Photoinitiated processes in 1-*p*-tolylsulfonylazo-2,4,6,8-tetrakis(*tert*-butyl)phenoxazine

T. E. Ivakhnenko,[a] ***N. I. Makarova,***[a] ***E. P. Ivakhnenko,***[a]* ***I. I. Chuev,***[b] ***S. M. Aldoshin,***[b]
V. I. Minkin,[a] ***and M. I. Knyazhanskii***[a]

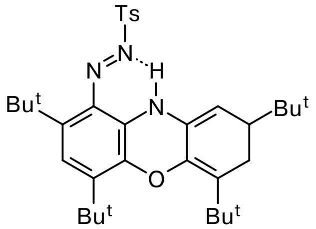
[a]*Scientific Research Institute of Physical and Organic Chemistry,*
Rostov State University,
194/2 prosp. Stachki, 344090 Rostov-on-Don, Russian Federation.
E-mail: Ivah@ipoc.rnd.runnet.ru
[b]*Institute of Problems of Chemical Physics, Russian Academy of Sciences,*
18 Institutskii prosp., 142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588. E-mail: sma@icp.ac.ru

New photochromic compound 1-*p*-tolylsulfonylazo-2,4,6,8-tetrakis(*tert*-butyl)phenoxazine containing the intramolecular hydrogen bond NH...N and the corresponding model structures 2,4,6,8-tetrakis(*tert*-butyl)-1-(veratroylazo)phenoxazine and 2,4,6,8-tetrakis(*tert*-butyl)-*N*-acetyl-1-(*p*-tolylsulfonylazo)phenoxazine were synthesized and studied. The data obtained suggested the mechanism of the photoreaction resulting in the accumulation of betaine 1-hydroxy-2,4,6,8-tetrakis(*tert*-butyl)-10-tolylsulfonylphenoxazin-9-one. The photochromic transformations in the molecule under study are due to intramolecular proton phototransfer followed by *E*—*Z*-isomerization about the N—N bond and the formation of betaine 1-hydroxy-2,4,6,8-tetrakis(*tert*-butyl)-10-tolylsulfonylphenoxazin-9-one. The molecular and crystal structure of the photoproduct was studied by X-ray analysis.

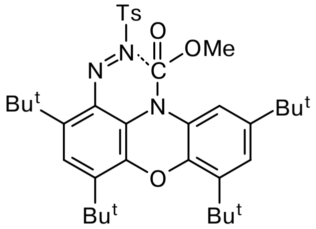
Key words: phenoxazine, structurally flexible systems, intramolecular proton phototransfer, *E*—*Z*-isomerization, molecular structure.

Various structural-nonrigid systems with the intramolecular hydrogen bond (IHB) OH...N, in which adiabatic excited state intramolecular proton transfer (ESIPT) is the primary stage of the processes determining the fluorescence[1] and photochemical (including photochromic)[2] properties, have been studied in detail.[3—6] However, similar processes in compounds with the IHB NH...N were studied much more poorly. Only some early works[7—9] have shown that fluorescence with the anomalous Stokes shift (ASS fluorescence) is due to the ESIPT N(1)H → N(2)H. Possible subsequent processes resulting in the adiabatic transformations of the structure and, the more so, adiabatic reactions involving the formation of metastable colored structures (photochromism) remain almost unstudied.

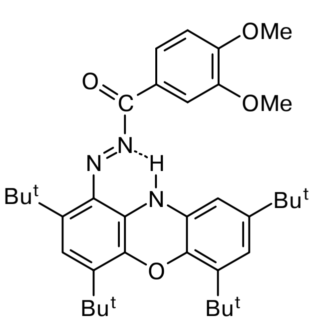
The purpose of this work was to study photoinitiated processes involving ESIPT in the structurally flexible molecular system containing the IHB NH...N (1-*p*-tolylsulfonylazo-2,4,6,8-tetrakis(*tert*-butyl)phenoxazine (**1**$_{azo}$)) and model structures in which ESIPT is excluded (**2**) or substantially modified (**3**).



1(**1**$_{azo}$)



2



3

Experimental

Electron absorption spectra were recorded on a Specord UV—Vis spectrophotometer. Spectral studies were carried out at 77 K in a quartz Dewar flask in a 1-cm cell cooled with liquid

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2014—2020, December, 2000.

1066-5285/00/4912-1981 $25.00

nitrogen. Solutions were irradiated with a DRSh-250 mercury lamp with plug-in glass light filters.

Polymeric films of the samples of compounds under study were prepared from polymethyl methacrylate (PMMC).

IR spectra were recorded on a Specord IR-71 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian VXR-300 spectrometer.

