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INTRAMOLECULAR PHOTOTRANSFER OF PROTONS AND THE QUENCHING OF FLUORESCENCE OF DERIVATIVES OF 2-(COUMARINYL-3)-5-(*ortho*-HYDROXYPHENYL)-1,3,4-OXADIAZOLE

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The spectral-luminescence properties of ortho-hydroxy derivatives of 2-(coumarinyl-3)-5-phenyl-1,3,4-oxadiazole have been studied. It is shown that the basic reason for the decreased quantum yield of emission for the compounds studied is the high-speed phototransfer of a proton (estimated as ~10^9 s^{-1}). Fluorescence of the products of this reaction (phototautomers) was not observed. It was confirmed by quantum-chemical calculations that the increase in efficiency of nonradiative dissipation of the electron excitation energy in phototautomeric forms of ortho-hydroxycoumarinyloxadiazoles is explained by an increase in intramolecular donor-acceptor interaction on introduction of the coumarin unit into the molecule. As a result of the high efficiency of nonradiative deactivation of the excited state, the ortho-hydroxyderivatives studied have promise as UV photostabilizers in polymeric materials.

Keywords: 2-(coumarinyl-3)-5-(*ortho*-hydroxyphenyl)-1,3,4-oxadiazole, intramolecular proton transfer, extinction of fluorescence.

Intramolecular phototransfer of protons (IMPTP) is one of the most thoroughly studied adiabatic photochemical processes [1-3], interest in which has scarcely decreased in more than 40 years [4-8]. This results not only from the importance of this process in the chemistry of the excited state and photobiology, but also from the range of technical applications in which IMPTP can be used (we mention only photochromic materials based on IMPTP molecules [9], organic scintillators [10, 11], photostabilisation of polymeric materials by protecting them from the ultraviolet radiation [12, 13], components of the active media of lasers in organic luminophores [14-16], concentrators of solar energy [17], etc.).

The principal structural factor necessary for IMPTP is the presence in an organic molecule of conjugated electron donor and electron acceptor groups, linked by an intramolecular hydrogen bond. If on transition to the excited state the acidity of the proton donor group and the basicity of the electron acceptor group are increased, conditions are created for phototransfer of a proton between them. The product of the IMPTP reaction (a phototautomeric form) is characterized by the existence of a more longwave emission spectrum and an anomalously large Stokes shift of the fluorescence in comparison with the intrinsic initial "normal" (or enolic) form. As a rule IMPTP is accompanied by efficient nonradiative dispersion of the electron excitation energy emanating principally in the phototautomeric form [3-5, 18-20]. As a result quantum yields for

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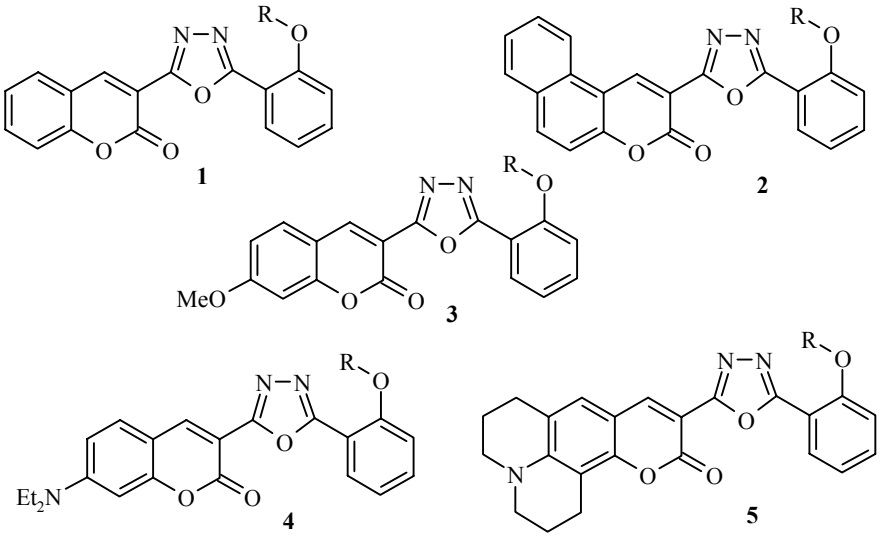
the fluorescence of IMPTP molecules seldom exceed 0.2, and in most cases they are at the level of a few percents. However, for one of the important technical applications of intramolecular phototransfer of protons – photostabilisation of polymeric materials – effective quenching of the excited state formed plays a determining role.

The objectives of our preceding work were *ortho*-hydroxy derivatives of 2,5-diphenyloxazole [18, 19] and 2,5-diphenyl-1,3,4-oxadiazole [20], for which the connection between the intramolecular redistribution of electron density on transfer to the excited state and the efficiency of IMPTP was described, and also extinction of fluorescence in the phototautomeric form.

In this paper *ortho*-hydroxy derivatives of 2-(coumarinyl-3)-5-phenyl-1,3,4-oxadiazole (**1a-5a**, R = H) and the corresponding methoxy derivatives (**1b-5b**, R = Me) will be discussed as model compounds.



Substitution of one of the benzene rings in *ortho*-hydroxydiphenyloxadiazole with an electron-acceptor coumarin unit should lead not only to an increase in the size of the π-conjugated system of the molecule but also to a notable increase in the strength of the intramolecular donor-acceptor interaction as, for example in the cases we have described [21]. This, in its turn, produces an important change in the spectral characteristics which to a considerable extent determine the IMPTP process and is connected with the subsequent nonradiative dissipation of the electron excitation energy.

