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Relationship between the structure and spectral-generation properties of coumarins benzopyrilium derivatives

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The spectral and generation parameters of new coumarins - benzopyrylium derivatives — in ethanol and acetonitrile under coherent excitation were studied. It was shown that these compounds are bichromophores. Based on quantum chemical calculations, it was established that for all the studied compounds the ground state (S_0) is characterized by an almost flat conformation of the aromatic part of their molecules. At the same time, the first excited state (S_1) is characterized by rotation of the perilium fragment by a certain torsion angle. The spatial orientation of the molecular orbitals of the structural elements of the molecules under study, the dipole moments and oscillator strengths of the $S_1 \rightarrow S_0$ electronic transition were determined. The relationship between these parameters and spectral and generation characteristics has been established. It has been shown that the nature of the substituents in the 6th and 7th positions of the coumarin backbone and benzopyrylium nucleus determines their lasing properties. Generation in the spectral region 715−740 nm was obtained using coumarin-class dyes.

Keywords: coumarins, benzopyrylium derivatives, absorption and fluorescence spectra, bichromophores, quantum chemical calculations, molecular orbitals, generation characteristics.

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Introduction

There are currently more than 60 pyrylium compounds for which generation has been observed [1]. These compounds are characterized by a large Stokes shift and have a rather high generation efficiency (up to 20%) [2]. In [3,4], benzopyran and benzopyrylium derivatives have been studied. It was shown that the condensation of benzoimidazole cycle with benzopyran derivatives allows not only to increase the generation efficiency, but also to increase significantly the photostability of active media [3]. Such compounds make it possible to shift the spectral range of generation of coumarin derivatives to the red region of the spectrum and expand significantly the range of smooth tuning of the generation wavelength [4].

It is known that the character of the solvate environment [5–8] has a great influence on the spectral-luminescence and generation characteristics of laser dyes. The fluorescence efficiency of polar and nonpolar dye solutions depends only slightly on the kind of anion [5]. In polar solutions, the quantum yield of fluorescence may not depend significantly on the species of anion. This is characteristic of the salt forms of dyes, including pyrylium salts. Complete dissociation of the dye salt occurs in polar solutions, and due to lability of the first excited singlet level, anions do not have time to diffuse to the dye molecule in the excited state [6]. If a non-polar solvent is used as an environment, molecules dissociate to a significantly lesser extent and the quenching anion remains in contact with the cation. This ultimately reduces the quantum yield of fluorescence. In addition, the position of the absorption, fluorescence, and generation bands [7] depends on the solvent type. The influence of the solvent, for example, depends on whether or not the dipole moment of the molecule and its spatial orientation change during the $S_0 \rightarrow S_1$ transition. A change of the solvent polarity in this process can affect the overlap of the absorption and fluorescence bands. It was shown in [8] that proton-donating solvents exert the strongest influence on the spectral-fluorescence and generation characteristics of benzopyran derivatives. The authors' analysis of their fluorescence characteristics showed that fixation of the diethylamino group by two saturated six-membered cycles leads to a change in the process of radiation-free deactivation of electronic excitation and stabilizes the molecule, which is reflected in the generation properties.

Studies of the relationship between the spectral and generation characteristics of new benzopyrylium derivatives and their molecular structure in various solvents are relevant in this context.

Experimental setup, objects, and measurement procedure

Absorption spectra of the studied compounds were measured with a Specord 200 spectrophotometer, and fluorescence spectra were recorded by a CM2203 SOLAR spectrofluorimeter under excitation to the maximum of the main absorption band of coumarins. A dye laser (DL) with

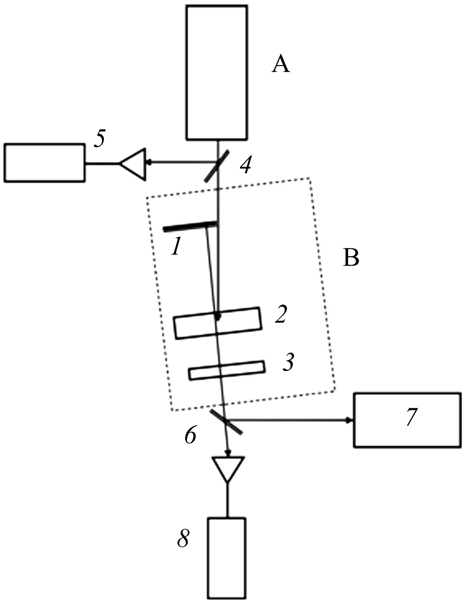


Figure 1. Diagram of the experimental setup: A — excimer laser; B — dye laser: *1, 3* — cavity mirrors, *2* — dye cuvette, *4, 6* — rotating plates, *5, 8* — energy meters, *7* — spectrograph.

coherent excitation was used to study the generation characteristics of benzopyrylium derivatives (Fig. 1). An electrodischarge excimer XeCl laser with a generation energy of 200 mJ, a wavelength of 308 nm, and a pulse duration of 60 ns served as the DL pump source. The XeCl laser radiation was focused by a cylindrical lens ($f = 10$ cm) onto a quartz cuvette 10×10 mm in size. The DL cavity with base $L = 15$ cm was formed by mirrors with reflection coefficients $R_1 \sim 100\%$ and $R_2 \sim 30\%$. Measurements of the DL generation energy and pumping energy control were carried out by IMO-2N meters. The broadband generation spectrum was recorded with an STE-1 spectrograph with light-guide transport of radiation.

New coumarins (benzopyrylium derivatives; see Fig. 2) under coherent excitation in ethanol and acetonitrile were the objects of the study. These compounds differ in that they contain a benzopyrylium nucleus with certain substituents in position 3 of the coumarin backbone.