1-*p*-Tolylsulfonylazo-2,4,6,8-tetrakis(*tert*-butyl)phenoxazine (1$_{\text{azo}}$). *p*-Toluenesulfonylhydrazine (0.88 g, 4.6 mmol) was added to a solution of 1*H*-1-oxo-2,4,6,8-tetrakis(*tert*-butyl)phenoxazine[10] (1.67 g, 4.6 mmol) in toluene (25 mL). The mixture was heated to boiling (15—20 min), and the solvent was removed *in vacuo*. The product that formed was washed with cold hexane to remove phenoxazinone residues, and the precipitate was recrystallized from *n*-hexane. A colorless bulky crystalline product was obtained. The yield was 0.69 g (26%), m.p. 153—154 °C. IR of **1**$_{\text{azo}}$, ν/cm^{-1}: 3460. ^{1}H NMR (CDCl$_3$), δ: 1.20, 1.40, 1.80, 2.20 (all s, 1 H each, Bu^t); 2.30 (s, 3 H, Me); 6.92—7.10 (m, 4 H, H arom.); 7.19, 7.25, 7.50 (all s, 1 H each, phenoxazine).

1-Hydroxy-2,4,6,8-tetrakis(*tert*-butyl)-*N*-4-methylphenylsulfonylphenoxazine (1′) was prepared by recrystallization of **1**$_{\text{azo}}$ from methanol. The white crystalline product (**1**$_{\text{azo}}$) was slowly dissolved by prolonged refluxing in methanol to form a blue solution, whose subsequent cooling gave colorless crystals of the product (**1′**) in almost 100% yield. M.p. 195—196 °C (with decomp.).

X-ray structural analysis. Compound **1′** is crystallized in monoclinic system. The main crystallographic parameters: $C_{70}H_{92}N_2O_4S_2$, a = 23.598(5), b = 15.057(3), c = 19.525(4) Å, β = 98.41(3)°, M = 1089.6, V = 6863(2) Å^3, Z = 4, d_{calc} = 1.055(2) g cm^{-3}, space group $P2_1/n$. The array of experimental data for a crystal 0.20×0.5×0.50 mm in size was obtained on a KM-4 four-circle diffractometer (KUMA DIFFRACTION) with Cu-Kα radiation. The number of measured reflections was 12080, and 4179 of them had $I > 2\sigma(I)$ (R_{int} = 0.0311).

The structures were solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation using the SHELX-97 program complex.[11] Hydrogen atoms were determined from the difference Fourier synthesis, and only positional parameters were refined for them. The R factor was equal to 0.0530, ωR = 0.1368, S = 0.899. The main bond lengths and bond angles are presented in Tables 1 and 2. The coordinates of atoms are deposited in the Cambridge Structural Database.

2,4,6,8-Tetrakis(*tert*-butyl)-*N*-acetyl-1-(*p*-toluenesulfonylazo)phenoxazine (2) was prepared by the interaction of a benzene solution of compound **1**$_{\text{azo}}$ with the equivalent amount of acetic anhydride. The mixture was separated on a column packed with silica gel. The yield was 35%, m.p. 148 °C. ^{1}H NMR (CDCl$_3$), δ: 1.18, 1.22, 1.26, 1.30 (all s, 9 H each, Bu^t); 2.3, 2.5 (both s, 3 H each, Me); 6.62—7.31 (m, 4 H, Ph and 3 H, phenoxazine). IR (Nujol), ν/cm^{-1}: 1750 (C=O).

Table 1. Main bond lengths (*d*) in molecules **1′a** and **1′b**

Bond	*d*/Å	
	1′a	**1′b**
S(1)—O(2)	1.428(2)	1.418(3)
S(1)—O(3)	1.433(2)	1.419(3)
S(1)—N(1)	1.692(3)	1.697(3)
S(1)—C(29)	1.747(4)	1.758(4)
O(1)—C(7)	1.398(4)	1.396(4)
O(1)—C(6)	1.404(4)	1.400(4)
N(1)—C(12)	1.446(4)	1.426(4)
N(1)—C(1)	1.449(4)	1.439(4)
C(2)—O(5)	1.378(4)	—
C(11)—O(5)	—	1.354(4)

