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Photochemical study of electrocyclization of 4-aryl-5-hetarylimidazolones for information optical recording

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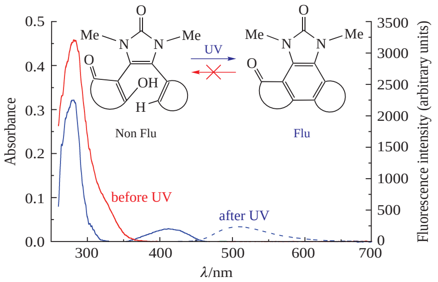
Irreversible photocyclization of 4-(het)aryl-5-(β-hydroxyvinyl) imidazolone derivatives into fused polycyclic structures proceeds with elimination of water molecule. A relationship between quantum yields, spectral characteristics and the structures of starting materials and cyclization products has been established. The results obtained are of interest in creation of optical recording media with fluorescent readout of the written information.



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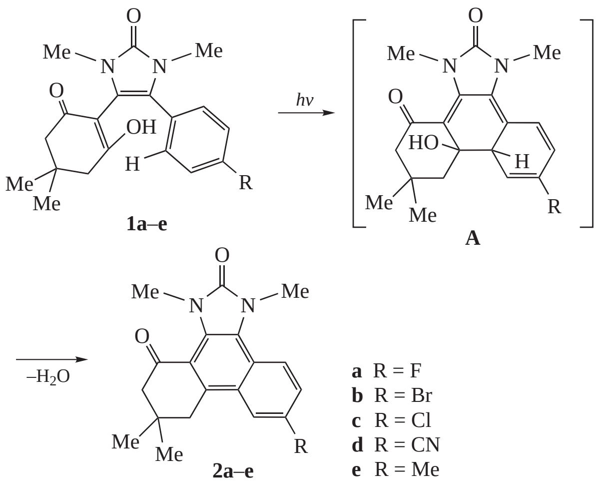
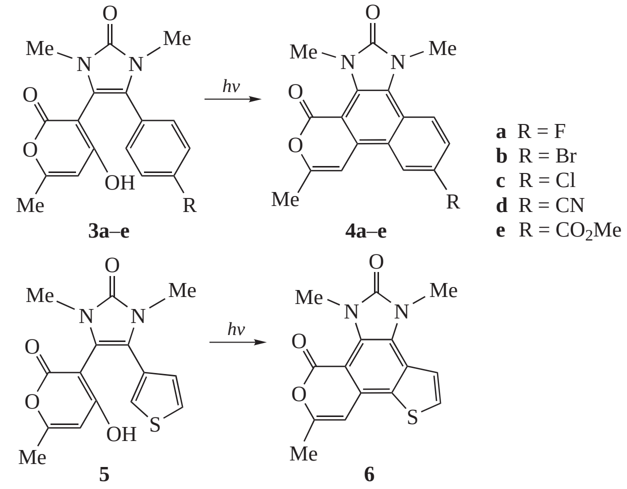
One of the problems of information technology is an insufficient capacity of modern carriers of optical information. Therefore, attempts to construct three-dimensional (3D) optical memory, in particular, optical discs with the two-photon recording and fluorescence reading of optical information of capacity more than 1 Tb seem very promising.[1] Photosensitive systems based on leucodyes and photogenerators of acids, chromones, and other organic substances that undergo irreversible photochemical transformations with the formation of fluorescent substrates are used for production of the optical discs of the archive type.[2–11] Photosensitive compounds of such design should possess absorption and fluorescence spectra compatible with the radiation of available laser sources, a high Stokes shift for the enhancement of contrast of images, a high photosensitivity to provide an appropriate speed of information recording, and the absence of fluorescence in the initial state.

