JOC The Journal of Organic Chemistry

Article

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Structural and Spectral Properties of Photochromic Diarylethenes: Size Effect of the Ethene Bridge

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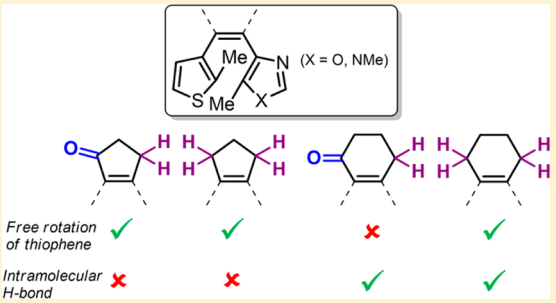
Supporting Information

ABSTRACT: The effect of the size of the ethene bridge on the structural and spectral properties of photochromic diarylethenes, which remains a poorly understood phenomenon, was studied as applied to diarylethenes containing unsymmetrical (cyclohexenone and cyclopentenone) and symmetrical (cyclohexene and cyclopentene) ethene bridges. Thiophene, oxazole, and imidazole derivatives were used as aryl moieties. An increase in the size of the ethene bridge in the cycloalkenone series was found to be accompanied by a hypsochromic shift of the absorption maximum of the photoinduced form, whereas no difference was found for cycloalkenes. A detailed analysis of the NMR spectra (including 2D experiments) revealed previously unknown effects associated with the existence of an intramolecular hydrogen bond (CH···N) between the six-membered ethene bridge and the azole substituents. The NMR experimental data obtained were confirmed by DFT quantum chemical calculations and X-ray analysis. It was found that an intramolecular hydrogen bond favors an increase of the quantum yield of the photocyclization reaction.



INTRODUCTION

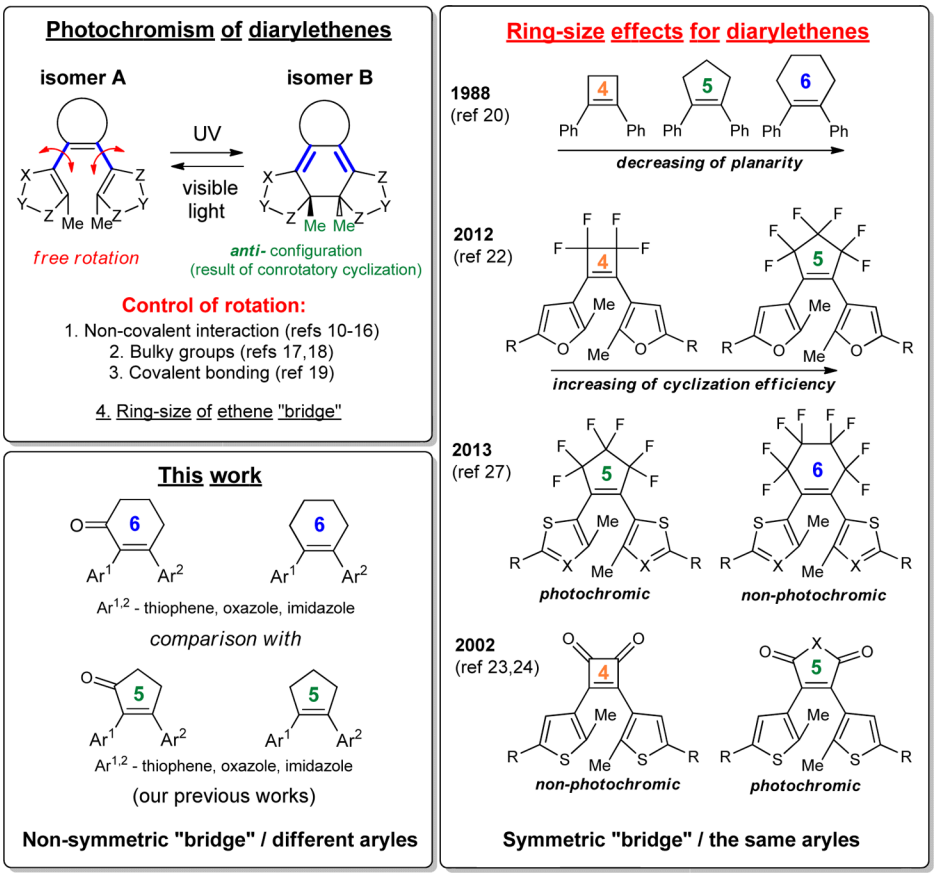
Organic compounds are becoming increasingly important in material and applied chemistry. The unlimited potential of organic synthesis enables one to subject the structure of the molecular core to various modifications and to fine-tune the properties of the molecules in required ranges as desired. These advantages have especially manifested themselves in the organic photochromes,[1] which are considered as promising compounds for the design of photocontrolled materials and devices with a wide range of practical applications,[2] in particular, as data storage elements[3] and molecular switches.[4] Besides, photochromes have attracted increasing attention in biology as an efficient tool for the spatial and temporal control of biological objects and systems,[5] as well as in photopharmacology.[6] Among organic photochromic compounds, diarylethenes bearing heterocyclic substituents have attracted much interest because of their high relative stability of the photoisomer and excellent fatigue resistance (Scheme 1).[7]

In recent years, an understanding of the nature of photoswitching and the use of advantages of an organic molecule, which are associated with the ease of modifications and opportunities for the utilization of various structural moieties, have allowed the solution of one of the key problems in this area of chemistry (photochromism) related to the design of photoswitches with high quantum yields.[8,9] A high efficiency, up to 98%[10] (which implies that each photon absorbed by the molecule is consumed in the photocyclization), can be achieved in three ways. First, the conformation can be stabilized through noncovalent interactions, such as hydrogen bonds (OH−N[11,12] and CH−N[13]), or other interactions (N−S,[10,14] N−F,[15] and N−P[16]). Another way is based on the introduction of bulky substituents into the ethene bridge.[17,18] The third method relies on the retention of the photoactive conformation through covalent bonding.[19] However, all these approaches have a number of drawbacks. In the case of noncovalent interactions, the nature of the solvent may have a considerable effect on the efficiency of cyclization. In the case of steric hindrance, the statistical character of the formation of diarylethenes adopting a required conformation is a disadvantage, which has not been

Received: November 3, 2016
Published: January 17, 2017

DOI: 10.1021/acs.joc.6b02665
J. Org. Chem. 2017, 82, 1477−1486

Scheme 1. Formulation of the Problem



overcome yet. Thus, for example, diarylethene comprising a benzobis(thiadiazolyl) fragment as ethene bridge and benzothienyl groups as aryl moieties and having no possibility for a conformational transition between antiparallel and parallel forms has been prepared by a cross-coupling reaction only with 50% of the photoactive form.[18a]