The hypothesis that the intramolecular donor-acceptor interaction is strengthened in the coumarinyloxadiazole series is confirmed with the example of compound **1b** for which the effect of the solvent on the spectral characteristics and the dipole moment in the excited state have been estimated (Table 1). The choice of this molecule (the methoxy derivative which is not substituted in the coumarin nucleus) and the group of solvents used is explained by the desire to avoid the effect of specific intra- and intermolecular interactions, therefore we excluded such polar proton-donor solvents as water, ethanol, formamide, etc. The molecular parameters required to estimate the nature of the intramolecular electron density redistribution by N. G. Bakshiev's modification of the method of spectral shifts [22, 23] (radius of the Onsager cavity (~7.2 Å) and the ground state dipole moment (~3.9 D) were determined in the AM1 semiempirical quantum-chemical approximation [24].

TABLE 1. Spectral-luminescent Characteristics* of 2-(Coumarinyl-3)-5-(2-methoxyphenyl)-1,3,4-oxadiazole (**1b**) in Aprotic Solvents with Different Polarities

Solvent	ε	*n*	ν_a	ν_f	$\Delta\nu_{ST}$	φ_f	τ_f	k_f	k_d
Dioxane	2.21	1.4224	29220	21950	7270	0.56	2.62	$2.1\cdot10^8$	$1.7\cdot10^8$
Benzene	2.28	1.5011	28500	22110	6390	0.46	2.24	$2.1\cdot10^8$	$2.4\cdot10^8$
Toluene	2.38	1.4961	28640	22180	6460	0.54	2.60	$2.1\cdot10^8$	$1.8\cdot10^8$
Xylene	2.57	1.5055	28620	22020	6600	0.56	2.34	$2.4\cdot10^8$	$1.9\cdot10^8$
Chloroform	4.70	1.4459	29400	21980	7420	0.54	2.73	$2.0\cdot10^8$	$1.7\cdot10^8$
Butyl acetate	5.01	1.394	29040	21940	7100	0.62	3.13	$2.0\cdot10^8$	$1.2\cdot10^8$
Ethyl acetate	6.02	1.3723	29080	21850	7230	0.55	3.12	$1.8\cdot10^8$	$1.4\cdot10^8$
Methylene chloride	8.90	1.4242	28620	21950	6670	0.54	2.73	$2.0\cdot10^8$	$1.7\cdot10^8$
Acetonitrile	36.2	1.3441	29280	21110	8170	0.48	3.42	$1.4\cdot10^8$	$1.5\cdot10^8$
Dimethylformamide	36.7	1.4303	29020	20400	8620	0.28	2.04	$1.4\cdot10^8$	$3.5\cdot10^8$

* ε and *n* are the dielectric permeability and refractive index of the solvent; ν_a, ν_f, and $\Delta\nu_{ST}$ are the positions of the maxima in the absorption and fluroescence spectra, and the Stokes shift of the fluorescence (cm^{-1}), φ_f is the quantum yield for fluorescence, τ_f is the fluroescence life time (ns), k_f and k_d are the rate constants for the initial photophysical processes, emission of fluorescence and nonradiative deactivation of the excited state (s^{-1}), calculated from the relations $k_f = \varphi_f/\tau_f$ and $k_d = (1 - \varphi_f)/\tau_f$.

It can be seen from the data cited in Table 1 that compound **1b** has relatively high quantum yields for luminescence which are not reduced much in solvents of high polarity. The extinction time for fluorescence is also relatively large and is no less than 2 ns even in highly polar solvents. These facts indicate the absence of any serious deactivating influence of the $n\pi^*$-states, introduced into the system of terms of this molecule with the introduction of the coumarin unit, on the spectral-luminescent characteristics of the molecules studied. Evidently the triplet levels of $n\pi^*$-type, localized on the carbonyl group of the coumarin lie at considerably greater energy than the lower singlet excited sate of molecules **1-5** (**a,b**) and intersystem conversion cannot occur concurrently with fluorescence at room temperature. It is possible that the efficiency of intersystem conversion in conditions of thermal activation would be increased, leading to a decrease in quantum yield and mission life time, however detailed study of this is outside the realms of the current work.

The Stokes shifts of the fluorescence of compound **1b** is quite large even in nonpolar solvents which may be interpreted as an indication of a change in conformation of this molecule in the excited state. However, the reason might also be redistribution of the intensities of the individual vibrational components in the emission spectrum, explained analogously in our previous discussion [25] with respect to the increased Stokes shift of unsubstituted 2,5-diphenyl-1,3,4-oxadiazole in comparison with their oxazole analogs.

The estimates of the values of the dipole moment in the excited state μ_e show the existence of an increase in the polarity of compound **1b** in the excited state: the dipole moment increases from 3.9 D (S_0, μ_G) to 9.4 D (S_1*), while the vector difference $\Delta\mu = \mu_e - \mu_G$ is 7.9 D. This corresponds approximately to a shift of 0.2-0.25 *e*, if one takes into account that pyrone ring is basically an electron acceptor while the methoxy substituent on the benzene ring is an electron donor system (the distance between the poles of the vector $\Delta\mu$ are averaged over the four possible conformers of compound **1b**). For comparison, the absolute value of the vector $\Delta\mu$ for *para*-OCH_3 substituted 2,5-diphenyl-1,3,4-oxadiazole is 3.8 D and it only reaches a value of 7.6 D for the corresponding *para*-$N(CH_3)_2$ derivative [26].

