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Synthesis and spectral properties of photochromic cyclopentenone diarylethenes with an additional π system in the ethene bridge

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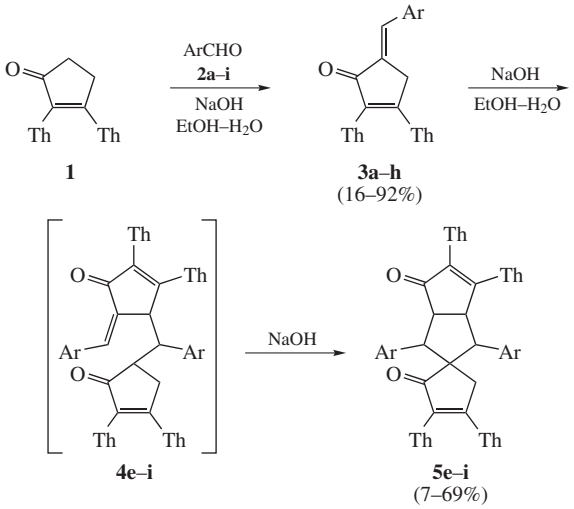
Photochromic diarylethenes with an additional π system in the ethene bridge were synthesized by the condensation of 2,3-bis(2,5-dimethyl-3-thienyl)cyclopent-2-en-1-one with aromatic aldehydes. Absorption bands maxima of the initial and cyclic forms of the substances were determined and their thermal stability was studied.

Photochromic diarylethenes are of interest for the development of molecular switches, optical memory systems, biosensors, and other photosensitive materials[1–6] because their photoinduced cyclic isomers are thermally stable.[7,8]

In the design of new photosensitive high-technology materials, an important issue is to evaluate structure–property relationships, which in turn requires the development of convenient methods for the synthesis and chemical modification of these compounds. Recently, we proposed a new type of photochromic diarylethenes, 2,3-diarylcyclopent-2-en-1-ones, which possess a significant potential for the chemical modification of a bridge fragment and obtained a wide range of compounds, whose spectroscopic and kinetic characteristics were studied.[9–12]

The aim of this work is to synthesize diarylcyclopentenones with an additional conjugation chain in the ethene bridge, to study their spectral properties, and to estimate correlations between structure and property of the series of compounds obtained. The introduction of an additional π system or the elongation of the conjugation chain of the hexatriene system, which is responsible for photochromic switching, can considerably change the spectral properties, in particular, cause a bathochromic shift of the absorption band maxima of these isomers.[13–19]



Th = 2,5-dimethylthiophen-3-yl

a Ar = Ph
b Ar = 2-HOC_6H_4
c Ar = 3-HOC_6H_4
d Ar = 2,4-$(MeO)_2C_6H_3$
e Ar = 3,4,5-$(MeO)_3C_6H_2$
f Ar = 4-$F_3CC_6H_4$
g Ar = 2-pyridyl
h Ar = 3-pyridyl
i Ar = 4-FC_6H_4

Scheme 1 Condensation of cyclopentenone **1** with aromatic aldehydes **2a–i**.

The condensation of compound **1** with aromatic aldehydes **2a–i** (method A, see Online Supplementary Materials) afforded a wide range of new diarylethenes **3a–h**† with an additional conjugation system in the bridge (Scheme 1).

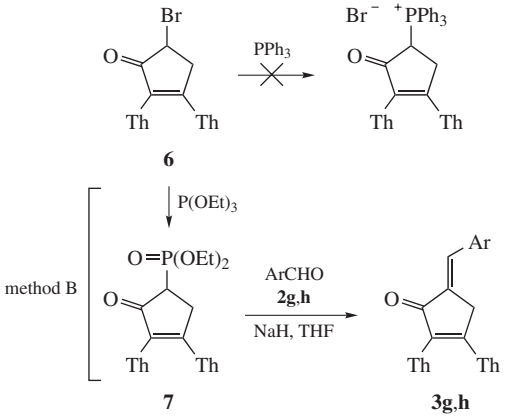
However, in the case of aromatic aldehydes **2e–i**, spiro compounds **5e–i** were isolated along with or in place of the condensation product (see Table S1 in Online Supplementary Materials). The formation of spiro compounds can be explained by the dimerization of molecules **3** as a result of two consecutive Michael-type addition reactions (see Scheme 1). The structures of diarylethenes **5e–i** were confirmed by NMR spectroscopy.[20–25]

An alternative procedure (method B) for the synthesis of compounds **3** (Scheme 2) based on the Horner–Wadsworth–Emmons reaction[26,27] was proposed to exclude the formation of side spiro compounds and to obtain diarylethenes **3** with a higher efficiency (we failed to obtain the target products by the Wittig reaction[28] with PPh_3; this was likely due to its insufficient nucleophilicity). Bromo derivative **6** was used as a starting compound,[10] and the target diarylethenes **3g**,**h** were prepared through intermediate phosphonates **7** with no impurities of spiro compounds **5**.

