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Synthesis and spectral properties of 3-(2-aryl-5-methyl-1,3-oxazol-4-yl)-2-(2,5-dimethylthiophen-3-yl)cyclopent-2-en-1-ones

Andrey G. Lvov,[a] Valerii Z. Shirinian,*[a] Alexey M. Kavun[b] and Mikhail M. Krayushkin[a]

[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 5328; e-mail: shir@ioc.ac.ru*
[b] *Higher Chemical College, Russian Academy of Sciences, 125047 Moscow, Russian Federation*

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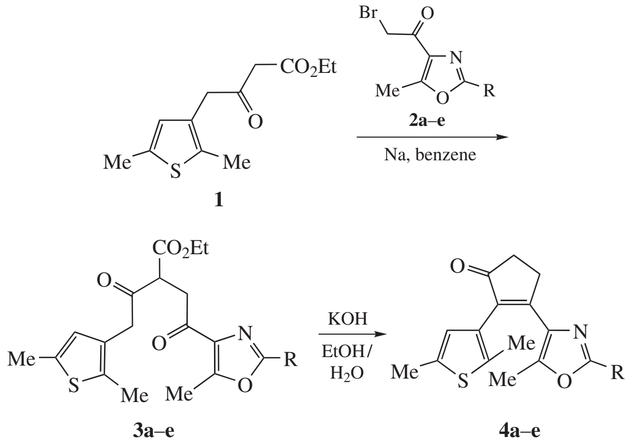
Alkylation of ethyl 4-(2,5-dimethylthiophen-3-yl)-3-oxobutanoate with 2-aryl-4-bromoacetyl-5-methyl-1,3-oxazole followed by decarboxylation–cyclization of the intermediate diketo ester affords the title photochromic compounds. Relationship between the fluorescent characteristics, thermal stability of photoinduced form as well as quantum yields of photochemical reactions and the structure of these compounds was evaluated.

Photochromic diarylethenes have been intensely studied to develop a new photoswitching materials and molecular devices.[1–4] For the practical application of diarylethenes it is necessary to improve some of their physical and chemical properties, such as thermal stability of photoinduced form and quantum yields of both photoreactions.[1] To reach this goal, relationship between the properties of photochromic molecules and their structures is to be derived. Typically, the photochromic reactivity of diarylethenes mainly depends on the type of heteroaryl groups and their electron donor/acceptor substituents.[5–8] Furthermore, much attention was paid to establishing a relationship between these properties and the substituents in the ethene bridge.[9–13] However, each class of photochromic compounds is specified by its own distinctive correlation between the structure and spectral characteristics. Moreover, small modifications in the structure can induce considerable changes in these properties. For these reasons, target synthesis of photoswitching compounds with predefined parameters remains quite difficult issue.

Recently, we proposed a new unique class of photochromic diarylethenes of cyclopentenone series comprising derivatives of benzene, thiophene, benzothiophene and naphthalene as aryl residues.[11] The presence of a carbonyl group in the ethene bridge contributes to various chemical modifications. The effect of substituents in the cyclopentenone ring on various photochromic characteristics has been studied.[11,14–16] Furthermore, the first unsymmetrical 2,3-diarylcyclopent-2-en-1-ones containing thiophene and oxazole derivatives as aryl substituents were synthesized and the dependence of the photoswitching properties on the asymmetry of molecule has been reported.[17] It was found that such isomeric photochromic diarylethenes show different thermal stability, absorption maxima, and quantum yields of cycloreversion reaction. The purpose of this work was to study the effect of substituents at the oxazole ring on the photoswitching characteristics of unsymmetrical diarylethenes bearing two different heterocyclic substituents, namely, thiophene and oxazole.

The target diarylethenes **4** were obtained according to the previously developed protocol[†] by alkylation of keto ester **1**[18] with bromo ketones **2** followed by cyclization in a water–alcohol alkaline solution (Scheme 1). Oxazoles **2a–e** with various substituents at the benzene ring have been synthesized by condensation of the corresponding benzaldehydes with acetylacetone oxime followed by reduction of the *N*-oxides and bromination of the resulting ketones.



a R = Ph
b R = 4-FC$_6$H$_4$
c R = 4-CF$_3$C$_6$H$_4$
d R = 4-(piperidin-1-yl)phenyl
e R = 4-MeOC$_6$H$_4$

Scheme 1

A study of spectral properties of the obtained compounds revealed that all diarylethenes display photochromic properties. Irradiation of their acetonitrile solution by UV light results in isomerization to give coloured form, whereas irradiation with visible light returns them to the initial colourless isomer. The spectral changes during photochromic reactions of all diarylethenes are characterized by the presence of isosbestic points at 330–350 nm.[‡] The typical absorption spectra of the initial form and the photoinduced form at the photostationary state (PSS) of diarylethenes **4a**,**c**,**d** in acetonitrile are shown in Figure 1.

