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Excited state intramolecular proton transfer reaction and luminescent properties of the *ortho*-hydroxy derivatives of 2,5-diphenyl-1,3,4-oxadiazole

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ABSTRACT: Luminescent properties of several *ortho*-hydroxy derivatives of 2,5-diphenyl-1,3,4-oxadiazole were studied in solvents of different polarity and protolytic ability and compared with the analogous derivatives of 1,3-oxazole, studied by us earlier. Evaluations of rate constants for the excited state intramolecular proton transfer (ESIPT) reaction and radiationless degradation of the energy of electronic excitation in the ESIPT reaction product, phototautomer form, were made on the basis of fluorescence quantum yields and fluorescence kinetic measurements. The proton phototransfer reaction is the most efficient primary photoprocess in the examined series of compounds. With rate constants of 10^{11}–10^{12} s^{-1} it exceeds the rates of other primary photophysical processes in these molecules by up to 2–3 orders of magnitude. A connection between the rate of the ESIPT reaction and the electron density redistribution on electronic excitation was revealed for the molecules under study. The electron donor substituents in 5-phenyl decrease the proton phototransfer rate constant up to complete inhibition of the ESIPT process in the case of the dimethylamino derivative of the oxazole series, whereas the electron acceptor substituents must accelerate this reaction. The determining role of the excited state increase of the proton donor group acidity was assumed on the basis of experimental data and quantum chemical calculations. The temperature investigations showed that the ESIPT reaction in the series of *ortho*-hydroxy derivatives of 2,5-diphenyloxazole and 2,5-diphenyl-1,3,4-oxadiazole has a very low activation barrier. However, the radiationless processes in the phototautomer form are characterized by the presence of a certain barrier in both examined series. A dependence of the radiationless dissipation rate in the phototautomer form on the excited state redistribution of the electron density in it was also found. The more efficient is the charge transfer from the *ortho*-phenolate fragment to the protonated heterocycle and the rest of the molecule, the more efficient are the radiationless losses. It was revealed that structural changes, which prevent the mentioned movement of electron density, result in an increase in the fluorescence efficiency of the phototautomer form and, hence, also to an increase in the total fluorescence quantum yield of the ESIPT molecule. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: 2,5-diphenyl-1,3,4-oxadiazole *o*-hydroxy derivatives; excited state intramolecular proton transfer reaction; luminescence

INTRODUCTION

In terms of important applications, the use of organic luminophores, which are characterized by abnormally high fluorescence Stokes shifts, seems to have more potential than the use of luminophores with 'normal' Stokes shift values.[1] The main advantage of the high Stokes shifts is the increase in light output as a result of low self-absorption of emitted light. Furthermore, in many cases decreases of light absorption by the environment, by products of possible photodegradation and by impurities also occurs. The last two factors are especially valid in scintillation techniques for the construction of scintillation detectors of large dimensions.[2] In biological systems, the 'abnormally red-shifted' fluorescence of the probe generally corresponds better to the region of higher transmittance of biomaterials.[3]

The excited state intramolecular proton transfer (ESIPT) reaction plays an important role within the limited quantity of known primary photochemical and photophysical processes which result in fluorescence with abnormally high Stokes shifts.[4–14] The product of the ESIPT reaction, excited phototautomer form, emits light in a longer wavelength region than the emission of the initial 'normal' form. The Stokes shift values typical of phototautomer forms vary in the range 6000–12 000 cm^{-1} for different ESIPT compounds.

Noticeable quenching of fluorescence, which accompanies proton phototransfer in most cases, is a considerable restriction for the wider practical usage of organic

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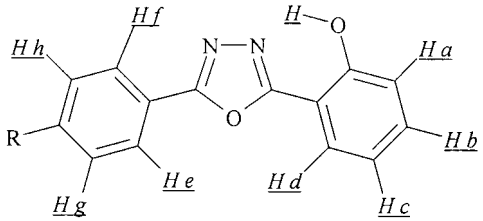
Table 1. Some physico-chemical characteristics of the *ortho*-hydroxy derivatives of 2,5-diphenyl-1,3,4-oxadiazole



Compound	R	Molecular formula	N(%): calc./ found	M.p. (°C)	^{1}HNMR: δ (ppm) H_a, 1H, d H_b, 1H, t H_c, 1H, t H_d, 1H, d	OH, 1H, s	H_{ef}, 2H, d	$H_{g,h}$, 2H, d	R
I	H	$C_{14}H_{10}N_2O_2$	11.76/ 11.8	163–164	7.133 7.071 7.508 7.948	10.315	8.136	7.668 3H,s (broad)	—
II	Cl	$C_{14}H_9ClN_2O_2$	10.27/10.2	175–176	7.130 7.065 7.506 7.948	10.296	8.128	7.726	—
III	OCH_3	$C_{15}H_{12}N_2O_3$	10.44/10.4	148	7.117 7.058 7.491 7.924	10.288	8.054	7.186	3.882, 3H,s
IV	$N(CH_3)_2$	$C_{16}H_{15}N_3O_2$	14.94/14.8	163–165	7.089 6.995 7.458 7.936	10.210	8.125	7.825	2.902, 6H,s
V	C_6H_5	$C_{20}H_{14}N_2O_2$	8.91/8.9	157	7.144 7.081 7.458 7.964	10.331	8.203	7.964	7.802(*o*), 2H,d 7.530(*m*,*p*), 3H,m
VI	$[CH]_3$	$C_9H_8N_2O_2$	15.9/16.0	147–149	6.906 6.868 7.386 7.809	10.057	—	—	4.671, 3H,s

fluorescent molecules which exhibit the ESIPT reaction.[4,6,8,10–15]

In spite of the large number of publications on ESIPT (several hundred), there are only a few which deal with the influence of the structure of organic compounds on the rate constants of proton transfer and radiationless deactivation connected with the discussed reaction (see, e.g., Refs. 16–49). Most of the publications cited deal with derivatives of salicylic acid, its esters and amides,[18,20–24,31–33,45] *o*-hydroxybenzaldehyde, acetophenone and related compounds,[19,38,41] *o*-hydroxybenzoxazoles,[21,42] benzothiazoles,[16,27,37] triazoles,[17,25,30,46] flavonols,[26,29,39,40] anthraquinones,[34–36] bipyridyls[28,47,49] and even such a simple model as malonic aldehyde.[48] There have also been several attempts to develop theoretical approaches for the connection between molecular structure and efficiency of ESIPT, for example, Nagaoka and Nagashima 'nodal planes.'[43,44] Unfortunately, the investigation of substituent effects in the above publications had mainly a non-systematic character: the number of examined substituents was small or, in many cases, the electronic properties of the substituents involved were similar one to another. These circumstances did not allow the authors of the original articles or numerous reviews to develop a general theoretical approach to the influence of molecular structure on the ESIPT process.

In a recent paper,[50] we examined the effect of the ESIPT reaction on the fluorescent properties of several *ortho*-hydroxy derivatives of 2,5-diphenyloxazole. The aim of this work was to investigate how the substitution of an electron-rich oxazole ring with a greater electron acceptor and less basic oxadiazole ring influences the fluorescent properties, the rate of the ESIPT reaction and the efficiency of radiationless decay within the studied series of compounds.

EXPERIMENTAL

The investigated *ortho*-hydroxy derivatives of 2,5-diphenyl-1,3,4-oxadiazole were synthesized by the following general scheme, analogous to that of Tandon and co-workers.[51,52] In the first step, the substituted aromatic acid chloride (0.1 mol), dissolved in 50 ml of toluene, was added to 50 ml of an aqueous solution of salicylic acid hydrazide (0.1 mol). Concentrated aqueous sodium carbonate was added dropwise with vigorous stirring to the reaction mixture to give a weakly alkaline medium. Stirring was continued for an additional 1 h, then the precipitate was filtered, washed with water and dried. In the case of compound **VI**, the salicylic acid hydrazide was stirred in acetic anhydride for 1 h at room temperature. After initial warming, during which the starting material dissolved completely, and following cooling of the reaction mass, a precipitate was formed. It was filtered, washed with water and dried. In the second step, the dry *N*-(*o*-hydroxybenzoyl)-*N*-acylhydrazine obtained was refluxed with a 10-fold excess of $SOCl_2$ for 1 h. The reaction mixture was cooled and poured over ice to yield a solid, which was filtered and washed with water until a neutral reaction of the filtrate. The solid was dried and recrystallized from octane. Typical yields were 50–65%.