Table 2. Main bond angles (ω) in molecules **1′a** and **1′b**

Angle	ω/deg	
	1′a	**1′b**
O(2)—S(1)—O(3)	119.5(1)	120.7(2)
O(2)—S(1)—N(1)	105.7(1)	105.1(2)
O(3)—S(1)—N(1)	104.7(1)	106.1(1)
O(2)—S(1)—C(29)	109.4(2)	108.9(2)
O(3)—S(1)—C(29)	109.8(2)	108.5(2)
N(1)—S(1)—C(29)	106.9(1)	106.6(1)
C(7)—O(1)—C(6)	117.8(2)	117.0(2)
C(12)—N(1)—C(1)	112.4(2)	112.7(2)
C(12)—N(1)—S(1)	114.6(2)	115.6(2)
C(1)—N(1)—S(1)	113.8(2)	114.2(2)
C(1)—C(6)—O(1)	118.9(3)	119.7(3)
O(1)—C(6)—C(5)	120.3(3)	120.3(3)
C(2)—C(1)—N(1)	119.4(3)	121.0(3)
C(6)—C(1)—N(1)	119.1(3)	117.3(3)
C(7)—C(12)—N(1)	118.9(3)	119.8(3)
C(11)—C(12)—N(1)	119.6(3)	118.4(3)
O(4)—C(11)—C(10)	118.7(6)	—
O(4)—C(11)—C(12)	121.1(6)	—
O(5)—C(2)—C(1)	120.6(3)	—
O(5)—C(2)—C(3)	119.3(3)	—
O(4)—C(2)—C(1)	—	124.4(6)
O(4)—C(2)—C(3)	—	115.7(5)
O(5)—C(11)—C(10)	—	119.4(3)
O(5)—C(11)—C(12)	—	120.8(3)

2,4,6,8-Tetrakis(*tert*-butyl)-1-(veratroylazo)phenoxazine (3) was prepared by the addition of 3,4-dimethoxybenzoylhydrazide (1.92 g, 0.01 mol) in small portions with stirring to a solution of phenoxazinone (4.21 g, 0.01 mol) in anhydrous benzene (40 mL). The mixture was refluxed for 1 h. Then the mixture was filtered off, and the solvent was evaporated. The yield was 3.2 g (52%), m.p. 252 °C (from hexane). ^{1}H NMR (toluene-d$_8$), δ: 1.54, 1.56, 1.58, 1.88 (all s, 9 H each, Bu^t); 2.10, 2.15 (both s, 3 H each, Me); 6.85—7.42 (m, 4 H, Ph and 3 H, phenoxazine). IR (Nujol), ν/cm^{-1}: 3400 (NH); 1720 (C=O).

Results and Discussion

Structure and absorption spectra of the starting product. The results of studying the compound with the assumed structure **1** by ^{1}H NMR and IR spectroscopy are presented in Experimental. The signals corresponding to the aromatic protons and to the proton of the NH group, whose signal exhibits a noticeable low-frequency shift (δ 7.5), are the most typical parameters that characterize the structure under study in the ^{1}H NMR spectra. However, the IR spectra contain pronounced absorption bands typical of stretching vibrations of the azo group (ν = 3460 cm^{-1}) and the NH group with the modification characteristic of IHB formation. Thus, it follows from the presented facts that the compound under study has structure **1**$_{\text{azo}}$, in which the phenoxazine fragment forms the weakened IHB NH...N with the azo group.

Table 3. Spectral parameters of compound **1**

Transition	Calculation					Experiment (in hexane)		
	λ/nm	ν/cm^{-1}	μ_e*	$\mu_e - \mu_g$**	f***	λ_{max}/nm (ε)	ν^{max}/cm^{-1}	f***
			D	D				
$S_1^{\pi\pi*}$ICT	270.5	39674	16.17	+7.11	0.21	278 (7750)	35971	0.13
$S_2^{n\pi*}$	376.6	26551	5.06	−4.00	0.04	No	—	<0.003
$S_1^{n\pi*}$	388.1	25767	11.03	+1.97	0.08	No	—	<0.001
T_5ICT	—	35347	22.62	+13.56	0	—	—	—
$T_4^{n\pi*}$	—	32421	10.20	+1.14	0	—	—	—
$T_3^{n\pi*}$	—	31955	6.37	−2.69	0	—	—	—
$T_2^{n\pi*}$	—	24793	8.20	−0.86	0	—	—	—
$T_1^{n\pi*}$	436.2	22925	17.99	+8.93	0	—	—	—

* The dipole moment of the molecule in the excited state.