Therefore, knowledge of the effect of the structural features on the photochromic properties is important for the design of new photoswitchable materials and devices with improved properties, including with high quantum yields. The conformation of the ethene bridge associated primarily with the size of the carbocycle is a very promising but poorly known factor that affects the quantum yield of the photocyclization reaction. It was demonstrated by both calculations and experimental studies[20] that the angle of rotation of the phenyl rings with respect to the bridge increases (and, correspondingly, the planarity of the molecule decreases) in a series of 1,2-diphenylcycloalkenes with an increase in the ring size of the bridge (from four- to six-membered), which should be favorable for an increase in the quantum yield. Taking into account this fact, as well as that an increase in the size of the bridge results in a hypsochromic shift, Irie and co-workers[21] proposed five-membered bridges as optimal units for the construction of photochromic diarylethenes. The first experimental evidence for the influence of the size of the bridge on the efficiency of the photocyclization reaction was obtained for furyl-bearing diarylethenes based on perfluorocyclobutene and perfluorocyclopentene as ethene bridge (Scheme 1, right column).[22] It was found that a decrease in the size of the ethene bridge leads to a considerable decrease in the cyclization quantum yield (and simultaneously to an increase in the efficiency of the cycloreversion reaction). This effect is more clearly manifested for the dithienyl derivative of cyclobutenedione.[23] This diarylethene, unlike, for example, related derivatives of maleic anhydride,[24] does not exhibit photochromic properties either in solution or in the crystalline phase. However, the photoactivity of diarylethenes based on squaric acid derivatives can be restored by introducing bulky heterocycles, such as thienothiophene[23] or thienypyrrole,[25] instead of thiophene or by modifying the bridge.[26] Another example of the critical effect of the size of the bridge was described for perfluorocyclohexenone derivatives containing 2-thienyl moieties,[27] which, unlike five-membered analogs, do not exhibit photochromic properties due to steric hindrance between the fluorine atoms of the bridge and the thiophene moieties. It should be noted that the effect of the size of the ethene bridge on the absorption maxima of photoisomers[28] and the crystal structures[29] was considered in a number of studies. Besides, a comprehensive investigation of this phenomenon was carried out for thienyl derivatives of cyclopentene and cyclohexene using calculation methods.[30]

Therefore, the general pattern of the effect of the size of the bridge on the physical and chemical properties of diarylethenes is still lacking. Moreover, known examples are related only to symmetrical derivatives and mainly of thiophene. This is due to the absence of facile and universal methods for the synthesis of photochromic compounds based on six-membered bridges derived not only from thiophene but also from other heterocycles, primarily azoles. The purpose of the present study is to synthesize photochromic derivatives of cyclohex-2-

DOI: 10.1021/acs.joc.6b02665
J. Org. Chem. 2017, 82, 1477−1486

Scheme 2. Syntheses of Diarylethenes Containing Six-Membered Bridges

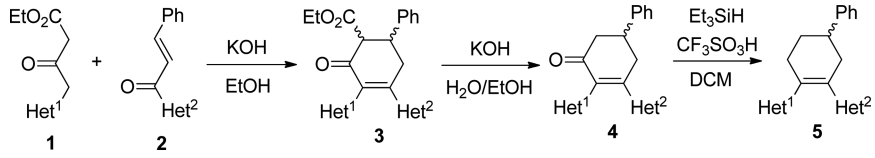
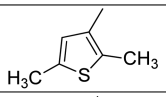
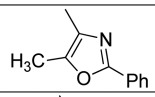
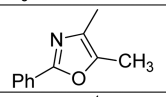
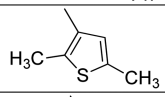
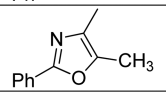
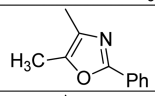
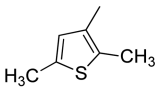
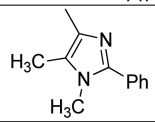
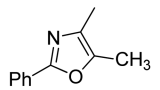
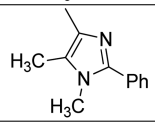
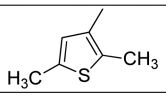
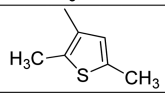


Table 1. Structures and Yields of Diarylethenes Containing Six-Membered Bridges 3−5

entry	structure			yield **3**	yield **4**	yield **5**
	№	Het^1	Het^2			
1	**a**			63%	61%	51%
2	**b**			43%	68%	-
3	**c**			32%	47%	-
4	**d**			60%*	39%	58%
5	**e**			37%	51%	-
6	**f**			26%	-	-

*Sodium ethoxide as the base.

en-1-one and cyclohexene and compare their structural and spectral properties with the five-membered analogs, which we synthesized previously. The earlier studies of our research team were devoted to the development of methods for the synthesis of thiophene[31] and azole[12,32] diarylethenes comprising cyclopent-2-en-1-one as ethene bridge, as well as of their cyclopentene analogs.[33]

RESULTS AND DISCUSSION

Synthesis. The classical method for the synthesis of cyclohex-2-en-1-one derivatives is based on the Robinson reaction of ketones bearing the methylene group at the α-position with chalcones. In particular, the condensation of acetoacetic ester with chalcones giving 3,5-diaryl-substituted cyclohexenones was studied in detail.[34] Meanwhile, there are no data[35] on this reaction with ethyl 4-aryl-3-ketobutanoates **1**, the condensation of which with chalcones **2** should afford 2,3,5-triaryl-substituted cyclohexenones as potential photochromes. The lack of data is attributed to the fact that until recently compounds **1** were virtually inaccessible. We have solved this problem relatively recently using readily available arylacetic acids as the starting compounds.[36]

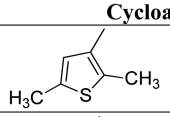
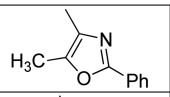
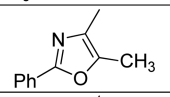
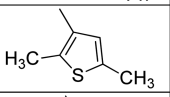
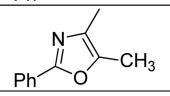
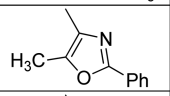
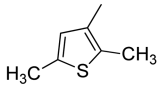
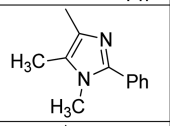
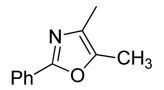
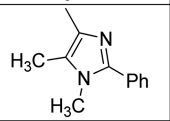
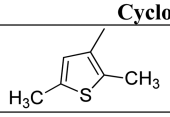
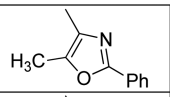
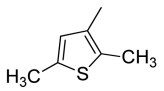
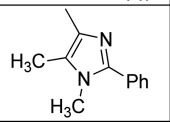
As expected, the reaction of keto esters **1** with chalcones **2** (thiophene, oxazole, and imidazole derivatives) in the presence of a base gave photochromic products, diarylethenes **3** (Scheme 2, Table 1). We have tested a series of bases (KOH, EtONa, piperidine, potassium carbonate). The best results were obtained by carrying out the reaction in the presence of potassium hydroxide in aqueous ethanol. The method for the synthesis of 2,3,5-triarylcyclohex-2-en-1-ones proved to be universal and allowed us to synthesize a series of previously unknown hetaryl-substituted cyclohexenones **3**. Because the presence of the ester group in these compounds is undesirable, we have carried out their saponification and decarboxylation. The reaction proceeds in one step in an aqueous ethanolic solution in the presence of alkali in moderate yields. This method was applied to synthesize isomeric diarylethenes bearing thiophene and oxazole as aryl moieties (**4a** and **4b**), bis-azole compounds **4c** and **4e**, and a derivative of thiophene and imidazole **4d**.

The carbonyl group in **4** was reduced by a procedure based on the ionic hydrogenation, which we developed earlier.[33] This reaction was applied to synthesize diarylethenes **5a,d** comprising thiophene and azoles (oxazole or imidazole) as heterocyclic substituents. However, as in the case of five-membered analogs,[33] we have failed to reduce diarylethenes **4b,c,e** bearing oxazole at the 2 position of the cyclohexenone ring.