† *2,3-Bis(2,5-dimethylthiophen-3-yl)-5-(phenylmethylidene)cyclopent-2-en-1-one* **3a**. Yield 0.04 g (32%), brown powder, mp 113–115 °C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.93 (s, 3H, Me), 1.97 (s, 3H, Me), 2.41 (s, 3H, Me), 2.43 (s, 3H, Me), 3.85 (s, 2H, $CH_2^{cyclopent}$), 6.59 (s, 1H, H^{thioph}), 6.68 (s, 1H, H^{thioph}), 7.36–7.48 (m, 3H, H^{Ph}), 7.53 (s, 1H, CHO), 7.64 (d, 2H, H^{Ph}, J 7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.34, 14.73, 15.21, 15.31, 37.25 ($CH_2^{cyclopent}$), 125.06, 126.73, 128.73, 129.37, 130.46, 131.37, 131.59, 133.23, 133.50, 135.34, 135.70, 135.84, 136.96, 137.24, 137.63, 158.86, 195.47 (C=O). MS, *m*/*z* (%): 390 (100, $[M]^+$), 375 (52, $[M-Me]^+$). HRMS, *m*/*z*: 413.1003 (calc. for $C_{24}H_{22}OS_2$ [M + Na]$^+$: 413.1004).

2,3-Bis(2,5-dimethylthiophen-3-yl)-5-[(3,4,5-trimethoxyphenyl) methylidene]cyclopent-2-en-1-one **3e**. Yield 0.03 g (22%), green powder, mp 127–128 °C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.95 (s, 6H, 2Me), 2.40 (s, 3H, Me), 2.42 (s, 3H, Me), 3.85 (s, 2H, $CH_2^{cyclopent}$), 3.92 (s, 9H, 3OMe), 6.56 (s, 1H, H^{thioph}), 6.63 (s, 1H, H^{thioph}), 6.87 (s, 2H, H^{Ph}), 7.43 (s, 1H, CHO). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.31, 14.75, 15.23, 15.32, 37.00 ($CH_2^{cyclopent}$), 56.39 (2OMe), 61.06 (OMe), 108.07, 125.02, 126.70, 129.38, 131.20, 131.51, 132.39, 133.51, 135.34, 135.89, 137.02, 137.43, 137.53, 139.75, 153.50, 158.38, 195.23 (C=O). IR (KBr, ν/cm^{-1}): 2938 (C–H^{arom}), 2913 (Me, C–H^{arom}), 2854 (Me, C–H^{arom}), 1693 (C=O), 1644, 1579, 1504, 1451, 1422, 1338, 1291, 1260 (C^{arom}–O), 1240, 1129, 1009, 822 (C–H^{Ph}), 754. MS, *m*/*z* (%): 480 (100, $[M]^+$), 465 (41, $[M-Me]^+$). HRMS, *m*/*z*: 481.1509 (calc. for $C_{27}H_{28}O_4S_2$ [M+H]$^+$: 481.1502).

For characteristics of compounds **3b–d**,**f–h**, see Online Supplementary Materials.



Scheme 2

We studied some spectral and kinetic characteristics of the compounds obtained. Figure 1 shows a typical spectrum of photoswitching characteristic of this class of compounds.[1,2] Table 1 indicates that the introduction of an additional polyene system into the ethene bridge considerably affects the spectral properties of photochromic 2,3-diarylcyclopent-2-en-1-ones.

The introduction of an additional conjugation chain into the bridge leads to a significant bathochromic shift in the λ_{max} of open form **A** in the case of donor substituents in the benzene ring (*cf.* 313 nm for **1** and 330–366 nm for **3b–e**, entries 1 and 3–6 in Table 1), whereas it has almost no effect in case of unsubstituted benzene (entries 1 and 2).

Some compounds with acceptor substituents (entries 8 and 12) have two absorption band maxima; the main maximum is hypsochromically shifted and the other as a shoulder is shifted to the long-wave region. As for the absorption spectra of isomers **A** of spiro compounds **5e–i**, their λ_{max} lie in the range 318–325 nm (entries 7, 9, 11, 13 and 14); that is, as compared with the values for corresponding alkenes **3e–i**, they are weakly shifted from the value for **1** (309 nm, entry 1). These results (the absence of a strong bathochromic shift) are reasonable, and they can be explained by the fact that, unlike **3e–i**, there is no additional π system in the ethene bridge of spiro compounds **5e–i**, which is responsible for the shifts of absorption bands of isomers **A**.

