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Photoinitiated Processes in Molecules of Schiff Bases Having an NH···N Intramolecular Hydrogen Bond*

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Abstract—Study of the absorption and luminescence spectra of Schiff bases derived from *o*-(*p*-tolylsulfonyl-amino)benzaldehyde has shown that these systems, like those derived from salicylaldehyde, are characterized by intramolecular proton transfer in the excited and ground electronic states. This process is responsible for the appearance at 77 K of fluorescence with an anomalous Stokes shift and formation of ketone structures. Unlike *o*-[alkyl(or aryl)iminomethyl]phenols, *o*-[alkyl(or aryl)iminomethyl]anilines do not give rise to acoplanarization of the ketone fragment, which could follow intramolecular proton transfer in the excited state and is responsible for fluorescence with an anomalous Stokes shift and formation of colored structures.

Intramolecular proton transfer (IPT) in excited state (ESIPT) is one of the most common and extensively studied adiabatic processes [1]. Excited state intramolecular proton transfer in structurally nonrigid molecules may be the first step of a series of adiabatic transformations leading to quenching of fluorescence with an anomalous Stokes shift (which is typical of ESIPT) [2–5] and/or formation of metastable colored structures [6, 7] (photochromism). A characteristic phototransformation of the latter type is associated with photochromic properties of Schiff bases derived from substituted anilines and *o*-hydroxybenzalde-hydes. These properties were formerly explained in terms of IPT OH→NH in the excited state [8] and were subsequently studied in a number of works (see, e.g., reviews [9–14]). Only in the recent time photochromic properties of Schiff bases were reasonably related to structural transformations which follow IPT in the excited state [7]. However, an important problem remains unsolved, namely that concerning the effect of intramolecular hydrogen bond, specifically of the nature of proton-donor center, on the feasibility of ESIPT and subsequent structural transformations responsible for fluorescent and photochromic properties of Schiff bases.

Previously, Chernova *et al.* were the only authors who studied [10] a series of compounds having an NH···N intramolecular hydrogen bond and model structures on the basis of *p*-tolylsulfonyl derivatives of Schiff bases. The observed fluorescence with an anomalous Stokes shift was reasonably assigned to IPT in the excited state.

The goal of the present work was to further study the nature of photoinitiated processes in molecules possessing an NH···N intramolecular hydrogen bond. For this purpose, we examined the absorption and luminescence spectra and photochemical properties of some *p*-tolylsulfonyl- and phenylamino derivatives of Schiff bases (compounds **I–VI**) and compared them with those of the corresponding derivatives of salicyl-aldehyde, *o*-(methyliminomethyl)phenol (**VII**) and *o*-(phenyliminomethyl)phenol (**VIII**).

The main parameters characterizing intramolecular hydrogen bond and also electron absorption and

I–VI   **VII, VIII**
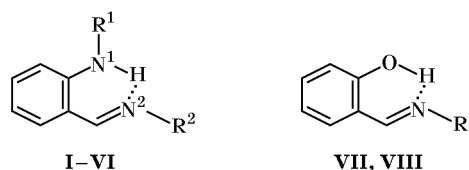
I, R^1 = Ts, R^2 = *iso*-C_3H_7; **II**, R^1 = Ts, R^2 = *tert*-C_4H_9; **III**, R^1 = Ts, R^2 = $(CH_2)_6CH_3$; **IV**, R^1 = Ts, R^2 = Ph; **V**, R^1 = Ts, R^2 = 2,6-(*iso*-C_3H_7)$_2C_6H_3$; **VI**, R^1 = Ph, R^2 = 2,6-(*iso*-C_3H_7)$_2C_6H_3$; **VII**, R^3 = CH_3; **VIII**, R = Ph.

