

Spectral-kinetic study of new hybrid photochromic coumarinopyrans with reversible fluorescence modulation

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Photochromic hybrid compounds based on coumarins with reversible fluorescence modulation have been synthesized for the first time. It was shown that UV irradiation leads to spectral and fluorescent changes due to the structure of the compounds.

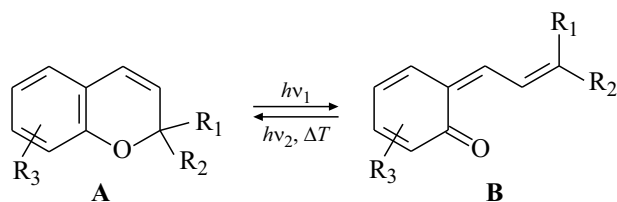
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Introduction

Photochromic organic compounds attract considerable interest, since they can be used to create various devices and materials that change their properties under the action of light. So, on the basis of organic photochromes, lenses for sunglasses, optical labels and other things are produced [1–3]. The development of this direction is also important for the development of optical devices for recording, reading and storing information [4], drugs with photocontrolled pharmacological activity [5].

The most promising photochromic compounds are benzo- and naphthopyrans (chromenes) [2], since they primarily have a higher photochemical stability compared to other organic photochromic compounds, in particular, spiropyrans and spirooxazines. In the cyclic (closed) form **A** they are colorless, but under the action of UV radiation or sunlight, the C–O– bond of the pyran ring is broken, followed by *cis-trans*-isomerization, resulting in the formation of an open colored form **B** capable of reversible photoinduced or thermal change in spectral characteristics (Scheme 1).



Scheme 1. Photochromic transformations of chromenes.

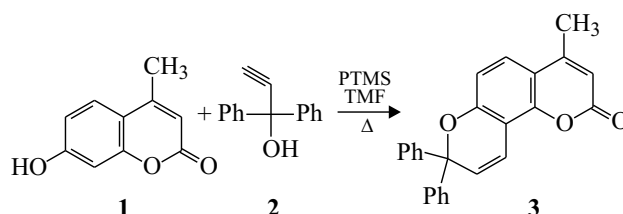
Preparation of hybrid compounds containing naphtho(benzo)pyran fragment in the molecule capable of photochromic transformations and a coumarin fragment possessing luminescent properties makes it possible to influence fluorescence through photochromic transformations

in the molecule. The spectral and kinetic properties of such compounds depend to a large extent on the nature of the substituents and their mutual configuration. We have previously synthesized a number of hybrid compounds, based 3-methyl-6-hydroxyperinaphthenone [6] and 3-methyl-6,9-dihydroxyphenalenone [7], which have luminescent properties, as substrates of 1,1-diaryl-2-propyn-1-ols of various structures.

The aim of this article is to synthesize and study the photochromic and luminescent properties of three new hybrid naphthopyrans containing coumarin as a fluorescent fragment.

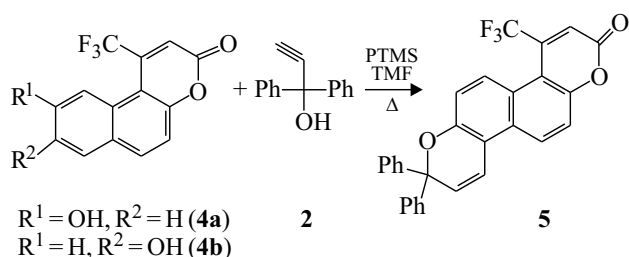
Experimental part

For the synthesis of new compounds, hydroxy-coumarins were used as starting materials. Thus, in the interaction of commercial 7-hydroxy-4-methyl-2H-chromen-2-on **1** with commercial 1,1-diphenyl-2-propyn-1-ol **2** using pyridinium *para*-toluenesulfonate or pyridinium trifluoromethanesulfonate as catalysts, 1-methyl-8,8-diphenylpyrano[3,2-f]chromen-3(8H)-on **3** was obtained (Scheme 2) with yield of 37%.



Scheme 2. Synthesis of chromene **3** using pyridinium trifluoromethanesulfonate (PTMS) catalyst in the presence of trimethylorthoformate (TMF).

The compound 8,8-diphenyl-4-(trifluoromethyl)chromeno[6,5-f]chromen-2(8H)-one **5** was obtained as a result of the interaction of 8-hydroxy-1-(trifluoromethyl)-3H-benzo[f]chromen-3-one **4b** with propargyl alcohol **2** (Scheme 3) with yield of 23%.



Scheme 3. Synthesis of chromene **5** using pyridinium trifluoromethanesulfonate (PTMS) catalyst in the presence of trimethylorthoformate (TMF).