Experimental results and discussion

The results of examination of benzopyrylium derivatives are presented in Table 1, where the name, structural formula of the compound, solvent (ethanol — EtOH, acetonitrile — ACN), absorption and fluorescence spectra, efficiency η_{gen}, and the spectral range of generation wavelength ($\Delta\lambda_{\text{gen}}$) are given.

As can be seen from Table 1, the absorption spectra in ethanol and acetonitrile of compound No. 1, which has no generating ability, and well-generating compound No. 3 are different. The presence of a diethylamino group in the benzopyrylium nucleus in position R_7 (compound No. 3) led to a significant difference in the structure and location of the main and side maxima in the absorption spectra. The main absorption maximum in ethanol (compound No. 1) is located at 420 nm, and the side absorption maximum is located at 660 nm. In acetonitrile, the opposite is true: the main maximum corresponds to 610 nm, while the side maximum is at 410 nm. In compound No. 3, the main maximum corresponds to 660 nm, and the side maxima are at 480 and 395 nm. The presence of two absorption bands in blue and red regions of the spectrum confirms the bichromophoric nature of these compounds. However, the presence of only one band in the fluorescence spectrum may be attributed to the localization of excitation exclusively at the coumarin backbone due to efficient charge transfer from the benzopyrylium nucleus. The fluorescence spectra are structureless, and the Stokes shift is 97 and 40 nm, respectively. A similar transformation of the absorption spectrum in acetonitrile is observed for compound No. 3.

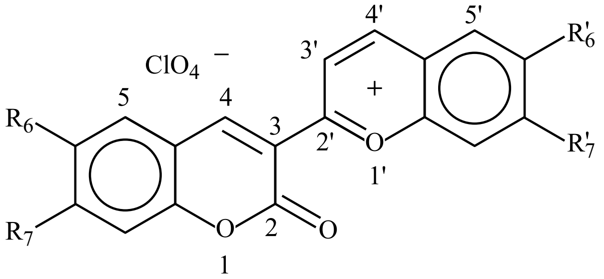
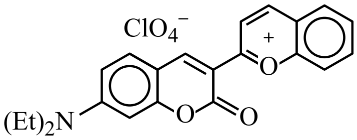
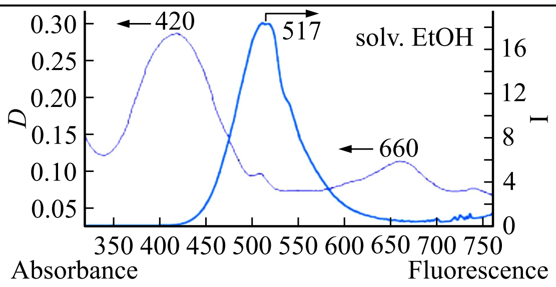
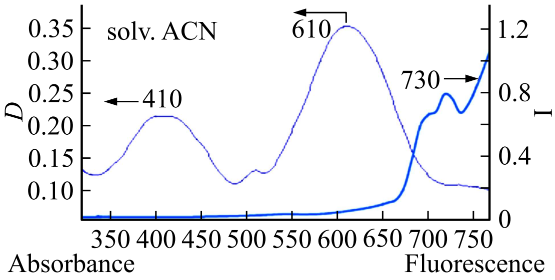
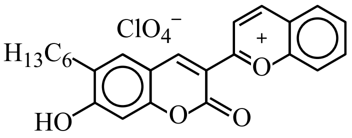
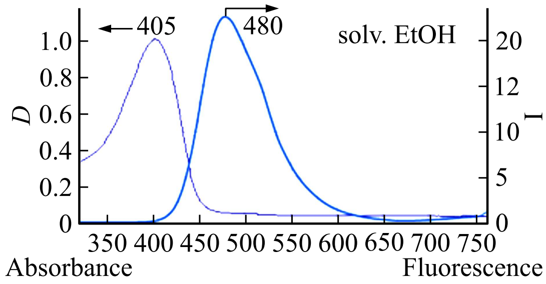
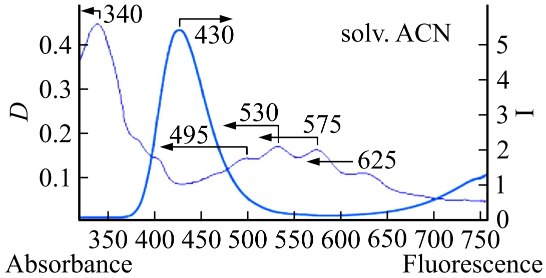


Figure 2. General structure of a benzopyrylium derivative: R_6 — C_6H_{13}; R_7 : $(Et)_2N$, OH; R'_6 — C_6H_{13}; R'_7 — $(Et_2)N$, OH.