Spectral Properties. Up to the present work, the effect of the size the ethene bridge on the spectral properties of symmetrical diarylethenes has been considered in a number of studies.[21,22,28,30a] The synthesis of pairs of cycloalkenones and cycloalkenes (compounds **6a−c**,[12] **6d**,[32] **7a,b**[33] were described by our scientific group earlier; compound **6e** was obtained for the first time) comprising the same aryl substituents (thiophene, oxazole, and imidazole) revealed some general features associated with the size of the bridge (Table 2). First, it should be noted that pairs of diarylethenes have absolutely

DOI: 10.1021/acs.joc.6b02665
J. Org. Chem. 2017, 82, 1477−1486

Table 2. Spectral Properties of 4−7 in Acetonitrile Solutions

entry	№	Structure		6 (X = CO), 7 (X = CH_2)		4 (X = CO), 5 (X = CH_2)	
		Het^1	Het^2	λ^{max}(A), nm	λ^{max}(B), nm	λ^{max}(A), nm	λ^{max}(B), nm
Cycloalkenone ethene "bridge" (compounds 6 and 4)[a]							
1	**6a/4a**			298	523	291	504
2	**6b/4b**			284	549	284	524
3	**6c/4c**			283	505	285	493
4	**6d/4d**			329	555	342	539
5	**6e/4e**			286	564	287	549
Cycloalkene ethene "bridge" (compounds 7 and 5)[b]							
6	**7a/5a**			290	452	293	457
7	**7d/5d**			293	460	292	462

[a]Spectral properties of diarylethenes **6a−c** (ref 12) and **6d** (ref 32) were described earlier. [b]Spectral properties of diarylethenes **7a,b** (ref 33) were described earlier.

identical chromophoric systems. These pairs differ only in the conformation of the ethene bridge and the planarity of the system of conjugated double bonds (primarily, in the degree of conjugation of the carbonyl group with the other part of the chromophoric system). Figure 1 presents the absorption spectra of **5d** in acetonitrile before and after UV irradiation.

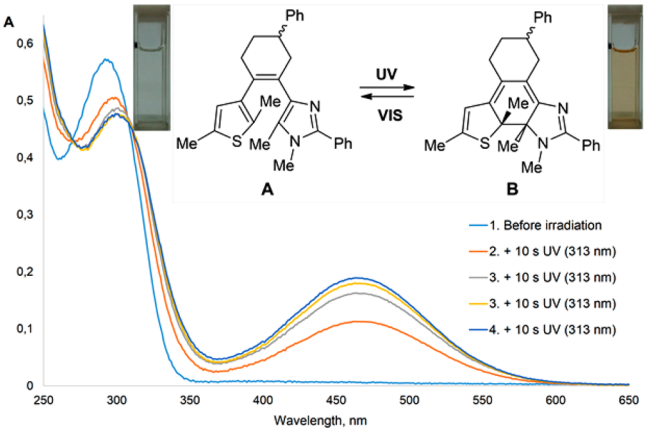


Figure 1. Changes of an absorption spectrum of compound **5d** under irradiation with UV light (313 nm) in acetonitrile ($c = 4.6 \times 10^{-5}$ M).

The reverse photoreaction occurs upon irradiation with visible light. An absorbance maximum of initial form **A** is observed at 292 nm and the photoisomer **B** exhibits this one in the visible region, at 462 nm.

It is difficult to establish the relationship between the spectral properties and the size of the ethane bridge for the form **A**. Meanwhile, there are clear correlations for the form **B** due probably to the more rigid structure of the photoisomer compared to the form **A**. An increase in the ring size of the bridge in the cycloalkenone series **6**/**4** leads to a hypsochromic shift of the absorption maxima of the photoinduced form by 12−25 nm. This effect can be attributed to a large distortion of the planarity of cyclohexenone molecules, resulting in a decrease in the efficiency of conjugation in the chromophoric system. On the other hand, an unexpected fact is that the absorption maxima of the form **B** have almost equal values for cycloalkene derivatives **7a**/**5a** and **7d**/**5d**. Apparently, this is due to the less rigid conformation of the carbocycle or the influence of intramolecular hydrogen bonding (see below). It should be noted that contradictory results were obtained previously for a pair of photochromic thiophene-based cyclopentene/cyclohexene derivatives. Thus, dithienylcyclohexenone was shown to have a longer-wavelength maximum,[30a] whereas indole and benzothiophene derivatives showed an inverse dependence.[28]

DOI: 10.1021/acs.joc.6b02665
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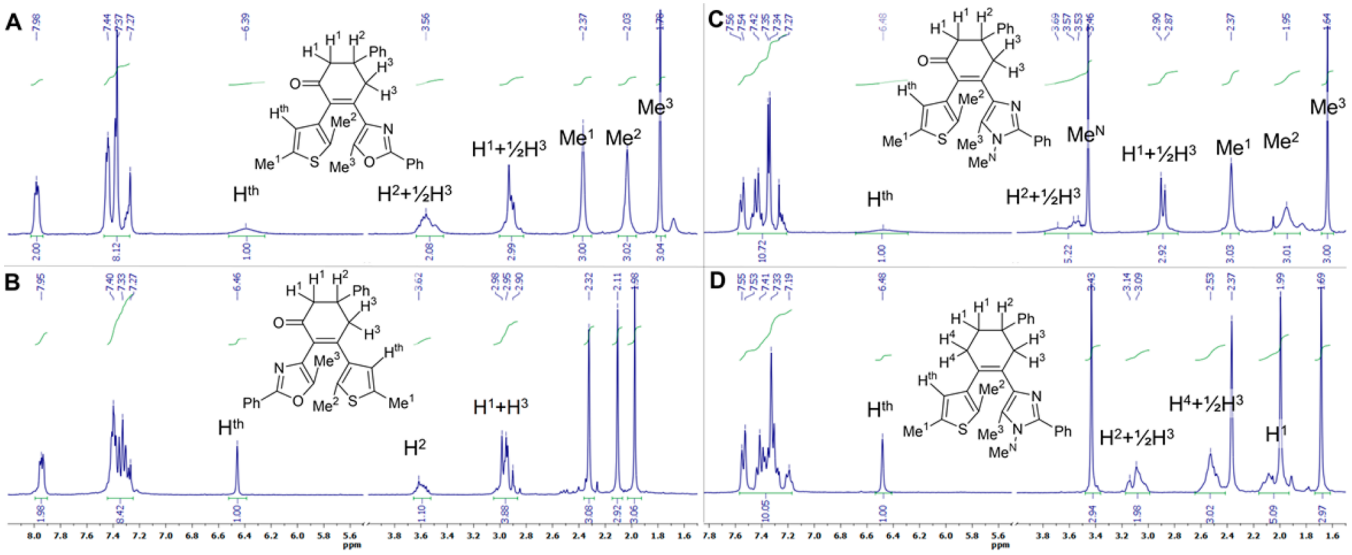

Figure 2. ^{1}H NMR spectra of diarylethenes **4a** (A), **4b** (B), **4d** (C), and **5d** (D) ($CDCl_3$, 300 MHz).

Structural Properties of Diarylethenes. A comparison of the ^{1}H NMR spectra of cyclopentenone and cyclohexenone diarylethenes and their reduced derivatives revealed some features indicating that the size of the bridge affects the structure of the photochromic molecule. Figure 2 shows the ^{1}H NMR spectra of compounds **4a**, **4b**, **4d**, and **5d**. The characteristic feature of these spectra is that the positions of the signals of the hydrogen atoms of the ethene bridge depend on the nature of the hetaryl substituents. The expected pattern is observed for compound **4b** (Figure 2B). Thus, a multiplet (integral = 1) of the aliphatic proton H^2 at the phenyl substituent appears at lower field (at 3.6 ppm), whereas signals for the protons H^1 and H^3 appear as a multiplet at 3.0 ppm. A different distribution of the signals for protons of the cyclohexenone moiety is observed for isomer **4a** (containing the oxazole moiety at the 3 position of the cyclohexenone ring). Thus, the spectrum shows a multiplet (integral = 2) at low field (at 3.6 ppm) and a multiplet (integral = 3) at high field. A similar situation is observed for diarylethene **4d** containing the imidazole moiety at the 3 position of the cyclohexenone ring and, which is more important, for cyclohexene derivative **5d**. The spectrum of the latter compound shows two additional aliphatic signals of the bridge, but it retains two signals at low field at 3.1 ppm, one of which is assigned to H^2.

