2050 *Russian Chemical Bulletin, International Edition, Vol. 51, No. 11, pp. 2050—2054, November, 2002*

Excited-state intramolecular proton transfer in 2,4,5-triarylimidazole molecules

A. I. Shienok, L. S. Kol´tsova, N. L. Zaichenko, and V. S. Marevtsev*

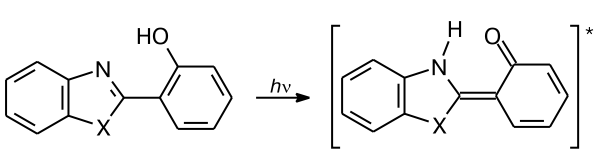
N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,
4 ul. Kosygina, 119991 Moscow, Russian Federation.
Fax: +7 (095) 137 8284. E-mail: marvic@polymer.chph.ras.ru

Excited-state intramolecular proton transfer (ESIPT) in the 2,4,5-triarylimidazole molecules was studied by spectral-luminescent technique. For 4,5-diphenyl-(2-hydroxyphenyl)imidazoles, the ESIPT occurs in both liquid and glassy matrices at 77 K. For 4,5-diphenyl-(2-hydroxynaphthyl)imidazole, the ESIPT requires rotation of molecular fragments and is not observed at 77 K.

Key words: triarylimidazoles, excited states of molecules, intramolecular proton transfer, luminescence.

Recently, excited-state intramolecular proton transfer (ESIPT) in molecules has been the subject of intensive studies owing to practical applications of some compounds as laser dyes,[1,2] photostabilizers,[3,4] and in biology.[5—7] Most of the studies concern three classes of heteroaromatic compounds, namely, 2-(2-hydroxyphenyl)benzothiazoles, 2-(2-hydroxyphenyl)benzoxazoles, and 2-(2-hydroxyphenyl)benzimidazoles and their derivatives. In these molecules, the ESIPT manifests itself as the abnormally large Stokes shift of the fluorescence maximum relative to the absorption spectrum of the initial molecule, which is due to fast (~100 fs) transfer of the hydroxyl proton to the N atom of the heterocycle in the excited state of the initial, enol (**E**), form of the molecule and the formation of excited molecule in the keto form (**K**), which emits luminescence (Scheme 1). After transition of **K** to the ground state the reverse proton transfer occurs and the molecule returns to the enol form **E**.

Scheme 1

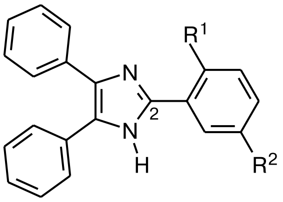


E **K**

X = S, O, NH

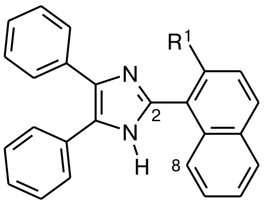
In this work we report the first study of the ESIPT in the molecules of triarylimidazole (TAI) compounds **1—5**.

Interest in these compounds is due to the possibility of varying their spectral-luminescent characteristics over a wide range[8—10] by introducing different substituents into the peripheral aryl rings.



1—3

1: $R^1 = R^2 = H$
2: $R^1 = OH, R^2 = H$
3: $R^1 = OH, R^2 = Br$



4, 5

4: $R^1 = H$
5: $R^1 = OH$

Compounds **1** and **4** contain no hydroxyl groups. They were chosen for comparison, since in this case the ESIPT is impossible.

Experimental

Absorption spectra were recorded on a Specord UV—Vis spectrophotometer. Luminescene measurements were carried out with a Jobin Yvon-3 (France) spectrofluorimeter. This instrument allows recording uncorrected fluorescence spectra; however, the spectral sensitivity of the R 777_01 photomultiplier used in the experiments was virtually constant in the spectral region from 400 to 500 nm. The solvents were EtOH, dioxane, and toluene ("spectroscopic" grade). Spectral studies were carried out at room temperature and at 77 K (for solutions in EtOH). In carrying out the luminescence measurements the optical density at the absorption maximum was at most 0.15, which allowed obtaining undistorted spectra. Semiempirical quantum-chemical calculations of the electron density and optimization of the molecular geometry was performed by the

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 1894—1898, November, 2002.