Thus the introduction of the coumarin ring in the molecule of *ortho*-methoxy (and in the *ortho*-hydroxy) derivative of 2,5-diphenyl-1,3,4-oxadiazole in fact leads to a notable increase in the intramolecular donor-acceptor interaction, which, in agreement with earlier conclusions [8-20], should have a notable effect on the spectral characteristics of the *ortho*-derivatives studied. In this way the possible negative consequences (from the point of view of the efficiency of luminescence) as a result of introduction (in the system of energy states of molecules **1-5**) of levels of the $n\pi^*$-type, localized in the CO group of the coumarin unit, will not appear.

The basic spectral characteristics and the parameters of the initial photophysical processes occurring in the excited states of the compounds studied are given in Table 2. The absence of longwave emission in the case of the tautomeric forms was somewhat unexpected. We expected it for the *ortho*-hydroxy derivatives **1a-5a**: the position and even the shape of the bands in their emission spectra differed little from those characteristic of the model *ortho*-methoxy derivatives **1b-5b**. The definite asymmetry of the spectral bands was similar for both groups of compounds. In our view this causes the absence from the spectrum of even one low intensity band of the fluorescence product of the IMPTP reaction and the appearance of vibrational structure only. Attempts to observe emission from phototautomeric forms, which might be formed in the case of compounds **1a-5a**, and their time-resolved fluorescence spectra, were unsuccessful.

TABLE 2. Spectral-luminescent Characteristics of Derivatives of Coumarinylphenyloxadiazoles*

Compound	Solvent	ν_a	ν_f	$\Delta\nu_{ST}$	φ_f	τ_f	k_f	k_d
1a	Toluene	28120	23100	5020	0.12	0.44	$2.7\cdot10^8$	$2.0\cdot10^9$
	Dioxane	28620	22210	6410	0.009	—	—	—
	Acetonotrile	28960	21820	7150	0.003	—	—	—
	Dimethylformamide	28840	21600	7240	0.0003	—	—	—
1b	Toluene	28640	22180	6460	0.54	2.60	$2.1\cdot10^8$	$1.8\cdot10^8$
	Acetonotrile	29280	21110	8170	0.48	3.42	$1.4\cdot10^8$	$1.5\cdot10^8$
	Dimethylformamide	29020	20400	8620	0.28	2.04	$1.4\cdot10^8$	$3.5\cdot10^8$
2a	Toluene	25340	21080	4260	0.11	0.74	$1.5\cdot10^8$	$1.2\cdot10^9$
	Acetonotrile	25660	21360	4300	0.07	0.37	$1.9\cdot10^8$	$2.5\cdot10^9$
	Dimethylformamide	25500	21240	4260	0.03	0.42	$1.0\cdot10^8$	$2.3\cdot10^9$
2b	Toluene	25660	21200	4460	0.53	3.43	$1.5\cdot10^8$	$1.4\cdot10^8$
	Acetonotrile	26140	21390	4750	0.74	3.85	$1.9\cdot10^8$	$0.7\cdot10^8$
	Dimethylformamide	26080	21020	5060	0.55	3.60	$1.5\cdot10^8$	$1.3\cdot10^8$
3a	Toluene	26960	22040	4920	0.13	0.86	$1.5\cdot10^8$	$1.0\cdot10^9$
	Acetonotrile	27220	22320	4900	0.09	0.36	$2.5\cdot10^8$	$2.5\cdot10^9$
	Dimethylformamide	27220	22250	4970	0.05	0.24	$2.1\cdot10^8$	$4.0\cdot10^9$
3b	Toluene	27380	21620	5760	0.58	2.48	$2.3\cdot10^8$	$1.7\cdot10^8$
	Acetonotrile	27860	22420	5440	0.74	2.59	$2.9\cdot10^8$	$1.0\cdot10^8$
	Dimethylformamide	27500	22090	5410	0.78	2.49	$3.1\cdot10^8$	$0.8\cdot10^8$
4a	Toluene	23280	20720	2560	0.48	2.34	$2.1\cdot10^8$	$2.2\cdot10^8$
	Acetonotrile	22850	20380	2470	0.42	1.58	$2.7\cdot10^8$	$3.7\cdot10^8$
	Dimethylformamide	22760	20000	2760	0.31	1.48	$2.1\cdot10^8$	$4.7\cdot10^8$
4b	Toluene	23760	20730	3030	0.49	2.33	$2.1\cdot10^8$	$2.2\cdot10^8$
	Acetonotrile	23240	20370	2870	0.53	2.08	$2.5\cdot10^8$	$2.3\cdot10^8$
	Dimethylformamide	23120	20100	3020	0.44	1.82	$2.4\cdot10^8$	$3.1\cdot10^8$
5a	Toluene	22480	20300	2180	0.42	2.64	$1.6\cdot10^8$	$2.2\cdot10^8$
	Acetonotrile	21830	19700	2130	0.55	3.36	$1.6\cdot10^8$	$1.4\cdot10^8$
	Dimethylformamide	21780	19460	2320	0.46	3.66	$1.3\cdot10^8$	$1.5\cdot10^8$
5b	Toluene	22920	20460	2460	0.43	2.57	$1.7\cdot10^8$	$2.2\cdot10^8$
	Acetonotrile	22220	19890	2330	0.52	3.14	$1.7\cdot10^8$	$1.5\cdot10^8$
	Dimethylformamide	22120	19650	2470	0.48	3.02	$1.6\cdot10^8$	$1.7\cdot10^8$

* Symbols as for Table 1.