It should be noted that during the synthesis of all the *ortho*-hydroxy derivatives of diphenyloxadiazole studied, highly fluorescent by-products were usually formed. Their emission spectra overlap significantly with the shorter wavelength emission region of the title compounds, that is why the compounds obtained were thoroughly purified by multiple recrystallizations from ethanol and octane. Coincidence of the fluorescence excitation spectra measured for normal form and phototautomer emission bands was chosen as the criterion of purity (the mean deviation did not exceeded 2–5% of the intensity in normalized spectra). Some physico-chemical characteristics of the synthesized compounds (melting points, element analyses and NMR data) are presented in Table 1.

Commercially available solvents (*n*-octane, toluene, acetonitrile) were purified and dried according to procedures described elsewhere (e.g. Ref. 53) to avoid traces of water, which may result in the presence of forms with intermolecular hydrogen bonds instead of intramolecular bonds. This might affect most of the conclusions concerning the peculiarities of the ESIPT process.[54,55] Normally, fluorescence excitation spectra and/or synchronous scanning spectra were used to monitor the purity both of the solvents used and of the investigated compounds dissolved in them.

Infrared spectra were measured on Specord M80 IR spectrometer. Proton NMR spectra were determined on a Brucker WP-100 Fourier transform spectrometer in DMSO-d_6.

Electronic absorption spectra were measured on a Hitachi U3210 spectrophotometer and fluorescence emission, excitation and 'both scan' spectra (all corrected for the instrument's response) on a Hitachi F4010 fluorescence spectrometer.

Fluorescence quantum yields were determined with reference to quinine sulfate in 1 N H_2SO_4 solution ($\varphi_0 = 0.546$[56]) using the equation

$$\varphi = \varphi_0 \cdot \frac{S(1-10^{-D_0})}{S_0(1-10^{-D})} \cdot \frac{n^2}{n_0^2}$$

where S and S_0 are the integral intensities of fluorescence spectra, D, and D_0 are the absorbances on the excitation wavelength and n and n_0 are the refractive indices of the solvents used. The subscript zero refers to the quinine sulfate solution. All fluorescence measurements were conducted for dilute solutions with an absorbance of 0.1–0.15 at the excitation wavelength (concentrations 10^{-5}–10^{-6} mol dm^{-3}).

The mathematical separation of individual bands in the fluorescence spectra was performed by a specially developed program, which uses the non-linear least-squares method (LSM) with the Fletcher–Pawell algorithm, and approximates the shape of individual fluorescence bands by a log-normal function.[57] When the intensity of the normal form and the phototautomer differed substantially, the separation procedure was conducted on the spectra in a semi-logarithmic representation.

The fluorescence kinetics were measured with a pulse single-photon counting spectrometer, working in the nanosecond range, described in previous papers.[58,59] Convolution of the fluorescence kinetic data was made by the non-linear least-squares method.[60–62] The accuracy of lifetimes obtained in such a way can be estimated to be 10–20 ps.

Quantum chemical calculations with optimization of the molecular geometry in the ground and excited states were made by the semiempirical full-valent AM1 method[63] with the use of the MOPAC 6.0 program. The spectral characteristics, which are necessary for the evaluation of fluorescence rate constants for the normal and phototautomer forms (see below), were obtained for their excited state optimized planar geometries by the ZINDO/S routine[64] (with 100 singly excited configurations). The k_f values were estimated from the calculated positions (wavenumber, ν, cm^{-1}) and intensities (f, oscillator strength) of the long-wavelength electronic transitions of the above-mentioned forms by the equation[65]

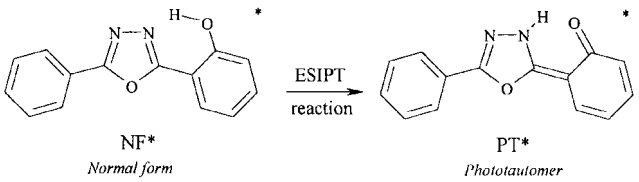
$$k_f = \frac{f \cdot \nu^2}{1.5}$$

Data for diagrams of the electron density redistribution at electronic excitation were obtained by the π-electron

semiempirical PPP CI method[66,67] with up to 100 singly excited configurations. Special semiempirical parameters, calibrated for systems with hydrogen bonding, were taken from Ref. 68. Several specific quantum-chemical indices were calculated for this purpose: the numbers of localization of electronic excitation (L_i; the sum of L_i of the atoms of any fragment in the molecule, L_{FR}, characterized the participation of the fragment in the excitation of the molecule as a whole) and the 'charge-transfer (CT) numbers,' l_{ij}, which help in understanding the directions of redistribution of the electron density in the molecule upon its transition to the electronically excited state.[69] The CT numbers, summarized on the atoms, included in a definite fragment of the molecule, could be classified to two types. The first, 'local' CT numbers, characterize the redistribution of electron density at excitation within the mentioned fragment. The second, interfragmental CT numbers, show the movement of electron density from one fragment of the molecule to another.

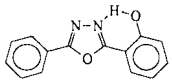
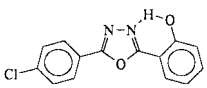
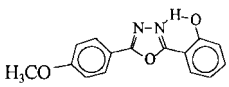
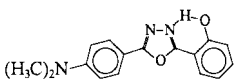
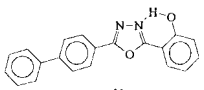
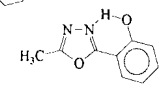
RESULTS AND DISCUSSION

The oxadiazole ring is characterized by lower basicity and can be considered as a stronger acceptor of electron density both in the ground and in the excited states in comparison with the oxazole ring. The $\Delta\nu_{OH}$ value (the shift of the stretching frequency of the hydroxy group of phenol upon hydrogen bond formation with proton accepting compounds in dilute solutions in CCl_4) is usually considered as a measure of the basicity of organic molecules at the stage of hydrogen bond formation.[70] For 2,5-diphenyloxazole this was found to be near 410 cm^{-1}, which is close to such strong organic bases as pyridine and quinoline.[70] In contrast, for the analogous 2,5-diphenyl derivative of 1,3,4-oxadiazole, the $\Delta\nu_{OH}$ value was estimated to be considerably lower, 325 cm^{-1}. The ESIPT reaction takes place along the intramolecular hydrogen bond between the *ortho*-hydroxy group and nitrogen atom of the heterocycle. Therefore, the marked difference in proton-accepting properties of these two heterocycles could influence the efficiency of proton phototransfer. This must result also in changes of spectral characteristics of the title compounds in comparison with their oxazolic analogs.[50]



The spectral properties of the *ortho*-hydroxy derivatives of 2,5-diphenyl-1,3,4-oxadiazole in three solvents,

Table 2. Spectral characteristics of the *ortho*-hydroxy derivatives of 2,5-diphenyl-1,3,4-oxadiazole in octane (Oc), toluene (Tol.) and acetonitrile (Ac.)[a]

	Compound	Solvent	ν_{abs} (cm^{-1})	ν_{fl}^{NF} (cm^{-1})	$\Delta\nu_{ST}^{NF}$ (cm^{-1})	ν_{fl}^{PT} (cm^{-1})	$\Delta\nu_{ST}^{PT}$ (cm^{-1})	φ_{fl}
I		Oc.	30720	27400	3320	19900	10820	0.021
		Tol.	31620	28280	3340	19980	11640	0.010
		Ac.	32080	27920	4160	20000	12080	0.015
II		Oc.	31280	26600	4680	19580	11700	0.015
		Tol.	31280	27220	4060	19420	11860	0.019
		Ac.	31880	27560	4320	19560	12320	0.009
III		Oc.	31340	27600	3740	19980	11360	0.011
		Tol.	31180	27740	3440	19980	11200	0.017
		Ac.	31680	27620	4060	20200	11480	0.013
IV		Oc.	30200	25770	4430	19940	10260	0.013
		Tol.	29980	24710	5270	19890	10090	0.036
		Ac.	30360	22370	7990	19970	10390	0.051
V		Oc.	30860	26180	4680	19880	10980	0.033
		Tol.	30700	26830	4320	19500	11200	0.037
		Ac.	31220	26720	4500	19040	12180	0.014
VI		Oc.	32560	29680	2880	21400	11160	0.012
		Tol.	32700	29420	3280	21660	11040	0.014
		Ac.	32880	27420	5460	21800	11080	0.009

[a] ν_{abs} and ν_{fl} are positions of maxima in the absorption and fluorescence spectra (NF denotes the normal form and PT the phototautomer); $\Delta\nu_{ST}$ and φ_{fl} are the Stokes shift and total quantum yield of fluorescence.