** The change in the dipole moment of the molecule on going from the ground (μ_g = 9.06 D) to excited state.

*** The oscillator intensity.

The data characterizing the electron states with the lowest energy and transitions in them with absorption, which were obtained experimentally and by quantum-chemical calculations by the semiempirical PM3 method[12] for structure $\mathbf{1}_{azo}$, are presented in Tables 3 and 4 and Figs. 1 and 2. Note that the experimental and calculated parameters corresponding to the experimentally observed longest-wave transition $S_0 \rightarrow S_1^{\pi\pi*}$ in structure $\mathbf{1}_{azo}$, coincide well (see Table 3). Analysis of the HOMO and LUMO responsible for this transition indicates a substantial contribution of the intramolecular charge transfer (ICT) from the phenoxazine fragment to the azo group, resulting in a dramatic increase in the dipole moment in the $S_1^{\pi\pi*}$ state (ICT) during excitation $S_0 \rightarrow S_1^{\pi\pi*}$ ($\Delta\mu \approx 7$ D) (see Table 3). This is experimentally manifested in a substantial long-wave shift of the absorption band with an increase in the solvent polarity on going from *n*-hexane to ethanol. According to the data of quantum-chemical calculations, structure $\mathbf{1}_{azo}$ has at least two low-energy singlet states $S^{n\pi*}$ and the corresponding triplet states $T^{n\pi*}$, which are not observed experimentally due to a very low intensity of transitions (see Table 3). However, the existence of these states typical of azo structures is confirmed by the absence of fluorescence even under the most favorable conditions (rigid matrix, 77 K). At the same time, due to the existence of the low-energy triplet states $T_{ICT}^{\pi\pi*}$, the appearance of rather long-lived fluorescence can be expected under these conditions. Also note the resemblance of the optical spectral parameters, including the absence of fluorescence of the studied compound $\mathbf{1}_{azo}$ and the nonplanar molecule of *cis*-azobenzene (λ_{max}= 280 nm, ε = 5200 L mol^{-1} cm^{-1}) rather than *trans*-azobenzene (λ_{max} = 320 nm, ε = 20000 L mol^{-1} cm^{-1})[13] (*cf.* Table 3). This resemblance is likely stipulated by the nonplanar structure $\mathbf{1}_{azo}$ due to steric hindrances of the *tert*-butyl and azo groups of the sterically hindered phenoxazine heterocycle. This can result in the observed weakening of the IHB and a low probability of the transfer of a proton in the ground electron state to form the hydrazo form, which is less stable than $\mathbf{1}_{azo}$ by 60 kJ mol^{-1} (according to the data of quantum-chemical calculations of the model compounds). Indeed, the formation of the latter is not observed in the absorption spectra on variation of both the temperature and polarity of the solvent within wide ranges.

Thus, the array of calculated and experimental data on the electronic absorption spectra and fluorescence properties along with the data of ^{1}H NMR and IR spectroscopy provides a reliable identification of starting structure $\mathbf{1}_{azo}$ and the nature of the absorption spectra responsible for the excitation of the photochemical processes.

Photoinitiated processes and structure of photoreaction products. The photoinitiated transformations of the absorption spectra upon the excitation of solutions in solvents with different polarities and in the polymeric matrix (PMMC) at 293 and 77 K with a steady-state light source at the long-wave absorption band are expressed as a change in the intensity of the initial absorption band and the appearance of two intense bands in the long-wave spectral region without formation of isosbestic points (see Figs. 1, 2 and Tables 3, 4). However, photochemical processes in liquid (293 K) and rigid frozen (77 K) solutions and in the polymeric matrix (PMMC, 293 K) dramatically differ both kinetically and by the spectral properties of the reaction products.

Table 4. Absorption spectra of photoproducts

Solvent	T/K	λ_1^{max}	λ_2^{max}	Structure
		nm	nm	
Isopentane	293	344	577	**1′**
	77	380	662	E-$\mathbf{1}_{hydrazo}$
Ethanol	293	363	617	**1′**
	77	380	660	E-$\mathbf{1}_{hydrazo}$
PMMC	293	360	560	**1′**
		370	620	E-$\mathbf{1}_{hydrazo}$

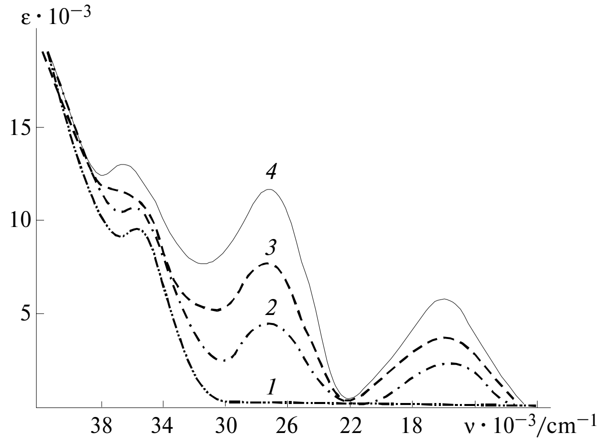


Fig. 1. Photoinduced changes in the electron absorption spectra of compound **1** in ethanol before irradiation (*1*) and after irradiation with a mercury lamp at λ = 313 nm for 8 (*2*), 13 (*3*), and 40 min (*4*).

The photoreaction in liquid solutions is very fast and thermally reversible only under short irradiation (≤2 min), whereas under long irradiation (~30 min) the photoreaction is irreversible. The photoreaction in rigid vitrified solutions (77 K) is thermally reversible, the photoproduct that formed under these conditions is completely transformed into starting form **1**$_{\text{azo}}$ when the temperature increases, and the process is polycyclic. However, unlike liquid solutions, in PMMC the reversible photoreaction with the inverse sharply retarded thermal process occurs along with the irreversible photoreaction. In all cases, the product of the irreversible photoreaction is characterized by two shorter-wave bands and endures a strong bathochromic shift with an increase in the solvent polarity, whereas two bands of the final photoproduct of the thermoreversible photoreaction lie in a much longer-wave region and do not exhibit substantial spectral shifts (see Table 4). Thus, at least two photoproducts form at ambient temperatures, and isosbestic points are absent during transformations of the spectra. With the purpose to study the structure of the molecule that forms in the irreversible photoreaction, we studied the preparatively isolated photoproduct **1′** by X-ray structural analysis.