The above-considered data provide indirect evidence for the nonequivalence of protons of one of the methylene groups of the cyclohexenone ring of diarylethenes containing azole at 3 position (diarylethenes **4a** and **4d**) and the cyclohexene ring of diarylethene **5d**. The same pattern is observed for related compounds **4c**,**e** and **5a** as well as the previously reported diarylethene[37] bearing a phenyl group at the 2 position and oxazole at the 3 position of the cyclohexenone ring.

To confirm the nonequivalence of the protons, we performed HSQC NMR experiments for **4a**, **4b**, **5a**, and **5d** [see Figures S1−S4 in the Supporting Information (SI)]. This heteronuclear NMR technique allows the determination of directly bonded proton−carbon pairs. Actually, signals for two hydrogen atoms H^3, which substantially differ in the chemical shift (by more than 0.5 ppm) but which are attached to the same carbon atom, were observed for diarylethenes **4a**, **5a**, and **5d** (however, this has not been registered for **4b**). Apparently, this effect in the NMR spectra is attributed to an intramolecular hydrogen bond between one of the protons H^3 and the sp^2-nitrogen atom of the azole heterocycle. Previously, it has been demonstrated that the protons involved in hydrogen bonding are less shielded than those that are not involved in such bonds.[38] In the case under consideration, this is manifested in a lower-field shift of the signal for one of the protons H^3.

Another indirect evidence of azole cycle fixation with hydrogen bonding is the absence of NOE interactions between the methyl group of the oxazole and the protons H^3 of cyclohexenone in the NOESY spectrum of diarylethene **4a** at 243, 273, and 303 K (see Figures S9 in the SI) in the presence of other NOE interactions. This fact indicates the spatial orientations of these groups.

A comparison of the spectra of isomers **4a** (A, Figure 2) and **4b** (B, Figure 2) shows a broadening of the signals for the aromatic thiophene proton H^{th} and protons of two methyl groups of **4a**. A similar pattern is observed for diarylethene **4d** (C, Figure 2), which contains an imidazole instead of the oxazole that is present in **4a**. On the basis of the partial assignment of NMR signals, the broadened signals of protons in the spectra of **4a** and **4d** were assigned to the thiophene moiety (Table S1 in the SI). It should be noted that an important difference between the ^{1}H NMR spectra of **4d** and **5d** is the broadening of the signals for the thiophene protons in the spectrum of the cyclohexenone compound (a similar pattern is observed for the **4a**/**5a** pair). This result attests to a hindered rotation of the thiophene substituent due to the steric effect of the carbonyl group. This is associated with the ring size of the bridge, because this phenomenon is not observed in the cyclopentenone series studied previously.[12,32] According to the literature data,[39] analysis of NMR spectra (section I.6 in the SI), and the calculated structure optimization (vide infra), the cyclohexenone moiety in compounds **4** in a wide range of temperatures from 343 to 303 K exists in the sofa (half-chair) conformation; i.e., the dynamic NMR effect is not a result of the conformational transformation of the cyclohexenone ring.

The temperature-dependent NMR spectra of compound **4a** confirmed the hindered rotation of the thiophene substituent (Figure 3 and Figure S8 in the SI for experiments at 243, 273, and 303 K). A double set of signals of the thiophene substituent

DOI: 10.1021/acs.joc.6b02665
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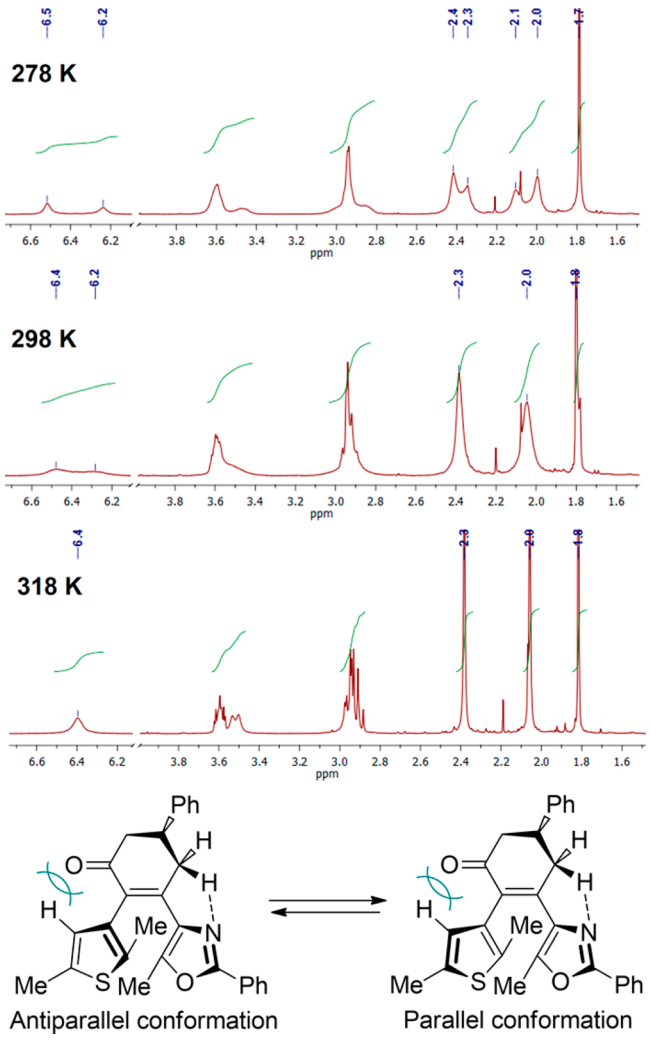


Figure 3. ^{1}H NMR spectra of diarylethene **4a** ($CDCl_3$, 600 MHz) at 278, 298, and 318 K (see explanation in the text).

terarylenes, primarily, the presence of attractive noncovalent interactions, which stabilize photoactive conformations.[10,14,41] The optimized structures for a series of diarylethenes with thiophene and imidazole moieties are given in Figure 4A.

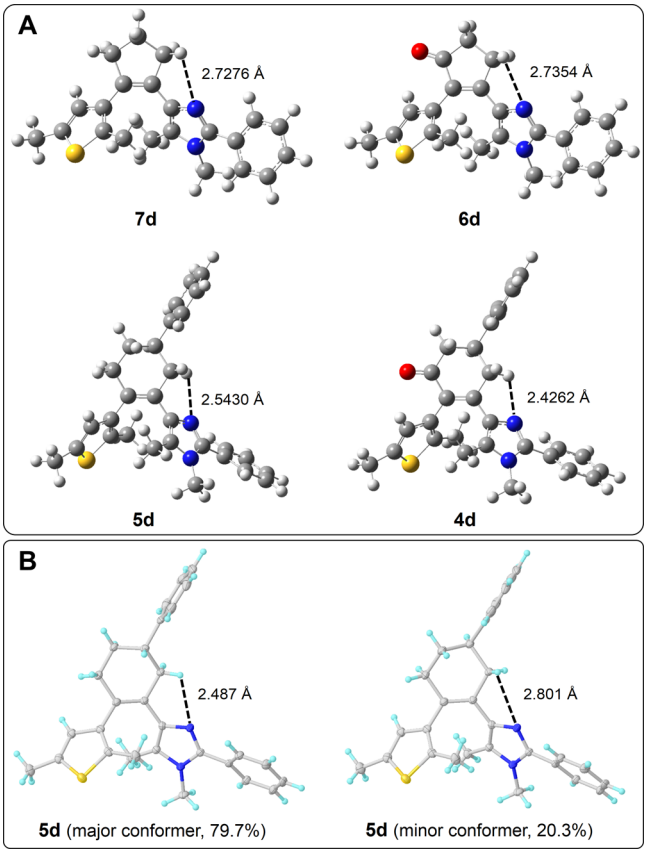


Figure 4. Optimized structures at the B3LYP/6-31G(d) level for diarylethenes **4d**, **5d**, **6d**, and **7d** (A) and X-ray analysis data for **5d** (B).