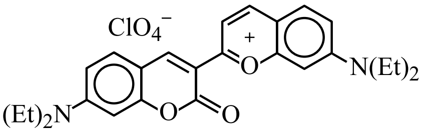
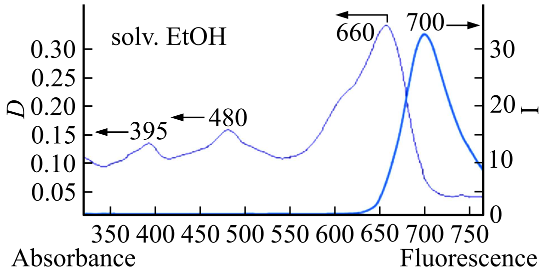
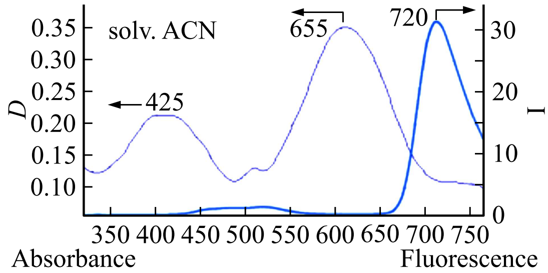
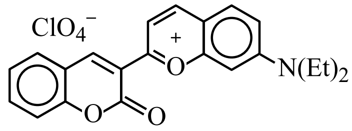
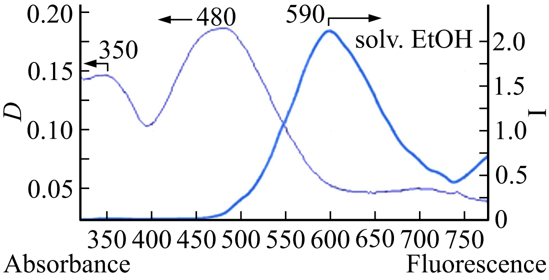
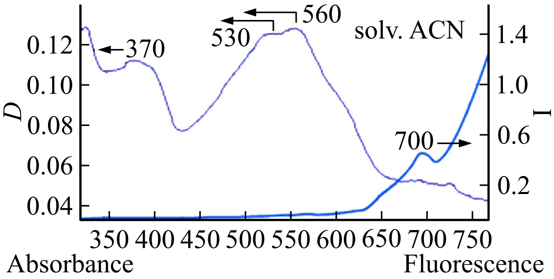
For compound No. 2 containing hydroxyl -OH(R_7)- and hexyl -C_6H_{13}(R_6)- groups in the coumarin core structure, the absorption and fluorescence spectra in ethanol have only one major maximum with wavelengths of 405 and 480 nm, respectively. The presence of only one short-wavelength absorption band indicates that the absorption of radiation is provided by the coumarin chromophore without the involvement of benzopyrylium. This is facilitated by the hexyl group located in the 7th position of the coumarin backbone. In acetonitrile, however, the pattern changes: a short-wavelength maximum ($\lambda = 340$ nm) and a long-wavelength structured absorption band ($\lambda = 495{-}625$ nm) of a lower intensity appear in the absorption spectrum. The peculiarity of acetonitrile is determined by the fact that it is an *n*-donor solvent possessing non-bonding unshared pairs of *n*-electrons, which lend basic properties to it. As a consequence, the charge oscillation along the conjugation chain, which also includes the benzopyrylium fragment, increases. The fluorescence spectrum has a typical appearance with a main maximum around 430 nm and increasing intensity in the long-wavelength region ($\lambda > 700$ nm). The lack of generation of compounds Nos. 1 and 2 may be attributed to the presence of a broad absorption band in the fluorescence region.

Table 1. Spectral and generation characteristics of benzopyrylium derivatives

№	Compound	Absorption, and fluorescence spectra, solvent	η_{gem}, , %	$\Delta\lambda_{gem}$ nm
1	2	3	5	6
1	 7-diethylamino-3-(benzopyrylium-2)-coumarin perchlorate		no generation	–
			no generation	–
2	 7-hydroxy-6-hexyl-3-(benzopyrylium-2)-coumarin perchlorate		no generation	–
			no generation	–

Compared to compound No. 3, compound No. 4 is characterized by the lack of a diethylamino group in position R_7 of the coumarin core. This resulted in the disappearance of the long-wavelength absorption band ($\lambda = 660$ nm, compound No. 3) and a significant increase in the intensity of the short-wavelength absorption band with maxima at 480 and 350 nm in ethanol. The presence of only one hypsochromic absorption band in this compound is indicative of the predominant role of the 7-diethylaminobenzopyrylium chromophore and weak coupling with the coumarin backbone due to the lack of a substituent in position R_7 of the coumarin core. Probably, the lack of group $N(Et)_2$ in the coumarin backbone does not ensure the formation of a single π-electron conjugation chain between coumarin and benzopyran fragments. The Stokes shift of the fluorescence spectrum was 110 nm; this compound has no generating ability. In acetonitrile (compared with ethanol solution), splitting of the main absorption maximum into two components and a bathochromic shift of the absorption band to 80 nm are observed. The fluorescence spectrum has an atypical shape with an anomalously large Stokes shift (110 nm) relative to

Table 1. (*Continued*).