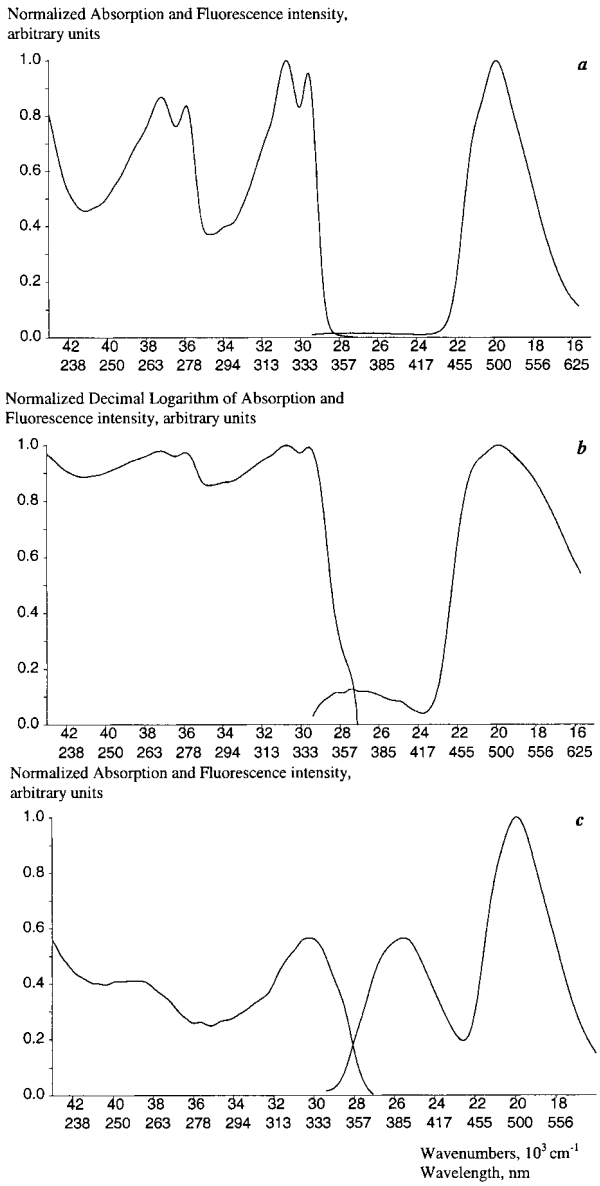


Figure 1. Absorption and fluorescence spectra of compound **I** [(a) and (b), respectively, in semi-logarithmic representation, normalized) and **IV** (c) in octane at 25 °C

which differ in polarity and protolytic ability, are presented in Table 2. The most typical absorption and emission spectra in octane are presented in Fig. 1.

As expected, two emission bands were observed in the fluorescence spectra of the studied compounds. Short-wavelength bands usually have Stokes shift values of 3000–5000 cm^{-1}. They belong to the emission of the normal (NF, enol) form. The long-wavelength bands are characterized by high Stokes shift values (10 000–12 000 cm^{-1}) and may be attributed to the emission of the phototautomer (PT, keto) form, which is formed as a result of the ESIPT reaction. As was emphasized in the Experimental section, the fluorescence excitation spectra, measured for the maxima of the normal form and the phototautomer, were practically identical within experimental error. They were also similar to the corresponding absorption spectra. These facts support our attribution of low-intensity short-wavelength emissions to the normal forms of the studied compounds. Also, we can conclude that phototautomer formation occurs only in the excited state, whereas in the ground state the equilibrium between these two species is completely shifted towards normal forms. Usually, the long-wavelength phototautomer emissions are 2–100 times more intense than those of the normal forms in the shorter wavelength region. Mean fluorescence decay times, measured within each of the observed bands, differ dramatically from one another. In most cases lifetimes of the normal forms lie below the lower measurement level of our instrument. In contrast to the normal forms, phototautomer lifetimes belong to the nanosecond time interval (see Table 3). Based on these facts, we can conclude that for the investigated compounds, as also for the previously studied derivatives of oxazole,[50] and for the most of the other cases known from the literature (see Introduction), the theoretically possible excited state equilibrium is significantly shifted towards the phototautomer form. The seeming exception of compound **IV** will be discussed later.

During the first decades of the investigation of ESIPT, there were extended discussions concerning the bipolar zwitterion or quinoid nature of phototautomer form.[4–14] In recent years most authors have tended to assume phototautomer forms to be quinoid-like. Our results confirm this statement. As follows from the data presented in Table 2, the positions of the fluorescence band of the phototautomer forms in the oxadiazole series are practically insensitive to the nature of the solvent. Such behavior might occur only if the polarity of the excited molecules does not differ significantly from that of the ground state. Taking into account the fact that a bipolar zwitterionic structure must have high dipole moment, we readily agree with numerous conclusions of other authors concerning the quinoid structure of the phototautomer forms. Only one seeming exception was observed: the fluorescence band of the phototautomer form is shifted by ca 1500–2000 cm^{-1} towards higher energies for compound **VI**, which has a methyl group in position 5 of the heterocycle, instead of substituted phenyl as in the other investigated compounds. However, the emission band of the normal form is also shifted to the short-wavelength region by nearly the same value for this molecule.

The fluorescence quantum yields within the studied series of *ortho*-hydroxy derivatives of diphenyloxadiazole are very low; in most cases they do not exceed 0.02, which is an order of magnitude lower than the mean φ_f value for the oxazole series.[50] It could therefore be concluded that effective intramolecular quenching of fluorescence accompanies the ESIPT reaction in the oxadiazole series.

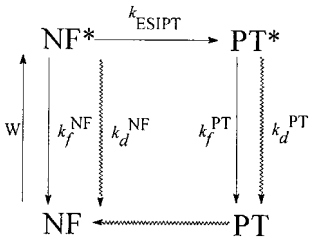
Combination of our spectral and kinetic data allows us to evaluate the ESIPT rates in the studied oxadiazole

Table 3. Rate constants of the ESIPT reaction and of radiationless decay in the phototautomer forms estimated on the basis of spectral and kinetic parameters in the series of *ortho*-hydroxy derivatives of 2,5-diphenyl-1,3,4-oxadiazole (**I–VI**) and analogous derivatives of 2,5-diphenyl-1,3-oxazole (**VII–XIII**, recalculated data from Ref. 50) in octane (oct.) and toluene (Tol.)[a]

Compound	R	Solvent	$\varphi_{fl}^{PT}/\varphi_{fl}^{NF}$	τ_{fl}^{PT} (ns)	k_{fl}^{NF} (s^{-1}) (cal.)	k_{fl}^{PT} (s^{-1}) (cal.)	k_{ESIPT} (s^{-1})	k_d^{PT} (s^{-1})
I	H	Oct.	52.5	0.18	4.0×10^8	1.4×10^8	4.1×10^{11}	5.4×10^9
		Tol.	25.0	0.30			1.8×10^{11}	3.2×10^9
II	Cl	Oct.	50.0	0.30	4.0×10^8	1.6×10^8	4.3×10^{11}	3.2×10^9
		Tol.	63.3	0.46			3.3×10^{11}	2.0×10^9
III	OCH_3	Oct.	7.7	0.29	4.1×10^8	1.5×10^8	6.5×10^{10}	3.3×10^9
		Tol.	12.5	0.42			8.1×10^{10}	2.2×10^9
IV	$N(CH_3)_2$	Oct.	1.4	0.22	4.1×10^8	1.6×10^8	1.6×10^{10} (1.7×10^{10})	4.4×10^9
		Tol.	0.44	0.26			4.5×10^9 (4.3×10^9)	3.7×10^9
V	C_6H_5	Oct.	12.4	0.45	4.7×10^8	1.7×10^8	9.7×10^{10}	2.0×10^9
		Tol.	11.2	0.67			5.8×10^{10}	1.3×10^9
VI	2-(2′-OH-phenyl)-5-CH_3-oxadiazole	Oct.	120	0.30	3.5×10^8	1.0×10^8	8.6×10^{11}	3.2×10^9
		Tol.	130	0.40			1.2×10^{12}	2.4×10^9
VII	H	Oct.	205	0.96	3.4×10^8	1.4×10^8	5.3×10^{11}	9.1×10^8
		Tol.	201	1.80			2.7×10^{11}	4.2×10^8
VIII	Cl	Oct.	120	0.91	3.4×10^8	1.4×10^8	3.1×10^{11}	9.5×10^8
		Tol.	219	1.37			3.8×10^{11}	5.9×10^8
IX	2,3,5-$(CH_3)_3$	Oct.	108	1.10	3.3×10^8	1.4×10^8	2.3×10^{11}	7.7×10^8
		Tol.	147	1.92			1.8×10^{11}	3.8×10^8
X	OCH_3	Oct.	54.2	0.66	3.4×10^8	1.4×10^8	1.8×10^{11}	1.4×10^9
		Tol.	76.9	0.98			1.8×10^{11}	8.8×10^8
XI	C_6H_5	Oct.	17.8	0.39	4.0×10^8	1.6×10^8	1.1×10^{11}	2.4×10^9
		Tol.	30.8	0.55			1.4×10^{11}	1.7×10^9
XII	β-$C_{10}H_6$	Oct.	20.6	0.45	4.3×10^8	1.6×10^8	8.7×10^{10}	4.3×10^9
		Tol.	34.2	0.97			9.0×10^{10}	2.4×10^9
XIII	2-(2′-OH-phenyl)-9,10-phenanthroxazole	Oct.	11.1	0.23	2.6×10^8	1.5×10^8	8.6×10^{11}	3.2×10^9
		Tol.	19.8	0.39			1.2×10^{12}	2.4×10^9

