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Dynamics of intramolecular processes in electronic-excited states of 2,4,5-triarylimidazole molecules

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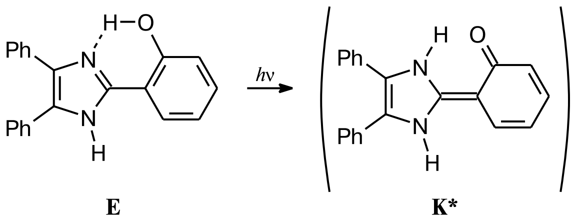
Intramolecular processes in electronic-excited states of 2,4,5-triarylimidazole molecules were studied by femtosecond laser spectroscopy. Experiments were carried out with two types of compounds, namely, those experiencing intramolecular proton transfer and two model compounds in which it is impossible. Schemes of the processes studied were proposed and the characteristic rate constants were determined. The excited-state intramolecular proton transfer (ESIPT) in the molecules with planar structure of the reaction center is a very fast process (≤100 fs). If the reaction center has a nonplanar structure and, hence, the intramolecular hydrogen bond is weakened, the ESIPT time is determined by the time of conformational rearrangement of the molecule.

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

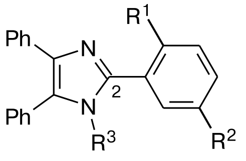
Recently, the phenomenon of excited-state intramolecular proton transfer (ESIPT) has been the subject of intensive studies. This is due to both great importance of this process and the possibility of practical use of compounds experiencing the ESIPT as laser dyes,[1] photostabilizers,[2] three-dimensional optical memory devices,[3] solar energy concentrators,[4] and electroluminescent materials with high photochemical stability.[5] This work is a continuation of our study[6] of the ESIPT in the triarylimidazole (TAI) molecules.

Earlier,[6] we have shown that electronic excitation of a hydroxyl-containing TAI molecule causes redistribution of the electron density in the initial, enol (**E**), form of the molecule, resulting in the ESIPT and in the formation of excited molecule in the keto form (**K***) followed by emission of fluorescence and by return of the molecule to the initial form **E** due to the ground-state intramolecular proton transfer.



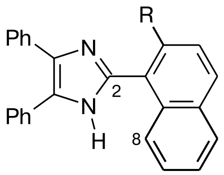
E **K***

Our steady-state study[6] of the spectral-luminescent properties of TAI showed that the ESIPT in 4,5-diphenyl-(2-hydroxyphenyl)imidazoles occurs in both liquid and glassy matrices at 77 K. The absence of the ESIPT in 4,5-diphenyl-(2-hydroxynaphthyl)imidazoles at 77 K was rationalized by the necessity of rotating particular molecular fragments until coincidence of the imidazole and naphthyl ring planes for the ESIPT to occur, which is impossible at this temperature. To confirm this assumption, in this work we studied the femtosecond dynamics of the photoinduced absorption spectra of TAI and determined the rate constants for elementary stages of the process. The following compounds were studied:



1, **2a—c**

	R^1	R^2	R^3
1	H	H	H
2a	OH	H	H
2b	OH	Br	H
2c	OH	H	Bu



3, **4**

R = H (**3**), OH (**4**)

Compounds **1** and **3** contain no hydroxyl groups. They were chosen for comparison, since in this case the ESIPT is impossible.

Experimental

Compounds **1**—**4** were synthesized following known procedures.[7—9] Purity of the TAI used was confirmed by the absence of impurity luminescence, by NMR spectroscopy, TLC, and

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by the melting temperatures which coincided with the published data.