When 9-hydroxy-1-(trifluoromethyl)-3H-benzo[f]chromen-3-one **4a** is used as a reagent, chromene synthesis does not occur.

The structure of the obtained compounds was confirmed by the data of the NMR spectra and mass spectroscopy.

Synthesis of **4a** and **4b** compounds was carried out according to the Pechman condensation method by the interaction of 2-hydroxy-6- and 2-hydroxy-7-methoxynaphthalene with trifluoroacetoacetic ester in polyphosphoric acid followed by demethylation.

Spectrophotometric measurements of **3** and **5** compounds solutions in toluene were carried out on „CARY 60 UV-Vis“ spectrophotometer and „CARY Eclipse“ spectrofluorimeter under irradiation with light of LC-4 xenon lamp by „Hamamatsu“. For photocoloration, a glass light filter UFS-1, which transmits UV radiation, was used, and for photodiscoloration, a glass light filter ZhS-12, which transmits visible light, was used.

Optimization of the geometry of molecules and the charge density on atoms was performed by the DFT method in the package Orca 4 using the functionality in the def2-SVP and 6-311G** basis sets.

Results and discussion

The absorption spectrum of the closed form **A** of the compound **3** has a narrow band with a maximum at 344 nm. Under the action of UV light, the compound **3** transforms into the open form **B** (Scheme 4), which has a wide band in the visible range from 400 to 750 nm (Fig. 1, curves 1, 2), which gives gray tint to the solution. Simultaneously, the intensity of the fluorescence band decreases with a maximum at 393 nm (Fig. 1, curve 6). The absorption spectrum of chromene coincides with the fluorescence

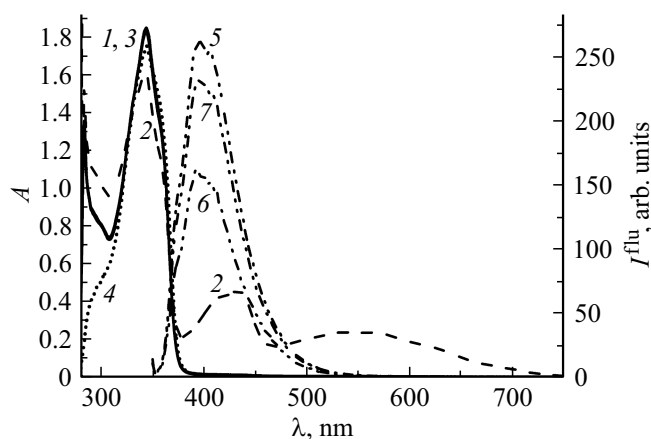


Figure 1. Spectra of absorption (1–3), fluorescence excitation when measuring at wavelength of 393 nm (4) and fluorescence when excited by light with wavelength of 344 nm (5–7) of the compound **3** in toluene up to (1, 4, 5), during irradiation through light filters UFS-1 (2, 6) and during dark spontaneous relaxation (3, 7).

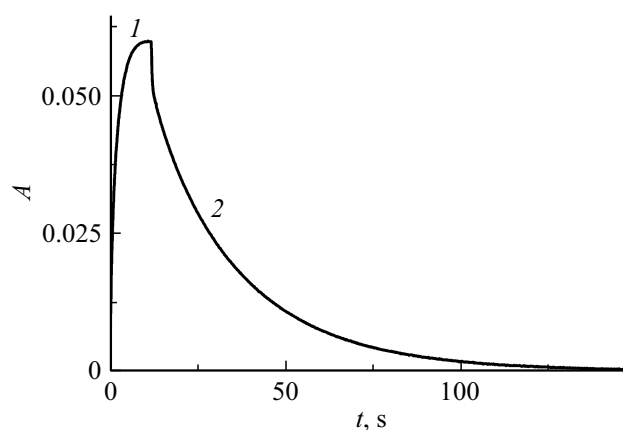
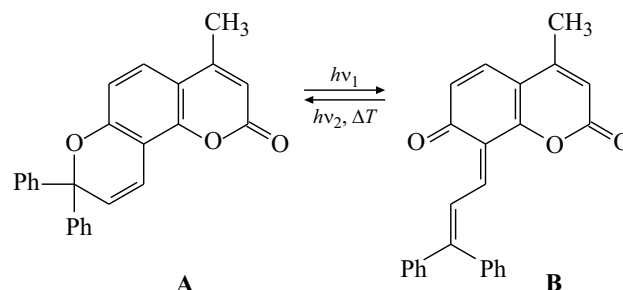


Figure 2. Kinetic curve of cyclic photocoloration (1) and dark discoloration (2) of compound **3** in toluene measured at 535 nm.

excitation spectrum.