[a] φ_{fl}^{NF} and φ_{fl}^{PT} are fractional fluorescence quantum yields of the normal form and the phototautomer (see description in text), τ_{fl}^{PT} the phototautomer lifetime, k_{fl}^{NF} and k_{fl}^{PT} radiative rate constants of the normal form and the phototautomer, evaluated by quantum-chemical calculations (AM1 + ZINDO/S), k_{ESIPT} the ESIPT reaction rate constant (values in parentheses for compound **IV** were obtained by the alternative method[58,59]) and k_d^{PT} the rate constant of radiationless decay of the phototatutomer form.

series. Let us consider the generalized scheme of primary photophysical and photochemical processes which act in the excited state of any molecule capable of ESIPT. Several pieces of evidence in favor of the irreversibility of the ESIPT process (the basis of the following scheme) could be found in numerous reviews.[4–14]



In this scheme NF refers to the normal form and PT to the phototautomer form, W is the rate of electronic excitation, k_f (with the appropriate indices) are radiative rate constants for the normal form and the phototautomer, k_d correspond to the radiationless deactivation rate constants and k_{ESIPT} is the rate constant of the ESIPT reaction. For conditions of a photostationary state, one can deduce the following equations for fluorescence quantum yields of normal (φ_{NF}) and phototautomer (φ_{PT}) forms, which can be determined experimentally:

$$\varphi_{NF} = \frac{k_f^{NF}}{k_f^{NF} + k_d^{NF} + k_{ESIPT}} \quad (1)$$

$$\varphi_{PT} = \varphi_{NF} \cdot \frac{k_{ESIPT}}{k_f^{NF}} \cdot \frac{k_f^{PT}}{k_f^{PT} + k_d^{PT}} \quad (2)$$

The rate constant of the ESIPT reaction can be easily derived from Eqns (1) and (2) taking into account that $1/(k_f^{PT}+k_d^{PT})$ corresponds to another experimentally measurable parameter, the lifetime of the phototautomer form

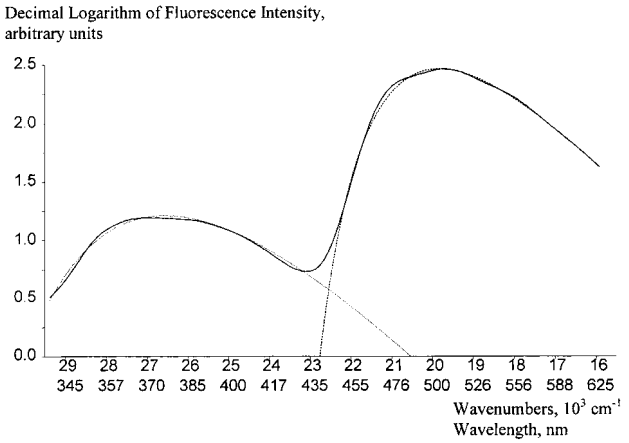


Figure 2. Example of separation of emission spectrum of compound **V** in octane into two individual fluorescence bands in semi-logarithmic representation

(τ_{PT}):

$$k_{ESIPT} = \frac{k_f^{NF}}{k_f^{PT}} \frac{\varphi_{PT}}{\varphi_{NF}} (k_f^{PT} + k_d^{PT}) \equiv \frac{k_f^{NF}}{k_f^{PT}} \frac{\varphi_{PT}}{\varphi_{NF}} / \tau_{PT} \qquad (3)$$

Owing to the fact that quantum yields, included in Eqn. (3), were measured with respect to the same absorbance value, the ratio $\varphi_{PT}/\varphi_{NF}$ can be substituted by the ratio of corresponding integral intensities. Separation of the fluorescence spectra of the investigated *ortho*-hydroxy compounds into two components is briefly described in the Experimental section. An example of the application of this procedure to the emission spectrum of compound **V** in octane (in a semilogarithmic representation) is presented in Fig. 2.

The rate constants of radiationless degradation of the energy of electronic excitation in the normal form and in the phototautomer can be estimated on the basis of their lifetime data:

$$k_d^{NF} = 1/\tau_{NF} - k_f^{NF} - k_{ESIPT} \qquad (4)$$

$$k_d^{PT} = 1/\tau_{PT} - k_f^{PT} \qquad (5)$$

One further point must also be clarified. The radiative rate constant for the normal form, k_f^{NF}, could be determined with satisfactory precision from the absorption spectra or from the quantum yield and lifetime. In contrast, the analogous value for the phototautomer, which does not exist in the ground state, k_f^{PT}, cannot be obtained from any spectral or kinetic experiment. That is why, by the analogy with our previous paper,[50] we evaluated k_f approximately for both the normal form and the phototautomer from the quantum-chemical calculations for their 'excited state optimized' planar geometries (understanding, however, that this approximation is not very precise).

The ratios of fractional quantum yields, experimental lifetimes of the phototautomer forms, k_f^{NF} values for the normal forms obtained from the absorption spectra in octane, k_f^{NF} and k_f^{PT} values obtained from the quantum-chemical calculations (AM1 excited state optimization + ZINDO/S), the rate constants of the ESIPT reaction and of radiationless decay of the phototautomer forms, evaluated by Eqns (3) and (5), are presented in Table 3. Data for acetonitrile solutions are not presented, because molecules of this solvent could form alternative hydrogen bonds with the OH groups of the investigated compounds. Such intermolecular hydrogen bonded complexes are unable to undergo the ESIPT reaction,[54,55,71] so they also must be taken in the above general scheme. Experimentally, the separate observation of such individual inter- and intramolecular hydrogen-bonded normal forms is hardly probable owing to the practically complete overlap of their emission spectra. The highest relative error of proton transfer rate constants, determined by this method, could be evaluated to be no worse than 50%, the phototautomer radiationless decay rate no worse than 30% (assuming limiting error levels for k_f values of 20% and absolute errors of lifetimes ($\leq$0.03 ns). As for quantum yield errors, we can consider them to be much lower than the 'traditional' 5–10%, because usually we substitute the quantum yield ratios by the corresponding ratios of integral fluorescence intensities, calculated from the same spectrum.