Femtosecond studies were carried out using a setup designed at the Laser Spectroscopy Laboratory, N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences.[10] The second harmonic (λ = 308 nm) was used as a pump pulse. The so-called supercontinuum (SC) was used as a probe pulse. Supercontinuum pulses were generated by focusing the femtosecond pulses on a cuvette filled with distilled water. Supercontinuum was stable over the wavelength range from 380 to 1000 nm except for the 580—630 nm range characterized by higher level of noise due to the properties of the SC (this spectral region was not included in the analysis). The delay time between the probe pulse and the pump pulse could be varied from 0 to 600 ps with an interval of 6.7 fs. Solutions of the compounds in acetonitrile, which exhibits no photoinduced absorption upon excitation by light with λ = 308 nm, were pumped through a quartz cell 1 mm thick. The TAI concentrations were chosen so that the absorption of the pump pulse in the cell was at most 70—80%. The spectra obtained were corrected using a known procedure.[11] The temporal resolution (70±5 fs throughout the spectral range studied) was determined from the kinetic curves measured for the signal of neat dioxane. All the TAI studied exhibited intense fluorescence. A portion of this fluorescence fell on the slit of a spectrometer, thus distorting the spectra. However, the excitation zone area was nearly an order of magnitude larger than the area affected by the probe pulse. Because of this, the integrated fluorescence of the sample was thought to be independent of the delay time. Therefore, the spontaneous emission spectrum recorded at a negative delay time was subtracted from the spectra obtained at all other delay times. All measurements were carried out at room temperature.

Results and Discussion

Preparatory to investigating proton transfer in hydroxyl-containing TAI, we studied the dynamics of photoinduced absorption spectra of compounds **1** and **3** in which no ESIPT occurs. Analysis of the experimental data revealed a common pattern of changes in the spectra of both compounds (Fig. 1). As can be seen, a broad band with a maximum at 480 nm for compound **1** (at 520 nm for **3**) appears during the first 250 fs. Then the spectrum undergoes some transformation to a time delay of 1 ps for **1** (250 fs for **3**) and remains unchanged up to 600 ps. Steady-state absorption spectra[6] of compounds **1**—**3** showed that irradiation with light (λ = 308 nm) causes transitions of molecules to either the S_2 state or the vibrationally excited S_1^v state (exact assignment requires complete interpretation of the absorption spectra, which will be done elsewhere). In any case the photoinduced band at 480 nm for **1** (at 520 nm for **3**) should be assigned to absorption from the first electronic-excited state S_1 of the initial molecule ($S_1 \rightarrow S_n$ transition). The kinetics of the rise of these bands obeys a single-exponent law with a rate constant of $9 \cdot 10^{12}$ s^{-1} for both compounds while the process is an internal conversion and/or vibrational relaxation to the S_1 state ($S_2 \rightsquigarrow S_1$ or $S_1^v \rightsquigarrow S_1$).

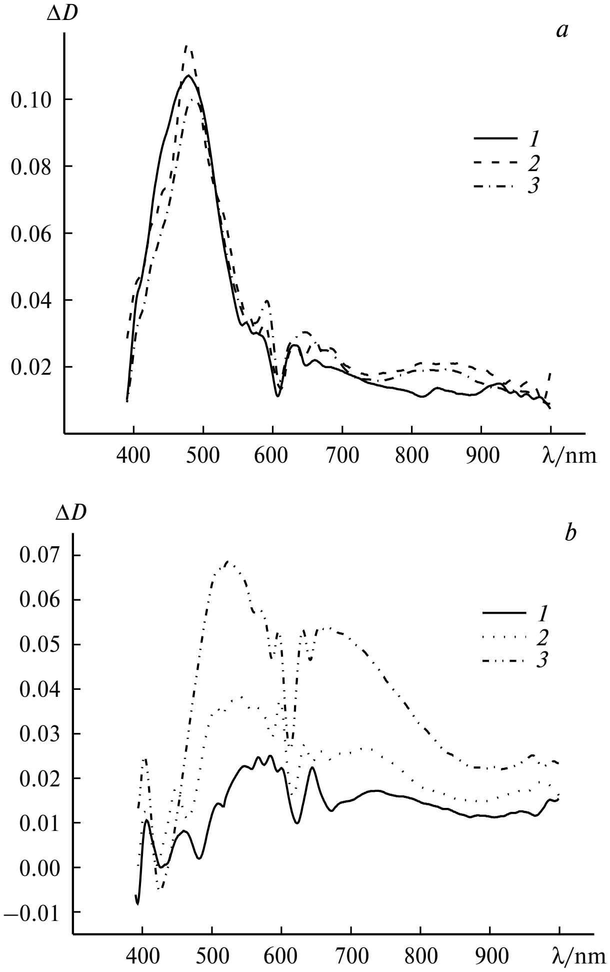


Fig. 1. Dynamics of photoinduced absorption spectra of compounds **1** (*a*) and **3** (*b*) in acetonitrile (photoinduced optical density): *a* — 250 fs (*1*), 1 ps (*2*), 190 ps (*3*); *b* — 0 (*1*), 75 (*2*), 250 fs (*3*).

