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Synthesis and Comparative Photoswitching Studies of Unsymmetrical 2,3-Diarylcyclopent-2-en-1-ones

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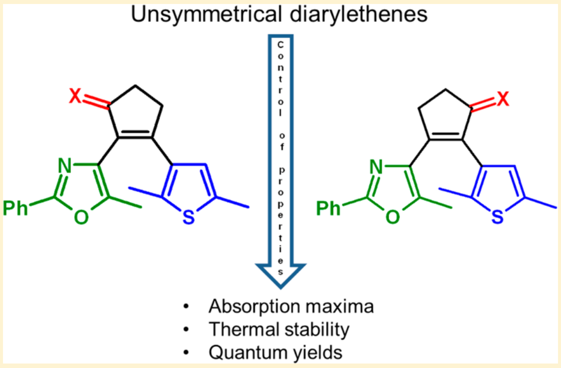
S Supporting Information

ABSTRACT: Photochromic diarylethenes (DAEs) based on the unsymmetrical ethene "bridge" bearing heterocycles of the different nature (oxazole and thiophene) as aromatic moieties have been designed and the photoswitching properties have been studied. The comparative studies of the photochromic characteristics of unsymmetrical isomeric 2,3-diarylcyclopent-2-en-1-ones have shown that the isomers have different thermal stability, absorption maxima, and quantum yields. It was found that the unsymmetrical diarylcyclopentenone bearing at second position of the cyclopentenone ring the thiophene unit displays high thermally stability, hypsochromic shift of absorption maxima wavelengths of initial and cyclic forms, and high quantum yields of cyclization and cycloreversion reactions. The replacement of the carbonyl group with oxime leads to a reduction of the difference in the photochromic properties of these isomers and just as the reduction of the carbonyl group to the hydroxy-group negates this difference to zero. The intramolecular hydrogen bond formation in the oxime and hydroxy derivatives was confirmed by IR and ^{1}H NMR spectral analysis, but the increase of the quantum yields of the cyclization reaction in a nonpolar hexane is observed only in the case of hydroxy derivatives that can be explained by the formation of more rigid six-membered heterocycle in hydrogen bonding.



INTRODUCTION

The molecular devices that can be activated using various external stimuli, e.g., chemical, electrochemical, and photochemical, hold enormous promise for the advancement of nanotechnology.[1−4] Considerable recent attention has been focused on photoswitch molecules as an active unit for photoreversible control of various physical and chemical properties.[5−8] The different types of photochromic compounds have been so far synthesized in an attempt to apply the compounds to optoelectronic devices.[9−12] Among the photochromic compounds, diarylethene derivatives are the most promising candidates for the applications because of their fatigue resistant and thermally irreversible properties.[12−15]

The photochromic properties of diarylethenes have been studied quite extensively, and the elucidation of relationships between structure and spectral properties of photochromic diarylethenes (DAEs) is at the center of ongoing investigations which aim at developing a molecule with improvement in switching properties that will ultimately be used in advanced photonic devices.[12−17] However, in spite of many of these studies, there are no widely available synthetic tools for the rational design of the DAE structure, including the directed synthesis of photochromic molecules with two or more improved features, and too often attempts to improve the certain characteristics leads to deterioration of other properties. Therefore, the development of new photochromic systems with the wide possibilities of chemical modification that would provide easily tunable switching properties is the actual point of this field.

In this context, recently we have proposed a new class of photochromic diarylethenes, 2,3-diarylcyclopent-2-ene-1-ones (DCPs), having high abilities to the chemical modification reactions of ethene "bridge",[18,19] and it has been obtained a wide range of photochromic compounds, whose spectroscopic and kinetic characteristics have been also studied (Chart 1).[18,20−22]

Chart 1. Photochromic 2,3-Diarylcyclopent-2-en-1-ones

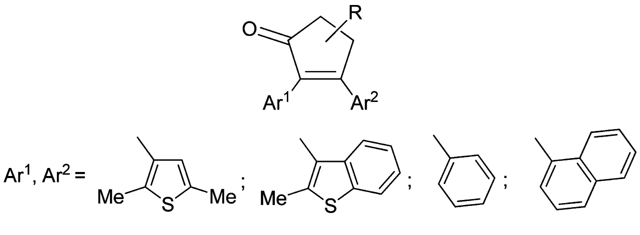


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Chart 2. Classification of Diarylethenes under Their Symmetry

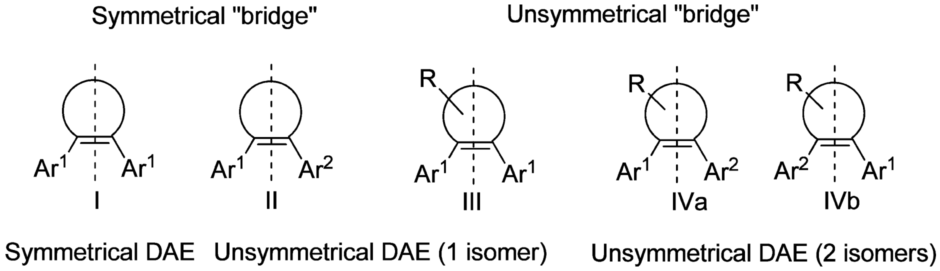
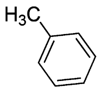
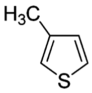
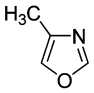
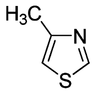
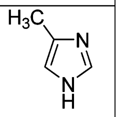
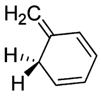
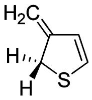
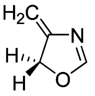
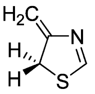
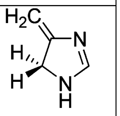


Table 1. Calculated Values of Ground State's Energy Differences of Model Structures

No.	1	2	3	4	5
Structure I					
Structure II					
$\Delta E_{II\text{-}I}$, kJ/mol	147.79	69.08	59.79	65.06	86.49

These studies have demonstrated that 2,3-diarylcyclopent-2-en-1-ones can be efficient to produce new photochromic systems with easily switchable properties and the presence of carbonyl groups in the ethene "bridge" not only greatly facilitates the introduction of functional groups but also gives molecule the nonsymmetry about the central ethene "bridge" and significantly affects the spectral properties.

The photochromic diarylethenes can be divided into three groups based on the symmetry of the molecule: the first type is symmetrical DAEs when the ethene "bridge" has the symmetry about the central double bond and aryl moieties are the same (Chart 2, structure **I**), the second group includes diarylethenes in which either the ethene "bridge" is a symmetrical and the aryl groups are different or the ethene "bridge" is a unsymmetrical and aryl residues are the same (Chart 2, structures **II** and **III**), and the third type involves the compounds in which the ethene "bridge" is unsymmetrical and the aryl moieties are not the same (Chart 2, compounds **IVa**,**b**). Only in the latter case, unlike the second type, there are two possible structural isomers that provide opportunities of a comparative study of photochromic properties of these compounds.

Most of known DAEs mainly belong to symmetrical molecules **I** (perfluorocyclopentene, cyclopentene, maleic anhydride, or maleimide derivatives) and both aryl residues are similar (thiophene or benzothiophene derivatives). The photochromic properties of unsymmetrical systems (structures **II** and **III**) have been studied in many works,[23−29] but such nonsymmetry suggests only one isomer and the study of the relationship between the nonsymmetry of the molecule and the spectral properties impossible. However, up to now there are no data on a comparative study of the spectral and kinetic properties of unsymmetrical diarylethenes having two structural isomers (structures **IVa** and **IVb**).