fluorescence spectra of compounds **I**–**III** and **IV**–**VI** [11–13] and *N*-salicylidenealkylamines (which were studied in detail previously), including Schiff bases **VII** and **VIII** [14–16], are generally similar. This suggests similarity in the mechanisms of photo-initiated processes in their molecules; in particular, it seems to be possible to use the results of previously performed quantum-chemical calculations to interpret on a qualitative level the absorption and fluorescence spectra of the compounds under study. Like salicyl-aldehyde derivatives [14], compounds **I**–**III** in non-polar solvents at room temperature exist in the enol form (E) with a strong intramolecular hydrogen bond. This bond weakens to some extent on introduction of bulky alkyl groups to the N^2 atom [11, 12]. The position and intensity of the long-wave absorption band A_E (λ_{max} 315 nm) do not depend on the size of the alkyl radical (Table 1) and are almost similar to the corresponding parameters of compound **VII** (λ_{max} 317 nm). Therefore, we can presume that the electron transition $S_0 \rightarrow S_1$ in **I**–**III**, as well as in **VII** [14], originates from intramolecular charge transfer (ICT) in structure E from the A ring (having a *p*-tolyl-sulfonylamino group) to the C=N moiety. Such ICT reduces the positive charge on N^2 and the dipole moment on excitation, leading [17] to blue shift of the long-wave absorption band in polar solvents (Table 1). As with compound **VII**, in going to polar solvents tautomeric equilibrium is displaced toward more polar ketone structure K, and intramolecular $N^1 \rightarrow N^2$ proton transfer in the ground state (GSIPT) gives rise to long-wave absorption band A_K (λ_{max} 400–410 nm) (Table 1). The N^2-aryl substituent in **IV**–**VI** substantially modifies the nature of the lowest electron transition. It should be kept in mind that, by analogy with **VIII** [14, 15], the modification involves additional ICT from the N–Ar acoplanar fragment to the C=N group. As a result, a red shift and struc-turization of the absorption band of **IV** is observed, presumably due to low-frequency (~1000 cm^{-1}) bending vibrations of the C=N–Ph fragment. The same factor leads to a blue shift and loss of fine structure of the absorption band of compound **V** because of acoplanarization of the C=N–Ar fragment and "freezing" of its bending vibrations, respectively, which are caused by introduction of bulky substituent to the N^2 atom (Table 1).

The above localization of the electron transition ensures a considerable decrease of the dipole moment on $S_0 \rightarrow S_1$ excitation ($\mu_{excit} < \mu_{ground}$), and the absorp-tion band shifts to shorter wavelengths as the solvent polarity increases (Table 1). Sharp reduction of the electron-donor power of the R^1N^1H fragment on

replacement of R^1 = Ts by R^1 = Ph (compound **VI**) weakens the intramolecular hydrogen bond so that the $S_0 \rightarrow S_1$ transition is localized mainly over the N^2–Ar fragment (in contrast to **IV** and **V**). The result is that a strong red shift of the absorption band is observed, the dipole moment does not change on excitation, and the corresponding shift of the absorp-tion band occurs on variation of the solvent polarity (Table 1). Unlike molecules **I**–**III**, significant reduc-tion of electron density on the C=N^2 group induced by delocalization of *n*-electrons on N^2 due to $n_{N^2}–\pi_{Ar}$ conjugation in **IV**–**VI** (as well as in the corresponding derivatives like **VIII** [7, 14]) does not favor GSIPT and formation of structure K even in polar solvents at room temperature. Therefore, the A_K band typical of structure K (λ_{max} 400–415 nm) is not observed in the spectra of compounds **IV**–**VI** (Table 1).

Lowering the temperature to 77 K, both in nonpolar and glassy polar solvents, leads to a sharp shift of the equilibrium of compounds **I**–**III** (in contrast to **IV**–**VI**) toward structure K due to IPT in the ground state, and a strong A_K absorption band appears with λ_{max} 400–415 nm (Table 1). This unusual pattern, which is also observed with *N*-salicylidenealkyl-amines, may be explained by specific spatial inter-actions between nonrigid molecular structures and glassy solvent matrix [14].

Excitation of compounds **I**–**VI** at the long-wave absorption maxima of either tautomeric structure in liquid solution in various solvents at room tempera-ture does not give rise to fluorescence (by analogy to compounds **VII** and **VIII**); however, unlike the latter, efficient photodecomposition of **I**–**VI** occurs. No photodecomposition but fluorescence is observed in glassy solutions of **I**–**VI** at 77 K. Compounds **I**–**III** in both polar and nonpolar solvents give rise to two fluorescence bands excited at the absorption bands of different tautomeric forms (Table 1). Tautomer K is characterized by a strong fluorescence (F_K) in the region λ_{max} 470–480 nm. Excitation of structure E induces F_{ASS} emission with an anomalous Stokes shift ($\Delta\nu > 11\,000$ cm^{-1}). As with *o*-hydroxy Schiff bases, such fluorescence is typical of dipolar structures in the S_1 state which are formed adiabatically as a result of $N^1 \rightarrow N^2$ ESIPT on excitation of tautomer E of compounds **IV** and **V** (Table 1). The situation caused by replacement of proton-donor substituent in the aldehyde ring is unusual for Schiff bases, and it may be interpreted in terms of the lack of ESIPT because of weakening (or rupture) of the $N^1H\cdots N^2$ intramole-cular hydrogen bond in the ground state and/or un-favorable localization of the lowest electron transition (see above).