Introduction of the hydroxyl group into position 2´ of the aryl ring changes the dynamics of photoinduced absorption spectra, which was reasonably associated with the ESIPT in these molecules. It should be noted that the spectral changes for compounds **2a**—**c** follow an identical pattern which is markedly distinct from that observed for **4**.

The dynamics of changes in the spectra of compound **2a** is shown in Fig. 2. As can be seen, the initial period is characterized by simultaneous rise of three bands with maxima at 415, 520, and 895 nm. Then, the long-wavelength bands virtually disappear to 10 ps with a characteristic decay time of 3.2 ps, whereas the intensity of the short-wavelength band remains nearly unchanged (small decrease in the optical density seems to be due to vibrational relaxation). Analysis of the kinetic curves presented in Fig. 3, *a* revealed complete coincidence of the kinetics in the bands at 520 and 895 nm, which allows these bands to be assigned to the same particle. Thus, the photoinduced absorption spectra indicate the existence of at least

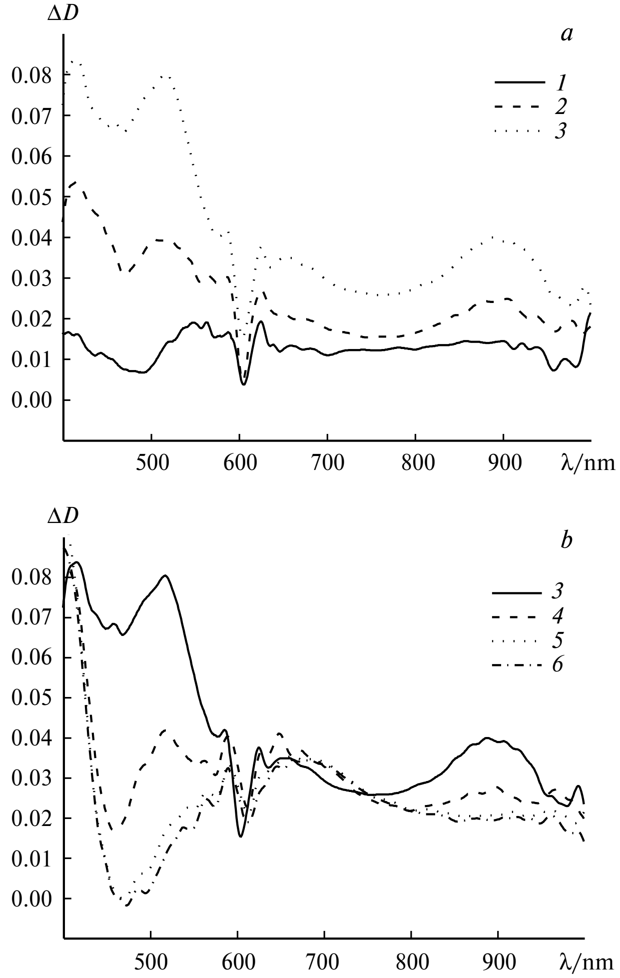


Fig. 2. Dynamics of photoinduced absorption spectra of compound **2a** in acetonitrile at delay times from 0 to 250 fs (*a*) and from 250 fs to 30 ps (*b*): 0 (*1*), 100 (*2*), 250 fs (*3*); 3 (*4*), 10 (*5*), 30 ps (*6*).