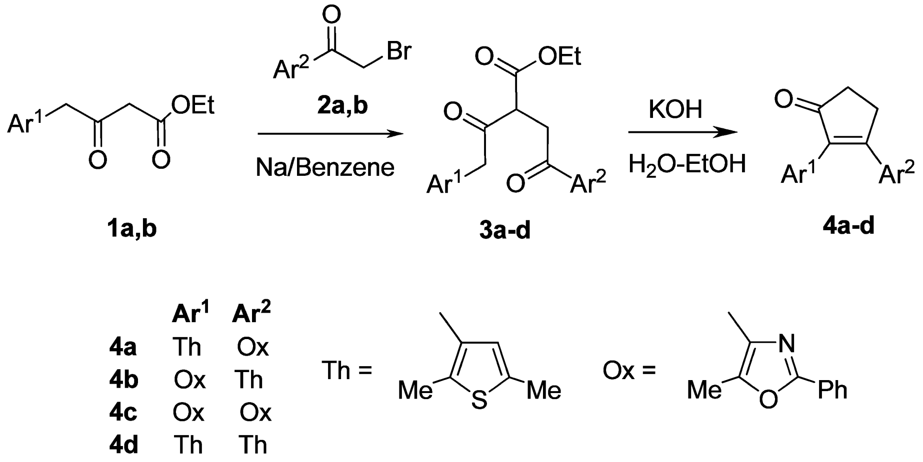
Our recent studies have shown that the photochromic features of isomeric unsymmetrical 2,3-diarylcyclopent-2-en-1-ones are quite different and strongly dependent on the substituent in the ethene "bridge", the nature of the aryl moiety, and the position of attachment of the aryl residue to the ethene "bridge".[18,21] Therefore, in this work we have synthesized and studied the photochromic properties of such unsymmetrical diarylethenes of cyclopentenone series bearing oxazole and thiophene derivatives as aryl moieties. The goal of the study was to perform the comparative analysis of the switch performance of unsymmetrical 2,3-diarylcyclopent-2-en-1-ones and to use the high abilities to the chemical modification of these compounds for the development of the photochromic DAEs with improved thermal stability and high quantum yields.

■ RESULTS AND DISCUSSION

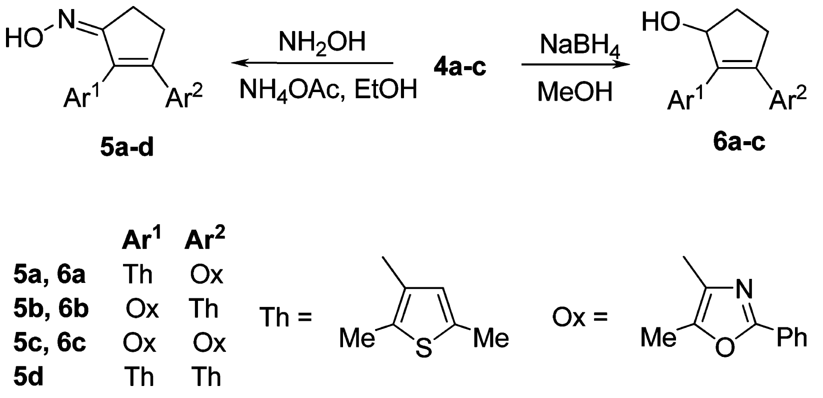
Design of Diarylethenes. To study the spectral properties of unsymmetrical diarylethenes and to develop the photochromic compounds with high thermal stability and improved quantum yields, the cyclopentenone ring was chosen as an ethene "bridge" and the thiophene and oxazole derivatives as aryl moieties. The diarylcyclopentenones as the main core have been chosen because as noted above of the unique ability of the ethene "bridge" of these compounds (cyclopentenone ring) to the different chemical modification.

The selection of oxazole ring along with thiophene as the aryl moiety was preceded by preliminary quantum-chemical calculations of the aromatic stabilization energy of 1,3-azole cycles, thiophene, and benzene rings based on density functional theory (DFT). Irie and co-workers previously pointed out that the aromatic stabilization energy of the aryl groups correlates well with the ground-state energy difference and the aromaticity is the key molecular property which controls the thermal stability of the closed-ring isomers.[12,17,31,32] The performed quantum chemical calculations are summarized in the Table 1. It was found that oxazole, thiazole, and thiophene rings have the low aromatic stabilization energies. However, the choice of thiophene and

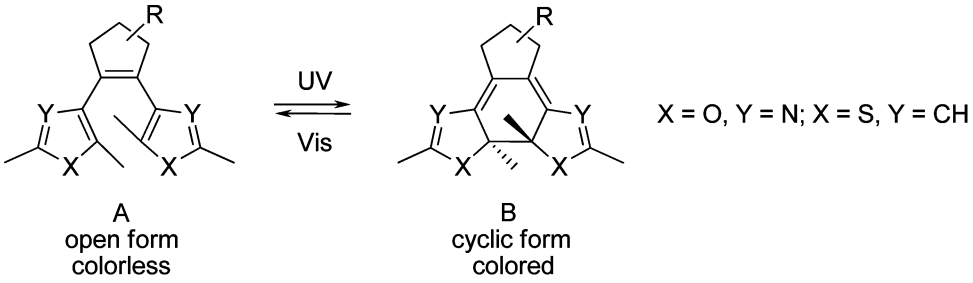
Scheme 1. Synthesis of 2,3-Diarylcyclopent-2-en-1-ones Bearing Thiophene and Oxazole Units



Scheme 2. Synthesis of Oxime and Hydroxy-Derivatives of 2,3-Diarylcyclopent-2-enes



Scheme 3. Photochromic Reactions of Dihetarylcyclopentene Derivatives



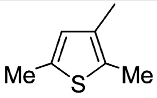
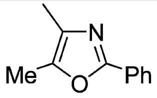
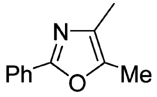
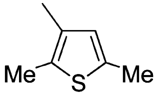
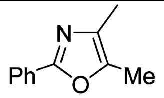
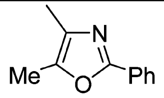
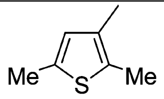
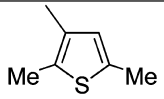
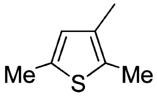
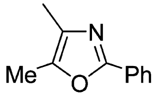
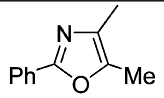
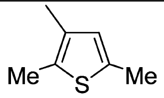
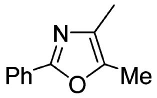
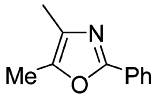
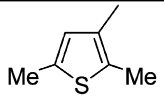
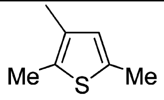
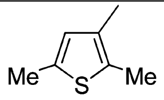
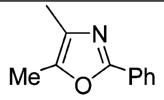
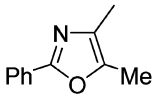
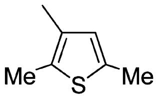
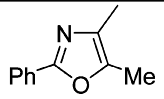
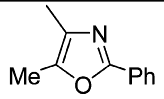
oxazole derivatives as aryl moieties was also dictated by the synthetic potential of these compounds.

In addition, an advantage in the selection of the thiophene and oxazole derivatives as the aryl moieties have been caused by other factors. At first, the thiophene derivatives are widely studied and have proven themselves as a promising photochromic DAEs. The presence of an sp^2-hybridized nitrogen atom in the oxazole ring is an important premise for the development of noncovalent bonds, including hydrogen. Noncovalent bonds have been used for the increasing of the quantum yields of the direct photoreaction due to the stabilization of the photoactive antiparallel conformation in more recent years.[33−37] Also the sp^2-hybridized nitrogen atom can participate in the formation of the supramolecular structures.[38−40] And finally, the azole compounds are more resistant to photoirradiation, acids, and oxidants, which make them more attractive as photoswitches.

Synthesis. The preparation of 2,3-diarylcyclopent-2-en-1-ones bearing thiophene and oxazole units as aryl moieties is based on our recently developed method.[18] The key stage of this synthetic protocol is the alkylation of ketoesters **1** by bromoketones **2** in the presence of metallic sodium in the absolute benzene. The subsequent cyclization in aqueous ethanol solution leads to photochromic diarylethenes **4** (Scheme 1). The presence of the acidic proton between the carbonyl and ester groups excludes the use of other reaction conditions than potassium hydroxide in aqueous alcoholic medium because the cyclization reaction is possible only after hydrolysis of the ester group.

