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Photo- and PH-switchable fluorescent diarylethenes based on 2,3-diarylcyclopent-2-en-1-ones with dialkylamino groups

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ABSTRACT

New dialkylamino groups-comprising diarylethenes of 2,3-diarylcyclopent-2-en-1-one (DCP) series have been synthesized and its photochromic, fluorescent as well as acidochromic features have been investigated. It was shown that photochromic properties of the substances depend strong on their structures; the non-symmetry of the photochromic molecule is a powerful tool to properly control and tune the parameters of diarylethenes. It has been found that the most promising of DCPs synthesized are those containing dialkylamino groups in ethene “bridge” (rather than in aryl moieties) because they possess photo- and pH-switchable emission along with thermal stability. It has been established that the introduction at the second position of the cyclopentenone ring the benzene residue leads to the disappearance of the photochromic properties.

1. Introduction

Design and synthesis of functional organic and hybrid materials has a high priority in the development of new technologies and smart devices [1–3]. Among them photochromic materials have been the focus of much attention because of their potential technological applications in display, high-density memory devices and other high technology fields [4–6]. One of promising classes of photochromic organic dyes are diarylethenes due to excellent thermal stability of its ring-open and ring-closed isomers, high fatigue resistance, rapid response, and photochromism in crystals [7–10].

The possible applications of diarylethenes are connected with design of photonic devices (optical memories and molecular photoswitches) [5,7], chemosensors [11–14], write-by-light/erase-by-heat recording systems [15,16], cell markers for biochemistry and medicine [17], smart devices and materials, *etc* [18,19]. To gain compounds with properties appropriate for definite purposes it is necessary first of all to study the correlations between chemical structures of compounds and their spectral properties, which, in turn, require the synthesis and modification of the structures.

One of interesting modifications of diarylethenes structures seems to be introduction into the molecules of electron donating dialkylamino groups including those forming merocyanine systems (conjugation between donating and withdrawing atoms – push-pull-system). To the best of authors' knowledge, a few of similar substances and systems have been synthesized as multi-chromophoric fluorescent switches [20–23] (including pH-sensitive ones [24–27]) and systems switching between P- and T-types [26]. In most cases dialkylamino-substituents, merocyanine dye [20] or spiropyran moieties [21] were attached to aryl groups (covalently or by hydrogen bonds [13]); there is also the only example of diarylethene with dimethylamino group in thiazole ethene “bridge” [25].

To extend the number of known diarylethenes with dialkylamino-substituents (essentially in ethene “bridge”, which actually has not been described) and to study thoroughly their properties and “structure-property” relationships it was proposed to synthesize the compounds based on photochromic 2,3-diarylcyclopent-2-en-1-ones (DCPs). DCPs have been reported earlier [28,29] to be promising class of photochromic diarylethenes with easily modifiable ethene “bridge” [30–34].

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Here, we have performed the design of three types of photoswitchable compounds with dialkylamino-groups. It was prepared new photochromic and fluorescent substances **4** and **6** (Scheme 1) comprising various electron donating dialkylamino groups both in aryl moieties (compounds **4**) and in cyclopentenone "bridge" (compounds **6**).

It is important to note that the introduction in diarylethene molecule of an additional conjugated π-system along with hexatriene is an effective way to design high-efficiency multifunctional photosensitive substances (materials). DCPs **4a**–**d** and **6a**–**e** include merocyanine system (conjugation between donating nitrogen atom and withdrawing oxygen atom) along with hexatriene system responsible to photochromic reaction. While in compounds **6a**–**e** merocyanine and hexatriene systems are separated from each other, in diarylethenes **4a**–**d** two systems intersect, whereas in DCPs **4e**,**f** merocyanine system is absent at all. The differences are certain to influence on photochromic and fluorescent characteristics of diarylethenes; the properties of dialkylamino groups-containing DCPs as well as their switching parameters have been investigated and are discussed below.