Table 1. Absorption and fluorescence of Schiff bases **I–VIII**

Compound no.	Solvent	Absorption, λ_{max}(A), nm ($\varepsilon \times 10^{-1}$, 1 mol^{-1} cm^{-1})			
		293 K		77 K	
		structure E (A$_E$)	structure K (A$_K$)	structure E (A$_E$)	structure K (A$_K$)
I	Isopentane	315 (4.4)	–	320	415 (0.14)[a]
	Ethanol	312	410 (0.18)[a]	320	410 (0.26)[a]
II	Isopentane	315 (4.5)	–	312	400 (0.16)[a]
	Ethanol	311	411 (0.17)[a]	320	400 (0.25)[a]
III	Isopentane	315 (4.5)	–	320	410 (0.14)[a]
	Ethanol	311	409 (0.19)[a]	320	410 (0.28)[a]
IV	Isopentane	338 (11.2)[b]	–	340	–
	Ethanol	336 (12.5)[b]	–	340	–
V	Isopentane	332 (7.2)	–	332	–
	Ethanol	322 (7.35)	–	330	–
VI	Isopentane	381 (11.0)	–	380	–
	Ethanol	380 (10.5)	–	380	–
VII	Isopentane	317	–	320	390 (10.0)[a]
	Ethanol	317	390 (2.5)[a]	320	390 (15.0)[a]
VIII	Isopentane	340 (6.25)[b]	–	342[b]	430 (0.01)[a]
	Ethanol	338	–	335	435 (0.05)[a]

Compound no.	Solvent	Fluorescence (77 K)					
		structure E (F$_{ASS}$)			structure K (F$_K$)		
		λ_{max}^{fl}, nm	λ_{max}^{exc}, nm	Stokes shift $\Delta\nu$, cm^{-1}	λ_{max}^{fl}, nm	λ_{max}^{exc}, nm	Stokes shift $\Delta\nu$, cm^{-1}
I	Isopentane	510	320	11 640	475	415	3045
	Ethanol	510	320	11 640	470	400	3725
II	Isopentane	515	320	11 830	480	400	4170
	Ethanol	515	320	11 830	480	400	4170
III	Isopentane	510	320	11 640	480	410	3560
	Ethanol	510	320	11 640	470	410	3110
IV	Isopentane	540	340	10 890	–	–	–
	Ethanol	540	340	10 890	–	–	–
V	Isopentane	525	330	11 255	–	–	–
	Ethanol	520	330	11 070	–	–	–
VI	Isopentane	440	380	3950	–	–	–
VII	Isopentane	500	320	11 250	465[c]	395	3800
VIII	Isopentane	512	340	9880	520	430	4025

[a] In parentheses is given the relative absorption intensity determined as $D(\lambda_{max}^K)/(c_0 \, l)$, where $D(\lambda_{max}^K)$ is the optical density at the absorption maximum of structure K, c_0 is the initial concentration, and l is the cell thickness (1 cm).
[b] Long-wave maximum of the structurized band.
[c] Fluorescence is also observed at 293 K.

Table 2. Melting points, IR spectra, and elemental analyses of Schiff bases **I–VI**[a]

| Comp. no.	mp, °C	Found, %				Formula	Calculated, %				IR spectrum, ν, cm^{-1}	
		C	H	N	S		C	H	N	S	C=N	SO$_2$
I	77–78	64.96	6.47	8.15	10.23	C$_{17}$H$_{20}$N$_2$O$_2$S	64.56	6.37	8.85	10.14	1635	1334, 1154
II	114–115	65.35	6.82	8.60	9.65	C$_{18}$H$_{22}$N$_2$O$_2$S	65.42	6.70	8.47	9.70	1640	1340, 1150
III	68–69	65.86	7.47	7.62	8.70	C$_{21}$H$_{28}$N$_2$O$_2$S	65.75	7.52	7.52	8.60	1630	1345, 1160
IV	107–108	68.41	5.03	8.23	9.12	C$_{20}$H$_{18}$N$_2$O$_2$S	68.55	5.18	7.99	9.15	1621	1342, 1160
V	164–165	71.75	7.00	6.35	7.28	C$_{26}$H$_{30}$N$_2$O$_2$S	71.80	6.91	6.45	7.18	1619	1340, 1160
VI	–	84.25	8.10	7.95	–	C$_{25}$H$_{28}$N$_2$	84.22	7.91	7.85	–	–	–

[a] Compounds **I–III** are yellow, compound **IV** is light yellow, and compounds **V** and **VI** are colorless.

Unlike molecules **VII** and **VIII** and also their derivatives having bulky *tert*-butyl groups [9, 13–16], even prolonged irradiation of glassy solutions of **I–V** does not give rise to reversible (on heating) accumulation of metastable colored species, i.e., compounds **I–V** exhibit no photochromic properties despite IPT in the excited state. Therefore, post-TICT structures K which are responsible for coloration and precursor structures K which are responsible for complete quenching of fluorescence (with an anomalous Stokes shift) of molecules **VII** and **VIII** and their *tert*-butyl derivatives in liquid solution [9, 15, 16] are not formed from compounds **I–V**. Obviously, the reason should be sought for not only in steric interactions, as in *tert*-butyl derivatives of **VII** and **VIII** but also

Scheme 1.

