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ENSEMBLES OF RINGS WITH A COUMARIN UNIT.
2.* SPECTRAL LUMINESCENT PROPERTIES AND SPIN–ORBIT COUPLING IN MOLECULES OF 3-(2-R-THIAZOL-4-YL)- AND 3-(4-R-THIAZOL-2-YL)COUMARINS

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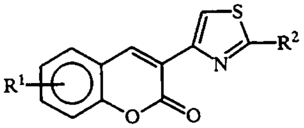
We have investigated the luminescent spectral properties of 3-(2-R-thiazol-4-yl)coumarins (R = CH_3, CH_2CN, Ar) and some isomeric 3-(4-R-thiazol-2-yl)coumarins (R = Ar) with substituents of different electronic types both in the coumarin and in the aryl moieties. We have obtained estimates of the rate constants for primary photophysical processes: emission of fluorescence and nonradiative degradation of the electronic excitation energy. We have calculated the matrix elements for the spin–orbit coupling operator, and based on these matrix elements we have calculated the intersystem crossing rate constants. We have shown that deterioration of the fluorescent properties of the studied thiazolyl derivatives of coumarin when π-conjugated moieties are introduced into the thiazole ring is determined by the enhancement of the spin–orbit interaction in a system of levels of the π,π-type.

The luminescent spectral and lasing properties of bis-coumarin luminophores, in which the basic chromophore moieties are connected through the 2 and 4 positions of a thiazole ring and consequently are not found in direct polar conjugation, have been rather intensely studied in recent years [2-5]. A great deal of attention has been paid to study of active laser media based on these compounds and also the process of intramolecular energy transfer between weakly bonded biscoumarin groups, especially important from the standpoint of more effectively choosing the polychromatic light for excitation in dye lasers with lamp pumping. However, in the investigations mentioned, there has been no systematic approach to solution of the problem of the effect on the luminescent spectral properties of 3-thiazolyl coumarins from expansion of the π-electron conjugated system of the molecule when aromatic moieties, including those containing pronounced electron-donor substituents, are introduced into the thiazole ring.



In this paper, we present the results of an investigation of the luminescent spectral properties of derivatives of 3-(2-R-thiazol-4-yl)coumarin, containing electron-donor substituents both in the coumarin moiety and in the 2 position of the thiazole ring (see Table 1).

In Table 2, we present the spectral characteristics of some isomeric compounds for which the coumarin chromophore is added at the 2 position of the thiazole ring. From comparison of the characteristics of compounds containing identical substituents in the coumarin chromophore, we can conclude that the thiazole ring added to the chromophore system at the 2

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*For communication 1, see [1].

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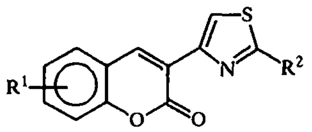
TABLE 1. Luminescent Spectral Characteristics of 3-(2-R-Thiazol-4-yl)coumarins in 2-Propanol



R^1	R^2	ν_a, cm^{-1}	ν_f, cm^{-1}	$\Delta\nu_{ST}$, cm^{-1}	φ_f	τ_f, nsec	k_f, sec^{-1}	k_d, sec^{-1}
1	2	3	4	5	6	7	8	9
H	CH_3	29660	24200	5180	0,223	1,226	$1,82 \cdot 10^8$	$6,34 \cdot 10^8$
	CH_2CN	29700	24380	5320	0,141	0,651	$2,17 \cdot 10^8$	$1,32 \cdot 10^9$
	C_6H_5	29040	23720	5320	0,130	0,607	$2,14 \cdot 10^8$	$1,43 \cdot 10^9$
	$4\text{-}CH_3OC_6H_4$	28340	21260	7080	0,0802	0,670	$1,20 \cdot 10^8$	$1,37 \cdot 10^9$
	$4\text{-}ClC_6H_4$	28500	23760	4740	0,104	0,633	$1,64 \cdot 10^8$	$1,42 \cdot 10^9$
$6\text{-}CH_3O$	CH_3	28100	23940	4160	0,0252	0,474	$5,3 \cdot 10^7$	$2,06 \cdot 10^9$
	C_6H_5	27180	23200	3980	0,0589	0,557	$1,06 \cdot 10^8$	$1,69 \cdot 10^9$
5,6-Benzo	CH_3	26640	23080	3560	0,527	2,885	$1,83 \cdot 10^8$	$1,64 \cdot 10^8$
	CH_2CN	26640	23180	3460	0,579	3,058	$1,89 \cdot 10^8$	$1,38 \cdot 10^8$
	C_6H_5	26280	22620	3660	0,185	1,107	$1,67 \cdot 10^8$	$7,36 \cdot 10^8$
	$4\text{-}CH_3OC_6H_4$	26080	21080	5000	0,108	0,850	$1,27 \cdot 10^8$	$1,05 \cdot 10^9$
	$4\text{-}ClC_6H_4$	26240	22700	3540	0,178	1,086	$1,64 \cdot 10^8$	$7,57 \cdot 10^8$