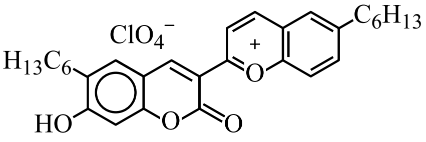
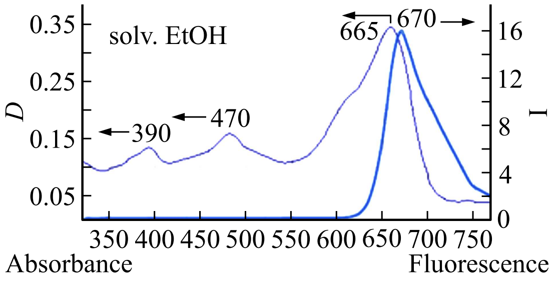
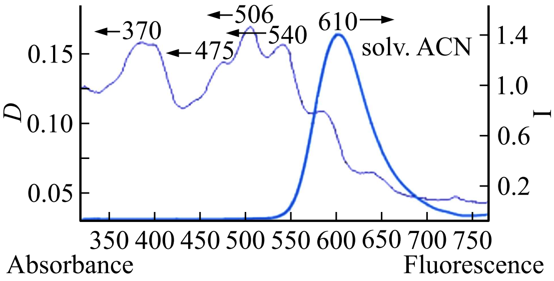
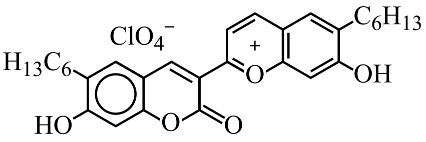
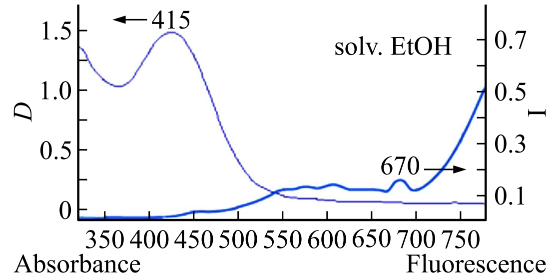
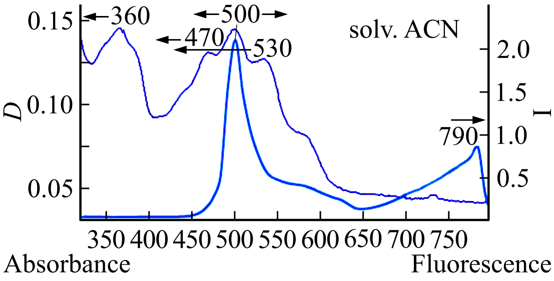
№	Compound	Absorption, and fluorescence spectra, solvent	η_{gem}, , %	$\Delta\lambda_{\text{gem}}$ nm
1	2	3	5	6
3	 7-diethylamino-3-(7-diethylamino-benzopyrylium-2)-coumarin perchlorate		3	715–730
			12.6	730–740
4	 3-(7-diethylamino- benzopyrylium-2)-coumarin perchlorate		no generation	–
			no generation	–

the weak maximum (700 nm) and increasing intensity in the > 750 nm region.

Comparing the absorption and fluorescence spectra of compounds Nos. 4 and 1, we note their similarity. Transfer of the 7-diethylamino group from the coumarin backbone to the benzopyrylium nucleus does not actually change the shape of absorption and fluorescence bands of the bichromophore; instead, it leads just to a bathochromic shift of the maxima in their spectra (~ 50 nm) in ethanol and their hypsochromic shift in acetonitrile (~ 30–50 nm).

For compounds Nos. 5 and 6 containing hexyl groups in positions R_6 and R'_6 and a hydroxyl group in position R_7 in the structure of the coumarin backbone and the benzopyrylium nucleus, the absorption spectra in ethanol and acentonitrile also differ significantly (Table 1). The absorption spectrum in ethanol (compound No. 5) is rather broad: in addition to the main band ($\lambda = 665$ nm), it contains maxima of a lower intensity located in the regions of 470 and 390 nm. The fluorescence spectrum is fairly narrow, and its feature is a large overlap with the long-wave absorption band. The Stokes shift is ~ 5 nm. In acetonitrile, broadening, sharp patterning, and short-wavelength shifts of the main absorption band by ~ 160 nm and fluorescence by ~ 60 nm are observed. The Stokes shift is 100 nm. The

Table 1. (*Continued*).

№	Compound	Absorption, and fluorescence spectra, solvent	η_{gem}, %	$\Delta\lambda_{gem}$ nm
1	2	3	5	6
5	 7-hydroxy-6-hexyl-3-(6- hexyl-benzopyrylium-2)-coumarin perchlorate		limit	725
			0.8	608–630
6	 7-hydroxy-6-hexyl-3-(7- hydroxy-6-hexyl-benzopyrylium-2)-coumarin perchlorate		limit	600
			0.8	555–567

intensity of the absorption maximum in the region of 370 nm in acetonitrile also increases significantly. The compound generates near-threshold emission in the region of 720 nm (ethanol) and 608–627 nm (acetonitrile). The emergence of generation on the long-wavelength wing of the fluorescence spectrum is associated with lower intrinsic absorption.

The presence of a hydroxyl group (R_7') in the benzopyrylium nucleus (compound No. 6) resulted in the transformation and emergence of only one main maximum (415 nm) in the ethanol absorption spectrum. The fluorescence spectrum contains a weak maximum around 670 nm and grows sharply in intensity in the long-wavelength region (700–800 nm). In acetonitrile, as with compound No. 5, broadening, patterning, and a bathochromic shift of the absorption band are observed. The main structured absorption maximum with a half-width of ~ 100 nm is in the region of 500 nm, and the short-wavelength one (narrower) is located at 360 nm. It is characteristic that the fluorescence spectrum also contains two bands. The first (narrowest) corresponds to the main absorption maximum (500 nm), and the second, of lower intensity, has a maximum in the region of 790 nm. Significantly, the fluorescence spectrum of the bichromophore is anomalously broad, and the main fluorescence band overlaps almost completely with the absorption spectrum. Despite this, the generation spectrum of compound No. 6 is located in the region of 555–567 nm.

The example of generating and non-generating compounds (Table 1) illustrates the important role of substituents in the 6th and 7th positions of the coumarin core, as well as in positions $6'$ and $7'$ of the benzopyrylium nucleus. The presence or lack of only electron-donor substituents in position 7 and unsubstituted positions $6'$ and $7'$ of the benzopyrylium nucleus leads to transformation of the absorption and fluorescence spectra and loss of generating ability of compounds. Conversely, the presence of electron-donor substituents in positions 6 or 7 of the coumarin backbone and electron-acceptor substituents -$N(C_2H_5)_2$ and -OH in position $7'$ of the benzopyrylium nucleus ensures efficient oscillation of π-electrons along the conjugation chain and the emergence of generation.