A considerable decrease in the quantum yield for fluorescence was also observed for compounds **1a-3a** in comparison with their methoxy analogs, which was effectively not observed for the dimethylamino and quinolizinyl derivatives **4a** and **5a**. The similarity of the spectral characteristics of the systems **4a,b** and **5a,b** in solvents of varying polarity should also be noted. This indicates an extremely small effect on their fluorescent properties of possibly formated non-luminescent TICT states, which are traditionally discussed as the basic cause for the decreased efficiency of luminescence of aromatic dialkylamino derivatives in polar solvents [27, 28]. Thus one can promote the suggestion that the decrease in emission intensity for compounds **1a-3a** is basically due to IMPTP and the subsequent effective intramolecular extinction of fluorescence of the phototautomeric forms produced. Unfortunately only indirect methods are available to determine the efficiency of proton phototransfer in the series of compounds studied because the more or less reliable direct estimation of the rate of this process from the kinetics of fluorescence is only possible in those case when emission of the normal and phototautomeric forms is observed.

Fluorescence (rate constant k_f^M) and the various nonradiative transitions, for example intra- and intersystem conversion (rate constant k_d^M) are ascribed to the first photoprocess which leads to "consumption" excitation of the methoxy derivatives. That the quantum yields of fluorescence for compounds **1b-5b** is notably less than unity shows that the second process takes place; the lifetime of the excited state of the methoxy derivatives depends on the rate constants of the initial photophysical processes:

$$1/\tau_M = k_f^M + k_d^M. \quad (1)$$

For the hydroxy derivatives there is another initial photochemical process, the proton phototransfer reaction (rate constant k_{EIPT}) which leads to dissipation of the excitation energy of the normal form. An analogous relation can be obtained for the extinction time for the fluorescence of the excited normal form:

$$1/\tau_{OH} = k_f^{OH} + k_d^{OH} + k_{ESIPT}. \quad (2)$$

If it is assumed that the rate constants for the initial photoprocesses for the series of hydroxy and methoxy derivatives are sufficiently close to one another ($k_f^{OH} \sim k_f^M$ and correspondingly $k_d^{OH} \sim k_d^M$), then the rate of the proton phototransfer can be estimated from a combination of equations (1) and (2):

$$k_{ESIPT} = (\tau_M/\tau_{OH} - 1)/\tau_M. \quad (3)$$

The estimates obtained in this way for toluene solutions are given in Table 3. Both the highly basic polar solvents and the proton donor solvents were excluded from the discussion as they may form intermolecular hydrogen bonds with the molecules of the hydroxy derivatives. In such solvate complexes intramolecular proton phototransfer becomes impossible [1-8], consequently it is necessary to discuss for solvents forming intermolecular hydrogen bonds a more complex scheme of initial processes and also intra- and intermolecular photochemical processes, the analysis of which is outside the realms of this paper.

An alternative indirect estimate of the rate of IMPTP is possible if it is assumed that the basis of the nonradiative process leading to the consumption of the normal forms of compounds **1a-5a** is proton transfer and other possible nonradiative processes cannot occur concurrently [1-8, 29] (however, this suggestion is not correct for **4a** and **5a**). Then

$$k_{ESIPT} = 1/\tau_{OH} - k_f^{OH}. \quad (4)$$

Values of k_f^{OH} were estimated from the absorption spectra according to [30] (Table 4), k_f^M and k_{ESIPT} were obtained from formulas (3) and (4). The rate constants for proton phototransfer for the coumarinyl derivatives of diphenyloxadiazole appear to be somewhat lower than the analogous values for the oxazole and

TABLE 3. Rate Constants* of Intramolecular Proton Phototransfer (k_{ESIPT}) in *ortho*-Hydroxysubstituted Compounds **1a-5a** in Toluene

ortho-Hydroxy derivatives			*ortho*-Methoxy derivatives			k_{ESIPT} (formula)	
Compound	τ_f^{OH}	k_f^{OH} (ESP)	Compound	τ_f^{M}	k_f^{OH} (ESP)	(3)	(4)
1a	0.44	$2.85 \cdot 10^8$	**1b**	2.60	$2.80 \cdot 10^8$	$1.8 \cdot 10^9$	$2.0 \cdot 10^9$
2a	0.74	$2.60 \cdot 10^8$	**2b**	3.43	$2.02 \cdot 10^8$	$1.1 \cdot 10^9$	$1.1 \cdot 10^9$
3a	0.86	$2.62 \cdot 10^8$	**3b**	2.48	$3.37 \cdot 10^8$	$7.7 \cdot 10^8$	$9.1 \cdot 10^8$
4a	2.34	$2.31 \cdot 10^8$	**4b**	2.33	$2.45 \cdot 10^8$	—	$(2.0 \cdot 10^8)$
5a	2.64	$2.28 \cdot 10^8$	**5b**	2.57	$2.33 \cdot 10^8$	—	$(1.5 \cdot 10^8)$

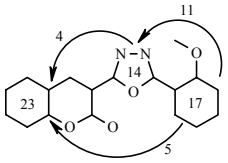
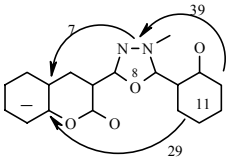
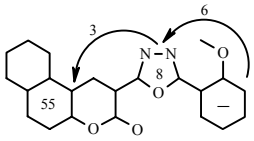
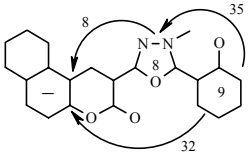
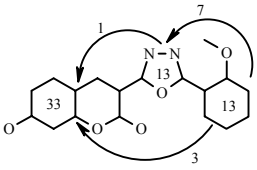
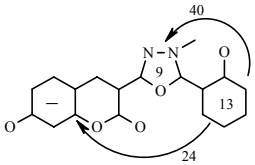
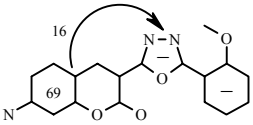
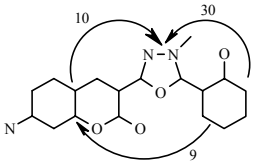
* k_f (ESP) – rate constants for emission of fluorescence estimated from the electronic absorption spectrum according to [30]. Figures in brackets are estimates in which it was observed that the deductions from formula (4) were not acceptable when the rate of IMPTP exceed the rates of the other initial photoprocesses.