appears upon a decrease in the temperature (278 K), while these signals coalesce upon an increase in the temperature to 318 K. The pattern observed in Figure 3 is attributed to the existence of molecule **4a** as a mixture of stable parallel and antiparallel conformers. This effect was observed in numerous NMR spectra at ambient or low temperature for structurally different diarylethenes.[40] Both conformers of **4a** are probably stabilized by an intramolecular CH−N hydrogen bond, which fixes the azole heterocycle, thus preventing its rotation about the C−C single bond. On the other hand, the rotation of the thiophene moiety is also hindered due to the carbonyl group of the ethene bridge, resulting in the existence of two conformers and the dynamic NMR effect. Importantly, in the case of the specially synthesized diarylcyclohexenone **3f** with two thiophene moieties, the hindered rotation of the heterocycle is not observed in the NMR spectrum. The foregoing demonstrates the key role of an intramolecular CH−N hydrogen bond, which fixes the azole cycle in the observed dynamic picture.

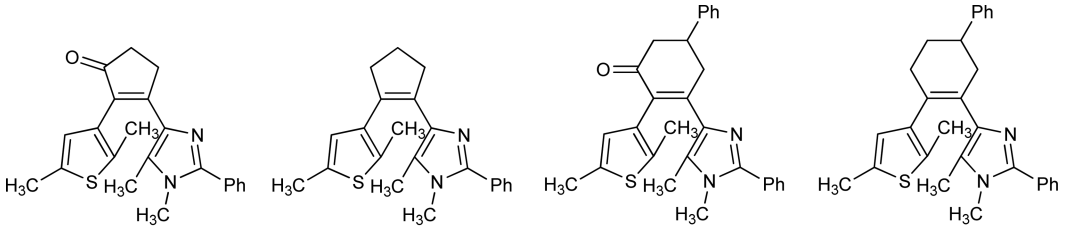
Structure Optimization and X-ray Analysis. To interpret the ^{1}H NMR spectroscopic data, we have optimized the structures of diarylethenes **4a,d**, **5a,d**, **6a,d**, and **7a,d** using the density functional theory (DFT) method at the B3LYP/6-31G(d) level. As shown earlier, this method provides an adequate interpretation of the data for photochromic

According to the calculated results, in all cases the photoactive antiparallel conformation of diarylethenes is the most stable one. The distance between the reactive carbon atoms in this conformation is shorter than 4.2 Å, which is a necessary condition[42] for the photocyclization in crystals (see section II in the SI for details). The ethene bridge in cyclopentene- (**7a,d**) and cyclohexenone-comprising (**4a,d**) diarylethenes adopts an envelope and sofa conformation, respectively, whereas the bridge in cyclopentenones **6a,d** is nearly planar. The cyclohexene ring in molecules **5a,d** has a half-chair conformation, which is a well-known fact.[43] Previously, it was demonstrated that this conformation is favorable also in the photochromic cyclohexene containing thiophene substituents.[30a]

The distance between one of the hydrogen atoms of the bridge and the nitrogen atom of the heterocyclic moiety is shown in Figure 4A. In the imidazole derivatives of diarylethenes bearing the six-membered bridge, this distance (**4d**, 2.4262 Å; **5d**, 2.5430 Å) is substantially shorter than the corresponding distance in the five-membered structures (**6d**, 2.7354 Å; **7d**, 2.7276 Å). Similar results were obtained for the oxazole derivatives (2.4537 Å in **4a** and 2.5513 Å in **5a** versus 2.7800 Å in **6a** and 2.7422 Å in **7a**). It can be seen that the distance between one of the methylene protons of the bridge and the azole nitrogen atom in the structures containing the six-

DOI: 10.1021/acs.joc.6b02665
J. Org. Chem. 2017, 82, 1477−1486

Chart 1



membered bridge is smaller than the sum of the van der Waals radii of the H (1.20 Å) and N (1.55 Å) atoms. This is indicative of the existence of an intramolecular CH···N attractive interaction, i.e., a hydrogen bond. The formation of this bond is possible due to the close arrangement of the atoms as a result of the ring expansion. Therefore, the results of calculations confirm the NMR spectroscopic evidence for the existence of an intramolecular hydrogen bond.

To confirm NMR data and results of the quantum chemical calculations, the structure of diarylethene **5d** has been studied by X-ray analysis (Figure 4B). This diarylethene was obtained as a cocrystal of two conformers with an antiparallel orientation of heterocycle moieties and a half-chair conformation of the ethene bridge. The structure of the major conformer (content is 79.7%) almost completely coincided with the results of the quantum chemical calculation, and the distance between the nitrogen atom and a hydrogen atom of ethene bridge was 2.487 Å. This is an added confirmation of the presence of an intramolecular hydrogen bond. On the other hand, the minor conformer (content is 20.3%) showed an elongated contact for this bond and is 2.801 Å. This indicates the absence of a hydrogen bond. The presence of the minor conformer indicates the nonrigidity of the ethene bridge (cyclohexene ring), which is not typical for diarylethene based on a cyclopentene ring. However, it should be noted that in the NMR spectra of compound **5d** only one conformation has been registered (single set of signals in the ^{13}C NMR spectrum).

Quantum Yields. The stabilization of the molecular geometry of photochromic diarylethenes by noncovalent interactions can result in a considerable increase in the quantum yield of the photocyclization reaction.[10−16] The revealed structural features of some diarylethenes using NMR spectroscopy and confirmed by DFT calculations allow us to expect that the efficiency of the cyclization reaction can be increased in the diarylethene series containing a six-membered bridge. To validate this hypothesis, we have determined the quantum yields for a series of compounds bearing thiophene and imidazole moieties (compounds **4d**, **5d**, **6d**, and **7d**, Chart 1). Photochromic diarylethenes based on the cycloalkenone and cyclopentene derivatives as ethene bridges have nearly equal efficiency in the photocyclization (31−40%). Meanwhile, the quantum yield of diarylethene **5d** based on the cyclohexene derivative as ethene bridge is 0.64, which can be attributed to effective stabilization of the molecular geometry due to a hydrogen bond between the cyclohexene bridge and the imidazole moiety. The relatively low quantum yield of **4d**, despite the presence of intramolecular hydrogen bonds, can be explained by steric hindrance of rotation of the thiophene ring, but this fact requires further investigation and confirmation.

CONCLUSION

So, the structural and spectral properties of the photochromic azole-comprising diarylethenes based on a five- or six-membered ethene bridge have been studied. It was found that an expansion of the ethene bridge in the cycloalkenone series, as opposed to the cycloalkene compounds, leads to a hypsochromic shift of the absorption maxima of the photo-induced form. A detailed study of ^{1}H NMR spectra revealed the effects associated with the existence of intramolecular hydrogen bonds CH···N between the six-membered ethene bridge and the azole substituent, which was confirmed by the geometry optimization of the molecular structures by the DFT method and by X-ray analysis. It was shown that an intramolecular hydrogen bond is favorable for an increase in the photo-cyclization quantum yield. The results of the present study significantly complement and extend the understanding of the effect of the carbocycle size of the bridge on the photochromic properties of diarylethenes.