PM3 method. The syntheses of compounds **1**—**5** were reported earlier.[11—13] Purity of the TAI used was confirmed by the absence of impurity luminescence, by NMR spectra, TLC, and by the melting points, which coincided with the published data.

Results and Discussion

All the compounds synthesized exhibit intense fluorescence in solutions at room temperature and at 77 K. The fluorescence excitation spectra of TAI **1**—**5** in the long-wavelength region virtually match the corresponding absorption spectra, thus proving the fact that the emitters of fluorescence are the molecules under study. The experimental extinction coefficients at the long-wavelength absorption maxima for solutions of compounds **2** and **5** in dioxane are $2.4 \cdot 10^4$ and $1.5 \cdot 10^4$ mol L^{-1} cm^{-1}, respectively. Table 1 lists the spectral characteristics and Figs. 1—4 present the absorption, fluorescence, and fluorescence excitation spectra of compounds **1**—**5**.

A feature of the spectra of hydroxyl-containing TAI **2** and **3** in non-aqueous solvents is abnormally large (compared to the spectrum of **1**) shift of the fluorescence maximum, ν_{fl}, relative to the corresponding long-wavelength maximum, ν_{abs}, in the absorption spectrum or in the fluo-

Table 1. Spectral characteristics of triarylimidazoles **1**—**5** in different solvents

Compound	Solvent	ν_{abs}	ν_{fl}	ΔE
		cm^{-1}		
1	Toluene	31446	26178	5268
	Dioxane	30769	26316	4453
	EtOH*	32051 (30769)	26525 (26810)	5526 (3959)
	Dioxane—water**	33333	25381	7952
2	Toluene	29851	21739	8112
	Dioxane	30303	21978	8325
	EtOH*	30581 (30030)	22831 (22989)	7750 (7041)
	Dioxane—water**	30769	22989	7780
3	Toluene	29240	21505	7735
	Dioxane	29240	21739	7501
	EtOH*	29240 (28902)	22472 (22727)	6768 (6175)
	Dioxane—water**	30488	22371	8117
4	Toluene	29412	24096	5316
	Dioxane	29412	23810	5602
	EtOH*	30303 (29851)	23529 (26316)	6774 (3535)
	Dioxane—water**	31056	23256	7800
5	Toluene	27397	21739	5658
	Dioxane	27778	21739	6039
	EtOH*	28329 (28571)	22831 (26455)	5498 (2116)
	Dioxane—water**	29412	21739	7673

* Listed are the values obtained at T = 300 and 77 K (in parentheses).

** In a 1 : 3 ratio.

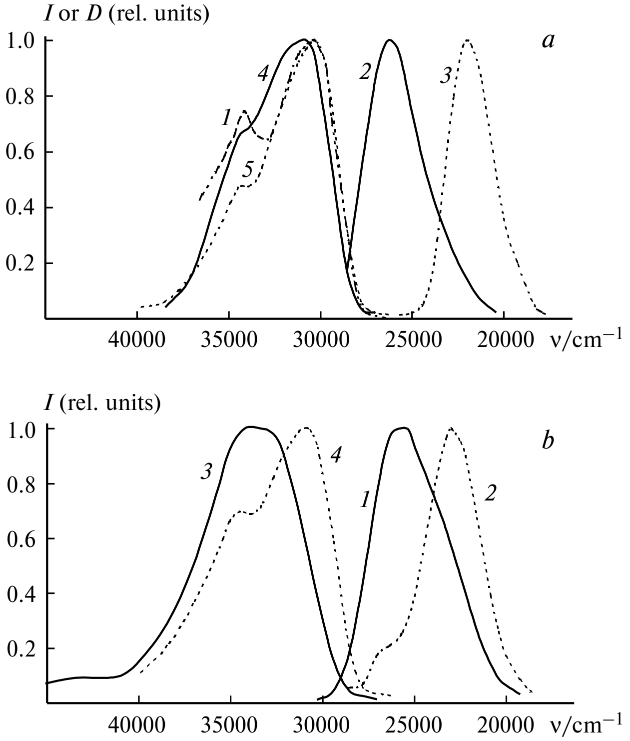
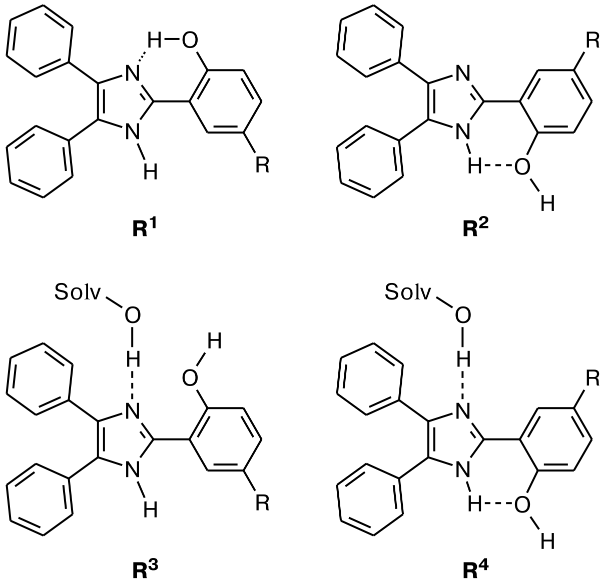