One can expect the possibility of reversible proton transfer reaction for compound **IV**, for which the fluorescence bands have comparable intensity. This circumstance urges us to apply to this compound the alternative procedure described previously.[58,59] The main idea is the simultaneous deconvolution of fluorescence decay curves not only with the excitation pulse, but also with the decay functions of the other excited species, which are present in the system. An analogous approach was used by others[72,73] in which the total fluorescence decay surface was taken into account to calculate the excited state photoreaction rates. Finally, with this method we are able to obtain not only lifetimes of all the components of the excited state reacting system, but also the kinetic rate constants of all the photoreactions between them. Moreover, this method gives statistically invalid or negative rate constants for the components which do not convert into one another in the excited state. Hence the discussed method can be used as a tool for the determination of the mechanism of the excited state chemical interaction in complicated cases, when no well-grounded choice can be made by any other methods. The main limitation of the discussed procedure is the requirement for a more or less high fluorescence intensity of the reacting species, so it cannot be applied to most of the molecules of the examined series except compound **IV**. The calculation

equations of two modifications of this method, integrational [Eqn. (6)] and derivative [Eqn. (7)], are presented in their general shape, adopted to the case of ESIPT reaction (equations for the decay of the phototautomer form are shown; the normal form decay was treated analogously); note that both discussed modifications of the method[58,59] gave similar results:

$$\frac{I_{PT}(t_2) - I_{PT}(t_1)}{\int_{t_1}^{t_2} E(t)\mathrm{d}t} = b \cdot \frac{k_f^{PT}}{S_{PT}} + k_{ESIPT} \cdot \frac{k_f^{PT} \cdot S_{NF}}{k_f^{NF} \cdot S_{PT}} \cdot \frac{\int_{t_1}^{t_2} I_{NF}(t)\mathrm{d}t}{\int_{t_1}^{t_2} E(t)\mathrm{d}t} - \frac{1}{\tau_{PT}} \cdot \frac{\int_{t_1}^{t_2} I_{PT}(t)\mathrm{d}t}{\int_{t_1}^{t_2} E(t)\mathrm{d}t} \quad (6)$$

$$\frac{\mathrm{d}I_{PT}(t)}{\mathrm{d}t} = E(t) \cdot b \cdot \frac{k_f^{PT}}{S_{PT}} + k_{ESIPT} \cdot \frac{k_f^{PT}}{k_f^{NF}} \cdot \frac{S_{NF}}{S_{PT}} \cdot I_{NF}(t) - \frac{1}{\tau_{PT}} \cdot I_{PT}(t) \quad (7)$$

where $I_{NF}(t)$ and $I_{PT}(t)$ are the fluorescence decay functions for the normal form and phototautomer (in their emission maxima), $E(t)$ the excitation pulse, S_{NF} and S_{PT} the integral intensities of the normalized fluorescence bands of the corresponding forms, b the instrument constant, which depends on the absorption of the excitation pulses by the investigated compounds ($b = 0$ for the phototautomer form and for all species which exist only in the excited state) and t_1 and t_2 are time integration limits. Usually integration and differentiation of decay curves were made numerically by the trapezium equations and by the Savitzky–Golay[74] method. All the kinetic curves were smoothed numerically[74] before their treatment by Eqns (6) and (7) with the linear multiparameter least-squares method.

Treatment of time-resolved fluorescence data of compound **IV** in octane and toluene by the reported method[58,59] allowed us to exclude the possibility of the backward ESIPT process (i.e. phototautomer* → normal form*) for this compound, because the corresponding rate constants were statistically invalid. From the other side, both approaches, Eqn. (3) and Eqns (6) and (7), give close results for this case (Table 3). This was additional confirmation of our statement about the irreversibility of the ESIPT process for compound **IV** and also for the other molecules investigated in this work.

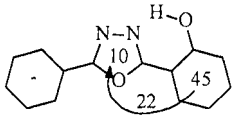
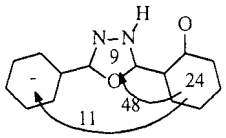
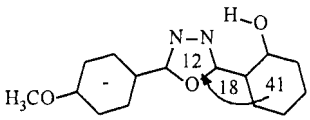
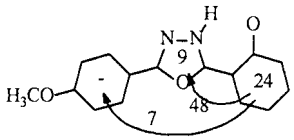
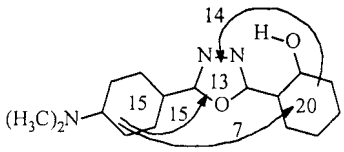
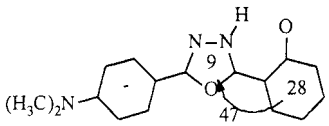
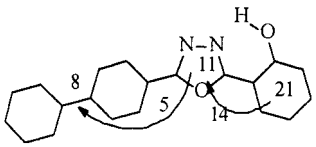
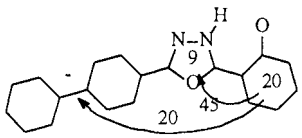
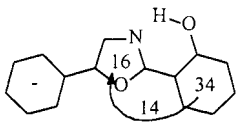
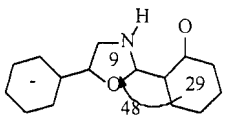
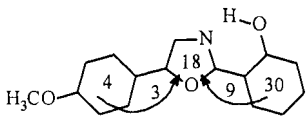
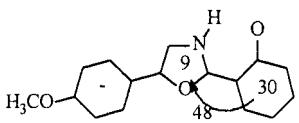
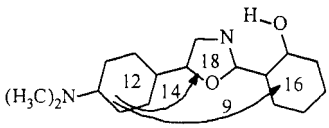
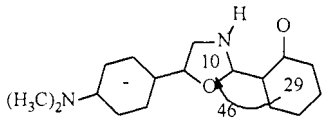
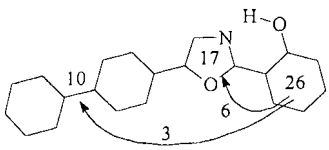
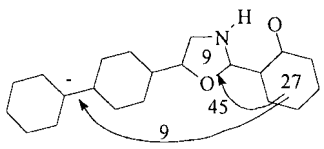
Based on the kinetic data obtained, the assumption could be made that proton phototransfer is the fastest, and correspondingly the main radiationless process of the normal form. The very low intensities of normal form fluorescence bands compared with those of the phototautomer are in agreement with this statement. Therefore, we do not consider any other valid radiationless losses in the normal form, except for the ESIPT reaction. This assumption is also supported, for example, by ESIPT process investigations in the series of *ortho*-acylamino derivatives of anthraquinone,[34–36] etc.

As one can see, the rates of proton phototransfer reaction in the oxadiazole series do not differ substantially from the derivatives of oxazole studied previously[50] (**VII–XIII**), which are also presented in Table 3. Hence the mentioned difference in basicity does not affect the rate of ESIPT significantly on changing the oxazole ring for the oxadiazole ring. However, a certain distinction between these two series of *ortho*-hydroxy molecules is typical for electron-donor substituted compounds. A noticeable decrease of the ESIPT rate constants under the influence of donor substituents introduced into the 5-phenyl radical was found both for the oxazole and oxadiazole derivatives. However, in contrast to the $N(CH_3)_2$-substituted *o*-hydroxydiphenyloxazole, for which no ESIPT reaction was observed at all, the corresponding representative of the oxadiazole series has two-banded fluorescence spectra. This is evidence of proton phototransfer. However, the estimated rate constant of the ESIPT reaction for this molecule is the smallest of those observed for all the compounds discussed here.

To clarify the reasons for such behavior, quantum-chemical calculations of the spectra and the excited state electron density redistribution were carried out for the investigated compounds. The special quantum-chemical indices (local CT) numbers are presented on the molecular diagrams in Table 4 within the corresponding fragments (normally, separate rings of the studied molecules). Interfragmental CT numbers are placed on the arrows, which show the directions of intramolecular charge transfer.

Let us consider the data for the normal forms presented in Table 4, starting from the studied earlier derivatives of oxazole. The main direction of charge redistribution in the excited molecule **VII** is from the *ortho*-hydroxy-substituted benzene ring containing the heterocycle. In terms of acid–base interactions this results in an increase in the acidity of the hydroxy group (the proton donor), and, correspondingly, in an increase in the basicity of the oxazole ring (the proton acceptor). Such coordinated

Table 4. Calculated characteristics [energies of electronic transitions (cm^{-1}), localization of the electronic excitation and charge redistribution in the S_1* state, π-electron approximation PPP CI] of the normal and phototautomer forms in the series of *ortho*-hydroxy derivatives of 2,5-diphenyloxazole and 2,5-diphenyl-1,3,4-oxadiazole[a]

	Normal form				Phototautomer form	
Compound	$\nu_{S_0}-S_1$	Δq_N	Δq_O	Charge transfer indices	$\nu_{S_0}-S_1$	Charge transfer indices
I	30550	−0.033	+0.196		21310	
III	30450	−0.033	+0.178		21560	
IV	29230	−0.020	+0.087		21590	
V	30930	−0.003	+0.149		20970	
VII	29760	−0.049	+0.152		21570	
X	29500	−0.053	+0.129		21660	
XIV	28100	−0.053	+0.062		21590	
XI	30545	−0.033	+0.196		21310	

[a] Δq_N and Δq_O are changes of π-charges on the nitrogen atom of the heterocycle and on the oxygen atom of the hydroxy group of normal forms in their excited states compared with the corresponding ground states.

changes of acid–base properties of the groups, connected to one another by an intramolecular hydrogen bond, constitute the driving force of the excited state proton transfer reaction.