To obtain the photochromic molecules capable of forming intramolecular hydrogen bonds and thereby to regulate the geometry of the molecule, oxime and hydroxy derivatives **5a−c** and **6a−c** have been synthesized by simple methods, respectively (Scheme 2). Alcohol derivatives **6a−c** bearing an

Table 2. Spectral and Kinetic Properties of Ketones 4a−d, Oximes 5a−d, and Alcohols 6a−c

Entry	Diarylethene structure			$\lambda_{max}{}^{A}$, nm (ε, M^{-1}cm^{-1})[a]	$\lambda_{max}{}^{B}$, nm (ε, M^{-1}cm^{-1})[a]	$\varphi_{A\text{-}B}$ (313 nm)[b]		$\varphi_{B\text{-}A}$[c]	
	No.	Ar^1	Ar^2			MeCN	Hexane	MeCN	Hexane
Ketones **4**									
1	**4a**			298 (2.60 × 10^4)	523 (0.76 × 10^4)	0.22	0.34	0.166	0.179
2	**4b**			284 (2.43 × 10^4)	549 (0.60 × 10^4)	0.20	0.10	0.012	<0.010
3	**4c**			283 (4.02 × 10^4)	505 (0.87 × 10^4)	0.27	0.22	0.041	0.056
4	**4d**			309 (0.94 × 10^4)	547 (0.46 × 10^4)	0,23	0.38	0.089	0.110
Oximes **5**									
5	**5a**			297 (2.58 × 10^4)	492 (0.77 × 10^4)	0.41	0.49	0.144	0.142
6	**5b**			290 (2.16 × 10^4)	500 (0.52 × 10^4)	0.32	0.36	<0.010	<0.010
7	**5c**			290 (3.69× 10^4)	477 (0.80 × 10^4)	0.23	0.24	0.051	0.070
8	**5d**			287 (1.72 × 10^4)	494 (0.50 × 10^4)	0.22	0.22	0.122	0.127
Alcohols **6**									
9	**6a**			289 (2.00 × 10^4)	457 (0.72 × 10^4)	0.53	0.47	0.170	0.210
10	**6b**			293 (1.42× 10^4)	457 (0.72 × 10^4)	0.46	0.61	0.055	0.040
11	**6c**			289 (2.86 × 10^4)	447 (0.91 × 10^4)	0.52	0.57	0.080	0.057

[a] Absorption maxima (extinction coefficients) of open-ring (A) and closed-ring (B) isomers. [b] Quantum yields of photocyclization. [c] Quantum yields of cycloreversion under irradiation with 517 nm for ketones and oximes and 436 nm for alcohols.

oxazole ring have been prepared by the reduction of the corresponding ketones **4a−c** with high yields under mild conditions. However, attempts to reduce **4d** to the corresponding alcohol were unsuccessful because the latter unlike oxazole analogues was unstable. Such a difference in the stability of these compounds can be attributed to the existence of intra- or intermolecular interaction of the hydroxy-group with sp^2-hybridized nitrogen atom in the oxazole derivatives.

The nonsymmetry of the molecules **5a** and **6a** (which are not capable of forming an intramolecular hydrogen bond) and compounds **5b** and **6b** (which can form intramolecular hydrogen bonds) is an excellent tool for studying the effect

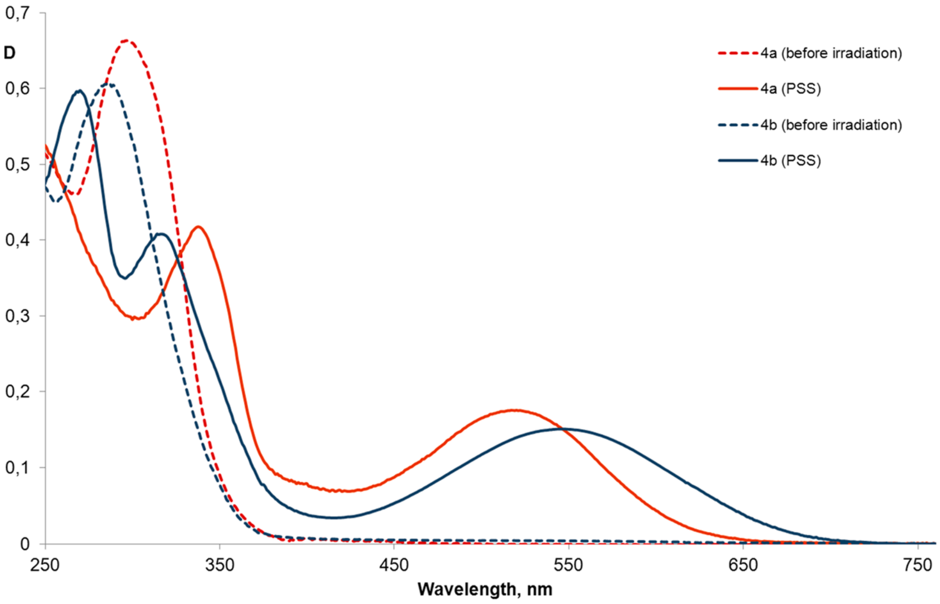


Figure 1. Absorption spectra of compounds **4a,b**, before irradiation and at PSS after irradiation with UV 313 nm in acetonitrile ($C = 2 \times 10^{-5}$ M) at 293 K.

of hydrogen bond interaction on the spectral and kinetic properties of diarylethene including the quantum yields of the photochromic cyclization reaction.

Photoswitching Properties of DCPs. The mechanism of the photochromic switching of DAEs involves the electrocyclic-cycloreversion reactions of the hexatriene system provoked by UV–vis light[6] (Scheme 3).

The photochromic characteristics of diarylcyclopentene derivatives have been measured in acetonitrile and hexane solutions at 293 K in the presence of air (oxygen) upon UV irradiation, and the colorless solutions of DCPs were converted into colored the ones with an absorption bands in visible range of spectrum and bleached back to colorless under visible light (Table 2).[41]

The measuring and comparing of the photochromic properties of the synthesized diarylethenes were used to estimate the correlations between their structures and different photoswitching characteristics such as absorption maxima, extinction coefficients of open- and closed-ring isomers, and thermal stability as well as the quantum yields of photocyclization and photobleaching reactions (Table 2). For the purpose of revealing the correlation between the molecular structures of the diarylcyclopentenone derivatives and the spectral properties, some previously published spectral properties of the diarylcyclopentenones **4d** and **5d** have been used.[18,21]

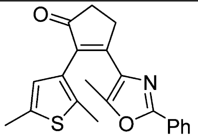
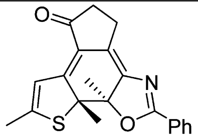
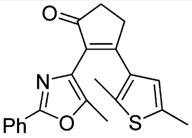
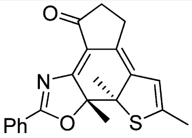
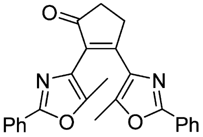
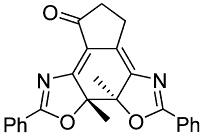
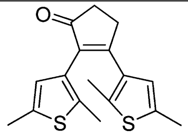
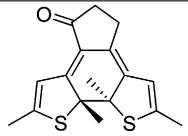
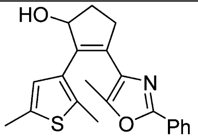
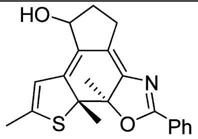
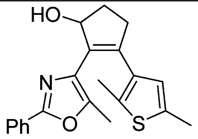
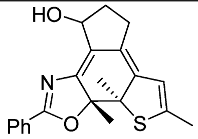
The photoswitching features of DAEs obtained have been studied by different methods: UV–vis, NMR spectroscopy, and IR spectrometry. It was found that all compounds show photochromic properties that are strongly dependent on the substituent in the ethene “bridge”, the nature of the aryl moiety, and the position of the aryl residue connection to the “bridge” (the nonsymmetry of the molecule). The typical changes observed in the absorption spectra of the photochromic reactions of diarylethenes **4a,b** in acetonitrile are shown in Figure 1. The spectral characteristics and quantum yields of the photoreactions are summarized in Table 2. As it can be seen from Table 2, the replacement of the thiophene ring with oxazole results in a hypsochromic shift of the absorption maximum of the colorless form A (compare λ^A values for compounds **4a–d** in Table 2) and the maximum shift is observed for the bis-oxazole derivatives **4c**.

The absorption maxima wavelengths of the photoinduced forms of the compounds studied also depend on the attached position of the aromatic residues. The maximum hypsochromic shift of the absorption band (42 nm) is observed for the bis-oxazolylcyclopentenone **4c** relative to bis-thiophene **4d**. But there are not any changes in absorption maxima of photo-induced form of 2-substituted oxazole isomer, while the absorption maximum of the isomer having an oxazole ring on C-3 position shifted hypsochromically compared to bis-thiophene derivative **4d** by about 23 nm. It was found that there is no direct correlation between the extinction coefficient and structure of these compounds. So the extinction coefficients of cyclic isomers differ little, but for open forms the highest value was found for photochromic bis-oxazole **4c** (4.02×10^4 M^{-1} cm^{-1}) and bis-thiophene **4d** has the lowest value (0.94×10^4 M^{-1} cm^{-1}).