oxadiazole derivatives we have studied [18-20] and also those known from the literature [1-8]. On one hand, this circumstance may arise from the decreased basicity of the proton accepting N atoms in the oxadiazole ring as a result of introduction of the electron acceptor coumarin unit, which in its turn, lowers the probability of proton phototransfer. However, it cannot be denied that the assumptions for the two equations (3) and (4) are sufficiently crude although it may be suggested that it is doubtful that the errors in carrying out the estimates even in the most unfavorable cases would exceed 50%. Nevertheless the tendency to decrease the rate of proton phototransfer in the series of compounds **1a-5a** with increasing electron donor character of the substituent in the coumarin unit of the molecules studied follows sufficiently clearly from the data in Table 3.

To clarify the principle of the phenomena described and to confirm them quantitatively we carried out quantum-chemical calculations using the PPP CI method with a special set of parameters [31], which showed its usefulness and efficiency for describing the spectral properties and the character of the redistribution of electron density in the excited state of molecular systems with IMPTP [18-20]. Special quantum-chemical indexes – the localization number of the excited electron L_i and the charge transfer (CT) number l_{ij} [32] (Table 4) – were also calculated. Three structural fragments were provisionally separated in the molecules **1a-5a**: coumarinyl, oxadiazolyl, and *ortho*-hydroxybenzene fragments. The diagrams of Table 4 show the general localization of the excited electron over the corresponding units. The CT number, which characterizes interfragment shift of the electron density within the fragments, the interfragment CT number is depicted approximately by arrows which show the direction of the transfer of electron density on transition to the excited state.

As has been noted, introduction of the coumarin nucleus into the diaryloxadiazole molecule changes the nature of the intramolecular donor-acceptor interaction considerably. Because of its considerable size the coumarin fragment plays a notable role in the formation of the excited states of compounds **1-5** – the general localization of the excited electron on this unit is quite large for all of the molecules studied. In distinction form the *ortho*-hydroxy derivatives of diphenyloxazole and oxadiazole, in which the heterocycle and the benzene ring with the hydroxy group take the principle part in redistribution of the electron density on electron excitation, in compounds **1-4** the role played by the coumarin nucleus is quite large in all cases. As in the case of the oxazole and oxadiazole derivatives in the compounds studied there is a tendency for a decrease in CT from the 2-benzene ring to the other parts of the molecule with increasing electron donor character of the substituent introduced into the opposite 5-position.

TABLE 4. Quantum-chemical Calculations of the Normal and Phototautomer Forms of Compounds **1a-4a** to Determine the Localization Numbers of the Excited Electron and the Charge Transfer Numbers [32]

Com-pound	Normal form*			Phototautomer form	
	ν_{S0-S1}	Δq_O	Scheme for the electron density redistribution	ν_{S0-S1}	Scheme for the electron density redistribution
1a	29080	0.086	36.0 33.8 30.2 	19160	21.0 33.0 46.1 
2a	27000	0.028	67.4 21.9 10.7 	18810	24.9 30.8 44.3 
3a	28760	0.065	43.8 31.9 24.3 	19570	19.0 34.1 46.9 
4a	23630	0.004	80.3 15.3 4.4 	19410	33.8 31.3 34.9 

* ν_{S0-S1} – relative energy of the excited state (cm^{-1}); Δq_O – change in charge on the O atom of the hydroxyl group in the normal form, reflecting the increased acidity of the hydroxyl group on transfer to the excited state (the change in basicity of the oxadiazole ring is approximately the same in all cases). Commentary on the molecular diagram is given in the text of the paper.

The notable decrease in CT in the end leads to a reduction in the rate of IMPTP [18-20]. In particular, in the series of compounds studied this effect aggravates the decrease in localization of the excited electron on the phenyl ring when a donor substituent is introduced into the coumarin fragment or when its π-system is widened (e.g., as a result of annelation, compound **2**). In the case of dialkylamine derivatives the effect becomes so much stronger that it can be accepted that the benzene ring in compounds **4** and **5** effectively takes no part in the formation of the excited state: the overall localization on this fragment ~4%. On the basis of the results obtained

TABLE 5. Some Physicochemical Characteristics of the Synthesized Derivatives of Coumarinylphenyloxadiazole