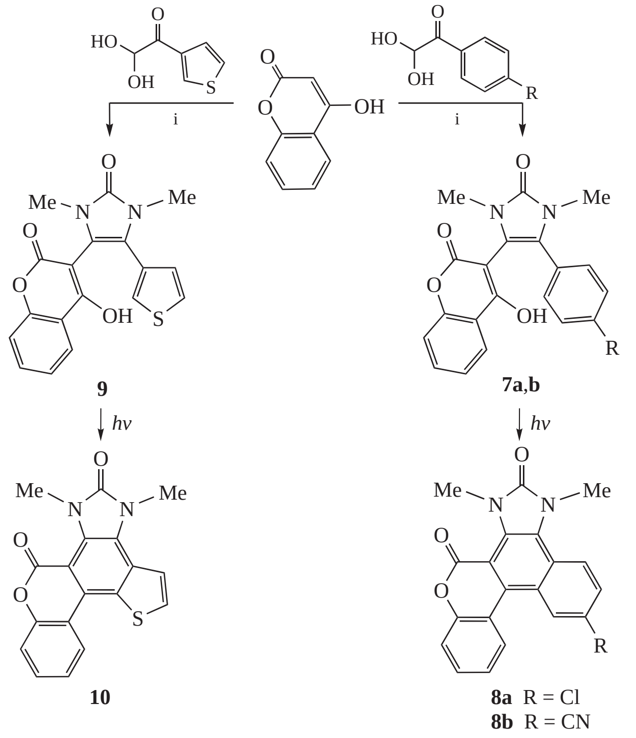
We have previously shown that nonfluorescent chromones and structurally related compounds are transformed under UV irradiation into fluorescent substrates.[12–14] The optical disc based on this transformation has been prepared and successfully tested for information optical recording.[1] We have also studied the behavior of imidazolone derivatives **1** and their analogues **3**, and **5** under the UV irradiation (Schemes 1,2). These compounds underwent photocyclization into fused substrates of type **A** which spontaneously eliminated water molecule to afford products **2**, **4** and **6**. In the most cases, the starting compounds **1**, **3**, and **5** had no fluorescence, whereas the photoproducts were highly fluorescent.[15]



Scheme 1



Scheme 2



Scheme 3 *Reagents and conditions*: i, MeNHC(O)NHMe, MeOH, reflux, 4 h.

In this paper we report on photochemical and photophysical studies of the series of the disubstituted imidazolones **1–6** and synthesis and properties of new coumarin derivatives **7–10**. The coumarin-containing substrates seem to be of certain interest in search for the compounds that can be used in creation of optical recording media, since the related coumarin derivatives have been shown to possess high photosensitivity.[16,17] Synthesis and characterization of compounds **1a–e**, **3a–e** and **5** and products of their photocyclization **2**, **4**, and **6** has earlier been reported (see Schemes 1, 2).[15] However, photochemical and photophysical study of their electrocyclization reactions was not previously performed. The synthesis of the new coumarin derivatives **7–10** is outlined in Scheme 3.

All the studied compounds **1a–e**, **3a–e**, **5**, **7a**,**b** and **9** underwent irreversible photocyclization[†] under UV irradiation in *N*-methyl-2-pyrrolidone (NMP) with formation of fused imidazolones **2a–e**, **4a–e**, **6**, **8a**,**b** and **10**, respectively (see Schemes 1–3).

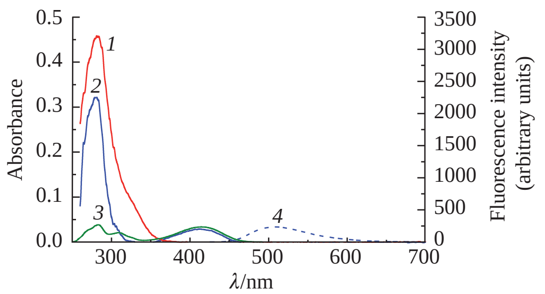


Figure 1 (*1*,*2*) Absorption spectra and (*3*) the fluorescence excitation spectrum measured at 503 nm and (*4*) the fluorescence spectrum under excitation at 415 nm for compound **1a** in NMP (*1*) before and (*2*–*4*) after UV irradiation.

