **TAL-A** in butyronitrile is shifted to short wavelength region compared with **TAL-A** fluorescence spectrum in ethanol (Fig. 6).

Anomalous large fluorescence Stokes shift of **TAL-A** indicates the existence of some process in the excited state. Solvent orientational relaxation induced by the changes of electrostatic moment of the anion at the excitation can be one of the possible processes. An increase in fluorescence intensity and a gradual shift to short-wavelength region occurs by temperature decreasing (Fig. 7).

The gradual short-wavelength shift of fluorescence spectrum in a polar solvent with an increase in viscosity is typical for systems with solvent orientational relaxation [25]. The smaller Stokes shift of **TAL-A** fluorescence in less polar butyronitrile also indicates the existence of solvent orientational relaxation.

Taking into account significant increase in carbonyl group basicity upon excitation the intermolecular proton transfer from protonated triethylamine (**BH+**) to the carbonyl oxygen of **TAL-A*** across the solvent with the formation of enol trans-tautomer **TAL-en-tr*** can be expected. In this tautomer as well as in **TAL-en*** the rotation of C(H)OH-group results in the twisted conformer (**TAL-en-r**) in which efficient radiationless deactivation is possible (Fig. 5). Such deactivation can be a cause of low fluorescence quantum yield of **TAL-A** in ethanol.



Conclusions

Fluorescence spectra of o-tosylaminobenzaldehyde (**TAL**) solutions consist of one band with an abnormally large Stokes shift and low quantum yield. This band belongs to product of excited state intramolecular proton transfer (ESIPT) from nitrogen atom of aminogroup to oxygen atom of carbonyl group. ESIPT in **TAL** is barrierless and irreversible according to quantum-chemical calculations. The low fluorescence quantum yield of the product ESIPT is caused by the efficient nonradiative deactivation. The rotation of C(H)OH group at 90 º to the plane of the substituted phenyl ring is one of the ways of this deactivation. The probability of internal conversion and intersystem crossing in resulting rotamer is high.

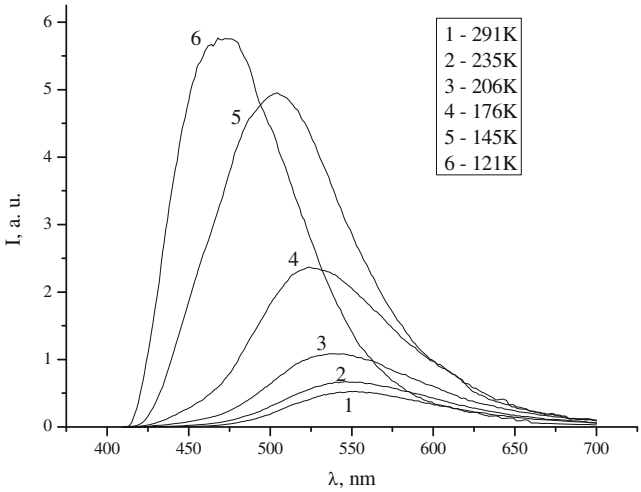


Fig. 7 The fluorescence spectra of **TAL-A** in ethanol at different temperatures

Abnormally large fluorescence Stokes shift of anionic form is reduced to normal value at temperature decreasing (viscosity increasing) and depends on solvent polarity. This Stokes shift of **TAL** anionic form is due to the solvent orientational relaxation induced by the changes of electrostatic moment of the anion at the excitation.

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