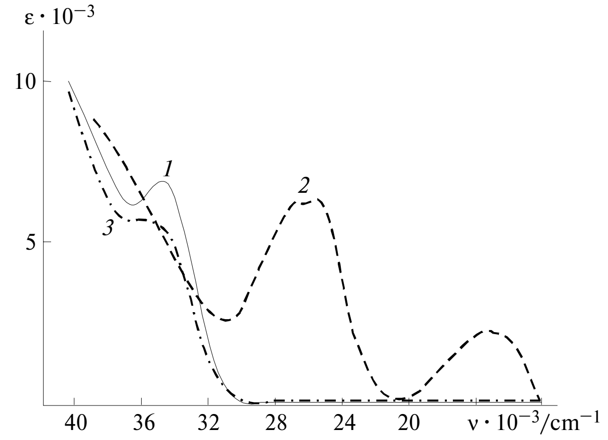


Fig. 2. Photoinduced changes in the electronic absorption spectra of compound **1** in isopentane before irradiation (*1*), after irradiation with a mercury lamp at λ = 313 nm for 15 min (*2*), and after defrosting (*3*).

Compound **1′** crystallizes as two independent molecules (see Fig. 3, *a*, *b*). The distinction in their molecular structures is mainly due to different orientations of the *tert*-butyl fragments. As a whole, all *tert*-butyl fragments are oriented in such a way that one of the methyl groups is almost coplanar to the plane of the benzoquinone fragment.

In molecule **1′a** the *tert*-butyl group at the C(10a) atom is disordered with populations of the positions 0.3 and 0.7. Two orientations of the *tert*-butyl group differ by a turn about the C(10a)—C(25a) bond by ~60°. In molecule **1′b** the *tert*-butyl group at the C(8b) atom is disordered with populations of the positions 0.3 and 0.7. Two orientations of the *tert*-butyl group differ by a twist about the C(8b)—C(21b) bond by ~30°.

The central fragment of molecules **1′a,b** is nonplanar. The angle between the planes of the benzene fragments C(1a)—C(6a) and C(7a)—C(12a) is 31.6° (**1′a**) and 34.3° (**1′b**). The N(1(a,b)) atom has a pyramidal configuration characterized by a sum of bond angles of 340.8° in molecule **1′a** and 342.4° in molecule **1′b**.

In this study, our special attention has been focused on the diffraction peaks localized at the atoms C(2a) (C(2a)—O(5a) 1.379 Å, population O(5a) 0.78), C(11a) (C(11a)—O(4a) 1.197 Å, population O(4a) 0.22), C(2b) (C(2b)—O(4b) 1.228 Å, population O(4b) 0.24), and C(11b) (C(11b)—O(5b) 1.354 Å, population O(5b) 0.76). Based on the chemical information and characteristic bond lengths, we ascribed these peaks to the O atoms.

For the O(5a) and O(5b) atoms, the C(2a)—O(5a) and C(11b)—O(5b) bond lengths correspond to the analogous values for the OH groups, while the consideration of the C(11a)—O(4a) and C(2b)—O(4b) bonds as double (by the value of the length) suggests the formation of stable free-radical or ionic structures in the crystal. The ESR study did not reveal paramagnetic centers in the crystal and, hence, these compounds have an ionic nature.

Let us consider the short intermolecular contacts of the O(5a), O(5b), O(4a), and O(4b) atoms with the neighboring atoms. The atoms corresponding to the hydroxyl groups form intramolecular (O(5a)...O(3a) 2.70 Å) and intermolecular (O(5b)...O(2a) 2.82 Å) hydrogen bonds. This is indicated by the elongation of the S(1a)=O(2a) (1.429 Å) and S(1a)=O(3a) (1.433 Å) bonds as compared to similar parameters of molecule **1′b** (S(1b)=O(2b) 1.418 Å, S(1b)=O(3b) 1.419 Å).