The results of photochemical and photophysical studies[‡] of imidazolones **1–10** are given in Table 1. As example of spectral characteristics, measurements for the compound **1a** are shown in the Figure 1.

The absorption band maxima of compounds **1a–e** are located in the 282–382 nm region of the electronic spectrum, whereas photocyclization products **2a–e** are characterized by a narrower absorption range with a significant bathochromic shift to the region of 403–415 nm. This shift is due to a substantial increase of the π-conjugation in the formed planar condensed imidazolones. Compounds **1a–e** show approximately the same efficiency of phototransformation. The measured quantum yields of the reactions are 0.3–0.4 (see Table 1). All the nonfluorescent starting compounds **1a–e** are converted into fluorescent products **2a–e** during the photocyclization. The fused photoproducts fluoresce in a spectral range of 500–505 nm. The starting compounds with Cl (**1c**) and CN (**1d**) substituents provide the photoproducts of the highest intensities of fluorescence.

Nonfluorescent pyranones **3a–e** and **5** reveal similar spectral kinetic properties of the irreversible electrocyclization into fluorescent photoproducts (see Table 1).

The absorption bands of compounds **4a–e** are shifted to the long-wavelength spectral range compared with their analogues **2**. Moreover, photosensitivity of imidazolones **3a–e** is substantially higher than that of **1a–e**. The quantum yields of photocyclization of compounds **3c–e** are close to $\varphi = 1.0$. It can be explained either by the participation of the intermediate photoproducts with the lower molar extinction coefficients in the photochemical reaction, or by the autocatalytic character of the photoreaction. The fluorescence bands of the condensed pyranones **4a–d** are located at 500–503 and 523 nm. The intensities of the fluorescence bands of the F-, Br-, and Cl-derivatives (**4a–c**, respectively) are approximately twice as much as those of their analogues **2a–c** (see Table 1).

Coumarin derivatives **7a**,**b** and **9** turned to possess fluorescence even before irradiation. The absorption and fluorescence spectral changes of the cyano-substituted compound **7b** during irradiation are shown in Figure 2(*a*) as an example. Its fluorescence intensity decreases along the UV irradiation (curve *4*) simultaneously

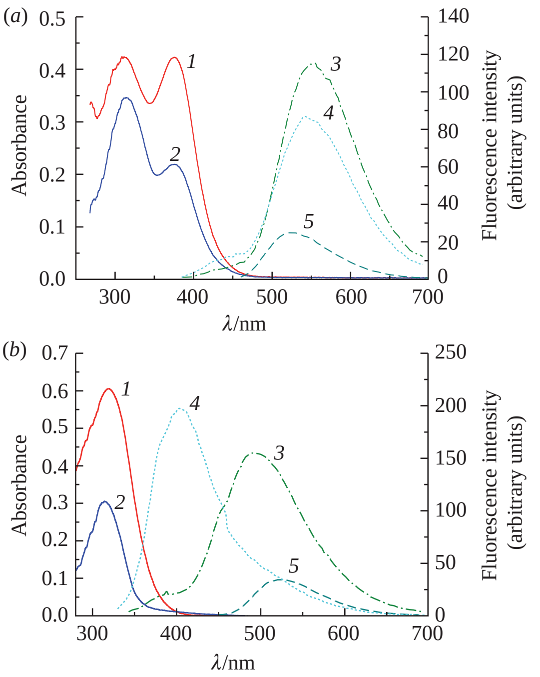


Figure 2 (*1*,*2*) Absorption and (*3*,*4*,*5*) fluorescence spectra of compounds (*a*) **7b** and (*b*) **7a** in NMP (*1*,*3*) before and (*2*,*4*,*5*) after UV irradiation. Excitation at (*3*,*4*) 320 nm (for **7a**) and 375 nm (for **7b**), and at (*5*) 440 nm (for **7a**) and 450 nm (for **7b**).