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9
7-OH	CH_3	27760	23520	4220	0,514	3,062	$1,68 \cdot 10^8$	$1,59 \cdot 10^8$
	CH_2CN	27920	22860	5060	0,553	2,712	$2,04 \cdot 10^8$	$1,65 \cdot 10^8$
	C_6H_5	28280	23040	4240	0,234	1,021	$2,29 \cdot 10^8$	$7,50 \cdot 10^8$
	$4\text{-}CH_3OC_6H_4$	27380	21920	5460	0,177	0,917	$1,93 \cdot 10^8$	$8,98 \cdot 10^8$
7-OH, 6-n-C_6H_{13}	CH_3	27320	23200	4120	0,615	3,045	$2,02 \cdot 10^8$	$1,26 \cdot 10^8$
	CH_2CN	27260	23120	4140	0,610	2,894	$2,11 \cdot 10^8$	$1,35 \cdot 10^8$
	C_6H_5	27040	22900	4140	0,231	1,065	$2,17 \cdot 10^8$	$7,22 \cdot 10^8$
	$4\text{-}CH_3OC_6H_4$	26800	22600	4600	0,225	0,995	$2,26 \cdot 10^8$	$7,79 \cdot 10^8$
7-N$(C_2H_5)_2$	CH_3	24540	21440	3100	0,565	3,145	$1,80 \cdot 10^8$	$1,38 \cdot 10^8$
	C_6H_5	24340	21100	3240	0,351	1,795	$1,96 \cdot 10^8$	$3,62 \cdot 10^8$
	$4\text{-}CH_3OC_6H_4$	24540	21300	3240	0,238	1,704	$1,40 \cdot 10^8$	$4,47 \cdot 10^8$
	$4\text{-}(CH_3)_2NC_6H_4$	24260	20420	3840	0,0334	0,362	$9,2 \cdot 10^7$	$2,67 \cdot 10^8$
7-O^-	CH_3	23880	21320	2560	0,387	3,846	$1,01 \cdot 10^8$	$1,59 \cdot 10^8$
	CH_2CN	23960	21060	2900	0,455	3,345	$1,36 \cdot 10^8$	$1,63 \cdot 10^8$
	C_6H_5	23600	20920	2680	0,163	1,351	$1,21 \cdot 10^8$	$6,20 \cdot 10^8$
	$4\text{-}CH_3OC_6H_4$	23580	20840	2740	0,156	1,619	$9,6 \cdot 10^7$	$5,21 \cdot 10^8$
7-O^-, 6-n-C_6H_{13}	CH_3	23140	20780	2360	0,482	3,901	$1,24 \cdot 10^8$	$1,33 \cdot 10^8$
	CH_2CN	22940	20780	2160	0,279	3,025	$9,2 \cdot 10^7$	$2,38 \cdot 10^8$
	C_6H_5	22680	20760	1920	0,124	0,977	$1,27 \cdot 10^8$	$8,97 \cdot 10^8$
	$4\text{-}CH_3OC_6H_4$	22820	20740	2080	0,206	1,603	$1,29 \cdot 10^8$	$4,95 \cdot 10^8$

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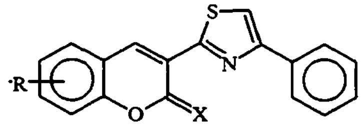
*ν_a and ν_f are the positions of the maxima for the absorption and fluorescence bands; $\Delta\nu_{ST}$, φ_f, and τ_f are the Stokes shift, the quantum yield, and the lifetime of fluorescence; k_f and k_d are the experimentally estimated values of the rate constants for emission of fluorescence and nonradiative degradation of the electronic excitation energy.