The results of spectral and kinetic studies of the photochromic compounds obtained are summarized in Table 1.[§] Synthesis of diarylethenes with various substituents at the benzene ring

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[†] Experimental procedures and characterization of the target and intermediate compounds as well as their ^{1}H and ^{13}C NMR spectra can be found in Online Supplementary Materials.

[‡] The absorption spectra of diarylethenes **4a–e** before and after UV irradiation are provided in Online Supplementary Materials.

[§] In order to evaluate a correlation between the structure and spectral properties, we have used the spectral characteristics of compound **4a** reported previously.[17]

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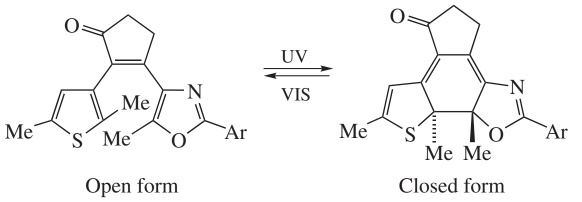
Table 1 Spectral and kinetic properties of diarylcyclopentenones **4a–e** in acetonitrile ($C = 2\times10^{-5}$ mol dm^{-3}) at 298 K.

Compound	λ^{A}_{max}/nm^a (ε/dm^3 mol^{-1} cm^{-1})^a	λ^{B}_{max}/nm^a (ε/dm^3 mol^{-1} cm^{-1})^a	φ_{A-B} (313 nm)^b	φ_{B-A} (517 nm)^c	$\tau^{B\to A}_{therm1/2}$/h^d
4a	298 (2.60×10^4)	523 (0.76×10^4)	0.22	0.166	3200
4b	293 (1.85×10^4)	517 (0.83×10^4)	0.23	0.109	2500
4c	308 (2.11×10^4)	522 (0.76×10^4)	0.22	0.138	500
4d	326 (3.00×10^4)	528 (0.93×10^4)	0.15	0.084	4700
4e	293 (2.86×10^4)	515 (0.86×10^4)	0.23	0.098	700

[a] Absorption maxima (extinction coefficients) of open-ring (A) and closed-ring (B) isomers. [b] Quantum yields of photocyclization under irradiation at 313 nm. [c] Quantum yields of cycloreversion under irradiation at 517 nm. [d] Half-life times of the ring-closed isomers in the dark.



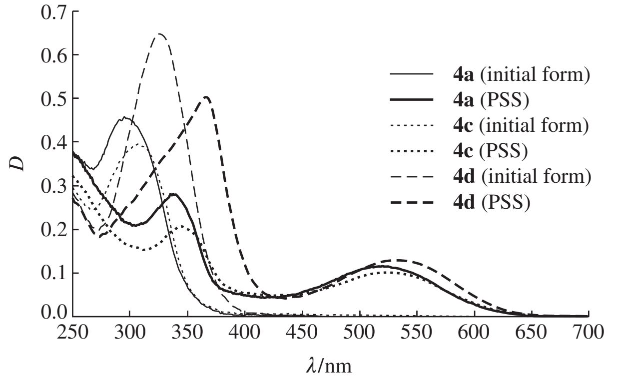


Figure 1 Absorption spectra of diarylethenes **4a,c,d** ($C \sim 2.5\times10^{-5}$ mol dm^{-3} in MeCN) before and after UV irradiation (λ = 313 nm) at 293 K.

allowed us to examine in detail their effect on the absorption maxima and the extinction coefficients of the open and cyclic forms. The introduction of a fluorine atom (compound **4b**) or methoxy group (compound **4e**) at the *para* position of the benzene ring results in a slight hypsochromic shift (by 5 nm) of the absorption maxima of the open form relative to that of diarylethene bearing an unsubstituted benzene substituent. However, the extinction coefficient decreases in the former case and increases in the latter case. A decrease in extinction is a result of the introduction of an electron-withdrawing trifluoromethyl group (compound **4c**), but in this case the absorption maximum shifts by about 10 nm to the long wavelength side. The largest bathochromic shift (by 28 nm) is caused by the introduction of an electron-donating dialkylamino group (compound **4d**) that also accompanied by an increase in absorption band intensity.