[†] *Photocyclization of imidazolones* **7a**, **7b** *and* **9** (*general procedure*). A solution of compound **7a**, **7b** or **9** (0.5 mmol) in NMP (5 ml) was irradiated with a Vilber Lourmat VL-6.LM lamp (365 nm, 6 W) at 20–25 °C for 6–20 h. The mixture was poured into water (100 ml), and the resulting precipitate was filtered off and recrystallized from MeOH to give the corresponding products **8a**,**b** and **10** (for characteristics, see Online Supplementary Materials).

[‡] For the procedure details, see Online Supplementary Materials.

Table 1 Photochemical and photophysical characteristics of imidazolones in NMP.[a]

Compound	λ_0/nm	ε/dm^3 cm^{-1} mol^{-1}	λ_0^{fl}/nm	I_0^{fl} (arbitrary units)	Photoproduct	$\lambda_{phot}{}^b$/nm	φ	λ_{phot}^{fl}/nm	I_{phot}^{fl} (arbitrary units)
1a	282	11250	–	–	**2a**	415	0.32	503	235
1b	287	18250	–	–	**2b**	410	0.39	501	275
	330	9000							
1c	284	18750	–	–	**2c**	407	0.30	505	455
	330	9500							
1d	280	16000	–	–	**2d**	403	0.39	500	400
	382	11000							
1e	284	17500	–	–	**2e**	405	0.35	505	225
3a	295	8750	–	–	**4a**	400	0.80	523	450
						430			
3b	296	–	–	–	**4b**	427	0.92	500	720
	325	9000							
3c	294	8750	–	–	**4c**	425	1.40	503	990
	325	8500							
3d	295	6250	562	35	**4d**	440	1.13	501	120
	380	7000							
3e	295	6100	–	–	**4e**	435	1.36	483	205
	377	7750							
5	270	12000	–	–	**6**	414	0.12	443	670
	308	11250							
7a	320	15250	486	155	**8a**	440	0.08	525	200
7b	310	10750	550	115	**8b**	450	0.44	547	85
	375	10500							
9	310	9250	500	300	**10**	410	0.19	459	505

[a] λ_0, λ_{phot}, λ_0^{fl}, λ_{phot}^{fl} are the wavelengths of the absorption and fluorescence band maxima in the initial compound and photoproduct, respectively; φ is the quantum yield of phototransformation; and I_0^{fl} and I_{phot}^{fl} are the fluorescence intensities at the maxima of the fluorescence bands of the initial compound and photoproduct, respectively. [b] In the visible spectral range.

with a decrease of the absorption band intensity (curve *2*) and the appearance of the fluorescence of the photoproduct (curve *5*).

The UV excitation of chloro-substituted coumarin **7a** provides different results. Unlike cyano-substituted compound **7b**, irradiation of **7a** leads to the change in the fluorescence spectrum of the starting compound [Figure 2(*b*), curve *3*] with the hypsochromic shift of the maximum (curve *4*). Besides, compound **7a** is characterized by the minimal quantum yield of the phototransformation as compared to all the studied compounds.

The fluorescence properies of imidazolones **7a**,**b** and **9** are caused, most likely, by the presence of the coumarin moiety in their structures. Therefore, the further search for target nonfluorescent substances that form fluorescent photoproducts upon UV irradiation should be performed on the basis of the structures of imidazolones **1** and **3**, which are not annelated with the benzene ring and have no substituents capable of elongating the π-conjugation system.

To conclude, UV irradiation of imidazolone derivatives **1**,**3**,**5**, **7**,**9** containing hydroxy function at the reaction center is a convenient access to fused imidazolones. The most of the starting compounds in the open form have no fluorescence, whereas the products of their photocyclization are fluorescent. Compound **5** best meets the requirements to efficient media for information optical recording.[1] Change of hydroxy functions in initial compounds for halogen atom or acyloxy group or similar transformations of these compounds can provide acid generation during cyclization reactions (these studies are in progress now). In turn, reactions with subsequent acidic photogeneration are of interest not only for optical recording of information, but also for use in biochemical studies.[18–26]

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.05.023.

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