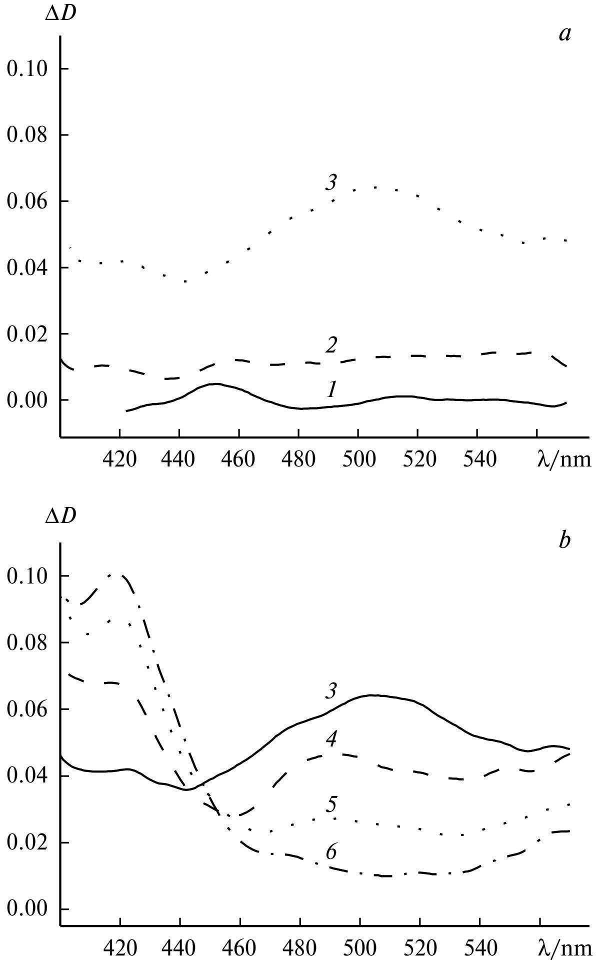
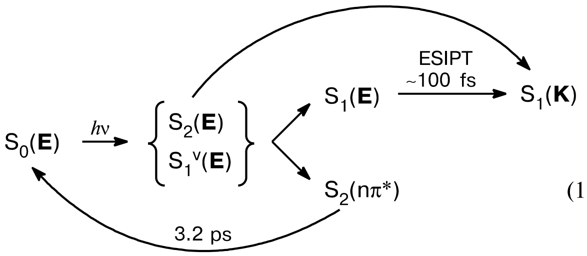


Fig. 3. Dynamics of photoinduced absorption spectra of compound **4** in acetonitrile at different delay times: −200 (*1*), 0 (*2*), 200 (*3*), 400 (*4*), 600 (*5*), 1000 fs (*6*).

two intermediate products. The long-lived (in the femtosecond time scale) species corresponding to the maximum at 415 nm is thought to be the keto form (**K**) of the molecule, produced as a result of the ESIPT and electronic-excited to the S_1 state (hereafter denoted as S_1(**K**)). Then, this species emits fluorescence with a large Stokes shift[6] relative to the absorption maximum of the molecule in the initial form **E** but remains apparently stable in the time range studied since the radiative times of complex organic molecules in solutions are usually of the order of several nanoseconds. Thus, by measuring the kinetics of the rise of absorption in the band at 420 nm one can estimate the ESIPT time (~100 fs for compounds **2a—c**). Naturally, this is an approximation since it is unknown in which state of the molecule **E** does the ESIPT occur (*i.e.*, are the S_2(**E**) and S_1^v(**E**) states involved in the process or the system initially relaxes to the S_1(**E**) state). However, these results are in good agreement with the data obtained for other molecules[12—14] which exhibit the ESIPT and have a planar structure of the reaction center.