A significant effect of the carbonyl group on the spectral characteristics of the unsymmetrical diarylethenes have also been observed in the NMR spectra of compounds **4a** and **4b** before and after irradiation with 365 nm at 293 K in $CDCl_3$.[42] It has been found that the signal of the hydrogen atom of thiophene ring of the compound **4a** (6.54 ppm) after UV irradiation has shifted downfield (to 6.84 ppm), whereas the same signal of the photochrome **4b** (6.64 ppm) has shifted upfield (to 5.78 ppm). The downfield shift of the thiophene ring proton in the ^{1}H NMR spectrum of the closed form of **4a** is likely due to the close proximity of the carbonyl group. In the second case, the effect of the carbonyl group is not possible, and a shift in the strong-field direction is only a consequence of a breach of the aromaticity of the thiophene ring. The upfield shift of thiophene proton of the cyclic form of the compound **4b** is in good agreement with the results for dithienylethenes obtained previously.[30,43]

The replacement of the carbonyl group with oxime leads to a hypsochromic shift of the maxima of cyclic forms, while the effect on the absorption maxima of open forms with the

Table 3. Thermal Stability of Dihetarylcyclopentenones 4a−d and Their Hydroxy Derivatives 6a,b

Entry	Compounds			Thermal stability ($\tau^{B\rightarrow A}_{1/2}$, h)
	No.	Open form (A)	Closed form (B)	
1	**4a**			3200
2	**4b**			1900
3	**4c**			9600
4	**4d**			940
5	**6a**			14200
6	**6b**			15700

exception for bis-thiophene derivative is not obvious. The difference in the absorption maxima of the open and cyclic forms of isomers **5a** and **5b** as well as its extinction coefficients is significantly less than that between the same parameters of compounds **4a** and **4b**. However, similar patterns are also observed for the oxime derivatives, and the longest wavelength of the absorption maximum is observed for isomer **5b**, where oxazole cycle is attached to the second position of cyclopentenone ring (500 nm) and the shortest wavelength of the absorption maximum is observed for bis-oxazole isomer **5c** (477 nm).

The reduction of the carbonyl group leads to hydroxy-derivatives **6a−c**. It should be noted that the reduction of bis-thiophene derivative **4d** leads to an extremely unstable compound and therefore there are no experimental data on its spectral properties. The hydroxy-group effect unlike the carbonyl or the oxime groups on the spectral properties was found to be small, and the difference in the spectral properties of isomeric compounds **6a−c** is strongly leveled. In the hydroxy-compounds, the oxygen atom of the hydroxy group is completely excluded from the chromophore system so the absorption maxima of the open and cyclic forms of these compounds are shifted toward the blue spectral region.

Thermal Stability of DCPs. The thermal stability (stability of open- and closed-ring isomers of DAEs for a long time in the dark) is a main property of photochromic compounds essential for their various applications.[12,16] Less aromatic stabilization energies of thiophene and oxazole as noted above are responsible for the stability of closed-ring isomers of diarylethenes by reducing the degree of destabilization of closed-ring isomers to the open-ring form. The half-lifetimes ($\tau_{1/2}$) of the closed-ring isomer of some photochromic compounds, ketones **4a−d** and alcohols **6a,b**, were measured in acetonitrile solutions ($C = 2 \times 10^{-5}$ mol L^{-1}) at 293 K in the presence of air (Table 3) and the dependence of this parameter on the structures of the photochromic compounds has been established. The thermal stability of oximes **5a−d** was not studied, so recently it was shown that the replacement with oxime group of carbonyl function results in a significant decrease of this photoswitching characteristic.[21]

The half-lifetime ($\tau_{1/2}$) of closed-ring isomer of bis-thiophene derivative **4d** was previously estimated to be 940 h at 293 K.[20] The replacement of the thiophene ring with oxazole, the latter has a smaller stabilization energy than thiophene (entries 2 and 3 in Table 1) leads to the improvement of the $\tau_{1/2}$ values to 1900 h for **4b**, to 3200 h for **4a**, and to 9600 h for bis-oxazole compound **4c** (entries 1, 2, and 3 in Table 3). The contribution to increase the half-lifetime ($\tau_{1/2}$) of closed-ring isomer of these compounds brings not only the low aromaticity of oxazole unit but also the nonsymmetricity of diarylethene molecule. For structurally isomeric DAEs **4a** and **4b**, the very different values of the half-lifetime (3200 h vs 1900 h, entries 1 and 2 in Table 3) were obtained. The reduction of the carbonyl group resulted in an unexpected results; the half-lifetime ($\tau_{1/2}$) of the closed-ring isomer for two hydroxy group bearing diarylethenes **6a**,**b** was estimated to be 14200 and 15700 h, respectively, and it is an order of magnitude more than that for the starting diarylcyclopentenones (entries 5 and 6 in Table 3).

Quantum Yields of Photocyclization and Photobleaching Reactions of DCPs. The efficiency of photochromic reactions of diarylethenes obtained has been estimated by quantum yield values. The efficient utilization of light energy in photochromic processes (high quantum yield) is an important performance, for example to reduce the time of light exposure on materials and objects, which is especially important for biological systems. In some work previously, the influence of the different substituted of diarylethenes on photochromic properties has been studied.[44−47] However, in fact, the quantum yield is the most difficult predictable property and to predict up to the actual synthesis of the molecule is almost impossible.[44]

Our earlier studies have also shown that it is very difficult to bring out the accurate correlation between the structure of diarylcyclopentenones and quantum yields of their photochromic reactions, however, some correlation between these parameters has been estimated.[18,21,48] The results of the measurements of quantum yields of cyclization and cycloreversion reactions of compounds obtained are given in Table 2. The quantum yields measurements were performed in acetonitrile and hexane solutions ($C \approx 3 \times 10^{-5}$ M) in the sequential irradiation of the filtered light (313 and 517 nm). As can be seen from Table 2, there are certain regularities between the structure and quantum yields of cyclization reaction of diarylethenes obtained depending on the polarity of the used solvent. First of all, it should be noted that in acetonitrile solution the quantum yields of the cyclization reaction of the ketones **4a**−**d** have the same order 20−27%, while in a nonpolar hexane ones depend strongly on the symmetry of the molecules. The quantum yields of the compounds bearing a thiophene unit at second position (compounds **4a** and **4d**) were found to be in two times higher values than ones of the compounds having on C-2 position an oxazole ring and were 34% and 38%, respectively. Such a feature is likely related to a presence of carbonyl group in these unsymmetrical diarylethenes, but in order to evaluate the accurate mechanism of this phenomenon, more detailed studies are needed.

In a solution the DAEs exist in two forms, parallel and antiparallel conformers.[31,49] According to the Woodward−Hoffmann rule,[50] the cyclization reaction occurs photochemically in a conrotatory mode and the conrotatory photocyclization reaction can only proceed from the antiparallel open-ring conformer. Because the interconversion between the conformers occurs in a time scale larger than the excited-state lifetime, only the light absorbed by the antiparallel form can induce photocyclization.[49] To achieve the large quantum yields, there were attempts to fix a conformation capable to photochemical cyclization.[51−53] Therefore, in addition to diarylcyclopentenones **4a**−**d**, in order to achieve the large quantum yields of the cyclization reaction, some diarylethenes bearing different functional groups (oxime and hydroxy groups) capable of forming intermolecular hydrogen bonds with the nitrogen atom of the oxazole ring (compounds **5a**−**d** and **6a**−**c**) have been prepared and the quantum yields have been measured.