Fig. 1. *a*. Absorption spectra (*1*), fluorescence spectra at ν_{exc} = 33333 (*2*) and 31250 cm^{-1} (*3*), and fluorescence excitation spectra at ν_{lum} = 26316 (*4*) and 21277 cm^{-1} (*5*) of compounds **1** (*2*, *4*) and **2** (*1*, *3*, *5*) in dioxane at 293 K. *b*. Fluorescence spectra at ν_{exc} = 35714 (*1*) and 32258 cm^{-1} (*2*) and fluorescence excitation spectra at ν_{lum} = 25000 (*3*) and 22222 cm^{-1} (*4*) of compounds **1** (*1*, *3*) and **2** (*2*, *4*) in dioxane—water (1 : 3) mixture at 293 K.



Solv — solvent

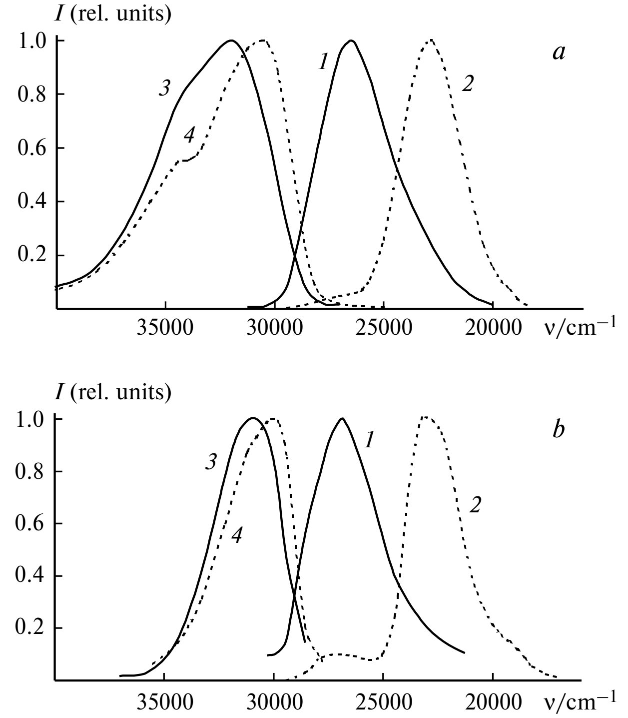


Fig. 2. *a*. Fluorescence spectra at ν_{exc} = 34483 (*1*) and 31250 cm^{-1} (*2*) and fluorescence excitation spectra at ν_{lum} = 25000 (*3*) and 22222 cm^{-1} (*4*) of compounds **1** (*1*, *3*) and **2** (*2*, *4*) in EtOH at 293 K. *b*. Fluorescence spectra at ν_{exc} = 33333 (*1*) and 29412 cm^{-1} (*2*) and fluorescence excitation spectra at ν_{lum} = 26316 (*3*) and 22222 cm^{-1} (*4*) of compounds **1** (*1*, *3*) and **2** (*2*, *4*) in EtOH at 77 K.