Scheme 4. Photochromic transformations of chromene **3**.

In the course of dark relaxation, the photoinduced absorption of the form **B** disappears and the intensity of both the absorption band (Fig. 1, curve 3) and the fluorescence of the form **A** is restored (Fig. 1, curve 7). The kinetic curve of the processes of photocoloration and dark discoloration

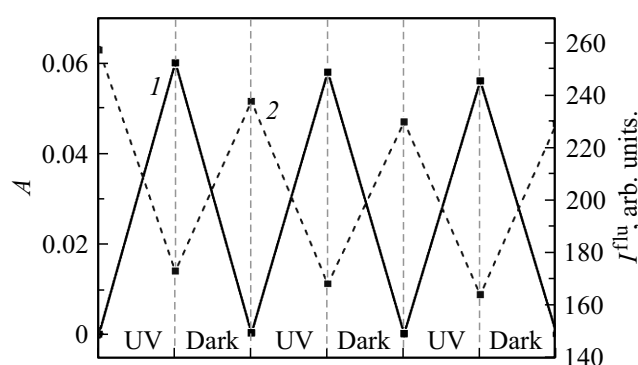


Figure 3. Absorption modulation when measuring at wavelength of 535 nm (1) and fluorescence intensity at wavelength of 394 nm (2) of the compound 3 in toluene under cyclic UV light irradiation and dark relaxation.

Calculation of charge density on hydroxyl fragments **4a** and **4b**

Atom	4a		4b	
	def2-SVP	6-311G**	def2-SVP	6-311G**
O	-0.191481	-0.651682	-0.202093	-0.657833
H	0.186223	0.173207	0.187243	0.168812

is shown in Fig. 2. These processes can be carried out repeatedly, as evidenced by the observed modulations of the absorption and fluorescence intensity during alternate irradiation with UV light and dark relaxation (Fig. 3).

The compound **5** is characterized by the same photoinduced spectral changes as for chromene **3**. However, the efficiency of these transformations turned out to be much lower (Fig. 4, curves 1, 2). Kinetic studies have shown that the rate of the photocoloration reaction is 4 times slower than that of the compound **3**. The dark reaction is slower by two orders of magnitude and has a two-exponential character. The values of the fluorescence intensity of the compound **5** are three times higher (Fig. 4, curve 5), and the efficiency of the photoinduced change in its intensity is also insignificant (Fig. 4, curve 6). The cyclicity of intensity modulation of absorption and fluorescence under alternate irradiation with UV and visible light is shown in Fig. 5. Similar photoinduced spectral changes were observed by us earlier for hybrid compounds based on hydroxyperinaphthenon [6] and dihydroxyphenalene [7].

To determine the factors influencing the course of the reaction of obtaining chromenes, the geometry of the initial compounds **4a** and **4b** was optimized using computational methods. The modeling results are shown in Fig. 6. The reason for the impossibility to obtain chromene using 9-hydroxy-1-(trifluoromethyl)-3H-benzo[f]chromen-3-one **4a**, apparently, is that cyclization reactions are hindered by steric hindrances in the *ortho*-position of the hydroxyl group of the compound **4a** (position of the 10th molecule) created by the adjacent trifluoromethyl group (Scheme 3).

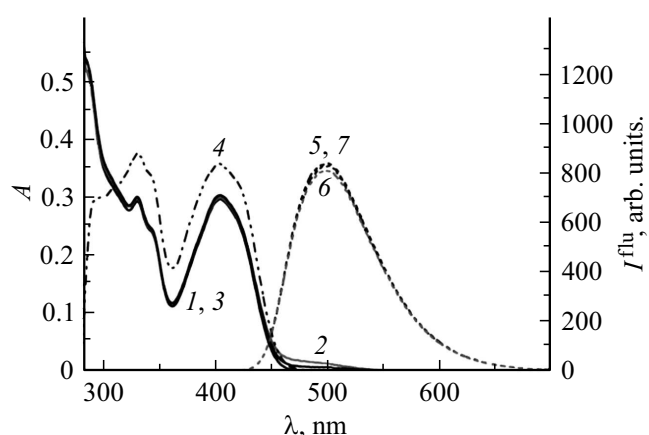


Figure 4. Spectra of absorption (1–3), fluorescence when excited by light with wavelength of 405 nm (5–7) and fluorescence excitation when measuring at wavelength of 501 nm (4) of the compound **5** in toluene, up to (1, 4, 5), during irradiation through a light filter UFS-1 (2, 6) and during dark relaxation (3, 7).