The difference in quantum yields of oximes **5a**−**d** in various solvents (acetonitrile and hexane) is not observed, although it was expected that owing to the formation of intramolecular hydrogen bonds between the atoms of the oxime group and the nitrogen atom oxazole ring the quantum yields in hexane should be higher than in acetonitrile. The quantum yields of unsymmetrical oximes **5a** and **5b** in both solvents is significantly higher than the ones of their ketone analogues **4a** and **4b** (Table 2). The reduction of carbonyl group to a hydroxy group leads to increasing of the quantum yields of the latter in both solvents (acetonitrile and hexane). The best results of quantum yields of the cyclization reaction (>50%) were achieved for alcohols **6a**−**c** in hexane solution. Moreover, the quantum yields of **6b**,**c** in hexane solution are considerably higher than that in acetonitrile, whereas for the compound **6a** the one in hexane conversely decreases. Such patterns can be explained by the presence of a hydrogen bond between the hydrogen atom of the hydroxy group and the nitrogen atom of the oxazole ring. To evaluate intramolecular interactions in these compounds in solution, we have performed the IR study of the two pairs of isomeric photochromes **5a**,**b** and **6a**,**b**. It was found that the compounds **5b** and **6b** in contrast to **5a** and **6a** form intramolecular hydrogen bonds, as evidenced by the presence of the broad signals at 3440 cm^{-1} for compound **5b** and at 3270 cm^{-1} for **6b** (Figure 2).[54]

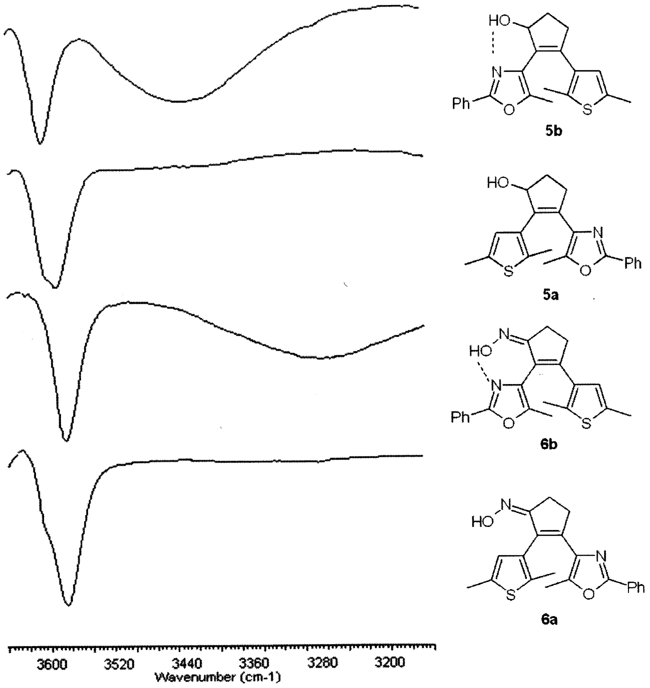
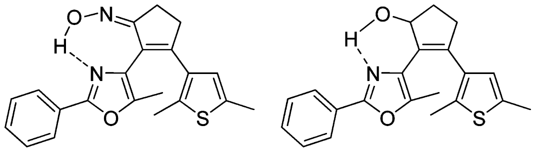


Figure 2. IR spectra of diarylethenes **5a**,**b** and **6a**,**b** in chloroform solutions (C = 0.005 M).

Thus despite the fact that the oxime and hydroxy derivatives form hydrogen bonds, but only in the latter case there is a relationship between the molecular "geometry" and the quantum yields. This is probably due to the fact that the intramolecular hydrogen bond between the oxime group and sp^2-nitrogen atom of oxazole ring leads to a seven-membered cycle formation, whereas the hydroxy-derivatives gives the six-membered ring (Chart 3). And as it is known the six-membered

Chart 3. The Intramolecular Hydrogen Bond of Compounds 9b and 10b



ring has a more rigid 'geometry' (conformation) than the seven-membered ring, and this in turn leads to an increase in the quantum yield of the direct reaction of hydroxy-substituted compounds **6b**,**c** in an apolar environment (hexane).

Additional confirmation of the existence of an intramolecular hydrogen bond between the hydroxy group and the nitrogen atom of the oxazole ring in the compound **6b** was obtained in the comparative analysis of ^{1}H NMR spectra of cyclic forms of isomeric alcohols **6a** and **6b**. The ^{1}H NMR spectrum of the sample of the cyclic form obtained by irradiation of diarylethene **6a** indicates the formation of two different photoproducts in the ratio 56:44 (Figure 3). The subsequent irradiation with visible light restores the initial ring-opened form that is clearly seen in the NMR spectrum. This fact, as well as an approximately equal ratio of the photoproducts, indicates that they are diastereomers **6a′** and **6a″**. A slight excess of one of them appears to be explained by the greater content of the conformers **6a′** that does not contain steric hindrance.

UV irradiation of the solution of compound **6b** also leads to the formation of two diastereomeric products, but the proportion is another, 76:24 (Figure 4). This process is also reversible. The high selectivity of a photoreaction product **6b′** (76%) indicates the presence of a hydrogen bond between hydroxy-group and nitrogen atom of oxazole ring, which can control the molecule conformation, and this in turn leads to the formation of predominantly one diastereomer pairs. It should be noted that the results obtained are in good agreement with literature data.[34,55]

We also evaluated the effectiveness of the cycloreversion reaction of diarylcyclopentenones synthesized. To date, there are no effective ways to improve the cycloreversion reaction efficiency (>50%). In many works,[44,56,57] it was attempted to study the effect of various factors on the quantum yields of cycloreversion, but the effective tool has not been found yet. However, some patterns are promising to improve this parameter. In particular, in the work[44] it has been shown that the introduction of various substituents at the reactive carbons leads to a significant change of the cycloreversion quantum yields. So the introduction of methoxy group leads to a strong suppression of the cycloreversion quantum yield to less than 10^{-4}, while cyano or a π-conjugated groups enhanced the reactivity to 41%.[44]

As it can be seen from Table 2, the cycloreversion reactivity of diarylcyclopentenones prepared appeared also strongly dependent on the symmetry of the diarylethene systems but does not depend on the solvent polarity. The quantum yields of the cycloreversion reaction of the isomeric ketones in

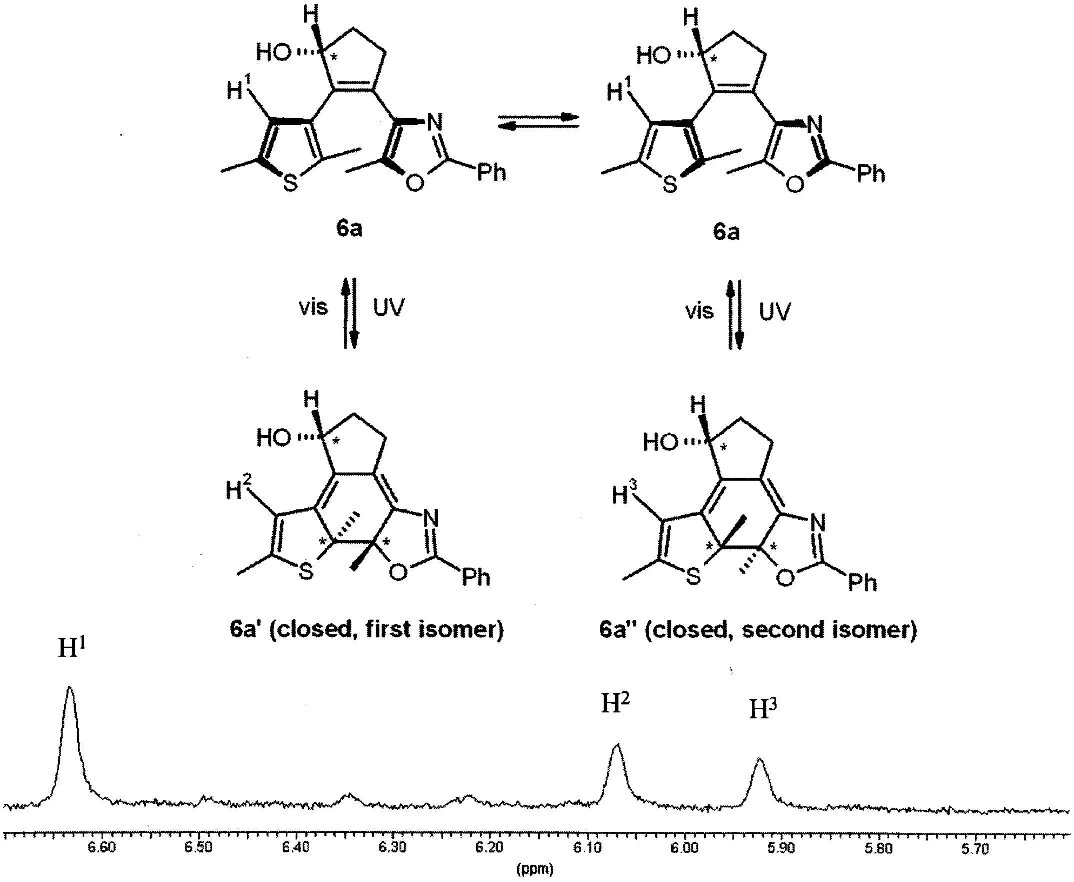


Figure 3. Structures of photogenerated diastereomers for **6a** and NMR spectra of **6a** in the field of protons of the thiophene ring after irradiation of benzene solution by UV light (254 nm). For convenience, the structure of only one stereoisomer of **6a** is given.