R = Alk, Ar.

in electronic properties of the N–Ts substituent which hampers formation of twisted structures K. Then, complete quenching of anomalous fluorescence of compounds **I–V** in liquid solutions does not result from formation of TICT structures (as with derivatives of **VII** and **VIII**) [7, 14, 18] but is caused by fast concurrent photodecomposition processes in the S$_1$ state, which are also responsible for fluorescence quenching of each tautomer of compounds **I–VI**.

The above data describing photoinitiated processes in molecules **I–V** in glassy solutions at 77 K may be represented by Scheme 1. According to this scheme, processes involving N$^1 \to$ N^2 ground state intramolecular proton transfer occur only for N^2-alkyl derivatives **I–III**. In keeping with the experimental data, the main difference of Scheme 1 from analogous schemes proposed for molecules **VII** and **VIII** [7, 14, 18] is the absence of ESIPT-following twisting of the A ring, which could give rise to formation of TICT and post-TICT structures in the S$_1$ and S$_0$ state, respectively. Here, it should be noted that weakening of intramolecular hydrogen bond and/or change of the localization of the lowest electron transition on variation of the R^1 substituent in the proton-donor R^{1}N^{1}H fragment (e.g., as in **VI**) could make the proposed scheme invalid. Thus Scheme 1 is not general for all molecules of Schiff bases in which N^{1}H$\cdots$N^2 intramolecular hydrogen bond is formed.

To conclude, we must emphasize a specific importance of our comparative results which suggest that photochromic properties of Schiff bases involving intramolecular hydrogen bond are determined by fine mechanisms of ESIPT-following structural transformations. Presumably, such transformations are typical only for Schiff bases derived from *o*-hydroxybenzaldehyde, in which O−H$\cdots$N intramolecular hydrogen bond is formed.
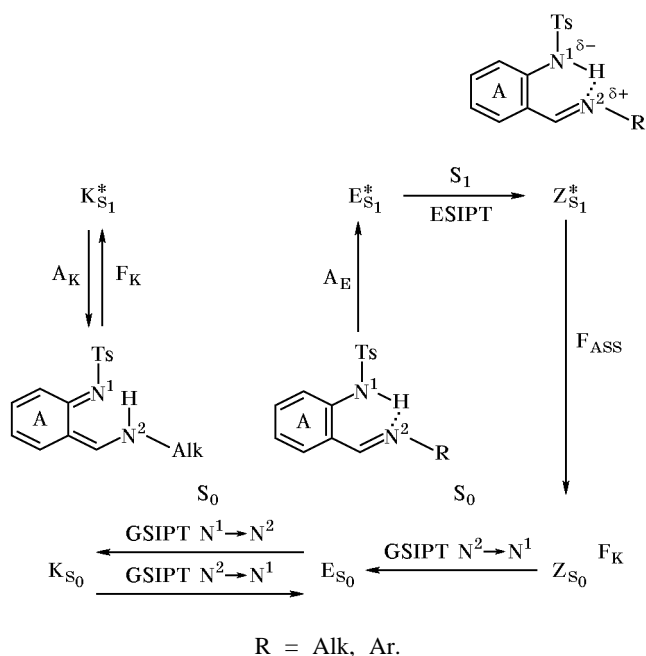
EXPERIMENTAL

The IR spectra were recorded on a Specord 71-IR spectrometer in mineral oil. Elemental analysis was performed at the Microanalysis Laboratory (Reseacrh Institute of Physical and Organic Chemistry, Rostov State University). The electron absorption spectra were measured on Specord M-40 and Varian Cary-100 spectrophotometers. The fluorescence spectra were obtained on Shimadzu RF-5001 PC and Elyumin-2M spectrofluorimeters equipped with an optical cryostat for low-temperature (77 K) measurements. The solvents used for recording absorption and fluorescence spectra were purified by standard procedures and were checked for impurities by luminescence spectra at 293 and 77 K.

Schiff bases **I**–**VI** were synthesized by condensation of 2-(*p*-tolylsulfonylamino)benzaldehyde [19] and the corresponding amine, according to the following procedure: a mixture of equimolar amounts of the aldehyde and amine in dry benzene was refluxed with a Dean–Stark trap until water separated competely (1–5 h) [11]. After cooling, the precipitate was filtered off, recrystallized from methanol, and dried at 70–100°C under reduced pressure. Table 2 contains the melting points, IR spectra, and analytical data of the compounds prepared.

Model compounds, *o*-(methyliminomethyl)phenol (**VII**) and *o*-(phenyliminomethyl)phenol (**VIII**), were synthesized by condensation of equimolar amounts of salicylaldehyde and methylamine or aniline in methanol on heating on a water bath for 1 h under reflux [20]. The properties of the products were consistent with published data.

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