TABLE 2. Luminescent Spectral Characteristics of 3-(4-Phenylthiazol-2-yl)coumarins and Their 2-Imino Analogs in 2-Propanol



R	X	ν_a, cm^{-1}	ν_f, cm^{-1}	$\Delta\nu_{ST}$, cm^{-1}	φ_f	τ_f, nsec	k_f, sec^{-1}	k_d, sec^{-1}
H	O	26700	20420	6280	0,529	4,390	$1{,}21 \cdot 10^8$	$1{,}07 \cdot 10^8$
	NH	26580	21580	5000	0,0137	0,723	$1{,}90 \cdot 10^7$	$1{,}36 \cdot 10^9$
6-CH_3O	O	25760	20400	5360	0,191	1,847	$1{,}03 \cdot 10^8$	$4{,}38 \cdot 10^8$
	NH	25620	20800	4820	0,0431	1,545	$2{,}79 \cdot 10^7$	$6{,}19 \cdot 10^8$
5,6-Benzo	O	24620	20000	4620	0,397	3,527	$1{,}13 \cdot 10^8$	$1{,}71 \cdot 10^8$

position exhibits more pronounced electron-acceptor properties than in the case of addition at the 4 position, since in the first case the long-wavelength transition in the absorption spectra is located about 2000-3000 cm^{-1} lower in energy. Thus, the thiazole chromophores in molecules of most of the investigated compounds exert a substantially lesser effect on the characteristics of the main coumarin chromophore moieties than in the case of the isomeric compounds presented in Table 2.

One more interesting conclusion follows from the data in Table 2. A rather large number of researchers have connected the low emission efficiency of unsubstituted coumarin with the unfavorable effect of the intersystem crossing process from the lower excited singlet π,π-type state of this molecule to the triplet n,π-level localized on the carbonyl group. In this case, replacing the oxygen atom of the carbonyl group by a nitrogen atom should lead to a substantial improvement in the fluorescent characteristics, since the n,π-levels of the C=N group are significantly lower in energy than the n,π-levels of the carbonyl group. However, in fact we not only do not observe an increase in the fluorescence efficiency in 2-iminocoumarins but we observe just the opposite: the quantum yield decreases by more than an order of magnitude. The decrease in fluorescence efficiency on going from coumarin to the corresponding 2-imino analog requires separate study; and the process of intersystem crossing involving the n,π levels of the carbonyl group of coumarin, if it occurs in the molecules under consideration, at least does not have the determining effect on their luminescence characteristics.

On the other hand, some isolation of coumarin from the thiazole moieties in the studied compounds promotes a nonplanar structure for their molecules. Thus, calculations by the molecular mechanics method (MMP2) in [6] with optimization of the geometry of the thiazolylcoumarins for different possible orientations of the heterocycles relative to each other showed that for the less polar conformers ($\mu \sim 2.5D$) with *anti* orientation of the hydrogen atoms in the 4 position of the coumarin moiety and the hydrogen atoms in the 5 position of the thiazole ring, the angle between the planes of the heterocyclic moieties is ~25°, while for the more polar *syn* conformers ($\mu \sim 3.8D$) the indicated angle is ~35°. The benzene ring introduced into the 2 position of the thiazole ring in both possible conformers does not deviate from the plane of the latter. Thus, conjugation between the coumarin and thiazole chromophore moieties in 3-thiazolylcoumarin molecules proves to be somewhat weakened compared with the hypothetical planar structure.

In considering the data presented in Table 1, we should especially note the small effect of the structural changes in the thiazole moiety on the energy of the lower excited singlet state of the studied compounds. We see no substantial effect both within the framework of a purely induction effect (going from CH_3- to CH_2CN-substituted) and within the framework of a conjugation effect (the series C_6H_5, 4-$CH_3OC_6H_4$, 4-$(CH_3)_2NC_6H_4$). Consequently, when the conjugated system of the thiazole-containing chromophore is expanded, the nature of the fluorescent state of the corresponding thiazolylcoumarin remains unchanged. The quantum chemical calculations performed also suggest that electronic excitation in the S_1 state in the studied systems is localized mainly on the coumarin moiety.

When the π system of the thiazole-containing chromophore is expanded by addition of an aryl moiety at the 2 position of the heterocycle, we observe a tendency toward a decrease in the fluorescence efficiency; this is even more clearly apparent when electron-donor substituents are introduced into the aforesaid aryl moiety.

Analysis of rate constants for emission of fluorescence and nonradiative degradation, estimated based on experimentally measured quantum yield and emission lifetime, suggests that an additional channel for nonradiative dissipation of excitation energy is included in the structural changes in the thiazole moiety of the studied 3-thiazolylcoumarins.