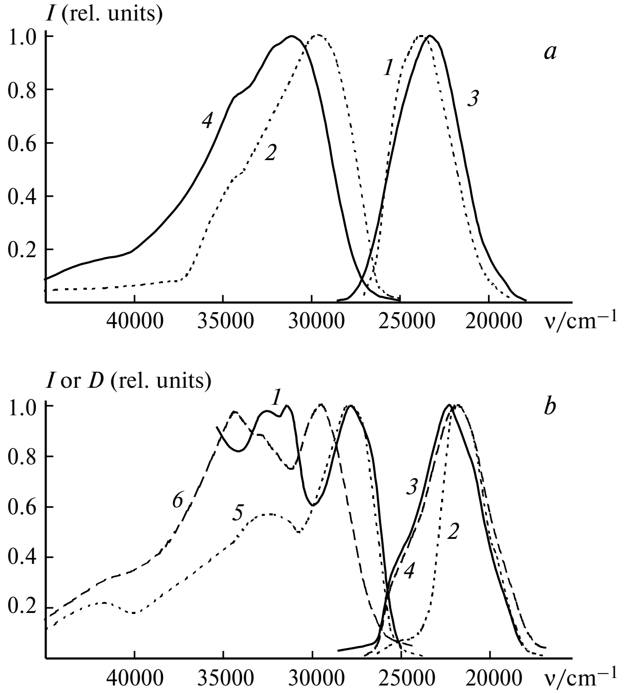


Fig. 3. *a*. Fluorescence spectra at ν_{exc} = 31250 (*1*) and 30303 cm^{-1} (*2*) and fluorescence excitation spectra at ν_{lum} = 23256 (*3*) and 22222 cm^{-1} (*4*) of compound **4** in dioxane (*1*, *3*) and in dioxane—water (1 : 3) mixture (*2*, *4*) at 293 K. *b*. Absorption spectrum (*1*), fluorescence spectra at ν_{exc} = 29412 (*2*), 35715 (*3*), and 28570 cm^{-1} (*4*), and fluorescence excitation spectra at ν_{lum} = 20833 (*5*) and 20833 cm^{-1} (*6*) of compound **5** in dioxane (*1*, *2*, *5*) and in dioxane—water (1 : 3) mixture (*3*, *4*, *6*) at 293 K.

rescence excitation spectrum (ΔE, see Table 1), which proves the occurrence of the ESIPT in these molecules. The fluorescence spectra of compounds **2** and **3** in aprotic solvents exhibit one band. This indicates stabilization of one out of two possible rotamers of the corresponding molecules, namely, $\mathbf{R^1}$, for which the intramolecular hydrogen bond favors the occurrence of the ESIPT.

However, the fluorescence spectra of TAI **2** and **3** in hydroxyl-containing solvents (EtOH, dioxane—water mixture) exhibit a shoulder in the short-wavelength region, which is absent in the fluorescence spectrum of **1** (see Figs. 1, *b* and 2, *b*). This result is consistent with the published data[14,15] for compounds characterized by the ESIPT and can be explained by the formation of an intermolecular hydrogen bond with the solvent, Solv—OH, and by stabilization of not only $\mathbf{R^1}$ but also solvated rotamers $\mathbf{R^3}$ or $\mathbf{R^4}$ (for them the ESIPT is impossible) in the solution.

It should be noted that even for molecule **1** in the dioxane—water mixture the ΔE value is comparable with or larger than the corresponding values for TAI **2** and **3** (see Table 1), though it is obvious that for compound **1** the ESIPT is impossible. The addition of water to dioxane causes a hypsochromic shift of the maxima of the fluorescence excitation spectra for all compounds, which is due to the solvatochromic effect, since the presence of water increases the medium polarity. The shift for TAI **1** (2564 cm^{-1}) is much larger than those for compounds **2** and **3** (466 and 1248 cm^{-1}, respectively). Under the same conditions the maximum of the fluorescence spectrum of compound **1** experiences a bathochromic shift, which can also be rationalized by solvatochromic effect in the framework of the four-level Jablonsky scheme. In contrast to this, a hypsochromic shift of ν_{fl} is observed for TAI **2** and **3**. This behavior is thought to be due to the fact that in the case of compounds **2** and **3** the emitter of fluorescence is the corresponding isomer **E** formed as a result of the ESIPT rather than the excited molecule **K**. Different spectral behavior of ν_{abs} and ν_{fl} in the dioxane—water mixture leads to large ΔE value for molecule **1**.