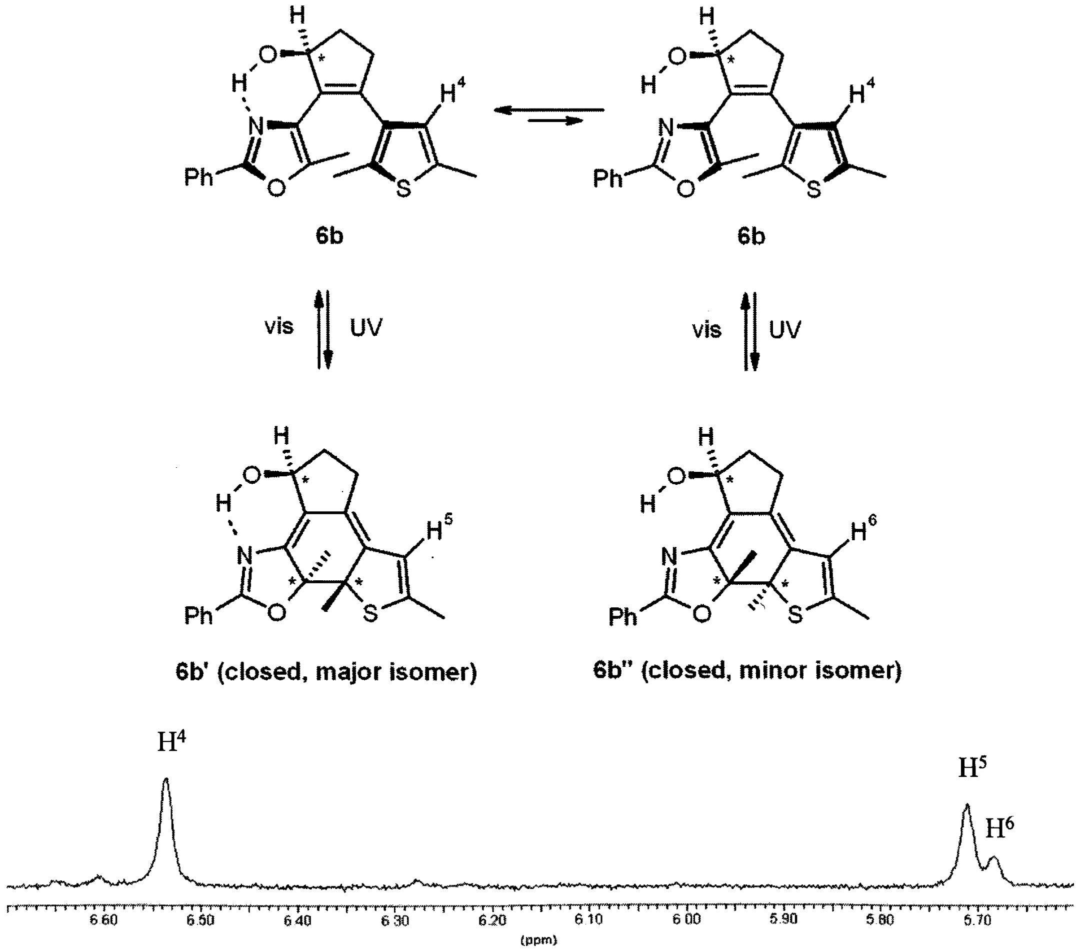


Figure 4. Structures of photogenerated diastereomers for **6b** and NMR spectra of **6b** in the field of protons of the thiophene ring after irradiation of benzene solution by UV light (254 nm). For convenience, the structure of only one stereoisomer of **6b** is given.

acetonitrile **4a** and **4b** were estimated to be 0.166 and 0.012, respectively. Interestingly, that similar tendency has been observed for the oxime (**5a**, 0.144, **5b**, <0.01, respectively) and hydroxy derivatives (**6a**, 0.170, **6b**, 0.055, respectively). Probably in each case the nature of these patterns is different because it is difficult to suggest that the influence of the carbonyl and hydroxy groups on the photochromic properties will be the same. The effect of solvent polarity on the efficiency of the cycloreversion reaction of the diarylethenes obtained has not been quite clear, but it should be noted that in most cases in hexane solution the quantum yields are higher than that in acetonitrile, although there are contradicting results. The results obtained on the influence of the solvent polarity on the quantum yields of the cyclization and cycloreversion reactions are in good agreement with literature data.[58]

■ CONCLUSION

Thus, novel unsymmetrical photochromic dihetarylcyclopentenones bearing thiophene and oxazole rings as aryl moieties have been developed. The relationship between structure of photochromic molecule and different switching properties (absorption maxima, thermal stability, and quantum yields) has been estimated. It was found that the spectral characteristics of these compounds depend on the substituents in cyclopentene ring, nature of aryl residues, and the positions of the attachment of the aryl groups to the ethene "bridge". The synthesis of the unsymmetrical DAEs consisting of two structural isomers has allowed us to perform a comparative analysis of the spectral and kinetic properties of these compounds. The study of the spectral properties of such unsymmetrical 2,3-diarylcyclopent-2-en-1-ones has shown that the isomers have different thermal stability, absorption maxima, and quantum yields. The replacement of the carbonyl group with oxime leads to a decrease of the difference in the photochromic properties of these isomers, and the reduction of the carbonyl function to the hydroxy-group absolutely removes this difference. It was demonstrated that by simple modifications of these diarylethenes photochromic compounds with improved performance (the thermal stability of photoinduced isomer and the quantum yields of the cyclization reaction) can be obtained. It has been found that DAEs bearing at the second position of the cyclopentene ring the oxazole unit as aryl moiety and an oxime or hydroxy group as the ethene "bridge" substituent are able to form the intramolecular hydrogen bond that in the case of the hydroxy-diarylethene leads to an increase of the quantum yield to 61% and the improvement of the diastereoselectivity (up to 76%).

■ EXPERIMENTAL SECTION AND METHODS

General Experimental Procedures. Proton nuclear magnetic resonance spectra (^{1}H NMR) and carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded in deuterated solvents on a spectrometers working at 300 MHz for ^{1}H and 75 MHz for ^{13}C. Both ^{1}H and ^{13}C NMR chemical shifts are referenced relative to the solvents residual signals ($CHCl_3$: δ 7.27 for ^1H NMR and δ 77.16 for ^{13}C NMR) and reported in parts per million (ppm) at 293 K. Data are represented as follows: chemical shift, multiplicity (s, singlet; d, doublet; m, multiplet; br, broad), coupling constants in hertz (Hz), integration, and assignment. Infrared spectra were measured on a FT-IR spectrometer in KBr pellets or abs $CHCl_3$ ($C = 0.005$ M) solutions and are reported in terms of frequency of absorption (cm^{-1}). Melting points (mp) were recorded using an apparatus and not corrected. Mass spectra were obtained on a mass spectrometer (70 eV) with direct sample injection into the ion source. High resolution mass spectra were obtained from a TOF mass spectrometer with an ESI source. Microanalyses were obtained using an automatic CHNS/O elemental analyzer. All chemicals and anhydrous solvents were purchased from commercial sources and used without further purification. Silica column chromatography was performed using silica gel 60 (70−230 mesh); TLC analysis was conducted on silica gel 60 F254 plates.

Theoretical Calculations. Ground-state energies of open- and closed-ring isomers were calculated by the B3LYP1 hybrid density functional method (basis set 6-31G(d)). The computations were performed with Firefly QC package,[59] which is partially based on the GAMESS (US)[60] source code.