EXPERIMENTAL SECTION

General Experimental Procedures. NMR spectra were recorded in deuterated solvents on spectrometers working at 300.13, 400.16, and 600.13 MHz for ^{1}H and 75.77, 100.63, and 150.91 MHz for ^{13}C. 2D spectra were set using standard parameters. The mixing time in NOESY was 0.7 s. Both ^{1}H and ^{13}C NMR chemical shifts are referenced relative to the residual solvents signals ($CHCl_3$: δ 7.27 for ^{1}H 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; t, triplet; br, broad), coupling constant in hertz (Hz), integration, and assignment. 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. 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 F_{254} plates.

Photochemical Studies. UV−vis spectra were recorded in 1.0 cm quartz cuvettes. The experimental measurements were performed in the presence of air in solutions of acetonitrile. The quantum yields of the photocyclization (Φ_{AB}) were measured by previously reported techniques (for details, see section III in the SI).[12]

Structure Optimization. DFT calculations were performed at the B3LYP/6-31G(d) level of theory as implemented in the Gaussian 09 program suite.[44]

X-ray Diffraction. Single crystals of **5d** were obtained by the slow evaporation of petroleum ether/ethyl acetate (6:1) solution. Crystals are triclinic, space group $P\bar{1}$, at 120 K; a = 8.6695(16) Å, b = 10.986(2) Å, c = 13.159(3) Å, α = 81.424(4)°, β = 76.719(4)°, γ = 69.087(4)°, V = 1136.3(4) Å^3, Z = 2, d_{calc} = 1.282 g cm^{-3}, μ(Mo Kα) = 1.63 cm^{-1}, F(000) = 468. Intensities of 16 588 reflections were measured using graphite-monochromated Mo Kα radiation (λ =

DOI: 10.1021/acs.joc.6b02665
J. Org. Chem. 2017, 82, 1477−1486

0.710 73 Å, ω-scans), and 5637 independent reflections [R_{int} 0.0463] were used in further refinement. The structure was solved by the direct method and refined by the full-matrix least-squares against F^2 in anisotropic approximation for non-hydrogen atoms; the central ring is disordered over two positions with the occupancies 0.797(4):0.203(4). The positions of hydrogen atoms were calculated, and they were refined in isotropic approximation in riding model. The refinement converged to wR2 = 0.1433 and GOF = 1.074 for all the independent reflections [R1 = 0.0597 was calculated against F for 4507 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using the SHELXTL PLUS 5.0 software.[45] CCDC 1524898 contains the supplementary crystallographic data, which can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis and Characterization of Diarylethenes 3a–c. To a solution of keto ester **1** (2 mmol) in ethanol (10 mL) were added chalkone **2** (2 mmol) and KOH (56 mg, 1 mmol), and the resulting suspension was mixed for 24 h at ambient temperature. After the completion of the reaction (TLC control), the mixture was poured into water (100 mL), extracted with ethyl acetate (3 × 50 mL), washed with brine (100 mL), dried over $MgSO_4$, and evaporated in vacuum. The residue was purified by column chromatography by eluting with petroleum ester/ethyl acetate (2:1 or 4:1).

*Ethyl 4-(2,5-Dimethylthiophen-3-yl)-5-(5-methyl-2-phenyloxazol-4-yl)-3-oxo-1,2,3,6-tetrahydro-[1,1′-biphenyl]-2-carboxylate (**3a**).* Pale red crystals, 63% yield (643 mg); mp 170 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.03–1.15 (m, 3H, CH_3), 1.78 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 2.88–3.06 (m, 1H, $^1/_2CH_2$), 3.46–3.62 (m, 1H, $^1/_2CH_2$), 3.85–4.15 (m, 4H, CH + CH + CH_2), 6.40 (br s, 1H, $H^{thiophene}$), 7.23–7.48 (m, 8H, H^{arom}), 7.92–8.02 (m, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 11.1, 14.0, 14.5, 15.1, 37.9, 43.0, 60.5, 60.9, 126.1 (2C), 127.0, 127.3 (3C), 127.7 (2C), 128.7 (4C), 130.2, 130.8, 134.9, 135.0, 135.1, 141.1, 147.6, 148.9, 159.9, 169.2; MS (EI) m/z (%) = 511 (100) $[M]^+$; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{31}H_{29}NO_4S$ 512.1890, found 512.1880.

*Ethyl 5-(2,5-Dimethylthiophen-3-yl)-4-(5-methyl-2-phenyloxazol-4-yl)-3-oxo-1,2,3,6-tetrahydro-[1,1′-biphenyl]-2-carboxylate (**3b**).* Purple crystals, 43% yield (440 mg); mp 167–169 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.08 (t, J = 7.0 Hz, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 2.91–3.06 (m, 2H, CH_2), 3.85–4.14 (m, 4H, CH + CH + CH_2), 6.49 (s, 1H, $H^{thiophene}$), 7.21–7.48 (m, 8H, H^{arom}), 7.85–7.97 (m, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 11.0, 14.0, 14.3, 15.0, 40.6, 43.2, 60.2, 60.9, 125.2, 126.1 (2C), 127.2 (2C), 127.4, 127.7, 128.5 (2C), 128.6, 128.8 (2C), 129.7, 130.5, 134.1, 136.1, 136.6, 140.9, 147.0, 156.2, 159.2, 169.0, 192.2; MS (EI) m/z (%) = 511 (45) $[M]^+$ 496 (40) $[M - CH_3]^+$, 406 (100); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{31}H_{29}NO_4S$ 512.1890, found 512.1906.

*Ethyl 4,5-Bis(5-methyl-2-phenyloxazol-4-yl)-3-oxo-1,2,3,6-tetrahydro-[1,1′-biphenyl]-2-carboxylate (**3c**).* Red crystals, 32% yield (357 mg); mp 192–194 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.07 (t, J = 7.0 Hz, 3H, CH_3), 1.96 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 2.95 (dd, J = 19.2, 10.6 Hz, 1H, $^1/_2CH_2$), 3.62 (dd, J = 19.2, 3.4 Hz, 1H, $^1/_2CH_2$), 3.88–4.13 (m, 4H, CH + CH + CH_2), 7.29–7.50 (m, 11H, H^{arom}), 7.90–8.02 (m, 4H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 11.2, 11.7, 13.9, 38.3, 42.9, 60.3, 60.9, 126.1 (4C), 126.9, 127.3 (2C), 127.4, 127.5, 127.7, 128.6 (2C), 128.7 (4C), 129.9, 130.3, 130.6, 134.8, 140.9, 147.1, 147.3, 150.9, 159.7, 160.2, 168.9, 192.4; MS (EI) m/z (%) = 558 (100) $[M]^+$; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{35}H_{30}N_2O_5$ 559.2227, found 559.2222.

*Ethyl 5-(1,5-Dimethyl-2-phenyl-1H-imidazol-4-yl)-4-(5-methyl-2-phenyloxazol-4-yl)-3-oxo-1,2,3,6-tetrahydro-[1,1′-biphenyl]-2-carboxylate (**3e**).* Purple crystals, 37% yield (422 mg); mp 150–151 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.06 (t, J = 7.0 Hz, 3H, CH_3), 1.83 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 2.89 (dd, J = 19.2, 11.1 Hz, 1H, $^1/_2CH_2$), 3.45 (s, 3H, NCH_3), 3.78 (dd, J = 19.2, 4.1 Hz, 1H, $^1/_2CH_2$), 3.87–4.10 (m, 4H, CH + CH + CH_2), 7.20–7.56 (m, 13H, H^{arom}), 7.92–8.04 (m, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 10.7, 10.9, 14.0, 32.0, 39.5, 42.9, 60.4, 60.8, 126.1 (2C), 127.2, 127.4 (2C), 127.8, 128.5, 128.6 (4C), 128.7 (4C), 129.0, 129.2, 129.7, 130.4, 131.8, 135.8, 141.4, 146.8, 147.9, 154.5, 159.4, 169.3, 193.0; MS (EI) m/z (%) = 571 (100) $[M]^+$; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{36}H_{33}N_3O_4$ 572.2544, found 572.2547.