At first sight, the benzene ring in position 5 of the heterocycle may be expected to have a minor influence on the rate of the ESIPT reaction. It hardly takes part in the main redistribution of electron density. The total localization of electron excitation on it is low. However, after the introduction of donor substituents into the 5-phenyl ring, its role in the charge redistribution and also its influence on the proton phototransfer reaction rate have a tendency to increase. Thus, when a methoxy group is introduced into the *para* position, nearly a 1.5-fold

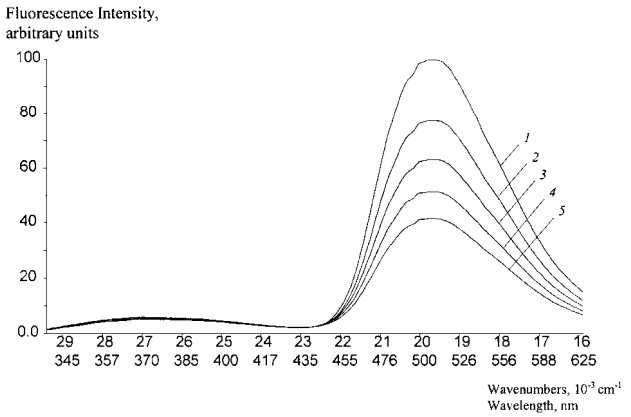


Figure 3. Fluorescence spectra of compound **V** in toluene at different temperatures (1, 298; 2, 308; 3, 318; 4, 328; 5, 338 K)

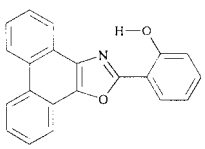
decrease in charge transfer from the —C_6H_4OH fragment to the heterocycle occurs. The decrease of the estimated ESIPT rate constant has nearly the same value. The stronger electron donor substituent, the —$N(CH_3)_2$ group, practically disables the movement of electron density from the —C_6H_4OH fragment to the heterocycle. Moreover, a definite amount of electron density is transferred in this case to the —C_6H_4OH fragment, making the excited state dissociation of its hydroxy group less probable than in the ground state. As a result, no ESIPT reaction was observed experimentally for 2-(2′-OH-phenyl)-5-(4″-$N(CH_3)_2$-phenyl)oxazole in solvents of different polarity and protolytic ability,[50] in polymer films and in the crystalline state. Based on these results, as also in our earlier publication,[50] we draw a conclusion about the determining influence of the increase of proton donor group acidity on the rate constant of the ESIPT reaction.

The replacement of the more basic oxazole ring by the less basic but more electron acceptor oxadiazole ring changes the situation. The efficiency of charge transfer increases by a 1.5-fold (compare structures **I** and **VII**). The mean increase in the hydroxy group acidity, which could be predicted from the change of charge on the hydroxylic oxygen, Δq_O, might exceed the corresponding value for its oxazole analog by approximately 25–30%. However, the relatively lower basicity of the oxadiazole ring determines nearly the same ESIPT rates for unsubstituted representatives of both investigated series of compounds.

At first sight, the donor substituents appear to behave similarly in the series of *ortho*-hydroxy derivatives of diphenyloxazole and oxadiazole: the decrease in the ESIPT rate constant was observed for the OCH_3-substituted compound **III**. However, the most noticeable difference in properties between the oxazole and the oxadiazole series was found for the $N(CH_3)_2$-substituted compounds **IV** and **XIV**. As in the case of the corresponding derivative of oxazole, an intense charge transfer from the —$C_6H_4N(CH_3)_2$ fragment to the heterocycle and also to the —C_6H_4OH fragment was observed. Although the electron-accepting ability of the oxadiazole ring is higher, the removal of electron density from the —C_6H_4OH fragment is retained fairly effectively. This is the main reason why the ESIPT reaction is still observed for the dimethylamino-substituted oxadiazole derivative **IV**. However, in this case the proton transfer reaction is the slowest among the two discussed series of compounds.

As in the previous case,[50] here we also make an attempt to evaluate the activation energies of the ESIPT reaction and the radiationless deactivation of the phototautomer. The temperature dependences of the fluorescence spectra and kinetics were studied for the biphenyl compound **V**, which is more or less similar in structure and spectral properties to the previously studied *ortho*-hydroxy derivative of 2-phenyl-9,10-phenanthroxazole.[50] The fluorescence spectra of compound **V** at temperatures from 25 to 65 °C are presented in Fig. 3 and the corresponding spectral and kinetic data are summarized in Table 5. If we choose an Arrhenius treatment for the investigated derivatives of oxazole and oxadiazole, a conclusion can be drawn that in both cases the ESIPT

Table 5. Spectral and kinetic parameters of compound **V** at different temperatures in toluene[a]

T(K)	$\varphi_{PT}/\varphi_{NF}$	τ_{PT} (ns)	k_{ESIPT} (S^{-1})	ESIPT	k_d^{PT} (s^{-1})	Radiationless degradation
298	10.2	0.64	4.3×10^{10}		1.4×10^9	
308	8.1	0.50	4.4×10^{10}	$\Delta E_{act} = 0.4 \pm 0.1$	1.8×10^9	$\Delta E_{act} = 4.4 \pm 0.4$
318	6.8	0.41	4.5×10^{10}	$(\Delta H^{\neq} = -0.2 \pm 0.2)$	2.3×10^9	$\Delta H^{\neq} = 3.8 \pm 0.4$
328	5.7	0.34	4.6×10^{10}	$\Delta S^{\neq} = -10.8 \pm 1.0$	2.8×10^9	$\Delta S^{\neq} = -4.0 \pm 1.0$
338	4.8	0.28	4.7×10^{10}		3.4×10^9	
 2-(2′-OH-phenyl)-9,10-phenanthroxazole (**XIII** recalculated data from Ref. 50)				$\Delta E_{act} = 0.7 \pm 0.2$ $(\Delta H^{\neq} = 0.1 \pm 0.2)$ $\Delta S^{\neq} = -8.1 \pm 0.6$		$\Delta E_{act} = 3.7 \pm 0.4$ $\Delta H^{\neq} = 3.1 \pm 0.4$ $\Delta S^{\neq} = -5.4 \pm 1.2$

[a] ΔE_{act} and $\Delta H^{\neq}$ values are in kcal mol^{-1} and $\Delta S^{\neq}$ values are in entropy units, cal mol^{-1} K^{-1}). Values in parentheses are 'statistical zero' values. All confidence intervals are given for the level of 95%.

reaction has very low, but in principle measurable, activation barriers (0.7 and 0.4 kcal mol^{-1}, respectively). However, if we consider the temperature data on the basis of Eyring' transition state theory, we can find that in both cases the ESIPT reaction is a practically barrierless process ($\Delta H^{\neq} \approx 0$). $\Delta S^{\neq}$, the entropy change during the proton phototransfer, was also found to be low. This may be attributed to the relatively small structural changes, such as intramolecular movement of one hydrogen atom, accompanied also by definite deformation of the molecular skeleton.[75,76] In contrast to ESIPT, radiationless deactivation of the excited phototautomer form has certain Arrhenius' activation barrier, ca 4 kcal/ mol^{-1}.

It is interesting that $\Delta S^{\neq}$ changes in this case are even slightly lower than that for the ESIPT process. Such a difference may be explained from the fact that intramolecular fluorescence quenching is connected with structural changes, which are even smaller than those of the ESIPT reaction. In our opinion, this result contradicts the TICT concept (twisted intramolecular charge-transfer states formation), very popular in recent years, in its application to ESIPT molecules. According to this, the main mechanism of radiationless deactivation of the excited phototautomer includes high-amplitude intramolecular motions and formation of non-planar biradicaloid non-luminescent TICT-like states.[27,77,78] In fact, there are many examples of ESIPT molecules for which TICT state formation is structurally impossible (flavonols, anthraquinones, several 'fixed' molecules[49]), but their quantum yields are low.