Photochemical Studies. UV−vis spectra were recorded in 1.0 cm quartz cuvettes. The experimental measurements were performed at 293 K in the presence of air in solutions of acetonitrile and hexane, respectively. Photocoloration and photobleaching reactions were carried out using a high-pressure mercury lamp as the exciting light source. The required wavelengths (313, 436, and 517 nm) were isolated by the use of the appropriate filters. Molar extinction coefficients of the photogenerated isomers were determined as follows: a diarylethene (10 mg) was dissolved in dichloromethane (3 mL), and the solution was irradiated with UV light (313 nm) for 30−45 min in 1.0 cm quartz cuvette. The obtained deeply colored solution was evaporated in the dark under vacuum, and the residue was used in preparation of samples for NMR and UV/vis spectroscopy studies. Molar extinction coefficients (ε_C) were calculated by eq 1:

$$\varepsilon_C = \frac{D}{\text{conv} \times c_0} \tag{1}$$

where D is the absorption at band maximum of photogenerated isomer, conv is the conversion of diarylethene, and c_0 is the total concentration of the compound.

Quantum yields of ring-closure and ring-opening processes were calculated by eqs 2 and 3, respectively:[61]

$$\ln \frac{D(\infty) - D(0)}{D(\infty) - D(t)} = 2.303 \times 10^3 \times I_0 \times \varepsilon_0 \times \varphi_{O-C} \times t \times \frac{c_0}{c_B(\infty)} \tag{2}$$

$$\ln \frac{D(0)}{D(t)} = 2.303 \times 10^3 \times I_0 \times \varepsilon_C \times \varphi_{C-O} \times t \tag{3}$$

where $D(\infty)$ is the absorption at band maximum of photogenerated isomer in photostationary state (PSS), $D(t)$ is the absorption at time t, and $D(0)$ is the initial absorption, I_0 is the irradiation light intensity, ε_0 and ε_C are molar extinction coefficients of initial and photogenerated isomers at the irradiation wavelength, respectively, c_0 and $c_B(\infty)$ are the total concentration and the concentration of photogenerated isomer in PSS, respectively, φ_{O-C} and φ_{C-O} are cyclization and ring-opening quantum yield, respectively, and $\varepsilon_0 \times c_0$ and $\varepsilon_C \times c_B(\infty)$ are lower than 0.2.

1,2-Bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene in hexane solution[45] and azobenzene in methanol solution[62] were used as a chemical actinometer.

Kinetic Studies. The half-lifes of thermal bleaching for the diarylethenes were determined as follows. The solution of open-ring form in acetonitrile ($C \approx 2 \times 10^{-5}$ M) was irradiated with UV light (λ = 313 nm) until reaching the photostationary state and was kept in dark at 293 K. The reaction yields were periodically determined by absorption spectroscopic measurement. The thermal bleaching process was determined as a first-order reaction (linearity for relationships between the logarithms of absorbance and exposal time) that is a well-known fact.[63]

Synthetic Procedures and Characterization Data. The ketoester **1b** was prepared from corresponding hetarylacetic acid[64] by the method used in ref 65. The ketoester **1a**,[65] bromoketones **2a**[66] and **2b**,[67] ketone **4d**,[18] and oxime **5d**[21] were synthesized according to known procedures.

*Ethyl 4-(5-Methyl-2-phenyl-1,3-oxazol-4-yl)-3-oxobutanoate **(1b)**.* Yield 1.87 g (65%), light-brown oil. IR (KBr, thin film), cm^{-1}: 2984, 2926, 1745, 1722, 1640, 1321, 1028, 715, 694. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.25 (t, J = 7.1 Hz, 3H, CH_3), 2.33 (s, 3H, CH_3), 3.59 (s, 2H, CH_2), 3.72 (s, 2H, CH_2), 4.17 (q, J = 7.1 Hz, 2H, CH_2), 7.39−7.44 (m, 3H, H^{phenyl}), 7.94−7.99 (m, 3H, H^{phenyl}). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.3, 14.1, 40.6, 48.4, 61.4, 126.1, 127.4, 128.7, 128.9, 130.1, 146.3, 160.0, 167.2, 199.4. MS (EI, 70 eV): m/z (%) = 287 (30), $[M]^+$, 241 (55), $[M - EtOH]^+$, 215 (70), $[M - EtOCO]^+$, 199 (35), $[M - MeCOOEt]^+$, 173 (90), 172 (100). HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{18}NO_4$, 288.1230; found, 288.1217.

2,3-Diarylcyclopent-2-en-1-ones (General Procedure). To a solution of ketoester **1** (10 mmol) in abs benzene (30 mL), sodium (0.23 g, 10 mmol) was added. The reaction mixture was stirred for 2 h, and bromoketone **2** (10 mmol) was added portionwise. The mixture was kept overnight, then poured into water (150 mL) and extracted with ethyl acetate (3 × 50 mL). The combined organic phases were washed with water (100 mL), dried with magnesium sulfate, and evaporated in vacuum. The residue was dissolved in ethanol (37 mL), and a solution of KOH (2.80 g, 50 mmol) in water (37 mL) was added. The reaction mixture was refluxed until completion of the reaction (monitored by TLC), then cooled, poured into water (100 mL), and extracted with ethyl acetate (3 × 50 mL). The combined organic phases were washed with water (100 mL), dried with magnesium sulfate, and evaporated in vacuum. The residue was purified by column chromatography by petroleum ester/ethyl acetate 3:1 and recrystallized from ethanol.

*2-(2,5-Dimethylthiophen-3-yl)-3-(5-methyl-2-phenyl-1,3-oxazol-4-yl)cyclopent-2-en-1-one **(4a)**.* Yield 1.40 g (40%), white powder, mp 174−176 °C. IR (KBr), cm^{-1}: 3061, 2920, 2859, 1696, 1630, 1580, 1561, 1482, 1447, 1404, 1380, 1263, 1188, 1143. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.85 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 2.63−2.70 (m, 2H, CH_2), 3.10−3.18 (m, 2H, CH_2), 6.54 (s, 1H, H^{thioph}), 7.43−7.52 (m, 3H, H^{phenyl}), 7.98−8.07 (m, 2H, H^{phenyl}). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.2, 14.4, 15.3, 29.3, 34.5, 126.2, 126.8, 127.1, 128.8, 129.0, 130.4, 133.3, 135.2, 135.5, 136.3, 149.0, 160.4, 161.4, 207.8. MS (EI, 70 eV): m/z (%) = 349 (70) $[M]^+$, 334 (20), $[M - CH_3]^+$. Anal. Calcd for $C_{21}H_{19}NO_2S$: C, 72.18; H, 5.48; N, 4.01. Found: C, 72.03; H, 5.36; N, 4.06.

*3-(2,5-Dimethylthiophen-3-yl)-2-(5-methyl-2-phenyl-1,3-oxazol-4-yl)cyclopent-2-en-1-one **(4b)**.* Yield 1.12 g (32%), gray crystals, mp 176−178 °C. IR (KBr), cm^{-1}: 2960, 2908, 2853, 1701, 1639, 1595, 1556, 1483, 1434, 1323, 1260, 1120, 1063. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.07 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.62−2.71 (m, 2H, CH_2), 2.94−3.04 (m, 2H, CH_2), 6.64 (s, 1H, H^{thioph}), 7.34−7.44 (m, 3H, H^{phenyl}), 7.90−8.00 (m, 2H, H^{phenyl}). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.1, 15.0, 15.1, 31.5, 35.0, 125.3, 126.3, 127.7, 128.6, 129.0, 129.9, 131.9, 133.4, 136.8, 137.3, 147.5, 160.2, 167.8, 206.8. MS (EI, 70 eV): m/z (%) = 349 (25) $[M]^+$, 244 (100). HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{20}NO_2S$, 350.1209; found, 350.1207.

*2,3-Bis(5-methyl-2-phenyl-1,3-oxazol-4-yl)cyclopent-2-en-1-one **(4c)**.* Yield 1.31 g (33%), red powder, mp 142−144 °C. IR (KBr), cm^{-1}: 3066, 2912, 2852, 1697,1650, 1601,1559, 1487, 1333, 1203, 1065, 1023. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.12 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.67−2.74 (m, 2H, CH_2), 3.16−3.23 (m, 2H, CH_2), 7.38−7.49 (m, 6H, H^{phenyl}), 7.94−8.03 (m, 4H, H^{phenyl}). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.5, 12.3, 29.7, 34.6, 126.2, 126.3, 127.1, 127.6, 128.7, 128.8, 128.8, 130.0, 130.4, 131.2, 133.1, 147.7, 149.3, 160.1, 160.3, 163.3, 206.9. MS (EI, 70 eV): m/z (%) = 396 (100), $[M]^+$, 381

(30), $[M - CH_3]^+$. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{25}H_{21}N_2O_3$, 397.1547; found, 397.1541.