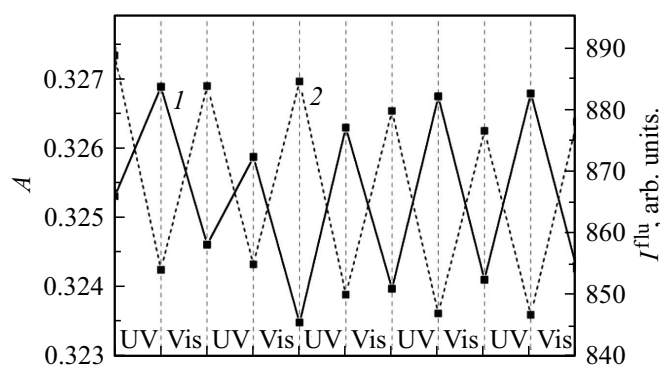


Figure 5. Intensity modulation of absorption at 404 nm (1) and fluorescence at 501 nm (2) of the compound **5** in toluene under cyclic irradiation with UV and visible light.

To confirm this assumption, an analysis of the electron density on the hydroxyl fragment was carried out. Since the electron density calculations strongly depend on the used functionality and basis, the electron density calculation was carried out in two different basis sets. The absolute values obtained using different bases (table) do not match. The relatively small SVP basis allows only for qualitative estimate of the electron density distribution, while the 6-311G** basis, a valence-extended basis set with the polarization function of hydrogen atoms, gives noticeably more accurate results when calculating the orbital occupancy. However, for both molecules, the calculated charges on the atoms of the hydroxyl fragment are close to each other, which also supports steric hindrance for the compound **4a**, which prevents the electrophilic substitution reaction in the 10 position.

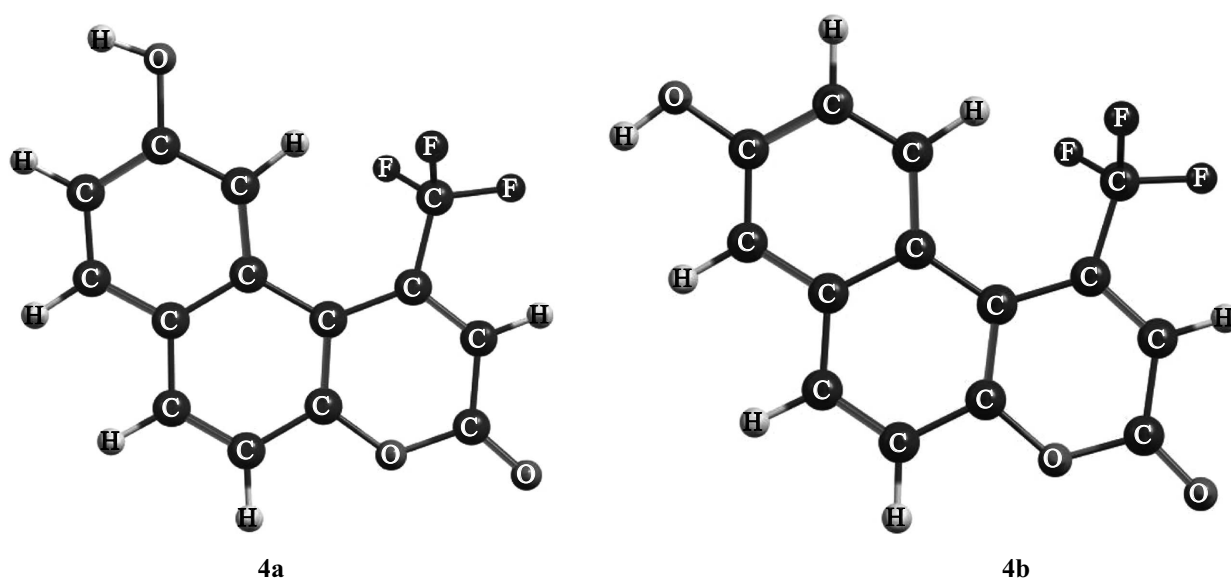


Figure 6. Optimized structures of **4a** and **4b** derivatives.

Conclusions

Thus, as a result of the performed study, new hybrid compounds **3** and **5** were synthesized, exhibiting photochromic transformations, as well as possessing the fluorescent properties of the original chromene form. Photochromic transformations of these compounds cause fluorescence modulation.

Introduction of a bulky substituent containing fluorine into hydroxycoumarin **4** prevents the synthesis of chromene with a hydroxy group in the 9th position and reduces the efficiency of photochromic transformations of the compound **5**. The performed quantum-chemical calculations confirm the obtained results.

The results obtained indicate the possibility of creating fluorescent photoswitches based on such hybrid compounds.

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Conflict of interest

The authors declare that they have no conflict of interest.

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