It could also be noted that for the oxazole series the efficiency of intramolecular quenching in the phototautomer forms displays a tendency to increase for compounds with electron acceptor substituents in the 5-phenyl group. This is typical also for compounds in which this phenyl radical is substituted for fragments with an extended π-conjugated system, such as biphenyl and naphthyl. The radiationless decay rate of oxadiazolic phototautomer forms is higher than that for the oxazole series and seems to be practically independent of the molecular structure. With the aim of finding any possible explanation for such behavior, we calculated the redistribution of electron density for the products of the ESIPT reaction, excited phototautomer forms, belonging to the oxazole and oxadiazole series. These results are also presented in Table 4. Based on these, it can be concluded that the efficiency of quenching might be connected with the redistribution of electron density from the —C_6H_4—O fragment of the phototautomer to the protonated heterocycle and the rest of the molecule. At this point, we should mention the fact that several decades ago electron transfer, followed immediately after the act of proton transfer, was already considered to be among the main reasons for the low fluorescent ability of molecules and molecular complexes capable of ESIPT.[8] Such electron transfer results in the formation of non-fluorescent biradicaloid structures. In fact, proton-assisted electron transfer became a subject of interest in several recent publications, e.g. Ref. 79. Numerous research groups interpreted effective radiationless decay in the phototautomer in terms of TICT state formation.[34,35,49,78] In spite of our sceptical attitude to this approach, let us note that TICT formation is also usually associated with, and is always initiated by, the primary noticeable separation of charges in the initially planar excited molecule.

One can see from the data in Table 4 that the phototautomer forms of the oxadiazole series differ from their oxazole analogs by the additional charge transfer from the —C_6H_4—O fragment to the phenyl radical in position 5 of the heterocycle. This result is in agreement with the higher efficiency of radiationless decay in the oxadiazole series. The electron acceptor substituents introduced into the 5-phenyl fragment must increase the efficiency of the discussed charge redistribution. The analogous increase of the discussed charge transfer in the phototautomer forms was also observed for biphenyl and naphthalene derivatives of *o*-hydroxydiphenyloxazole. In this paper we have already mentioned the fact that substituents of different electronic nature influence dramatically the rate constant of the ESIPT reaction in the series of *ortho*-hydroxy derivatives of oxazole and oxadiazole. It seems to us logical to assume the analogous influence of molecular structure on the radiationless deactivation of the excited phototautomer form. Thus, any structural modifications of ESIPT molecules, which could prevent the above-discussed charge transfer in phototautomer forms, might result in a decrease of their radiationless deactivation efficiency.

Some arguments in favor of the above assumption were found during the analysis of spectral properties of compound **XV**:

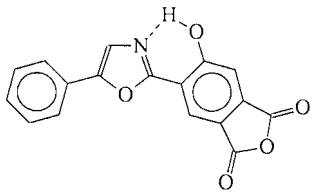


Table 6. Spectral and kinetic parameters of compound **XV** in toluene and acetonitrile[a]

Solvent	ν_{abs} (cm^{-1})	ν_{fl}^{PT} (cm^{-1})	$\Delta\nu_{ST}^{PT}$ (cm^{-1})	τ_{fl} (ns)	φ_{fl}
Toluene	29480	20340	9140	4.76	0.40
Acetonitrile	30260	20440	9820	5.19	0.45

[a] Data for octane are not presented owing to the very low solubility of compound **XV** in this solvent.

Owing to the presence of strong electron-accepting groups in the proton donor 'phenolic' part of this molecule, the rate of ESIPT for **XV** is out of the range that we can evaluate with our spectral and kinetics devices. We failed to find even traces of normal-form fluorescence in this case. On the other hand, the unusually high fluorescence intensity and unusually slow fluorescence decay of the phototautomer form are typical of compound **XV** (Table 6). We can describe such behavior by the following scheme: the presence of two strong electron-accepting C═O groups in close proximity to and one of them, in direct conjugation with the proton donor center, makes the excited state dissociation of the OH group more probable in comparison with the other *ortho*-hydroxy compounds **I–XIV**. That is why the ESIPT rate of **XV** is the highest among the examined series. Further, in this case, the excessive electron density, which is formed immediately after the act of proton transfer, does not delocalize towards the protonated heterocycle and aromatic rings in the 5-position. It moves to the strong acceptor center, composed of two carbonyls and an oxygen bridge atom between them. No or much less electron density is redistributed to the heterocycle in this case, so the probability of a radiationless process, which might be connected with the charge transfer in this direction, becomes low. As a result, experimentally we observe both an increase in ESIPT rate and an increase in fluorescence quantum yield of phototautomer form of compound **XV**. Further steps towards confirmation of the above hypothesis, including the synthesis and examination of photophysical properties of compounds having strong electron acceptor substituents in proton donor fragments of ESIPT molecules, will be the subject of future publications.

CONCLUSION

The proton phototransfer reaction is the most efficient primary photoprocess in the series of *ortho*-hydroxy derivatives of 2,5-diphenyl-1, 3-oxazole and 1,3-oxadiazole. With rate constants of 10^{11}–10^{12} s^{-1} it exceeds the rates of other primary photophysical processes in these molecules by to 2–3 orders of magnitude. A connection between the rate of the ESIPT reaction and the electron density redistribution on electronic excitation was revealed for the molecules under study. Electron donor substituents in the 5-phenyl group decrease the proton phototransfer rate constant up to its complete inhibition in the case of the dimethylamino derivative in the oxazole series. The determining role of the excited state increase of proton donor group acidity was assumed on the basis of our data.

The ESIPT reaction in the series of *ortho*-hydroxy derivatives of 2,5-diphenyloxazole and 2,5-diphenyl-1,3,4-oxadiazole has practically no activation barrier. However, the radiationless processes in the phototautomer form are characterized by the presence of certain barriers in both series examined.

A possible connection between the character of the electronic density redistribution in the excited phototautomer form and the efficiency of radiationless decay has been assumed. This opens up a possible way to increase the total fluorescence efficiency of ESIPT molecules by their purposeful structural modification.

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REFERENCES

1. Vollmer F, Rettig W, Birckner E. *J. Fluorescence* 1994; **4**: 65–69.
2. Birks JB. *The Theory and Practice of Scintillation Counting*. Pergamon Press: Oxford, 1967.
3. Lakowicz JR. *Principles of Fluorescence Spectroscopy*. Plenum Press: New York, 1983.
4. Weller A. *Prog. React. Kinet.* 1961; **1**: 188–214.
5. Ireland JF, Wyatt PAH. *Adv. Phys. Org. Chem.* 1976; **12**: 131–211.
6. Klöpffer W. *Adv. Photochem.* 1977; **10**: 311–358.
7. Martynov UY, Demyashkecich AB, Uzhinov BM, Kuzmin MG. *Russ. Chem. Rev.* 1977; **46**: 1–31.
8. Krasheninnikov AA, Shablia AV, Ermolaev VL. *Spectroscopy of Phototransformations in Molecules*. Nauka: Leningrad, 1977; 46–61. (in Russian).
9. Kasha M. *J. Chem. Soc., Faraday Trans. 2* 1986; **82**: 2379–2392.
10. Formosinho SJ, Arnaut LG. *J. Photochem. Photobiol. A: Chem.* 1993; **75**: 1–20.
11. Formosinho SJ, Arnaut LG. *J. Photochem. Photobiol. A: Chem.* 1993; **75**: 21–48.
12. Ormson SM, Brown RG. *Prog. React. Kinet.* 1994; **19**: 45–91.
13. Le Gourrierec D, Ormson SM, Brown RG. *Prog. React. Kinet.* 1994; **19**: 211–275.
14. Douhal A, Lahmani F, Zewail AH. *Chem. Phys.* 1996; **207**: 477–498.
15. Martynov IY, Uzhinov BM, Kuzmin MG. *Khim. Vys. Energ.* 1977; **11**: 443–447.
16. Heller A, Williams DL. *J. Phys. Chem.* 1970; **74**: 4473–4480.
17. Shizuka H, Matsui K, Hirata Y, Tanaka I. *J. Phys. Chem.* 1977; **81**: 2243–2246.
18. Acuna AU, Amat-Guerri F, Catalan J, Gonzalez-Tablas F. *J. Phys. Chem.* 1980; **84**: 629–631.
19. Catalan J, Toribio F, Acuna AU. *J. Phys. Chem.* 1982; **86**: 303–306.
20. Toribio F, Catalan J, Amamt F, Acuna AU. *J. Phys. Chem.* 1983; **87**: 817–822.
21. Mordzinski A, Grabowska A, Kuhnle W, Krowszynski A. *Chem. Phys. Lett.* 1983; **101**: 291–296.
22. Shabestary N, El-Bayomi MA. *Chem. Phys. Lett.* 1984; **106**: 107–110.
23. Sanchez-Cabezudo M, De Paz JLD, Catalan J, Amat-Guerri F. *J. Mol. Struct.* 1985; **131**: 277–289.
24. Acuna AU, Toribio F, Amat-Guerri F, Catalan J. *J. Photochem.* 1985; **30**: 339–352.
25. Shizuka H, Machii M, Higaki Y, Tanaka M, Tanaka I. *J. Phys. Chem.* 1985; **89**: 320–326.
26. Strandjord AJG, Smith DE, Barbara PF. *J. Phys. Chem.* 1985; **89**: 2362–2366.
27. Woessner G, Goeller G, Rieker J, Hoier H, Stezowski JJ, Daltozzo E, Neureiter M, Kramer HEA. *J. Phys. Chem.* 1985; **89**: 3629–3636.