TABLE 3. Calculation of Spin–Orbit Coupling in Molecules of Model 3-(2-R-Thiazol-4-yl)coumarins

R	X	$E(S_1)/f$	L_C	L_T	L_X	$E(T_i)/\beta_{ii}$	L_C	L_T	L_X	$k_{D(i)}$	φ (k_F, k_D)
1	2	3	4	5	6	7	8	9	10	11	12
H	H	30775/0,770	85,5	14,5	—	12886/0,0008	85,5	14,5	—	$7\cdot10^3$	0,204 ($4{,}86\cdot10^8$, $1{,}90\cdot10^9$)
						19363/0,0128	94,6	5,4	—	$6{,}6\cdot10^6$	
						21272/0,0122	51,4	48,6	—	$8{,}8\cdot10^6$	
						24887/0,0048	46,2	53,8	—	$2{,}8\cdot10^6$	
						27976/0,0911	95,5	4,5	—	$1{,}87\cdot10^9$	
						29893/0,0047	40,9	59,1	—	$7{,}3\cdot10^6$	
H	C_6H_5	30067/0,794	68,6	26,6	4,8	13624/0,0004	85,8	13,7	0,5	$2\cdot10^3$	0,197 ($4{,}79\cdot10^8$, $1{,}95\cdot10^9$)
						19933/0,0072	38,2	37,8	23,9	$2{,}7\cdot10^6$	
						21013/0,0094	53,8	16,3	29,8	$5{,}7\cdot10^6$	
						23933/0,0060	63,5	21,9	14,6	$4{,}2\cdot10^6$	
						26596/0,0081	36,4	28,7	34,9	$1{,}3\cdot10^7$	
						28080/0,0843	95,2	3,6	1,2	$1{,}89\cdot10^9$	
						29505/0,0102	32,1	41,3	26,6	$3{,}7\cdot10^7$	
H	4-$CH_3OC_6H_4$	29747/0,777	66,4	27,8	5,7	14375/0,0084	83,2	16,2	0,6	$1{,}3\cdot10^6$	0,176 ($4{,}58\cdot10^8$, $2{,}15\cdot10^9$)
						19826/0,0103	23,7	34,3	42,0	$5{,}8\cdot10^6$	
						20816/0,0112	65,8	10,3	24,0	$8{,}3\cdot10^6$	
						23802/0,0093	58,3	27,5	14,2	$1{,}0\cdot10^7$	
						26553/0,0097	42,0	31,7	26,3	$2{,}0\cdot10^7$	
						28069/0,0802	4,8	5,1	90,1	$1{,}82\cdot10^9$	
						28117/0,0280	90,0	4,2	5,8	$2{,}2\cdot10^8$	
						29339/0,0132	32,5	30,8	36,6	$6{,}3\cdot10^7$	

TABLE 3 (continued)

1	2	3	4	5	6	7	8	9	10	11	12
H	4-$(CH_3)_2NC_6H_4$	28282/0,621	55,3	27,9	16,8	14126/0,0264	82,0	17,1	0,9	$1{,}6 \cdot 10^7$	0,134 (3,31 · 10^8, 2,14 · 10^9)
						16735/0,0227	1,9	15,3	82,8	$2{,}0 \cdot 10^7$	
						20938/0,0124	82,2	14,8	3,0	$1{,}4 \cdot 10^7$	
						21655/0,0098	0,2	2,5	97,3	$1{,}0 \cdot 10^7$	
						23462/0,0194	58,6	33,8	7,6	$5{,}7 \cdot 10^7$	
						26197/0,0212	34,5	43,2	22,3	$1{,}2 \cdot 10^8$	
						27475/0,0092	4,6	4,3	91,1	$2{,}8 \cdot 10^7$	
						28171/0,0697	89,0	7,7	3,3	$1{,}88 \cdot 10^9$	
7-CH_3O	H	30216/0,852	83,4	16,6	—	—	—	—	—	$1{,}87 \cdot 10^9$	0,217
7-CH_3O	C_6H_5	29702/0,879	74,8	21,2	4,0	—	—	—	—	$1{,}90 \cdot 10^9$	0,214
7-CH_3O	4-$CH_3OC_6H_4$	29541/0,875	73,2	22,3	4,1	—	—	—	—	$2{,}02 \cdot 10^9$	0,201
7-CH_3O	4-$(CH_3)_2NC_6H_4$	28964/0,829	61,4	25,1	13,5	—	—	—	—	$2{,}10 \cdot 10^9$	0,178
7-$N(CH_3)_2$	H	27224/0,890	91,7	8,3	—	—	—	—	—	$1{,}65 \cdot 10^9$	0,210
7-$N(CH_3)_2$	C_6H_5	27004/0,933	88,2	10,2	1,6	—	—	—	—	$2{,}24 \cdot 10^9$	0,168
7-$N(CH_3)_2$	4-$CH_3OC_6H_4$	27082/0,945	87,7	10,6	1,7	—	—	—	—	$2{,}17 \cdot 10^9$	0,175
7-$N(CH_3)_2$	4-$(CH_3)_2NC_6H_4$	26944/0,969	83,4	12,7	3,9	—	—	—	—	$2{,}10 \cdot 10^9$	0,183