The clearest correlations were found between the structures of the synthesized compounds and the λ_{max} of their photoinduced isomers **B**. The elongation of the conjugation chain in the ethene bridge of cyclopentenone **1** by the introduction of an arylmethylidene substituent into the 5-position of the bridge (compounds **3a–e**) leads to a bathochromic shift of the λ_{max} of coloured isomer **B** by ~36–44 nm (entries 1 and 2 in Table 1). In the case of electron-acceptor substituents in the benzene ring, it results in an even stronger bathochromic shift: λ_{max} reaches 608 nm for a *para*-trifluoromethylphenyl substituent (compound **3f**).

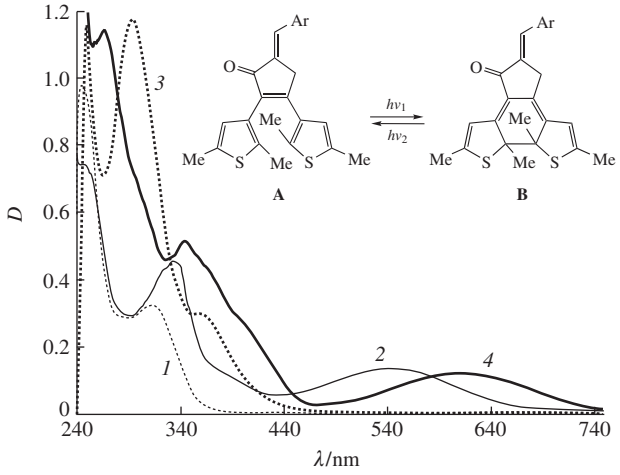


Figure 1 Absorption spectra of compounds (*1*,*2*) **1** and (*3*,*4*) **3f** (C = = 2.0×10^{-5} mol dm^{-3} in MeCN) (*1*,*3*) before and (*2*,*4*) after UV irradiation (λ = 365 nm, t = 70 s) at 293 K.

Table 1 Spectral characteristics of initial and photoinduced isomers of 2,3-diarylcyclopent-2-en-1-ones obtained in acetonitrile solutions (C = = 2×10^{-5} mol dm^{-3}) at 293 K in the presence of air.

Entry	Compound	λ_A^a/nm	ε^a/dm^3 mol^{-1} cm^{-1}	λ_B^b/nm	$\tau_{1/2\ therm}^{B\to A}$[c]/h
1	**1**	309	6.43×10^3	547	939
2	**3a**	313	1.61×10^4	585	98
3	**3b**	348	1.42×10^4	587	1094
4	**3c**	330	2.15×10^4	589	605
5	**3d**	366	2.52×10^4	583	1008
6	**3e**	339	3.51×10^4	591	41
7	**5e**	320	2.25×10^4	563	287
8	**3f**	294	4.17×10^4	608	8190
		355	1.39×10^4		
9	**5f**	238	7.01×10^4	567	313
		325	9.48×10^3		
10	**3g**	310	4.44×10^4	597	148
11	**5g**	318	2.69×10^4	565	238
12	**3h**	293	1.05×10^5	603	220
		345	9.04×10^3		
13	**5h**	245	4.25×10^4	565	4260
		318	2.53×10^4		

[a]Absorption maxima and extinction coefficients of open-ring isomers of diarylcyclopentenones. [b]Absorption maxima of closed-ring isomers of diarylcyclopentenones. [c]Half-life times of the ring-closed isomers in the dark.

We have also studied the reaction kinetics of thermal decolouration of the photoinduced isomers **B** in the acetonitrile solutions in the dark at 293 K. Based on these data, we have found that thermal decolouration is a first-order reaction (a linear relationship between the logarithm of the optical density of the photoinduced isomers and the exposure time in the dark was observed), and calculated the times ($\tau_{1/2\ therm}^{B\to A}$) in which the concentrations of isomers **B** of diarylethenes decreased by 50% and which, in essence, are a measure of the thermal stability of these compounds. We have found correlations between the structures of diarylethenes and their thermal stability. The introduction of a 5-positioned phenylmethylidene fragment (compound **3a**) leads to a decrease in the thermal stability of initial diarylethene **1** (entries 1 and 2 in Table 1) by a factor of almost 10. The introduction of a pyridine substituent (compounds **3g** and **3h**) into the bridge exerts the same effect: the thermal stability of coloured isomers **B** decreases (entries 1, 10 and 12). The introduction of the acceptor trifluoromethyl group into the benzene ring is the most promising modification: the value of $\tau_{1/2\ therm}^{B\to A}$ for diarylethene **3f** is 8190 h (~1 year). The thermal stability of compounds **3b–e** with donor substituents in the benzene ring is of the same order of magnitude or lower than that in starting cyclopentenone **1** (939 h). The cyclic isomers of compounds **5e–h** are less thermally stable than the closed form of cyclopentenone **1**.

Thus, we have accessed previously unknown photochromic diarylethenes of the cyclopentenone series with an additional π system in the ethene bridge, studied their spectral properties and found structure–property correlations.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2013.09.010.

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