We can make some assumptions of the nature of the species corresponding to the spectral maxima at 520 and 895 nm. First, this can not be the **E** form of the molecule in the first electronic-excited state, S_1(**E**), since in this case the molecule should undergo transition to the S_1(**K**) state during 100 fs as a result of the ESIPT. Second, due to ultrafast ESIPT process in the S_1(**E**) state treatment of this species as triplet-excited molecule in the **E** form, produced as a result of the S_1(**E**) $\rightsquigarrow$ T_1(**E**) intersystem crossing, seems to be hardly probable. Third, this can not also be the triplet-excited molecule in the **K** form (T_1(**K**)), since its formation must be accompanied by a decrease in the absorption in the region near 420 nm as a consequence of the S_1(**K**) $\rightsquigarrow$ T_1(**K**) process. The most probable assumption is that the excited **E** form of the molecule is in such a state from which no proton transfer is possible. This can be, *e.g.*, an $n\pi^*$ electronic-excited singlet state. This assumption is substantiated[15—19] by the fact that the (2,2´-bipyridyl)-3,3´-diol (bipy(OH)$_2$) molecule is characterized by close positions of the $S_1(\pi\pi^*)$ energy level, where the ESIPT occurs, and the $S_2(n\pi^*)$ energy level. The latter is populated in a competing manner during vibrational relaxation of higher excited states of the **E*** form, that is, a portion of molecules goes to the $S_1(\pi\pi^*)$ state while another portion of molecules goes to the $S_2(n\pi^*)$ state. Deactivation of the $S_2(n\pi^*)$ state to the ground state, S_0, occurs radiationlessly, the lifetime of the former state being about several picoseconds. Structural similarity of the reaction centers of the bipy(OH)$_2$ and TAI molecules and close lifetimes of the species detected in this work and of the $S_2(n\pi^*)$ state of the bipy(OH)$_2$ molecule suggest that the **E** form of the molecule in the $S_2(n\pi^*)$ state is also produced in the case of compound **2a**. Therefore, the processes occurring after excitation with light at λ = 308 nm can be represented as follows:



(1)

The results obtained in studies of compounds **2b**,**c** confirm the scheme proposed. Some distinctions consist in different positions of the absorption maxima and in the lifetimes of the $S_2(n\pi^*)$ state (Table 1).

A feature of the molecular structure of compounds **3** and **4** is that the imidazole and 2-naphthyl ring planes do not coincide.[6] As shown above, in the case of compound **3** containing no OH group the nonplanar structure of the reaction center causes no significant changes in the dynamics of photoinduced spectra compared to **1**. However, nonplanar molecular structure of compound **4** characterized by a longer distance between the N atom and the H atom of the hydroxyl group and, hence, by weaker hydrogen bond between them compared to the hydrogen bond in molecule **2a** must affect the ESIPT process. As mentioned above, in solutions the ESIPT occurs in compounds **2a—c** and **4**. In a glassy matrix (ethanol) at 77 K the ESIPT occurs only in compounds **2a—c**, whereas compound **4** emits luminescence with a small Stokes shift, which corresponds to the initial form **E**.

Table 1. Results of femtosecond study of solutions of compounds **2a—c** in acetonitrile

TAI	Transition wavelength/nm		Characteristic relaxation time
	$S_2(n\pi^*)\to S_n(\mathbf{E})$	$S_1(\mathbf{K})\to S_n(\mathbf{K})$	$S_2(n\pi^*) \rightsquigarrow S_0(\mathbf{E})$/fs
2a	520, 895	415	3200
2b	500, 930	420	1055
2c	525, 905	~390	1520

It was reasonable to expect that peculiarities of the molecular structure of compound **4** will also affect the dynamics of photoinduced absorption spectra. Indeed, as can be seen in Fig. 4 this compound behaves in essentially different manner compared to **2a**. At times between 0 and 200 fs, a band with a maximum ~510 nm appears. Then, this band disappears and simultaneously a new band with a maximum at 420 nm appears with a characteristic time of 350 fs. The newly appeared band remains unchanged up to a time of 600 ps. The kinetic curves measured at 420 and ~510 nm are shown in Fig. 3. As in the preceding case, the short-wavelength band can be assigned to absorption of a long-lived fluorescent state of the keto form of the molecule, $S_1(\mathbf{K})$. However, in contrast to com-