28. Bulska H, Grabowska A, Grabowski ZR. *J. Lumin.* 1986; **35**: 189–197.
29. Itoh M, Fujiwara Y, Sumitani M, Yoshihara K. *J. Phys. Chem.* 1986; **90**: 5672–5678.
30. Bigger SW, Ghiggino KP, Leaver IH, Scully AD. *J. Photochem. Photobiol. A: Chem.* 1987; **40**: 391–399.
31. Gormin D, Kasha M. *Chem. Phys. Lett.* 1988; **153**: 574–576.
32. Gormin D. *J. Phys. Chem.*, 1989; **93**: 5979–5980.
33. Heldt J, Gormin D, Kasha M. *J. Chem. Phys.* 1989; **136**: 321–334.
34. Smith TP, Zaklika KA, Thakur K, Barbara PF. *J. Am. Chem. Soc.*, 1991; **113**: 4035–4036.
35. Smith TP, Zaklika KA, Thakur K, Walker GC, Tominaga K, Barbara PF. *J. Phys. Chem.* 1991; **95**: 10465–10475.
36. Smith TP, Zaklika KA, Thakur K, Walker GC, Tominaga K, Barbara PF. *J. Photochem. Photobiol. A: Chem.* 1992; **65**: 165–175.
37. Rieker J, Lemmeri-Schmitt E, Goeller G, Roessler M, Stueber GJ, Schettler H, Kramer HEA, Stezowski JJ, Hoier H, Henkel S, Schmidt A, Port H, Wiechmann M, Rody J, Rytz G, Slongo M, Birbaum J-L. *J. Phys. Chem.* 1992; **96**: 10225–10234.
38. Mitra S, Das R, Mukherjee S. *Chem. Phys. Lett.* 1993; **202**: 549–554.
39. Chou PT, Martinez ML, Clements JH. *Chem. Phys. Lett.* 1993; **204**: 395–399.
40. Ormson SM, Brown RG, Vollmer F, Rettig W. *J. Photochem. Photobiol. A: Chem.*, 1994; **81**: 65–72.
41. Chou PT, Ming C, Clements JH, Martinez ML, Chang CP. *Chem. Phys. Lett.* 1994; **220**: 229–234.
42. Kaufmann JM, Litak PT, Boyko WJ. *J. Heterocycl. Chem.* 1995; **32**: 1541–1555.
43. Nagaoka S, Nagashima U. *Chem. Phys. Lett.* 1996; **206**: 353–362.
44. Nagaoka S, Shinde Y, Mukai K, Nagashima U. *J. Phys. Chem.* 1997; **101**: 3061–3065.
45. Lahmani F, Zehnacker-Rentien A. *J. Phys. Chem.* 1997; **101**: 6141–6147.
46. Tibita S, Yamamoto M, Kurahayashi N, Tsukagoshi R, Nakamura Y, Shizuka H. *J. Phys. Chem. A* 1998; **102**: 5206–5214.
47. Borowicz P, Grabowska A, Les A, Kaczmarek L, Zagrodski B. *Chem. Phys. Lett.* 1998; **291**: 351–359.
48. Cuma M, Thompson C, Scheiner S. *J. Comput. Chem.* 1998; **19**: 129–138.
49. LeGourrierec D, Kharlanov V, Brown RG, Rettig W. *J. Photochem. Photobiol. A: Chem.* 1998; **117**: 209–216.
50. Doroshenko AO, Posokhov EA, Shershukov VM, Mitina VG, Ponomarev OA. *High Energy Chem.* 1997; **31**: 428–435 (in Russian).
51. Tandon SK, Dovel DS, Shanker K, Sinke JK. *Pharmazie* 1982; **37**: 388–389.
52. Sharma BL, Tandon SK. *Pharmazie* 1984; **39**: 858–859.
53. Gordon AJ, Ford RA. *The Chemist's Companion*. John Wiley & Sons: New York, 1972.
54. McMorrow D, Kasha M. *J. Am. Chem. Soc.* 1983; **105**: 5133–5134.
55. McMorrow D, Kasha M. *J. Phys. Chem.* 1984; **88**: 2235–2243.
56. Melhuish WH. *J. Phys. Chem.* 1961; **65**: 229–235.
57. Siano DB, Metzler DE. *J. Chem. Phys.* 1969; **51**: 1856–1861.
58. Ponomarev OA, Doroshenko AO, Mitina VG. *Khim. Fiz.* 1989; **8**: 1369–1376 (*Russ*.).
59. Doroshenko AO, Kirichenko AV, Mitina VG, Ponomarev OA. *J. Photochem. Photobiol. A: Chem.* 1997; **94**: 15–26.
60. Ware WR, Doemeny LJ, Nemzek TL. *J. Phys. Chem.* 1973; **77**: 2038–2048.
61. Grinvald A, Steinberg IZ. *Anal. Biochem.* 1974; **59**: 583–598.
62. Basharin SK, Gachko GA, Kivach LN, Maskevich SA, Maskevich AA, Udovydchenko BP. *Zh. Prikl. Spektrosk.* 1990; **52**: 48–53.
63. Dewar MJS, Zoebich EG, Healy EF, Stewart JJ. *J. Am. Chem. Soc.* 1985; **107**: 3902–3909.
64. Ridley JE, Zerner MC. *Theor. Chim. Acta* 1973; **32**: 111–124.
65. Parker CA. *Photoluminescence of Solutions*. Elsevier: Amsterdam, 1968.
66. Parr RG. *Quantum Theory of Molecular Electronic Structure*. W.A. Benjamin: New York, 1964.
67. Nishimoto K, Mataga N. *Z. Phys. Chem.* 1957; **12**: 335–339.
68. Griffits J. *Dyes Pigments* 1982; **3**: 211–233.
69. Luzanov AV. *Usp. Khim.* 1980; **69**: 2086–2117.
70. Murthy ASN, Rao CNR. *Appl. Spectrose. Rev.*, 1968; **2**: 69–101.
71. Denisov GS, Golubev NS, Schreiber VM, Shajakhmetov SS, Shurukhina AV. *J. Mol. Struct.* 1997; **437**: 153–160.
72. Bechem JM, Ameloot M, Brand L. *Chem. Phys. Lett.* 1985; **120**: 466–472.
73. Ameloot M, Bechem JM, Brand L. *Chem. Phys. Lett.* 1986; **129**: 211–219.
74. Savitzky A, Golay MJE. *Anal. Chem.* 1967; **37**: 1627–1639.
75. Sekiya H, Habu M, Ujita H, Tsuji T, Mori A, Takeshita H, Nishimura Y, Petek H, Yoshihara K. *Chem. Phys. Lett.* 1993; **215**: 641–648.
76. Scully AD, Bigger SW, Ghiggino KP, Vogl O. *J. Photochem. Photobiol. A: Chem.* 1991; **55**: 387–393.
77. Potter CAS, Brown RG, Vollmer F, Rettig W. *J. Chem. Soc., Faraday Trans.* 1994; **90**: 59–67.
78. Vollmer F, Rettig W. *J. Photochem. Photobiol. A: Chem.* 1996; **95**: 143–155.
79. Del Re G, Brahimi M, Peluso A. *Chem. Phys. Lett.* 1999; **299**: 511–517.