Compound	Empirical formula (molecular mass)	Found N, % / Calculated N, %	mp, °C	IR spectra, ν, cm^{-1} (assignment)	^{1}H NMR spectra, chemical shifts, δ, ppm (assignment)				Yield, %
					1H, s, OH	1H, s, 4-H	H_{arom}	other protons	
1	2	3	4	5	6	7	8	9	10
1a	$C_{17}H_{10}N_2O_4$ (306.28)	9.23 / 9.15	229-231	3155 (OH) 1744 (C=O) 1607 C=C)	10.15	9.01	7.04 (1H, t, 4'-H); 7.09 (1H, d, 3'-H) 7.40-7.49 (3H, m, 6-,7-,8-H) 7.74 (1H, t, 5'-H); 7.89 (1H, d, 6'-H) 7.96 (1H, d, 5-H)	—	79
1b	$C_{18}H_{12}N_2O_4$ (320.30)	8.71 / 8.75	157-159	1744 (C=O) 1606 (C=C)	—	8.91	7.17 (1H, t, 4'-H); 7.30 (1H, d, 3'-H) 7.46 (1H, t, 6-H); 7.50 (1H, d, 8-H) 7.64 (1H, t, 5'-H); 7.76 (1H, t, 7-H) 7.93 (1H, d, 6'-H); 8.00 (1H, d, 5-H)	3.95 (3H, s, OCH_3)	57
2a	$C_{21}H_{12}N_2O_4$ (356.34)	7.89 / 7.86	246-248	3180 (OH) 1744 (C=O) 1623, 1563 (C=C)	10.18	9.61	7.08 (1H, t, 4'-H); 7.12 (1H, d, 3'-H) 7.44 (1H, t, 5'-H) 7.59-7.68 (2H, m, 7-, 10-H) 7.80 (1H, t, 6-H) 8.01-8.10 (2H, m, 6'-, 5-H) 8.31 (1H, d, 8-H); 8.71 (1H, d, 9-H)	—	82
2b	$C_{22}H_{14}N_2O_4$ (370.36)	7.49 / 7.56	225-228	1735 (C=O) 1606, 1563 (C=C)	—	9.54	7.15 (1H, t, 4'-H); 7.24 (1H, d, 3'-H) 7.56-7.69 (3H, m, 5'-,7-,10-H) 7.80 (1H, t, 6-H); 8.00 (1H, d, 6'-H) 8.07 (1H, d, 5-H); 8.29 (1H, d, 8-H) 8.64 (1H, d, 9-H)	3.97(3H, s, OCH_3)	78
3a	$C_{19}H_{14}N_2O_5$ (350.33)	8.09 / 8.00	259-260	3198 (OH) 3058, 2988 (CH) 1743 (C=O) 1615 (C=C)	10.11	8.90	6.96 (1H, d, 6-H); 7.03 (1H, s, 8-H) 7.07-7.14 (2H, m, 3'-,4'-H) 7.46 (1H, t, 5'-H); 7.84 (1H, d, 5-H) 7.89 (1H, d, 6'-H)	1.44 (3H, t, OCH_2CH_3) 4.19 (2H, q, OCH_2CH_3)	69

TABLE 5 (continued)

1	2	3	4	5	6	7	8	9	10
3b	$C_{20}H_{16}N_2O_5$ (364.36)	7.74 / 7.69	199-200	3034, 2978 (CH) 1744 (C=O) 1604 (C=C)	—	8.81	6.95 (1H, d, 6-H); 7.01 (1H, s, 8-H) 7.12 (1H, t, 4'-H); 7.21 (1H, d, 3'-H) 7.57 (1H, t, 5'-H); 7.84 (1H, d, 5-H) 7.91 (1H, d, 6'-H)	1.45 (3H, t, $OCH_2C\underline{H}_3$) 3.96 (3H, s, $OC\underline{H}_3$) 4.20 (2H, q, $OC\underline{H}_2CH_3$)	82
4a	$C_{21}H_{19}N_3O_4$ (377.40)	11.07 / 11.13	223	3197 (OH) 2982, 2927 (CH) 1735 (C=O) 1623, 1591 (C=C)	10.09	8.67	6.58 (1H, s, 8-H); 6.75 (1H, d, 6-H) 7.01-7.10 (2H, m, 3'-,4'-H) 7.44 (1H, t, 5'-H) ;7.62 (1H, d, 5-H) 7.89 (1H, d, 6'-H)	1.19 (6H, t, $N(CH_2C\underline{H}_3)_2$) 3.51 (4H, q, $N(C\underline{H}_2CH_3)_2$)	77
4b	$C_{22}H_{21}N_3O_4$ (391.42)	10.81 / 10.74	175-178	2972, 2932 (CH) 1726 (C=O) 1620, 1590 (C=C)	—	8.62	6.61 (1H, s, 8-H); 6.82 (1H, d, 6-H) 7.15 (1H, t, 4'-H); 7.29 (1H, d, 3'-H) 7.63 (1H, t, 5'-H); 7.68 (1H, d, 5-H) 7.88 (1H, d, 6'-H)	1.17 (6H, t, $N(CH_2C\underline{H}_3)_2$) 3.92 (3H, s, $OC\underline{H}_3$) 3.50 (4H, q, $N(C\underline{H}_2CH_3)_2$)	61
5a	$C_{23}H_{19}N_3O_4$ (401.42)	10.55 / 10.47	248-250	3230 (OH) 2944, 2840 (CH) 1719 (C=O) 1617, 1578 (C=C)	10.12	8.51	7.02-7.13 (2H, m, 3'-,4'-H) 7.18 (1H, s, 5-H); 7.44 (1H, t, 5'-H) 7.87 (1H, d, 6'-H)	1.95 (4H, m, $N(CH_2C\underline{H}_2CH_2)_2$) 2.80 (4H, m, $N(CH_2CH_2C\underline{H}_2)_2$) 3.36 (4H, t, $N(C\underline{H}_2CH_2CH_2)_2$)	56
5b	$C_{24}H_{21}N_3O_4$ (415.45)	10.26 / 10.11	210-212	2940, 2846 (CH) 1720 (C=O) 1623, 1592 (C=C)	—	8.43	7.12 (1H, t, 4'-H); 7.17 (1H, s, 5-H) 7.21 (1H, d, 3'-H); 7.56 (1H, t, 5'-H) 7.87 (1H, d, 6'-H)	1.96 (4H, m, $N(CH_2C\underline{H}_2CH_2)_2$) 2.80 (4H, m, $N(CH_2CH_2C\underline{H}_2)_2$) 3.35 (4H, t, $N(C\underline{H}_2CH_2CH_2)_2$) 3.96 (3H, s, $OC\underline{H}_3$)	68

it may be concluded that proton phototransfer should be considerably retarded on the introduction of electron donor substituents, until it is completely blocked in dimethylamino-, and even more in quinolizine-substituted *ortho*-hydroxycoumarinylphenyloxadiazole.