We cannot distinguish intermolecular interactions that stabilize the ionic structure in the crystalline environment of the atoms O(4a) and O(4b) (O(4a)...N(1a) 2.73 Å, O(4a)...O(2a) 2.86 Å, O(4a)...C(28a) 2.44 Å, O(4a)...O(4b) 2.92 Å, O(4b)...N(1b) 2.80 Å,

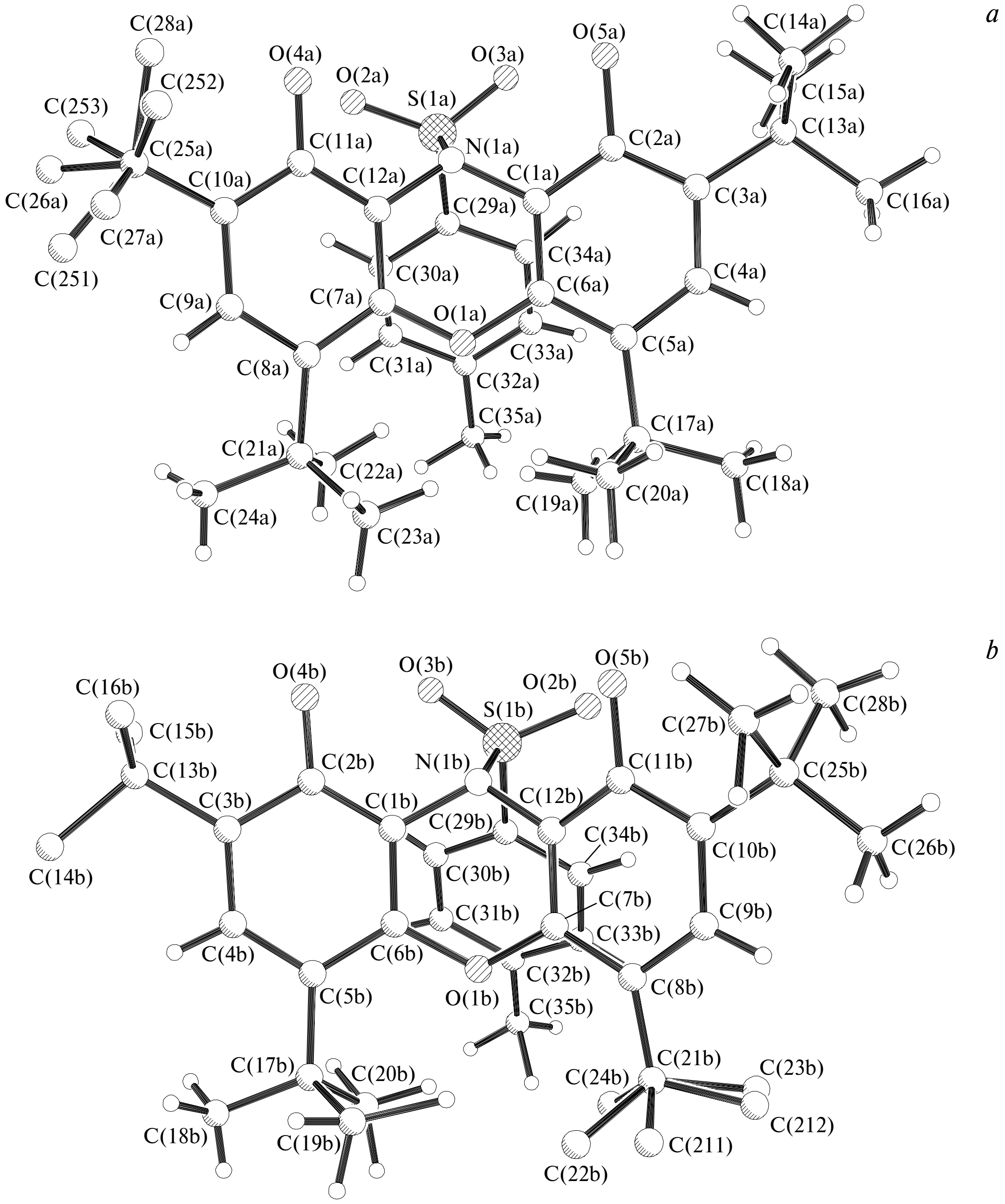


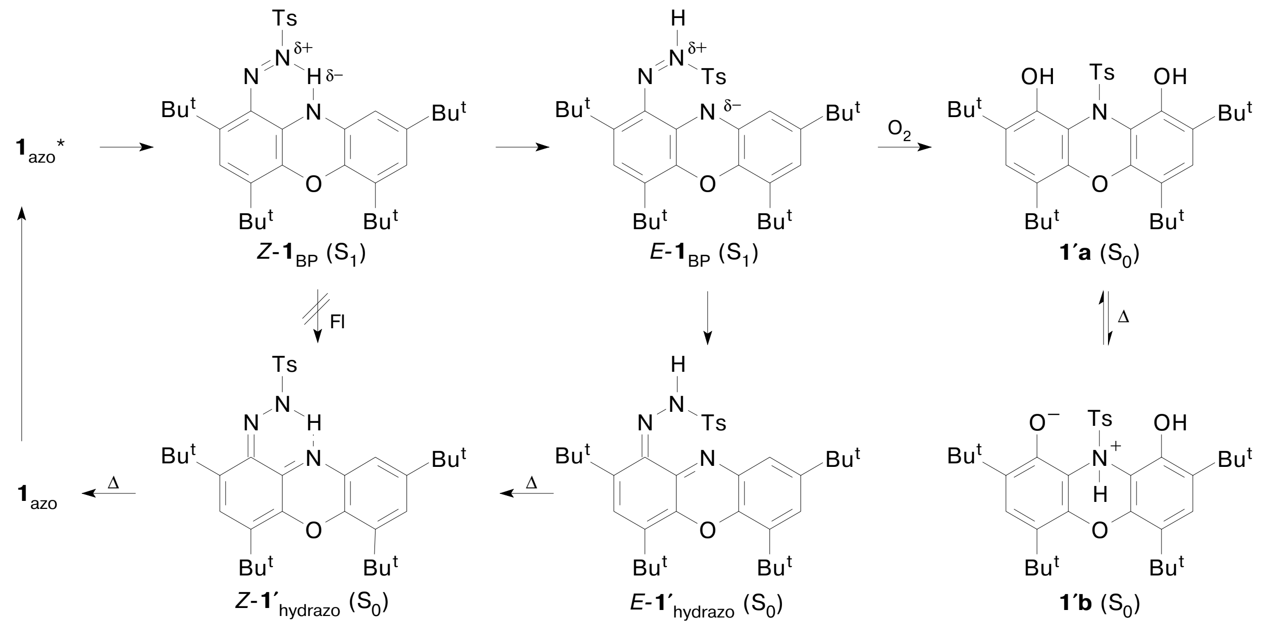
Fig. 3. General view of molecules **1′a** (*a*) and **1′b** (*b*).

O(4b)...O(2a) 2.82 Å, O(4b)...O(3b) 2.85 Å, O(4b)...C(16b) 2.78 Å). However, reliable conclusions will be drawn after additional physicochemical analysis of these crystals.

It follows from the X-ray data that compound **1′** is a superposition of two tautomeric forms of the photooxidation product of polar structure (**1′a** and **1′b**), which explains the experimentally observed strong long-wave shift of the absorption bands in the proton-donating solvent (ethanol) as compared to that in isopentane (see Table 4). The characteristic feature of this structure is the presence of the tosyl group at the N atom of the phenoxazine part of the molecule. Such a structure of the photoproduct can indicate that the *Z* and *E* forms of the bipolar structure **1** ($\mathbf{1}_{BP}$) are intermediates in the reaction (Scheme 1).

To draw conclusions about the photoproduct structure and the mechanism of the reversible photoreaction, we studied the photoinitiated processes in model compounds **2** and **3**. Compound **2**, in which the H atom is replaced by the acyl group, is not photoactive and does not fluoresce at either 293 K or 77 K upon excitation at the absorption band of the transition with the same nature as that of compound $\mathbf{1}_{azo}$ (λ^{max}_{ab} = 295 nm). By