At the same time, the compounds with the highest generative efficiency are those with an $N(Et)_2$-group in position 7 of the coumarin backbone and position $7'$ of the benzopyrylium nucleus. The most efficient generation was obtained in compound No. 3, which emits in the far red region of the spectrum (730–740 nm) with a sufficiently high efficiency — 12.6% (acetonitrile). Compounds containing a hydroxyl OH-group in these positions are characterized by a lower generation efficiency. The presence of a hexyl group in positions 6 and $6'$ does not affect significantly the generating ability of the studied compounds.

Quantum-chemical calculations of the molecular structure, dipole moments, and oscillator strengths of the $S_1 \to S_0$ transition were carried out to further elucidate the peculiarities of influence of these substituents and the reasons for the difference in spectral and generation properties of benzopyrylium derivatives. Quantum-chemical calculations of the studied compounds were performed in the Firefly 8.0.1 [9] software package. The electron density functional method with the B3LYP three-parameter hybrid functional [10,11] and the 6-31G(d,p) basis function set [12] was applied in these calculations. Calculations were performed for single coumarin molecules in the gas phase (in vacuum) in zero electrostatic fields. First, we optimized the geometry of molecules in the ground singlet (S_0) electronic state to obtain an equilibrium geometry corresponding to the energy minimum. The resulting equilibrium geometry was used to calculate the equilibrium structure of molecules in the first excited singlet (S_1) state. Calculations and analyses of the Franck–Condon states of molecules have not been performed.

Optimization of state S_1 of the studied molecules revealed that the primary changes in the geometry of molecules in the search for an energy minimum in the excited state are due to rotation of their benzopyrylium fragment (BF) relative to the coumarin (C) fragment. To determine the position of fragments relative to each other, we introduce angle φ between planes m and n (Fig. 3). We will consider this angle as the main numerical parameter characterizing the geometry of molecules. The position of plane m is determined by atoms C2, C3, and C2$'$, and atoms C3, C2$'$, and O1$'$ define the position of plane n. Thus, angle φ is the C2–C3–C2$'$–O1$'$ torsion angle. The values of angle φ, dipole moment d for the studied benzopyrylium derivatives in states S_0 and S_1, and transition oscillator strength f are presented in Table 2.

The results of calculation of excited state S_1 of benzopyrylium derivatives showed that compounds Nos. 2 and 3 are characterized by a flat conformation of the aromatic part (angle φ for them is even smaller than in the S_0 state), while compounds Nos. 1, 4, 5, and 6 have a non-planar conformation of the aromatic part with their torsion angle φ being close to 90°. The analysis of HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) boundary molecular orbitals shows that they are localized on different aromatic fragments in the equilibrium excited state for compounds Nos. 1, 4, 5, and 6 (Table 3). Thus, the spatial overlap between them is negligibly small. This is the reason for the extremely low value of oscillator strength f of electronic transition S_1–S_0. Consequently, these benzopyrylium derivatives should have a very low value of fluorescence quantum yield (γ), which is confirmed experimentally to be of the order of a few percent. This may also be the reason for the lack or weakness of generation of these compounds. Since these benzopyrylium derivatives have boundary molecular orbitals localized on different aromatic fragments, the electric charge distribution of these molecules is non-uniform and leads to an increase in electric dipole moment d compared to state S_0 by a factor of more than 2 (and a factor of more than 3 for compound No. 6). In turn, derivatives Nos. 2 and 3 have very high oscillator strength values and low values of the electric dipole moment, since the orbitals for these derivatives are localized almost uniformly throughout the molecule.

Table 3 shows that the presence and type of substituents in positions R_6, R_7, R'_6, and R'_7 significantly affects the spatial position and electron density distribution along the molecular orbitals of coumarin and benzopyran fragments.

For compound No. 1, which does not contain substituents in positions R6$'$ and R7$'$ of the benzopyrylium nucleus, the spatial orientation of boundary MOs shows that the S_0 state is characterized by an almost flat LUMO and HOMO conformation ($\varphi \sim 1.7^\circ$). However, in state S_1, the LUMO is localized only on the benzopyrylium backbone, while HOMO is localized on the coumarin core with a torsion angle of $\sim 90^\circ$. The dipole moments of states S_1 and S_0 differ by a factor of ~ 2 and the oscillator strength is negligible ($\sim 10^{-5}$). These compounds have no generating ability.

For compound No. 2 containing a hexyl group (R6) in the coumarin core, the electron density distribution over the LUMO and HOMO in the S_0 state covers both backbones, and torsion angle φ assumes a negative value of $\sim -12.53^\circ$. At the same time, the LUMO hexyl group is virtually non-excited. In state S_1, the LUMO is localized only on the benzopyrylium fragment, while the HOMO is localized only on the coumarin backbone, including the hexyl group. In