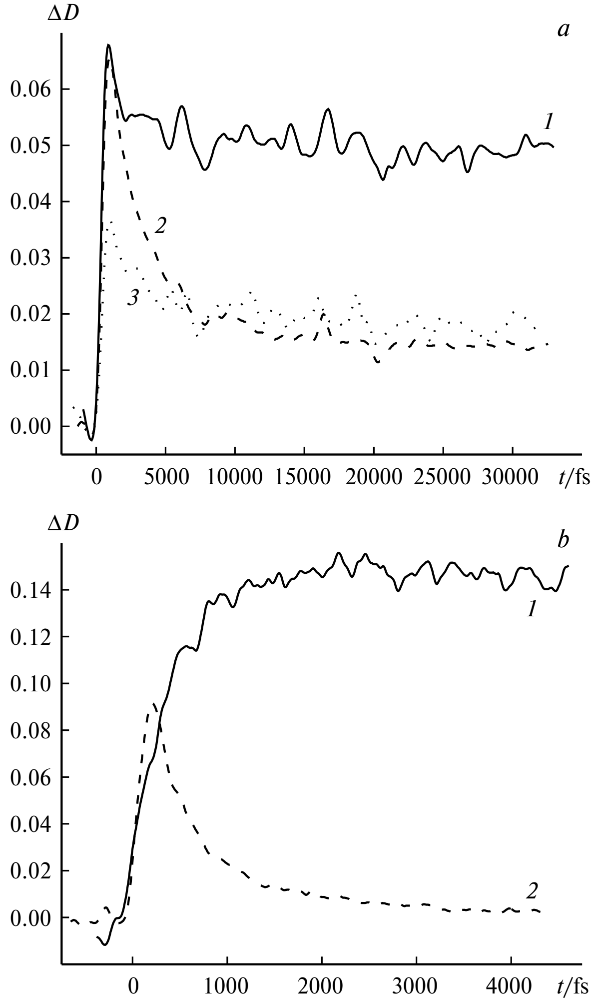


Fig. 4. Curves of changes in the optical density with time at different wavelengths for solutions of compounds **2a** (*a*) and **4** (*b*) in acetonitrile: *a* — 420 (*1*), 530 (*2*), 900 nm (*3*); *b* — 420 (*1*), 510 nm (*2*).

pound **2a**, the S_1(**K**) state is produced synchronously with the decrease in the absorption at 510 nm. This allows one to assign the absorption at 510 nm to S_1(**E**) and to explain the change in the optical density in the band maxima at 420 and 510 nm by the ESIPT process. Thus, proton transfer in molecule **4** occurs at least 3.5 times slower than in molecule **2**. Taking into account the results of the steady-state study,[6] it makes sense to assume that this behavior is associated with the necessity of rotating the 2-hydroxynaphthyl fragment in the excited state of molecule **4** (**E*** form) for the ESIPT to occur. It is the rotation stage that is the limiting state of the process. The presence of this stage extends the measured time of the ESIPT in molecule **4** and is responsible for the absence of this process in the rigid ethanol matrix at 77 K.

Two features should also be pointed out. First, as can be seen in Fig. 3, *b* and Fig. 4, the S_1(**K**) state of molecule **4** is produced only in the $S_1(\mathbf{E}) \to S_1(\mathbf{K})$ process, which implies the absence of the ESIPT from the S_2(**E**) or $S_1{}^v$(**E**) states. This means that the times of internal conversion and vibrational relaxation to the S_1(**E**) state are much shorter than the time of conformational rearrangement of the molecule (350 fs), which is necessary for the ESIPT to occur. Rotation of molecular fragments followed by fast ESIPT (~100 fs) becomes possible only in the relatively long-lived S_1(**E**) state. Second, the results obtained showed that molecule **4** does not undergo transition to the $S_2(n\pi^*)$ state. This is not surprising since annelation of the benzene ring can cause significant changes in positions of the electronic-excited energy levels of molecule **4** compared to **2a**. Then, the processes occurring in molecule **4** after excitation by light with λ = 308 nm can be described by the following scheme:

$$S_0(\mathbf{E}) \xrightarrow{h\nu} \left\{\begin{matrix} S_2(\mathbf{E}) \\ S_1{}^{v}(\mathbf{E}) \end{matrix}\right\} \longrightarrow S_1(\mathbf{E}) \xrightarrow{a} \\ \longrightarrow S_1{}^{r}(\mathbf{E}) \xrightarrow{b} S_1(\mathbf{K}), \qquad (2)$$

a, rotation (350 fs), *b*, ESIPT (~100 fs).

where $S_1{}^r$(**E**) is the molecule in the first electronic-excited state after rotation of the imidazole and 2-hydroxynaphthyl fragments.

The results obtained suggest that the ESIPT time is extremely short (≤100 fs) in compounds with planar structure of the reaction center and is determined by the time of conformational rearrangement of the molecule in compounds with nonplanar structure of the reaction center and, hence, weakened intramolecular hydrogen bond.

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