Scheme 1



contrast, compound **3**, being excited at the long-wave absorption bands of the azo form in isopentane (λ^{max}_{ab} = 303 nm, ε = 14000 mol L^{-1} cm^{-1}, for shoulder λ_{sh} = 316.5 nm, ε = 8000 mol L^{-1} cm^{-1}) and ethanol (λ^{max}_{ab} = 303 nm, ε = 15125 mol L^{-1} cm^{-1}, for shoulder λ_{sh} = 322 nm, ε = 9500 mol L^{-1} cm^{-1}), exhibits at 77 K in both vitrifying solvents intense ASS fluorescence ($\lambda^{max}_{flu} \approx$ 500 nm, $\Delta\nu^{\alpha-f} \approx$ 11000 cm^{-1}) typical of ESIPT, which is absent from liquid solutions. Structurally flexible molecules similar to molecule **3** are characterized by the absence or a low intensity of the ESIPT of ASS fluorescence in nonviscous media due to the adiabatic formation (following ESIPT) of twisted structures that damp ASS fluorescence.[5,6] Unlike the nonfluorescent structure $\mathbf{1}_{azo}$, the fluorescent compound **3** exhibits no photochemical activity in both liquid (293 K) and solid (293, 77 K) media. Therefore, we may assume that in compounds of the studied type ESIPT fluorescence appears, similar to **3**, only in the absence of structural transformations, which efficiently compete with the emission in the S_1 state and lead, similar to $\mathbf{1}_{azo}$, to the formation of the photoreaction products. Such conformational changes are usually manifested in a substantial moderation or complete retardation of the inverse dark reaction in the ground electron state with an increase in the viscosity of the medium in the polymeric matrix (PMMC) or vitrified solvent (77 K). The reversible photoreactions of compound $\mathbf{1}_{azo}$ are characterized by precisely these kinetic features.