As the temperature decreases down to 77 K, the fluorescence excitation spectra of compounds **1**—**3** experience a bathochromic shift. Earlier, an analogous behavior of the long-wavelength absorption band was observed for many compounds and explained either by dimerization of the compounds under study upon reduction of temperature[16,17] or by enhancement of conjugation between dif-

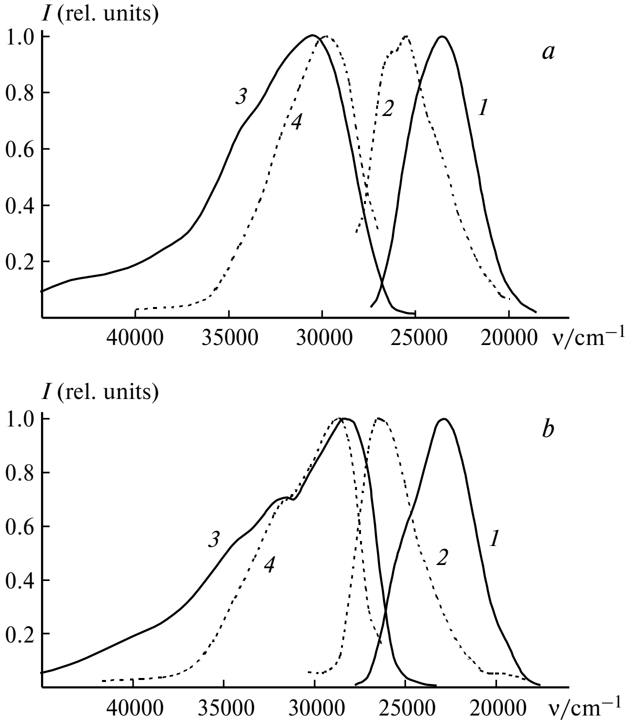


Fig. 4. *a*. Fluorescence spectra at ν_{exc} = 28570 (*1*) and 30303 cm^{-1} (*2*) and fluorescence excitation spectra at ν_{lum} = 22727 (*3*) and 25000 cm^{-1} (*4*) of compound **4** in EtOH at 293 (*1*, *3*) and 77 K (*2*, *4*). *b*. Fluorescence spectra at ν_{exc} = 33333 (*1*) and 32258 cm^{-1} (*2*) and fluorescence excitation spectra at ν_{lum} = 21277 (*3*) and 23810 cm^{-1} (*4*) of compound **5** in EtOH at 293 (*1*, *3*) and 77 K (*2*, *4*).

ferent molecular fragments due to the absence of rotation of these fragments in the rigid glassy matrix at 77 K.[18,19] At this temperature, the Stokes shift, ΔE, substantially decreases; however, for TAI **2** and **3** it remains rather large and much exceeds the corresponding value for compound **1**, thus indicating that the ESIPT also occurs at 77 K.

Figures 3 and 4 present the spectra of the naphtho derivatives **4** and **5**. A salient feature of the molecular structure of these compounds compared to TAI **1—3** is deviation of the aryl substituent in position 2 from the plane of the imidazole ring. Optimization of the molecular geometry of **4** and **5** showed that the dihedral angle between the imidazole and naphthyl ring planes in rotamer $\mathbf{R^1}$ is ~40 and 30°, respectively. Such a specific structure strongly affects the spectral-luminescent properties of the molecules. For instance, the fluorescence spectra of TAI **5** in toluene (see Table 1) and dioxane (see Fig. 3, *b*) already exhibit a short-wavelength shoulder, which points to the existence of at least two equilibrated rotamers ($\mathbf{R^1}$ and $\mathbf{R^2}$) in the medium containing no hydroxyl groups. By analogy with TAI **2** and **3** we believe that the emitter of short-wavelength luminescence is rotamer $\mathbf{R^2}$ for which the ESIPT is impossible. The intramolecular hydrogen bond in the $\mathbf{R^1}$ rotamer of compound **5** seems to be substantially weakened due to the nonplanar structure of the rotamer compared to the TAI **2** and **3**, thus stabilizing the $\mathbf{R^2}$ rotamer. The addition of water to the solution of TAI **5** in dioxane considerably increases the concentration of those rotamers for which the ESIPT is impossible. This manifests itself as an increase in the relative intensity of the short-wavelength shoulder in the luminescence spectrum and as an increase in the intensity of the band at 34480 cm^{-1} in the fluorescence excitation spectrum, which can be assigned to the absorption of the last-mentioned type of rotamers. Excitation into this band causes an insignificant shift of the fluorescence spectrum toward the short-wavelength region (see Fig. 3, *b*), which also proves the existence of several rotamers in the solution. A comparison of the spectra of compounds **4** and **5** (see Fig. 3, *a*,*b*) shows that, as in the case of TAI **1—3**, the fluorescence spectrum of hydroxyl-containing TAI **5** in the dioxane—water mixture experiences a hypsochromic shift, while the spectrum of compound **4** experiences a bathochromic shift. This is an indirect proof of the occurrence of the ESIPT in molecule **5**.