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*R^1 and R^2 are the substituents (see Table 1);

$E(SI)$ is the energy of the lower excited singlet state (cm^{-1});

$E(T_i)$ are the energies of the triplet states (cm^{-1});

f is the oscillator strength of the S_0-S_1 transition;

β_{i1} is the matrix element of the spin–orbit coupling operator for the SI and T_i states (cm^{-1});

L_C, L_T, L_X are numbers indicating percentage localization of the electronic excitation respectively on the coumarin and thiazole moieties and on the substituent X;

k_F and k_D are the rate constants for emission of fluorescence and intersystem crossing (for compounds with R_1 = H, in column 11 we give the partial constants for intersystem crossing from the lower singlet state to a specific triplet level; in column 12, we give the overall constant; the data for the rest of the compounds are given in abbreviated form);

φ is the fluorescent quantum yield, calculated on the basis of the values obtained for k_F and the overall k_D.

Since the energy of the fluorescent $\pi\pi$-state remains practically unchanged (and also especially the energy of the singlet and triplet n,π states localized on the carbonyl group, which are generally not very sensitive to changes in the molecular structure), a likely reason for the deterioration in the fluorescent characteristics may be enhancement of the efficiency of intersystem crossing within the system of singlet and triplet levels of the π,π-type. In order to test the hypothesis advanced, we estimated the matrix elements of the spin–orbit coupling operator for the corresponding excited states, based on which we then calculated the intersystem crossing constants in the molecules of the studied thiazolylcoumarins (Table 3).

Our calculations are approximate, but nevertheless we can use them to draw certain conclusions. Thus, introducing a benzene ring into the 2 position of the thiazole ring of the thiazolylcoumarin molecule and then introducing electron-donor substituents into the indicated benzene ring does not lead to a substantial change in the nature and position of the lower singlet and triplet states. At the same time, the energy of a number of higher excited triplet levels is decreased; some of them even drop below the S_1 state. A special effect on the luminescent spectral properties comes from the lowering of the energy of the higher excited triplet levels, characterized by a more substantial spin–orbit coupling with the fluorescent S_1 state. And although the calculated matrix elements of the spin–orbit coupling operator are relatively small, 0.01-0.09 cm^{-1} (which should be expected when considering interaction between levels of the same orbital type), the small energy intervals between the S_1 level and the above-noted Ti terms lead to an appreciable increase in the efficiency of intersystem crossing, which in turn also is responsible for the decrease in the fluorescent quantum yield.

Thus, the deterioration in fluorescent properties of the studied thiazolyl derivatives of coumarin when π-conjugated moieties are introduced into the thiazole ring, including moieties containing pronounced electron-donor substituents, is determined by the increase in the spin–orbit coupling in the system of π,π-type levels.

EXPERIMENTAL

The investigated compounds were synthesized as in [1, 7]. The absorption spectra were measured on a Specord M-40 spectrophotometer; the fluorescence spectra were measured on a Hitachi F4010 spectrofluorimeter. The fluorescent quantum yields were determined relative to quinine bisulfate in 1 N sulfuric acid ($\varphi = 0.55$ [8]), introducing a quadratic correction for the difference between the refractive indices of the reference solution and the solutions to be measured. The optical densities of the solutions in the quantum yield determination were no greater than 0.2 for thickness of the absorbing layer equal to 1 cm. The kinetics of fluorescence were studied on an apparatus operating in the single-photon counting mode in the nanosecond range [9]. Mathematical treatment of the decay curves was done by the least-squares method [10, 11]. Quantum chemical calculations by the PPP SCF CI method taking into account up to 100 singly excited configurations were done with the set of parameters in [12, 13]. The matrix elements of the spin–orbit coupling operator for the $\pi\pi$-states were calculated according to the data in [14-19]; estimates of the rate constants for primary photophysical processes were obtained as in [17-19].

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