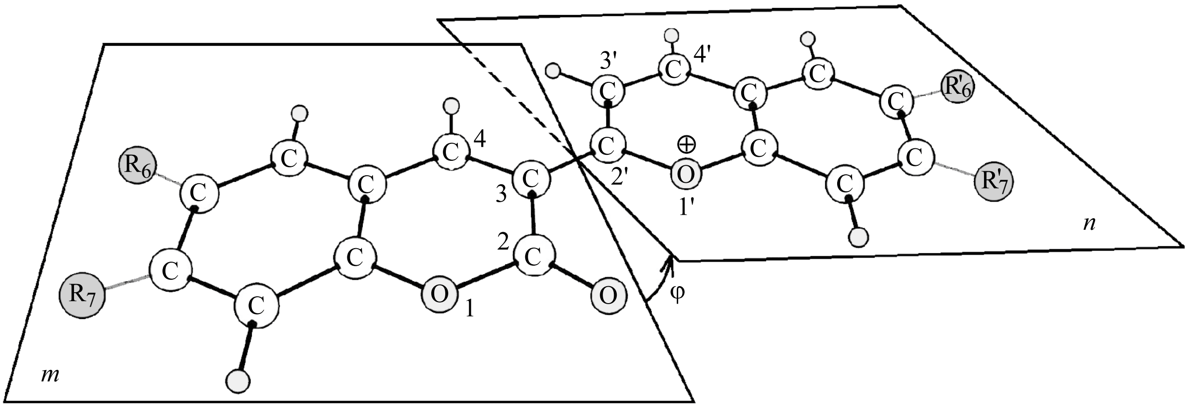


Figure 3. Spatial structure of the aromatic part of molecules of benzopyrylium derivatives: R_6, R_7, R'_6, R'_7 — lateral substituents (Table 2).

Table 2. Torsion angle φ, dipole moment d, and oscillator strength f of transition $S_1 \to S_0$ of benzopyrylium derivatives

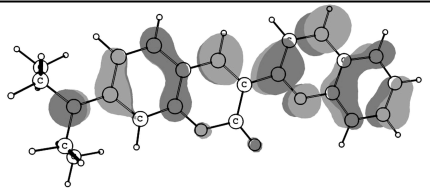
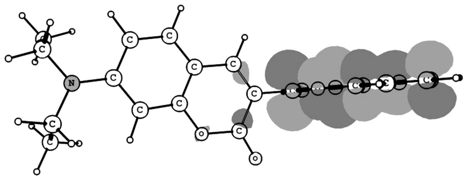
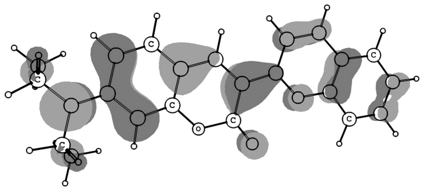
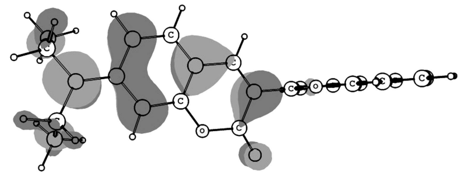
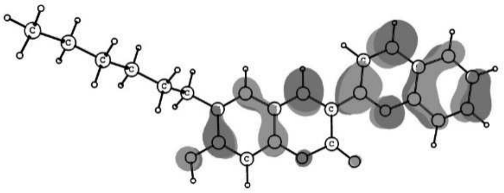
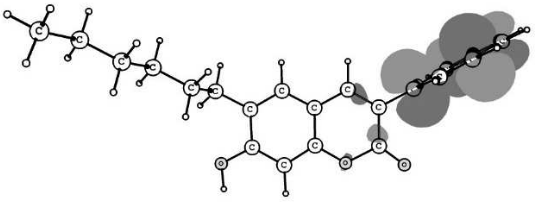
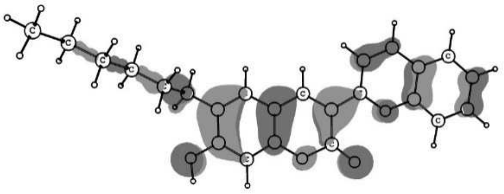
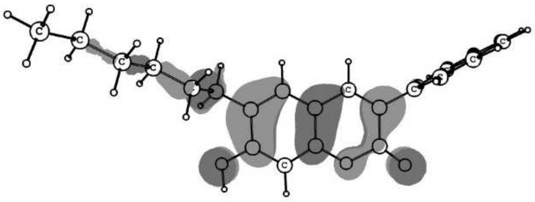
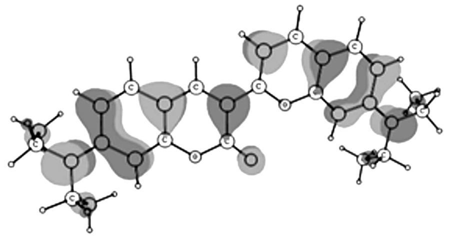
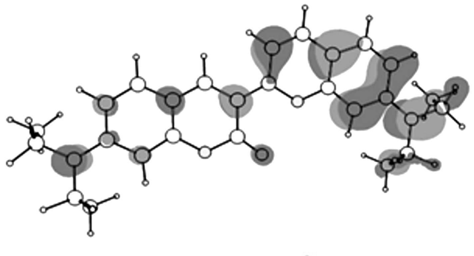
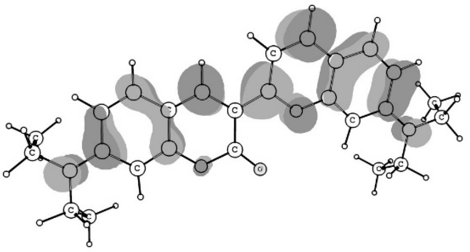
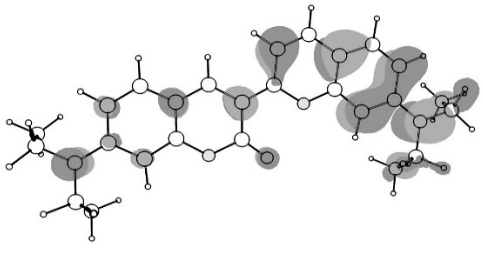
№	Compound name	Substituents				φ		d, D		f
		R_6	R_7	R'_6	R'_7	S_0	S_1	S_0	S_1	$S_1 \to S_0$
1	7-diethylamino-3-(benzopyrylium-2) -coumarin perchlorate	H	$N(C_2H_5)_2$	H	H	1.70o	89.66°	13.88	28.97	10^{-5}
2	7-hydroxy-6-hexyl-3-(benzopyrylium-2) -coumarin perchlorate	H	$N(C_2H_5)_2$	H	$N(C_2H_5)_2$	−12.53°	−0.47°	5.99	3.92	0.427
3	7-diethylamino-7-(3-diethylamino -benzopyrylium-2)-coumarin perchlorate	H	H	H	$N(C_2H_5)_2$	−27.38°	−0.0°	6.85	10.66	0.221
4	3-(7-diethylamino-(benzopyrylium-2) -coumarin perchlorate	C_6H_{13}	OH	H	H	7.53°	88.79°	9.44	24.50	10^{-4}
5	7-hydroxy-6-hexyl-3 -(6-hexylbenzopyrylium-2)-coumarin perchlorate	C_6H_{13}	OH	C_6H_{13}	H	10.20°	88.81°	9.16	25.17	10^{-4}
6	7-hydroxy-6-hexyl-3-(7-hydroxy-6-hexylbenzopyrylium-2) -coumarin perchlorate	C_6H_{13}	OH	C_6H_{13}	OH	14.82°	88.38°	7.60	25.32	10^{-4}