The solution of TAI **5** in EtOH at room temperature also contains a mixture of two rotamers, as was indicated by the short-wavelength shoulder in the fluorescence spectrum (see Fig. 4, *b*). However, a decrease in the solution temperature down to 77 K substantially reduces the ΔE value to 2116 cm^{-1}, which points to the impossibility for the ESIPT to occur at this temperature. The structureless fluorescence spectrum recorded at 77 K (a band of low intensity at 19230 cm^{-1} can be attributed to the phosphorescence of TAI **5**) indicates stabilization of one rotamer under these conditions. According to quantum-chemical calculations of the $\mathbf{R^1}$ and $\mathbf{R^2}$ rotamers of molecule **5**, the ground-state energy of $\mathbf{R^1}$ is ~4 kcal mol^{-1} lower than that of $\mathbf{R^2}$. Hence, one can suggest that it is the $\mathbf{R^1}$ rotamer that is stabilized at 77 K. The absence of the ESIPT for compound **5** in the EtOH glassy matrix cannot be rationalized only by solvation, since in this case the ESIPT could also not be observed in compounds **2** and **3**. One can assume that the ESIPT in molecule **5** can occur only after rotation of the 2-hydroxynaphthyl fragment by some angle until coincidence of its plane and the imidazole ring plane. Naturally, such a rotation in the rigid glassy matrix at 77 K is hindered. Therefore, the need for conformational rearrangement as a prerequisite for the ESIPT fundamentally differs molecule **5** from the molecules of compounds **2** and **3** characterized by the desired arrangement of the imidazole and 2-hydroxyphenyl rings in their ground states.

To gain a deeper insight into the ESIPT mechanism, we carried out quantum-chemical calculations of isolated molecule **2** in the ground state (**E**) and in the first singlet electronic-excited state (**K**) (Table 2). Excitation of the

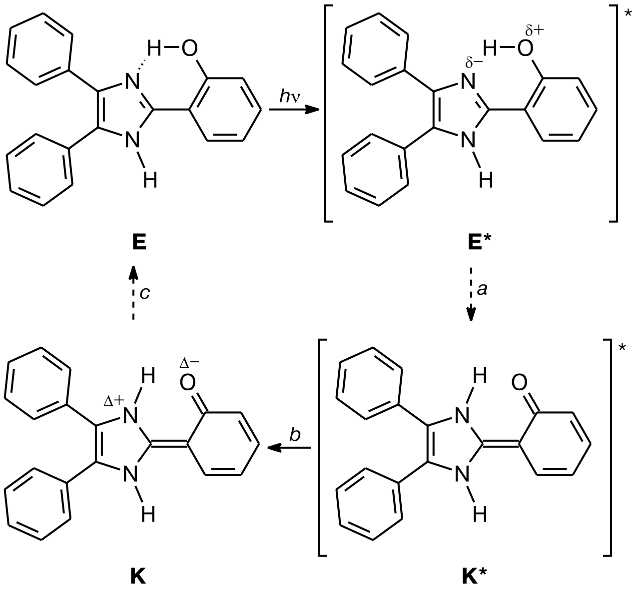
Table 2. Atomic charges (q) of N(3) and O in the enol (**E**) and keto form (**K**) of molecule **2** calculated by the PM3 method

Molecular form	q/a.u.	
	N(3)	O
E	−0.147	−0.264
E*	−0.172	−0.236
K	+0.233	−0.489

molecule in the **E** form causes an increase in the atomic charge of N(3) and a decrease in the atomic charge of O, thus leading to the ESIPT (*a*) and to the formation of **K***. After emission of fluorescence (*b*) the molecule is in the ground state **K** characterized by a large positive atomic charge of N(3) and a negative atomic charge of O. As a consequence, the reverse intramolecular proton transfer (*c*) occurs, thus resulting in the formation of the initial molecule (**E**).