The absorption maxima of the photoinduced form of the diarylethenes **4** lie in the green region of the optical spectrum (515–528 nm). The effect of the trifluoromethyl group (compound **4c** depriving of electron pair conjugated with the benzene ring) on the absorption maximum of the photoinduced form is very weak, whereas the presence of fluorine substituent (compound **4b**) leads to a hypsochromic shift by 6 nm. In the case of compounds with electron-donating substituents, a shift of absorption maximum to the blue spectral region is observed for methoxy derivative **4e** (hypsochromic shift by 6 nm), whereas for piperidino derivative **4d** this shift is bathochromic. The presence of substituents with two unshared electron pairs leads to increasing the extinction coefficient of the photoinduced form (compounds **4b**,**d**,**e**), whereas similar parameters of diarylethenes **4a** and **4c** do not differ.

An ^{1}H NMR study of the open and cyclic forms of the diarylethenes obtained has shown that the effect of substituents at the benzene ring on the chemical shifts of protons is insignificant in both forms.¶ The chemical shifts of the aromatic proton of the thiophene ring of diarylethenes **4a–e** in open form are observed at δ 6.54 ppm, whereas those of the cyclic isomer are observed at δ 6.82–6.86 ppm. While the effect of electron-donating and electron-withdrawing substituents on the chemical shifts of thiophene ring and methyl group protons is very small, the downfield shift by 0.28–0.32 ppm of the thiophene protons in cyclic form relative to that of the open form is quite unusual and is not typical of diarylethenes. At the same time, the signals of methyl group protons in the thiophene ring in cyclic form are shifted upfield relative to those of the open form, which is logical and explainable. Such shift of the signal of the proton of the thiophene ring in cyclic form can be only explained by a deshielding effect of closely spaced carbonyl group,[17] as a thiophene ring with formation of a cyclic form loses its aromaticity, and this in turn, on the contrary, should result in an upfield shift.

The efficiency of light energy utilization measured as the quantum yield of the photochemical reaction is an important characteristic of photochromic diarylethenes.[19–21] Measurement of the quantum yield of the cyclization reaction of the compounds obtained indicates that replacement of a hydrogen atom by fluorine one or trifluoromethyl or methoxy group nearly does not affect this value. On the other hand, introduction of a dialkylamino group results in a considerable decrease in cyclization efficiency (by 7%). The unexpected result was obtained for the quantum yield of the cycloreversion (ring-opening) reaction. Introduction of any substituent leads to a decrease of its value relative to that of unsubstituted photochrome. Some interesting patterns can be observed by comparing the values of cycloreversion quantum yields and extinction coefficients, in particular, it was identified that an increase in the extinction coefficient of cyclic form results in a decrease in the quantum yield of the reverse photochromic reaction. In fact, diarylethene **4d** that has the largest extinction coefficient (9300 dm^3 mol^{-1} cm^{-1}) exhibits also the smallest cycloreversion efficiency (8.4%), whereas diarylethenes **4a** and **4c** with extinction values of 7600 dm^3 mol^{-1} cm^{-1} manifest high yields, 16.6 and 13.8%, respectively.

The thermal stability of the photoinduced form is yet another important photoswitching property of diarylethenes. We have found that replacement of a hydrogen atom in **4a** by a dialkylamino group (**4d**) provides a considerable increase in half-life period (from 3200 to 4700 h, Table 1). On the other hand, the introduction of miscellaneous substituents reduces thermal stability, down to 500 h in the case of diarylethene **4c**.

Among all obtained compounds, only diarylethene **4d** with a strong electron-donating dialkylamino group possesses fluorescent properties. This characteristic of the photochromic diarylethenes is important for the development of non-destructive readout

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¶ The characteristic signals in the ^{1}H NMR spectra of forms A and B of diarylethenes **4a–e**, as well as the full NMR spectra of compound **4e** before and after UV irradiation are available in Online Supplementary Materials.

memory elements.[1,4] The open form of compound **4d** emits light at 570 nm under UV irradiation at the absorption maximum of initial form A (326 nm).[††] The Stokes shift is rather large and amounts to 13 131 cm^{-1}, apparently due to competition between the emission and photoswitching processes. UV irradiation leads to the formation of a photoinduced isomer and an almost threefold decrease in emitted light intensity. Irradiation with visible light results in formation of the initial form of the diarylethene and recovery of starting fluorescence; this process can be repeated several times.

In conclusion, we have prepared novel unsymmetrical photochromic diarylethenes of the cyclopentenone series bearing oxazole moieties with various aromatic substituents and identified relationships between their spectral characteristics and structural features.

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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.2014.09.010.

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[††] For the modulation plot of the fluorescent properties of compound **4d**, see Online Supplementary Materials.