this case, the benzopyrylium moiety is rotated relative to the coumarin backbone by torsion angle $\varphi = 0.47°$ and is not excited, the dipole moments decrease significantly, by a factor of 2 (S_0) and 7 (S_1), and the transition oscillator strength increases ($f_{S_1-S_0} \sim 0.427$). Thus, the difference in localization of molecular orbitals on coumarin and benzopyrylium backbones in states S_0 and S_1 does not ensure their conjugation in the excited state, which is a possible reason for the significant hypsochromic shift of the absorption spectrum in acetonitrile (by ~ 100 nm), the lack of generation, and the weak fluorescence ability of this compound.

The presence of a diethylamino group in position R7′ of the benzopyrylium nucleus (compound No. 3) changes the situation significantly compared to compound No. 1. The LUMO and HOMO electron density in the S_0 state is distributed over coumarin and benzopyrylium backbones, despite the increased value of torsion angle $\varphi \sim -27°$. In excited state S_1, the LUMO and HOMO are localized on both fragments of the molecule and are in the same plane. The smallness of the torsion angle ($\varphi \sim -0.05°$) facilitates the establishment of a conjugation chain of π-electron shells on both backbones, including two terminal diethylamino groups. As a consequence, the absorption and fluorescence spectra of compound No. 3 are significantly shifted to the red region and their maxima are located in the 660 and 700 nm regions, respectively. At the same time, the difference between dipole moments of the transition in states S_0 and S_1 decreases by a factor of ~ 1.5 and oscillator strength f increases significantly to ~ 0.2. This compound generates radiation quite well.

For compound No. 4, which is characterized by the lack of a diethylamino group in the coumarin backbone (R7), the spatial distribution of molecular orbitals in the S_0 state (LUMO and HOMO) shows that they are also localized on the coumarin and benzopyrylium moieties with torsion angle $\varphi \sim 7.5°$. However, in the S_1 excited state, the HOMO is localized only on the benzopyrylium backbone and the -$N(C_2H_5)_2$-group, which is rotated relative to the coumarin fragment by $\varphi \sim 88.8°$. This is probably why

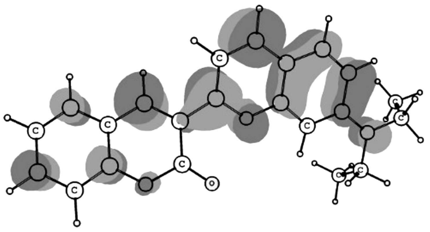
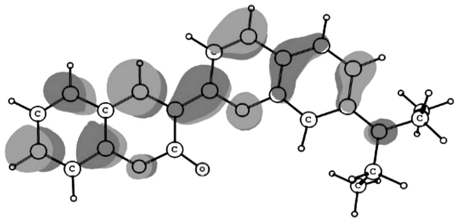
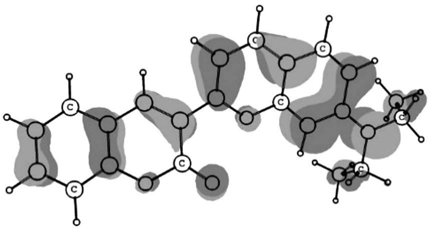
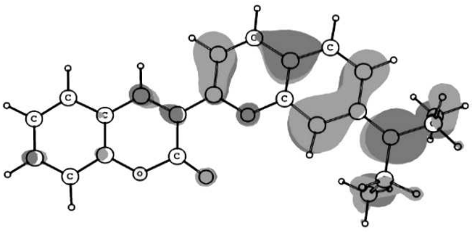
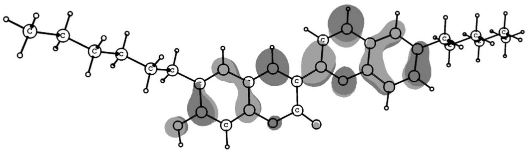
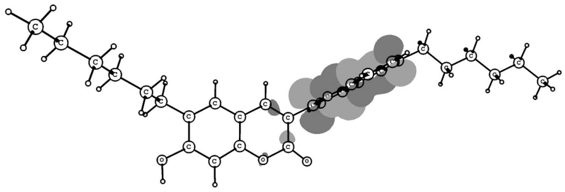
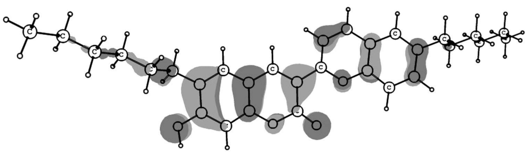
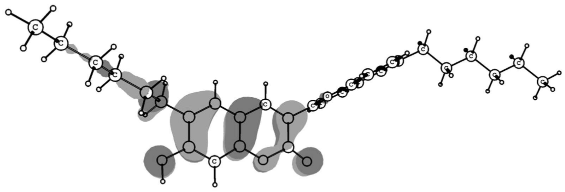
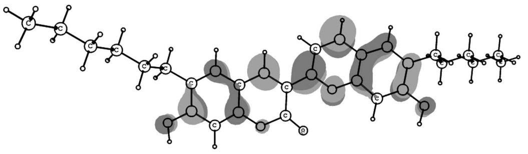
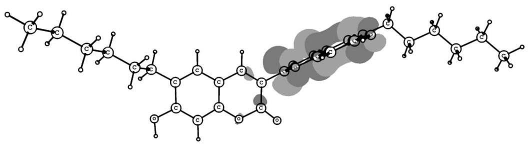
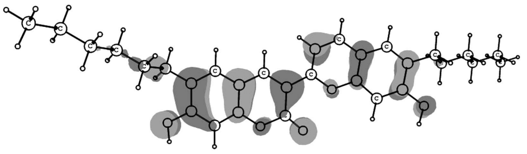
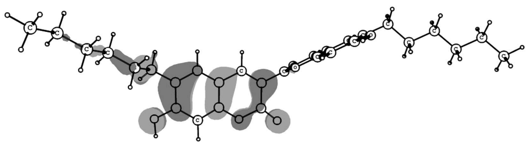
Table 3. Optimized geometry of benzopyrylium derivative molecules and their HOMO and LUMO boundary molecular orbitals in ground (S_0) and excited (S_1) equilibrium states