Thus, the processes occurring in molecules **2** and **3** can be described by Scheme 2.

Scheme 2



In the case of TAI **5** this scheme must include an additional stage of rotation of the excited molecule (**E***) until coincidence the imidazole and naphthyl ring planes, which is followed by the ESIPT.

This work was carried out with partial financial support of the Russian Foundation for Basic Research (Project No. 00-03-32095).

References

1. P. T. Chou, M. L. Martinez, and J. H. Clements, *Chem. Phys. Lett.,* 1993, **204**, 395.
2. P. T. Chou, M. L. Martinez, and J. H. Clements, *J. Phys. Chem.*, 1993, **97**, 2618.
3. G. J. Stueber, M. Kieniniger, H. Schettler, W. Busch, B. Goeller, J. Franke, H. E. A. Kramer, H. Hoier, S. Henkel, P. Fischer, H. Port, T. Hirsch, G. Rytz, and J.-L. Birbaum, *J. Phys. Chem.*, 1995, **99**, 10097.
4. J. C. Crawford, *Prog. Polym. Sci.*, 1999, **24**, 7.
5. G. C. Lin, E. S. Awad, and M. A. El-Sayed, *J. Phys. Chem.*, 1991, **95**, 10442.
6. P. J. Rossky and J. D. Simon, *Nature (London)*, 1994, **370**, 263.
7. S. M. Dennison, J. Guharay, and P. K. Sengupta, *Spectrochim. Acta, Part A: Molec. Biomolec. Spectrosc.*, 1999, **55**, 1127.
8. V. S. Marevtsev, A. I. Shienok, and M. I. Cherkashin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 2469 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 2292 (Engl. Transl.)].
9. C. R. Moylan, R. D. Miller, R. J. Twieg, K. M. Betterton, V. Y. Lee, T. J. Matray, and C. Nguyen, *Chem. Mater.*, 1993, **5**, 1499.
10. J. F. Hayes, M. B. Mitchell, and C. Wicks, *Heterocycles*, 1994, **38**, 575.
11. D. Davidson, M. Weiss, and M. Jelling, *J. Org. Chem.,* 1937—1938, **2**, 319.
12. S. Kory and S. Narisava, *Asahi Garasu Kenkyu Hokoku*, 1962, **12**, 55; *Chem. Abstrs*., 1963, **59**, 1621h.
13. Pat. Fr. 1395112, 1965; *Chem. Abstrs.,* 1965, **63**, 1793e.
14. K. Das, N. Sarkar, A. K. Ghosh, D. Majumdar, D. N. Nath, and K. Bhattacharyya, *J. Phys. Chem.,* 1994, **98**, 9126.
15. F. Rodriguez-Prieto, J. C. Penedo, and M. Mosquera, *J. Chem. Soc.*, *Faraday Trans.,* 1998, **94**, 2775.
16. N. W. Tyer and R. S. Becker, *J. Am. Chem. Soc.*, 1970, **92**, 1289.
17. P. Appriou, R. Guglielmetti, A. Botrei, and A. Le Beuze, *J. Photochem.*, 1978, 73.
18. V. G. Luchina, Yu. D. Khamchukov, V. S. Marevtsev, A. T. Gradyushko, A. V. Lyubimov, and M. I. Cherkashin, *Zh. Prikl. Spektrosk.*, 1989, **50**, 398 [*J. Appl. Spectr. USSR*, 1989, **50** (Engl. Transl.)].
19. O. V. Sverdlova, *Elektronnye spectry v organicheskoi khimii* [*Electronic Spectra in Organic Chemistry*], Khimiya, Leningrad, 1985, 248 pp. (in Russian).

Received May 25, 2001;
in revised form May 16, 2002