Introduction of a coumarin ring also markedly changes the character of the intramolecular donor-acceptor interaction in the product of the IMPTP reaction, the phototautomer form. As a result of proton phototransfer to the benzene ring a considerable excess of electron density arises which is then redistributed to the other parts of the molecule. In one of our papers [20] a suggestion was made about the connection between the efficiency of extinction of fluorescence in the phototautomer form and the intensity of intramolecular CT between units in it. According to the calculations cited, introduction of the electron acceptor coumarin ring considerably strengthens the expected redistribution of electron density, which is 1.5 to 2 times as great for the compounds studied than for the derivatives of oxazole and oxadiazole studied previously [20]. In the case of the dialkylamine derivatives the presence of such strong electron donor substituents in the opposite part of the molecule can only decrease a similar redistribution of charge to a small extent. So on the basis of the results of the calculations a considerable increase in the efficiency of intramolecular extinction of fluorescence of the phototautomer forms of the compounds studied can be forecast.

The experimental results (Tables 2 and 3) confirm this proposal. For example, the absence of emission bands for the phototautomer forms of **1a-3a** is explained by the considerable increase in the efficiency of their nonradiative deactivation, whereas the absence of IMPTP in compounds **4a** and **5a** reflects the localization of the excited electron on their 7-dialkylamine substituted coumarin units. The increased efficiency of fluorescence as a result of the increased electron donor power of the substituents introduced is indicated by the decrease in the rate of proton phototransfer in the series H, OCH_3, $N(C_2H_5)_2$, quinolizine, leading to practically blockage in the last two cases.

Taking into account the high efficiency of nonradiative deactivation of the excited states of molecules **1a-3a**, compounds of this type have potential for use as UV protectors for polymeric materials.

EXPERIMENTAL

Derivatives of coumarinylphenyl-1,3,4-oxadiazole were synthesized by a previously described method [33]. 2-Iminocoumarin-3-carboxamides and hydrazides of salicylic or 2-methoxybenzoic acids were used as starting materials. Nitrogen elemental analysis results agreed with the calculated values (Table 5).

IR spectra of the compounds synthesized as 1% suspensions in KBr pellets were recorded with a Specord M-80 spectrometer. A strong band of the C=O group of a lactone ring was observed at 1719-1744 cm^{-1}, while vibrations of the C=C bonds of the aromatic and heterocyclic rings were observed at 1578-1623 cm^{-1}. Broad weak vibrations of the associated O–H bond were observed in the 3155-3230 cm^{-1} for the *ortho*-hydroxy derivatives.

^1H NMR spectra of DMSO-d_6 solutions with TMS as internal standard were recorded with a Varian VXR-400 instrument. For the compounds synthesized signals for the aromatic protons were observed at 6.57-8.71 ppm, a singlet for the proton at position 4 of the coumarin ring was observed at 8.43-9.61 ppm, and the signal for the OH proton was observed at 10.09-10.18 ppm. This signal was replaced by the singlet for the methoxy group at 3.92-3.97 ppm in the corresponding methoxy derivatives.

Absorption spectra were measured with Hitachi U-3210 and Specord M-40 spectrophotometers, while fluorescence spectra and quantum yields were measured with a Hitachi F4010 spectrofluorometer. A solution of quinine hydrogen sulfate in 1 N sulfuric acid ($\varphi_f = 0.546$) [34] was used as the standard for determination of the quantum yield of fluorescence. In all cases RMS corrections for the difference in refractive indexes of the measured and standard solutions were introduced [35].

Kinetics and time-resolved fluorescence spectra were measured with an apparatus [36, 37] working in a photon counting regime with a nanosecond range. The lifetime of the fluorescence was calculated with a

nonlinear least squares method [38, 39]. To estimate the dipole moment of the molecule of **1b** in the ground state quantum-chemical calculations were carried out in the semiempirical AM1 method with optimization of the geometry of the different planar conformations of this compound, which differ in the mutual orientation of the coumarin unit, oxadiazole ring, and the *ortho*-methoxysubstituted phenyl unit. The effective dipole moment of structure **1b** (~3.9 D) was estimated as the weighted mean of the geometric dipole moments of the four possible conformers taken with statistical weights, with inverse squares of their heats of formation, with the weight of the most energetically suitable conformer adjusted to unity. The Onsager radius of polarity was taken as equal to the radius of the sphere in which the conformer having the greatest linear dimension (7.2 Å) can be placed. The quantum-chemical calculations in the π-electron approximation was carried out by the PPP KV method using 100 once excited configurations and using a set of semiempirical parameters [31].