Oximes 5 (General Procedure). A mixture of ketone **4** (2.0 mmol), hydroxylamine hydrochloride (0.40 g, 6.0 mmol), and anhydrous sodium acetate (0.64 g, 6.0 mmol) in ethanol (7 mL) was refluxed for 3 h and poured into water (70 mL). The residue was filtered off, washed with water (2 × 30 mL), and recrystallized from ethanol.

*2-(2,5-Dimethylthiophen-3-yl)-3-(5-methyl-2-phenyl-1,3-oxazol-4-yl)cyclopent-2-en-1-one Oxime (**5a**).* Yield 0.65 g (90%), yellow powder, mp 95−97 °C. IR (KBr), cm^{-1}: 3273, 2917, 1701, 1628, 1488, 1448, 1193, 867, 692. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.83 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 1.85−1.97 (m, 2H, CH_2), 3.00−3.17 (m, 2H, CH_2), 6.59 (s, 1H, H^{thioph}), 7.40−7.53 (m, 3H, H^{phenyl}), 7.93−8.06 (m, 2H, H^{phenyl}). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.9, 14.3, 15.3, 24.6, 32.5, 126.2, 127.0, 127.4, 128.8, 130.0, 130.1, 131.7, 133.3, 134.5, 136.2, 145.7, 146.9, 159.8, 168.4. MS (EI, 70 eV): *m*/*z* (%) = 364 (25), $[M]^+$, 347 (100), $[M - OH]^+$. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{21}H_{21}N_2O_2S$, 365.1318; found, 365.1299.

*3-(2,5-Dimethylthiophen-3-yl)-2-(5-methyl-2-phenyl-1,3-oxazol-4-yl)cyclopent-2-en-1-one Oxime (**5b**).* Yield 0.62 g (85%), yellow powder, mp 165−166 °C. IR (KBr), cm^{-1}: 3262, 2917, 1643, 1555, 1488, 1448, 1334, 1143, 963, 775, 693. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.85 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.82−2.99 (m, 4H, CH_2), 6.52 (s, 1H, H^{phenyl}), 7.34−7.51 (m, 3H, H^{phenyl}), 7.99 (br s, 1H, OH), 8.05−8.15 (m, 2H, H^{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.6, 14.7, 12.2, 25.0, 34.3, 125.6, 126.6, 127.3, 127.7, 128.5, 129.8, 130.0, 133.8, 134.5, 136.5, 146.8, 151.2, 160.1, 166.6. MS (EI, 70 eV): *m*/*z* (%) = 364 (15), $[M]^+$, 347 (30), $[M - OH]^+$. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{21}H_{21}N_2O_2S$, 365.1318; found, 365.1315.

*2,3-Bis(5-methyl-2-phenyl-1,3-oxazol-4-yl)cyclopent-2-en-1-one Oxime (**5c**).* Yield 0.72 g (87%), yellow powder, mp 190−192 °C. IR (KBr), cm^{-1}: 3283, 3055, 2914, 1615, 1488, 1449, 1334, 1196, 991, 867, 690. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.02 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.90−3.02 (m, 2H, CH_2), 3.04−3.14 (m, 2H, CH_2), 7.34−7.48 (m, 6H, H^{phenyl}), 7.93−8.00 (m, 2H, H^{phenyl}), 8.05−8.12 (m, 2H, H^{phenyl}). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.2, 11.7, 24.7, 32.8, 126.2, 126.5, 127.4, 127.6, 128.6, 128.8, 130.0, 130.2, 133.1, 146.7, 146.8, 160.1, 160.3, 167.0. MS (EI, 70 eV): *m*/*z* (%) = 411 (55) $[M]^+$, 394 (100), $[M - OH]^+$. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{25}H_{22}N_3O_3$, 412.1656; found, 412.1644.

Alcohols 6 (General Procedure). A ketone **4** (0.5 mmol) was dissolved in methanol (3 mL), and sodium borohydride (0.095 g, 2.5 mmol) was added slowly. The solution was stirred for 2 h, poured into water (100 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic phases were washed with water (100 mL), dried with magnesium sulfate, and evaporated in vacuum.

*2-(2,5-Dimethylthiophen-3-yl)-3-(5-methyl-2-phenyl-1,3-oxazol-4-yl)cyclopent-2-en-1-ol (**6a**).* Yield 0.16 g (93%), yellow powder, mp 115−117 °C. IR (KBr), cm^{-1}: 2918, 1704, 1604, 1556, 1448, 1448, 1380, 1083, 825, 689. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.83 (s, 3H, CH_3), 1.92−2.03 (m, 4H), 2.35−2.52 (m, 4H), 2.66−2.81 (m, 1H), 3.09−3.23 (m, 1H), 5.04−5.13 (m, 1H, CH), 6.63 (s, 1H, H^{thioph}), 7.38−7.51 (m, 3H, H^{phenyl}), 7.93−8.04 (m, 2H, H^{phenyl}). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.8, 14.3, 15.3, 32.7, 33.6, 80.8, 126.1, 127.6, 128.7, 129.9, 132.7, 133.4, 133.5, 133.9, 136.3, 137.2, 145.8, 159.5. MS (EI, 70 eV): *m*/*z* (%) = 351 (40) $[M]^+$, 333 (30), $[M - H_2O]^+$. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{21}H_{22}NO_2S$, 352.1366; found, 352.1361.

*3-(2,5-Dimethylthiophen-3-yl)-2-(5-methyl-2-phenyl-1,3-oxazol-4-yl)cyclopent-2-en-1-ol (**6b**).* Yield 0.16 g (93%), yellow powder, mp 149−150 °C. IR (KBr), cm^{-1}: 3331, 2917, 2852, 1554, 1488, 1449, 1143, 1072, 693. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.77 (s, 3H, CH_3), 1.96−2.10 (m, 4H), 2.37−2.51 (m, 4H), 2.74−3.85 (m, 2H, CH_2), 4.33 (s, 1H, OH), 5.20−5.27 (m, 1H, CH), 6.54 (s, 1H, H^{thioph}), 7.40−7.51 (m, 3H, H^{phenyl}), 7.96−8.05 (m, 2H, H^{phenyl}). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.6, 14.3, 15.2, 29.8, 31.2, 36.4, 80.2, 126.1, 127.3, 128.8, 130.2, 131.2, 132.8, 133.1, 134.6, 136.3, 137.8, 145.9, 159.4. MS (EI, 70 eV): *m*/*z* (%) = 351 (10), $[M]^+$, 333 (30), $[M - H_2O]^+$. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{21}H_{22}NO_2S$, 352.1366; found, 352.1363.

*2,3-Bis(5-methyl-2-phenyl-1,3-oxazol-4-yl)cyclopent-2-en-1-ol (**6c**).* Yield 0.19 g (95%), yellow powder, mp 180−181 °C. IR (KBr), cm^{-1}: 3307, 2912, 2852, 1625, 1553, 1484, 1449, 1086, 1025, 721, 693. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.94 (s, 3H, CH_3), 1.98−2.09 (m, 4H), 2.45−2.54 (m, 1H), 2.94−3.02 (m, 2H, CH_2), 5.15−5.25 (m, 1H, CH), 7.41−7.49 (m, 6H, H^{phenyl}), 7.97−8.05 (m, 4H, H^{phenyl}). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.5, 29.8, 31.2, 34.8, 80.4, 126.2, 126.2, 127.3, 127.5, 128.8, 130.2, 130.3, 131.9, 132.7, 133.5, 145.6, 145.7, 159.78, 160.0. MS (EI, 70 eV): *m*/*z* (%) = 398 (15), $[M]^+$, 380 (60), $[M - H_2O]^+$. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{25}H_{23}N_2O_3$, 399.1703; found, 399.1696.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^1H, ^{13}C NMR spectra of compounds, UV−vis spectra of diarylethenes **4**−**6**, and IR spectra of diarylethenes **5a**,**b** and **6a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(41) Full version of the Table 2 is available in the Supporting Information.

(42) ^{1}H NMR spectra of the compounds **4a** and **4b** are available in the Supporting Information.

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