№compound 1	Orbital 2	S_0 3	S_1 4
1	LUMO		
	HOMO		
2	LUMO		
	HOMO		
3	LUMO		
	HOMO		

there is a significant difference (~ 2.5 times) between the dipole moments of the S_0 and S_1 states, and the oscillator strength is very low ($f \sim 10^{-4}$). Thus, the difference in localization of molecular orbitals of coumarin and benzopyran fragments in states S_0 and S_1 does not ensure the formation of a single π-electron conjugation chain of the molecule. This confirms the observed large hypsochromic shift of absorption (180 nm) and fluorescence (~ 100 nm) spectra compared to compound No. 3.

For bichromophores Nos. 5 and 6 differing only in the presence or absence of a hydroxyl group -ON in position R7′ of the benzopyrylium nucleus, LUMO and HOMO states S_0 are distributed over coumarin and benzopyrylium backbones in the main plane of molecules with torsion

Table 3. (*Continued*)

№compound 1	Orbital 2	S_0 3	S_1 4
4	LUMO		
	HOMO		
5	LUMO		
	HOMO		
6	LUMO		
	HOMO		

angles φ of $\sim 10.2^\circ$ and 14.8°, respectively. The hexyl groups contained in the structure of both backbones (in position R6′) are perpendicular to the main plane of molecules.

In the excited S_1 state, the lowest vacant MO is localized only on the benzopyrylium moiety and is rotated by $\sim 88.8^\circ$ (compound No. 5) and $\sim 88.4^\circ$ (compound No. 6) relative to the plane of the coumarin core. However, the HOMO in this state encompasses both backbones despite the difference in their spatial orientation. This is probably the reason why the π-electron conjugation chain between two fragments of the molecule is provided, which is confirmed by the higher fluorescence quantum yield and generating ability of these compounds. The difference of dipole moments of states S_0 and S_1 is also significant and equal to ~ 16 and ~ 18 D, respectively.

Thus, the results of quantum-chemical calculations have shown that for generating compounds in the S_0 state, an almost flat conformation of the aromatic part of these molecules is typical, which is achieved due to the small torsion angle of rotation. In the S_1 state, both planar and orthogonal conformations of the molecule are possible, which are determined by the presence of substituents in certain positions of the coumarin and benzopyrylium nuclei and ensure the formation of a single chain of π-electron conjugation between the benzopyrylium and coumarin fragments.

Conclusion

The study of spectral-luminescent properties of benzopyrylium derivatives in ethanol and acetonitrile showed that their absorption and fluorescence spectra contain several maxima. The structuring and broadening of spectra are associated with the bichromophoric structure, which includes a coumarin backbone and a benzopyrylium nucleus, of these compounds. The structuring of absorption spectra is more evident in acetonitrile. The absorption spectra of the studied compounds are located in the range of 350−750 nm, while the fluorescence spectra are localized in the region of 500−800 nm, have weak intensity, and are broadened.

The relation between the spectral and generation properties of benzopyrylium derivatives and the spatial arrangement of molecular orbitals has been studied. It is shown that the difference in localization and spatial position of MOs of the coumarin and benzopyrylium fragments in the S_0 and S_1 states does not ensure the formation of π-electron conjugation between them, which is confirmed by a large hypsochromic shift of the absorption and fluorescence spectra and, accordingly, by the lack of generation.

It is shown that the presence of substituents in certain positions of the coumarin backbone and the benzopyrylium nucleus changes the conformation of the molecule and, accordingly, the dipole moments and transition oscillator strengths. The generating ability in coumarins of this class is manifested only in the presence of the strongest donor substituents in position 7, such as Et_2N- and -ON, and sufficiently strong acceptors in positions R'_6 and R'_7.

Conflict of interest

The authors declare that they have no conflict of interest.

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