REFERENCES

1. A. Weller, *Progr. React. Kinet.,* **1**. 188 (1961).
2. W. Klopffer, *Adv. in Photochem.*, **10**, 311 (1977).
3. J. F. Ireland and P. A. H. Wyatt, *Adv. Phys. Org. Chem.,* **12**, 131 (1976).
4. I. Yu. Martynov, A. B. Demyashkevich, B. M. Yzhinov, and G. Kuz'min, *Usp. Khimii*, **46**, 3 (1977).
5. S. J. Formosinho and L. G. Arnaut, *J. Photochem. Photobiol. A. Chem.,* **75**, 21 (1993).
6. S. M. Ormson and R. G. Brown, *Progr. React. Kinet.*, **19**, 45 (1954).
7. D. LeGourrierec, S. G. Ormson, and R. G. Brown, *Progr. React. Kinet.,* **19**, 211 (1994).
8. A. Douhal, F. Lahmani, and A. H.Zewail, *Chem. Phys.,* **207**, 477 (1996).
9. M. E. Kletskii, A. A. Milov, A. V. Metelitsa, and M. I. Knyazhansky, *J. Photochem. Photobiol. A. Chem.,* **110**, 267 (1997).
10. M. L. Martinez, W. C. Cooper, and P. T. Chou, *Chem. Phys. Lett.,* **193**, 151 (1992).
11. J. M. Kaufmann, P. T. Litak, and W. J. Boyko, *J. Heterocycl. Chem.,* **32**, 1541 (1995).
12. J. Rieker, E. Lemmert-Schmitt, G. Goeller, M. Roessler, G. J. Stueber, H. Schettler, H. E. A. Kramer, J. J. Stezowski, H. Hoier, S. Henkel, A. Schmidt, H. Port, M. Wiechmann, J. Rody, G. Rytz, M. Stlongo, and J.-L. Birbaum, *J. Phys. Chem.,* **96**, 10225 (1992).
13. G. J. Stueber, M. Kieninger, H. Schetteer, W. Busch, B. Goeller, J. Franke, H. E. A. Kramer, H. Hoier, S. Henkel, P. Fisher, H. Port, T. Hirsch, G. Rytz, and J.-L. Birbaum, *J. Phys. Chem.,* **99**, 10097 (1992).
14. M. Kasha. *Acta Phys. Polon. A,* **71**, 717 (1987).
15. D. A. Patthenopolous, D. McMorrow, and M. Kasha, *J. Phys. Chem.,* **95**, 2668 (1991).
16. P. T. Chou, M. L. Martinez, and J. H. Clements, *Chem. Phys. Lett*., **204**, 395 (1993).
17. F. Vollmer and W. Rettig, *J. Photochem. Photobiol. A. Chem.,* **95**, 143 (1996).
18. A. O. Doroshenko, E.A. Posokhov, V. M Shershukov, V. G. Mitina, and O. A. Ponomarev, *Khim. Vysok. Energ.,* **31**, 395 (1997).
19. A. O. Doroshenko, E. A. Posokhov, and V. M. Shershukov, *XVIIIth Intern. Conf. on Photochem.,* 3-8 August 1997, Warsaw, Poland, 1997, 211.
20. A. O. Doroshenko, E. A. Posokhov, A. A. Verezubova, and L. M. Ptyagina, *The Jablonski Centennial Conf. on Luminescence and Photophysics,* 23-27 July, 1998, Torun, Poland, 1998, 217.
21. A. O. Doroshenko, V. V. Ivanov, S. N. Kovalenko, I. A. Zhuravel', S. N. Yarmolenko, and O. A. Ponomarev, *Khim. Fizika*, **16**, No. 11, 40 (1997).
22. N. G. Bakhshiev, *Optika i Spektroskopiya*, **13**, 43 (1962).
23. N. G. Bakhshiev, *Optika i Spektroskopiya*, **19**, 345 (1965).
24. M. J. S. Dewar, E. G. Zoebich, E. F. Healy, and J. J. P. Stewart. *J. Amer. Chem. Soc.,* **107**, 3902 (1985).
25. A. O. Doroshenko, V. T. Skripkina, E. A. Posokhov, E. N. Obukhova, and V. M. Shershukov, *Khim. Geterotsikl. Soedin.,* 988 (1997).

26. N. A. Popova, E. G. Yushko, B. M. Krasovitskii, V. I. Minkin, A. E. Lyubarskaya, and M. G. Gol'dberg, *Khim. Geterotsikl. Soedin.,* 26 (1983).
27. Z. R. Grabowski, *Acta Phys. Polon. A,* **71**, 743 (1987).
28. F. Vollmer and W. Rettig, *J. Photochem. Photobiol. A. Chem.,* **95**, 143 (1996).
29. P. T. Smith, K. A. Zaklika, K. Thakur, G. C. Walker, K. Tominaga, and P. F. Barbara, *J. Phys. Chem.,* **95**, 10465 (1991).
30. A. N. Terenin, *Photonics of Dyestuff Molecules and Natural Organic Compounds* [in Russian], Nauka, Leningrad (1967).
31. J. Griffith, *Dyes Pigm.,* **3**, 211 (1982).
32. A. V. Luzanov, *Usp. Khimii*, **49**, 2086 (1980).
33. S. N. Kovalenko, K. M. Sytnik, V. M. Nikitchenko, S. V. Rusanova, V. P.Chernykh, and A. O. Porokhnyak, *Khim. Geterotsikl. Soedin.,* 190 (1999).
34. W. H. Melhuish, *J. Phys. Chem.,* **65**, 229 (1961).
35. S. I. Kotelevskiy, *J. Luminescence,* **79**, 211 (1998).
36. O. A. Ponomarev, A. O. Doroshenko, and V. G. Mitina, *Khim. Fizika*, **8**, 1369 (1989).
37. A. O. Doroshenko, A. V. Kirichenko, V. G. Mitina, and O. A. Ponomarev, *J. Photochem. Photobiol. A. Chem.,* **94**, 15 (1996).
38. W. R. Ware, L. J. Doemeny, and T. L. Nemzek, *J. Chem. Soc.*, **77**, 2038 (1973).
39. S. K. Basharin, G. A. Gachko, L. N. Kivach, S. A. Maskevich, A. A. Maskevich, and V. P. Udovydchenko, *Zh. Prikl. Spektroskopii*, **52**, 48 (1990).