Synthesis and Characterization of Diarylethene 3d. To a solution of keto ester **1a** (480 mg, 2 mmol) in dry ethanol (7 mL) was added metallic sodium (46 mg, 2 mmol). After completion of hydrogen evolution, chalkone (600 mg, 2 mmol) was added, and the resulting suspension was refluxed for 2 h. After the completion of the reaction (TLC control), the mixture was poured into water (100 mL), extracted with ethyl acetate (3 × 50 mL), washed with brine (100 mL), dried over $MgSO_4$, and evaporated in vacuum. The residue was purified by column chromatography by eluting with petroleum ester/ethyl acetate (1:1).

*Ethyl 5-(1,5-Dimethyl-2-phenyl-1H-imidazol-4-yl)-4-(2,5-dimethylthiophen-3-yl)-3-oxo-1,2,3,6-tetrahydro-[1,1′-biphenyl]-2-carboxylate (**3d**).* Yellow powder, 60% yield (630 mg); mp 150–151 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.06 (t, J = 7.0 Hz, 3H, CH_3), 1.64 (s, 3H, CH_3), 1.95 (br s, 3H, CH_3), 2.36 (br s, 3H, CH_3), 2.84–3.00 (m, 1H, $^1/_2CH_2$), 3.46 (s, 3H, NCH_3), 3.55–4.16 (m, 5H, CH + CH + CH_2 + $^1/_2CH_2$), 6.46 (br s, 1H, $H^{thiophene}$), 7.17–7.63 (m, 10H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 10.1, 14.0, 14.4, 15.2, 31.9, 40.0, 45.3, 60.6, 60.7, 126.7, 126.9, 127.1, 127.4, 128.6 (4C), 128.8 (4C), 130.6, 131.7, 132.2, 134.1, 136.1, 136.5, 141.5, 143.6, 147.5, 152.7, 169.6; MS (EI) m/z (%) = 524 (10) $[M]^+$, 509 (20) $[M - CH_3]^+$; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{32}H_{32}N_2O_3S$ 525.2206, found 525.2190.

Synthesis and Characterization of Diarylethene 3f. To a solution of keto ester **1a** (240 mg, 1 mmol) in ethanol (5 mL) were added chalkone (242 mg, 1 mmol) and KOH (28 mg, 0.5 mmol), and the resulting suspension was mixed for 24 h at ambient temperature. The resulting precipitate was filtered, washed with water and ethanol, and dried on the air.

*Ethyl 4,5-Bis(2,5-dimethylthiophen-3-yl)-3-oxo-1,2,3,6-tetrahydro-[1,1′-biphenyl]-2-carboxylate (**3f**).* Yellow amorphous powder, 26% yield (120 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.11 (t, J = 7.1 Hz, 3H, CH_3), 1.94 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 2.33 (s, 6H, CH_3), 2.94–3.02 (m, 2H, CH_2), 3.84–3.96 (m, 2H, CH_2), 4.02–4.12 (m, 2H, CH_2), 6.28 (s, 1H, $H^{thiophene}$), 6.38 (s, 1H, $H^{thiophene}$), 7.24–7.38 (m, 5H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 14.0, 14.3, 14.4, 15.0, 15.1, 40.2, 43.4, 60.4, 61.0, 125.2, 127.2 (2C), 127.4, 127.7, 128.8 (2C), 130.8, 132.3, 134.3, 134.6, 134.8, 136.1, 136.5, 141.1, 153.6, 169.3, 192.8; MS (EI) m/z (%) = 464 (100) $[M]^+$; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{27}H_{28}O_3S_2$ 465.1553, found 465.1561.

Synthesis and Characterization of Diarylethenes 4a–e. To a solution of diarylethene **3** (0.4 mmol) in ethanol (2 mL) was added a solution of KOH (112 mg, 2.0 mmol) in water (2 mL), and the resulting mixture was refluxed until completion of the reaction (TLC control). The resulting solution was poured into water (50 mL), extracted with ethyl acetate (3 × 30 mL), washed with brine (50 mL), dried over $MgSO_4$, and evaporated in vacuum. The residue was purified by column chromatography by eluting with petroleum ester/ethyl acetate (2:1 or 4:1).

*4-(2,5-Dimethylthiophen-3-yl)-5-(5-methyl-2-phenyloxazol-4-yl)-1,6-dihydro-[1,1′-biphenyl]-3(2H)-one (**4a**).* Purple crystals, 61% yield (107 mg); mp 188–189 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.78 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.83–3.00 (m, 3H, CH_2 + $^1/_2CH_2$), 3.45–3.65 (m, 2H, CH + $^1/_2CH_2$), 6.39 (br s, 1H, $H^{thiophene}$), 7.24–7.49 (m, 8H, H^{arom}), 7.92–8.02 (m, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.0, 14.4, 15.2, 38.4, 40.0, 45.2, 126.0 (2C), 126.8 (2C), 126.9, 127.1, 127.8, 128.7 (4C), 130.2, 131.3, 134.5, 135.0, 135.3, 143.2, 145.9, 147.2, 148.9, 159.8, 206.8; MS (EI) m/z (%) = 439 (100) $[M]^+$, 424 (60) $[M - CH_3]^+$. HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{28}H_{25}NO_2S$ 440.1679, found 440.1671.

*5-(2,5-Dimethylthiophen-3-yl)-4-(5-methyl-2-phenyloxazol-4-yl)-1,6-dihydro-[1,1′-biphenyl]-3(2H)-one (**4b**).* Purple crystals, 68% yield (119 mg); mp 115–117 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.98 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 2.86–3.06 (m, 4H, CH_2 + CH_2), 3.54–3.65 (m, 1H, CH), 6.46 (s, 1H, $H^{thiophene}$), 7.23–7.50 (m, 8H, H^{arom}), 7.89–7.99 (m, 2H, H^{arom}); ^{13}C NMR (75

DOI: 10.1021/acs.joc.6b02665
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MHz, $CDCl_3$) δ = 10.9, 14.3, 15.0, 40.2, 40.7, 44.9, 125.3, 126.1 (2C), 126.7 (2C), 127.0, 127.8, 128.5 (2C), 128.8 (2C), 129.5, 129.7, 131.0, 133.7, 136.4, 136.7, 142.9, 146.7, 156.4, 159.3, 197.0; MS (EI) m/z (%) = 439 (10) $[M]^+$, 424 (15) $[M\text{-}CH_3]^+$, 334 (100); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{28}H_{25}NO_2S$ 440.1679, found 440.1667.

*4,5-Bis(5-methyl-2-phenyloxazol-4-yl)-1,6-dihydro-[1,1′-biphenyl]-3(2H)-one (**4c**).* Red crystals, 47% yield (91 mg); mp 173−175 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.97 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.84−3.05 (m, 3H, CH_2 + $^1/_2CH_2$), 3.44−3.73 (m, 2H, CH + $^1/_2CH_2$), 7.19−7.59 (m, 11H, H^{arom}), 7.86−8.08 (m, 4H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 11.0, 11.6, 38.5, 39.9, 45.0, 126.1 (2C), 126.2 (2C), 126.7, 126.8 (2C), 127.0, 127.3, 127.4, 128.5, 128.6 (2C), 128.7 (2C), 128.8 (2C), 128.9, 129.9, 130.3, 135.1, 143.0, 146.8, 151.2, 159.7, 160.1, 197.1; MS (EI) m/z (%) = 486 (100) $[M]^+$, 471 (15) $[M - CH_3]^+$; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{32}H_{26}N_2O_3$ 487.2016, found 487.2010.