Thus, based on the structural, spectral, and photochemical data obtained for $\mathbf{1}_{azo}$ and model compounds **2** and **3**, we can represent the scheme of photoinitiated processes in compound $\mathbf{1}_{azo}$, including the formation of the metastable photoproduct responsible for photochromism (see Scheme 1). The excitation in the azo structure ($\mathbf{1}_{azo}$) of the ICT transition ($\mathbf{1}_{azo} \rightarrow \mathbf{1}_{azo}$*) from the N atom of the phenoxazine fragment to the azo group provides the conditions for ESIPT to form the bipolar structure *Z*-$\mathbf{1}_{BP}$. In compound **3**, the further transformation of the structure does not occur, and structure *Z*-$\mathbf{3}_{BP}$ corresponding to *Z*-$\mathbf{1}_{BP}$ is responsible for ASS fluorescence. In compound $\mathbf{1}_{azo}$ ESIPT is only the primary stage followed by the fast *Z*→*E* isomerization to form structure *E*-$\mathbf{1}_{BP}$, due to which emission from structure *Z*-$\mathbf{1}_{BP}$ is not manifested. As we should expect, the processes characteristic of molecules **1** and **3** cannot occur in molecule **2** without IHB, which stipulates the absence of both fluorescence and photochemical transformations. In compound $\mathbf{1}_{azo}$ the bipolar structure *E*-$\mathbf{1}_{BP}$ is intermediate in the photoreaction that occurs in two competing directions. The reversible photochromic process results in the formation of the metastable colored (in the ground electron state) *E*-hydrazo form. The subsequent inverse dark process begins from the *E*→*Z*-isomerization of the hydrazo structure (*E*-$\mathbf{1}_{hydrazo} \rightarrow$ *Z*-$\mathbf{1}_{hydrazo}$), which is controlled by the medium viscosity and completed by the inverse intramolecular proton transfer to form the starting azo form (*Z*-$\mathbf{1}_{hydrazo} \rightarrow \mathbf{1}_{azo}$). The irreversible process includes the addition of the residue of the tosyl group to the N atom of the phenoxazine fragment in the bipolar structure *E*-$\mathbf{1}_{BP}$ and the elimination of the azo group accompanied by the oxidation of the phenoxazine fragment. The last process is controlled by oxygen diffusion and is especially efficient in liquid solutions. The irreversible process is completely excluded in frozen solutions at 77 K.

Thus, ESIPT in compounds with the IHB NH...N, like the similar process in compounds with the IHB OH...N, is the initiating primary stage of both adiabatic transformations of the structure and diabatic reactions, including the reversible formation of metastable colored structures and deep irreversible destructive transformations.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 96-15-97476, 98-03-33063, and 99-03-32485).

References

1. S. G. Formosinho and L. G. Arnaud, *J. Photochem. Photobiology, A: Chem.,* 1994, **75**, 21.
2. E. Hadjoudis, in *Photochromism, Molecules and Systems,* Eds. H. Durr and H. Bouas-Laurent, Elsevier, Amsterdam, 1990, 685.
3. A. Grabowska, K. Kowacki, and L. Kaczmarek, *Acta Phys. Polon., A (Ingl.),* 1995, **88**, 1081.
4. M. I. Knyazhanskii and A. V. Metelitsa, *Fotoinitsiirovannye protsessy v molekulakh azometinov i ikh strukturnykh analogov* [*Photoinitiated Processes in Azomethine Molecules and Their Structural Analogs*], Izd. Rostovskogo-na-Donu Univ., Rostov-on-Don, 1992, 77 pp. (in Russian).
5. M. I. Knyazhansky, A. V. Metelitsa, A. Ia. Bushkov, and S. M. Aldoshin, *J. Photochem. Photobiology, A: Chem.*, 1996, **97**, 121.
6. M. E. Kletskii, A. A. Milov, A. V. Metelitsa, and M. I. Knyazhansky, *J. Photochem. Photobiology, A: Chem.,* 1997, **110**, 267.
7. B. K. Andzulene and T. B. Esene, *J. Appl. Spectr.*, 1978, **28**, 649.
8. Z. A. Starikova, A. E. Obodovskaya, and B. M. Bolotin, *J. Struct. Chem.*, 1982, **23**, 128.
9. L. Sh. Aphonasiady, B. M. Bolotin, and N. F. Levchenko, *Chem. Heterocycl. Compnd.,* 1980, **3**, 390.
10. J. V. Karsanov, E. P. Ivakhnenko, and A. Z. Rubezhov, *J. Organomet. Chem.,* 1989, **11**, 1.
11. G. M. Sheldrick, *SHELXL-97; Program for Crystal Structure Determination and Refinement of Crystal Structures*, University of Göttingem (Germany), Göttingem, 1997.
12. J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209.
13. Yu. P. Kitaev, *Khimiya gidrazonov* [*Chemistry of Hydrazones*], Nauka, Moscow, 1977, 207 pp. (in Russian).

Received June 6, 2000