*5-(1,5-Dimethyl-2-phenyl-1H-imidazol-4-yl)-4-(2,5-dimethylthiophen-3-yl)-1,6-dihydro-[1,1′-biphenyl]-3(2H)-one (**4d**).* Yellow crystals, 39% yield (71 mg); mp 169−172 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.64 (s, 3H, CH_3), 1.95 (br s, 3H, CH_3), 2.37 (br s, 3H, CH_3), 2.82−2.97 (m, 3H, CH_2 + $^1/_2CH_2$), 3.46 (s, 1H, NCH_3), 3.47−3.77 (m, 2H, CH + $^1/_2CH_2$), 6.48 (br s, 1H, $H^{thiophene}$), 7.23−7.59 (m, 10H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 10.1, 14.5, 15.2, 31.9, 39.6, 40.0, 45.3, 126.7, 126.9 (2C), 128.2, 128.4, 128.6 (4C), 128.8 (3C), 130.6, 132.2, 134.0, 134.2, 136.5, 143.6, 147.5, 152.8, 194.5; MS (EI) m/z (%) = 452 (55) $[M]^+$, 437 (100) $[M - CH_3]^+$. HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{29}H_{28}N_2OS$ 453.1995, found 453.2011.

*5-(1,5-Dimethyl-2-phenyl-1H-imidazol-4-yl)-4-(5-methyl-2-phenyloxazol-4-yl)-1,6-dihydro-[1,1′-biphenyl]-3(2H)-one (**4e**).* Purple crystals, 51% yield (102 mg); mp 167−170 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.84 (s, 3H, CH_3), 1.98 (s, 3H, CH_3), 2.84−3.04 (m, 3H, CH_2 + $^1/_2CH_2$), 3.46 (s, 1H, NCH_3), 3.47−3.78 (m, 2H, CH + $^1/_2CH_2$), 7.23−7.62 (m, 13H, H^{arom}), 7.95−8.11 (m, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 10.6, 10.8, 31.9, 39.7, 39.9, 45.1, 126.1 (2C), 126.8, 126.9 (2C), 127.8, 128.5 (2C), 128.6 (2C), 128.7 (2C), 128.8 (2C), 128.9, 129.7, 132.1, 136.1, 143.4, 146.5, 147.7, 159.4, 197.8; MS (EI) m/z (%) = 499 (100) $[M]^+$; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{33}H_{29}N_3O_2$ 500.2333, found 500.2320.

Synthesis and Characterization of Diarylethenes 5. To a solution of diarylethene **4** (0.6 mmol) in absolute (abs) dichloromethane (3 mL) under inert atmosphere (argon) were added solutions of triethylsilane (140 mg, 1.2 mmol) in abs dichloromethane (3 mL) and trifluoromethanesulfonic acid (180 mg, 1.2 mmol) in abs dichloromethane (3 mL) simultaneously. The resulting emulsion was mixed at ambient temperature (diarylethene **4a**) or refluxed (diarylethene **4d**) until complete conversion of **4** (TLC control). The resulting solution was poured into a 5% water solution of $NaHCO_3$ (100 mL) and extracted with dichloromethane (2 × 30 mL). The combined organic phases were washed with water (100 mL), dried over $MgSO_4$, and evaporated in vacuum. The residue was purified by flash chromatography with petroleum ether (150 mL, for removing of silicon-containing impurities) and petroleum ether/ethyl acetate (6:1).

*4-(4-(2,5-Dimethylthiophen-3-yl)-1,2,5,6-tetrahydro-[1,1′-biphenyl]-3-yl)-5-methyl-2-phenyloxazole (**5a**).* Yellow powder, 51% yield (130 mg); mp 137−139 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.81 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 1.97−2.15 (m, 2H, CH_2), 2.36 (s, 3H, CH_3), 2.47−2.60 (m, 3H, CH_2 + $^1/_2CH_2$), 2.94−3.16 (m, 2H, CH + $^1/_2CH_2$), 6.44 (s, 1H, $H^{thiophene}$), 7.17−7.52 (m, 8H, H^{arom}), 7.91−8.03 (m, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 10.7, 14.1, 15.2, 30.1, 32.4, 37.6, 40.3, 125.9 (2C), 126.1, 126.5, 126.9, 127.0 (2C), 127.8, 128.4 (2C), 128.6 (2C), 129.6, 131.3, 132.6, 135.1, 136.9, 139.1, 144.4, 146.6, 159.0; MS (EI) m/z (%) = 425 (100) $[M]^+$; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{28}H_{27}NOS$ 426.1886, found 426.1873.

*4-(4-(2,5-Dimethylthiophen-3-yl)-1,2,5,6-tetrahydro-[1,1′-biphenyl]-3-yl)-1,5-dimethyl-2-phenyl-1H-imidazole (**5d**).* White powder, 58% yield (152 mg); mp 127−128 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.69 (s, 3H, CH_3), 1.88−2.16 (m, 2H, CH_2), 1.99 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.43−2.62 (m, 3H, CH_2 + $^1/_2CH_2$), 2.98−3.19 (m, 2H, CH + $^1/_2CH_2$), 3.43 (s, 3H, CH_3), 6.48 (s, 1H, $H^{thiophene}$), 7.15−7.58 (m, 10H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 9.7, 14.1, 15.1, 30.2, 31.7, 32.4, 38.6, 40.6, 125.0, 125.8, 127.0, 127.1 (2C), 128.1, 128.2 (2C), 128.4 (2C), 128.8 (2C), 129.8, 130.3, 131.2, 131.4, 134.1, 138.5, 139.8, 146.0, 147.0; MS (EI) m/z (%) = 438 (70) $[M]^+$, 423 (100) $[M - CH_3]^+$; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{29}H_{30}N_2S$ 439.2202, found 439.2186.

*3-(1,5-Dimethyl-2-phenyl-1H-imidazol-4-yl)-2-(5-methyl-2-phenyloxazol-4-yl)cyclopent-2-enone (**6e**).* Compound **6e** was prepared according to a previously reported method.[12] Yellow powder, 26% yield; mp 122−125 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.89 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.61−2.72 (m, 2H, CH_2), 3.20−3.30 (m, 2H, CH_2), 3.53 (s, 3H, NCH_3), 7.36−7.48 (m, 6H, H^{arom}), 7.53−7.63 (m, 2H, H^{arom}), 7.96−8.05 (m, 2H, H^{arom}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 10.8, 11.3, 30.3, 32.0, 34.7, 126.2 (2C), 127.6, 128.6 (4C), 128.7, 129.0 (2C), 129.1, 129.5, 129.9, 130.2, 130.6, 133.6, 147.3, 148.4, 160.0, 167.2, 207.4; MS (EI) m/z (%) = 409 (90, $[M]^+$), 304 (100); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{26}H_{23}N_3O_2$ 410.1863, found 410.1851.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02665.

Copies of ^{1}H and ^{13}C NMR and HRMS spectra for all new compounds, 2D NMR (HSQC, NOESY) characterization of target compounds, and corresponding *Z*-matrix of the optimized structures (PDF)

Crystallographic data for **5d** in CIF format (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support by Russian Foundation for Basic Research (RFBR Grant 16-33-60013) is gratefully acknowledged. Authors are grateful to E. Mel'nikova for the synthesis of some starting compounds.

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DOI: 10.1021/acs.joc.6b02665
J. Org. Chem. 2017, 82, 1477−1486