2. Experimental

2.1. Materials and methods

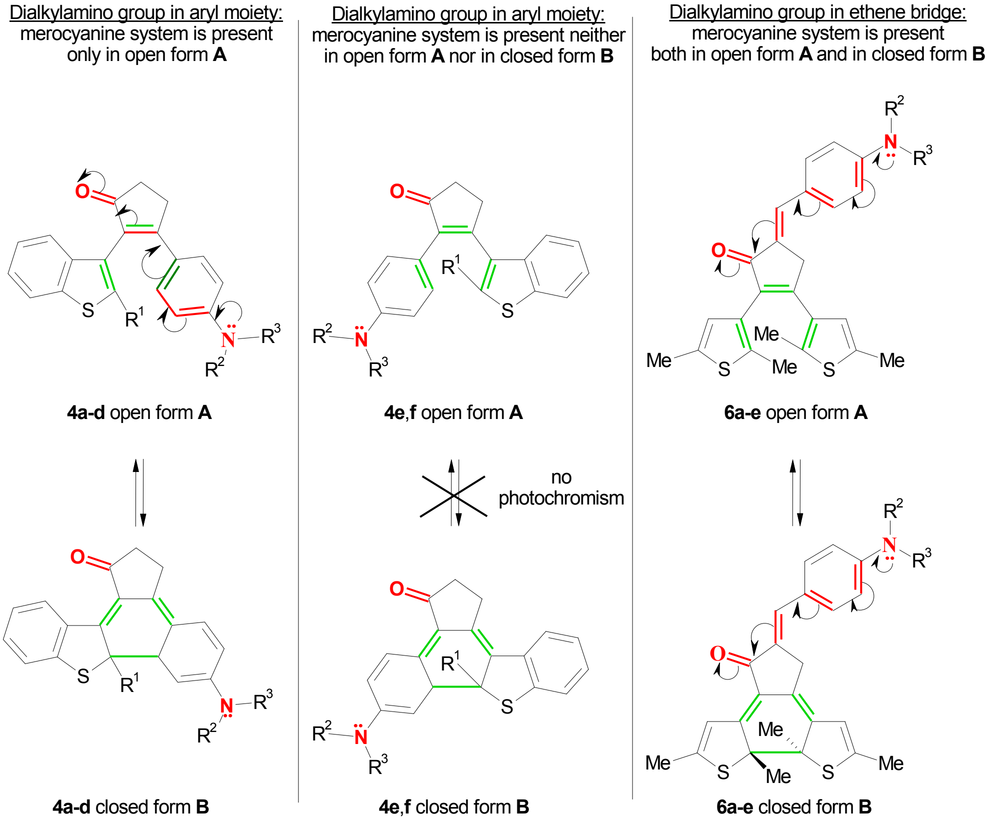
^{1}H and ^{13}C NMR spectra were recorded in deuterated solvents on a Bruker AM-300 spectrometer working at 300 MHz for ^{1}H, 75 MHz for ^{13}C. Mass spectra were obtained on a Kratos mass spectrometer (70 eV) with direct sample injection into the ion source. Melting points were measured on a Boetius hot stage and were not corrected. IR spectra were obtained on a Specord M80 or M82 spectrometer in KBr pellets. High resolution mass spectra were obtained from a TOF mass Bruker maXis spectrometer with an ESI source. Microanalyses were obtained using a PerkinElmer 2400 Series II CHNS/O Elemental Analyzer.

Electronic absorption spectra were recorded on a LOMO SF-56 spectrophotometer. Fluorescence spectra were measured using a Fluorat®-02-Panorama spectrofluorometer. The experiments were performed in acetonitrile solutions ($C = 2 \cdot 10^{-5}$ mol L^{-1} for absorption spectra and $C = 2 \cdot 10^{-6}$ mol L^{-1} for emission ones) at 293 K in the air presence. Photocoloration was carried out using 6W Vilber Lourmat (France) UV-lamp model VL-6.LC (365 nm light); the emission was induced at maxima of excitation spectra. Quantum yields of ring-closure ($\varphi_{A\rightarrow B}$) and ring-opening ($\varphi_{B\rightarrow A}$) processes were calculated by previously reported technique [28,35]. The fluorescence quantum yields were determined by using as references the solutions of 4-dimethylamino-4′-nitrostilbene in benzene ($\varphi_f = 0.53$) [36] (for compounds **6b**,**e**), quinine in 0.1 N sulfuric acid ($\varphi_f = 0.55$) [37] (for compounds **4b**,**c**,**g**), naphthalene in methylcyclohexane ($\varphi_f = 0.23$) [38] (for compounds **4e**,**f**), coumarin-1 in ethanol ($\varphi_f = 0.73$) [39] (for compounds **4a**,**d**) or coumarin-30 in acetonitrile ($\varphi_f = 0.67$) [39] (for compounds **6a**,**c**,**d**).

Commercially available reagents and solvents were used. Column chromatography was performed using silica gel 60 (70–230 mesh); TLC analysis was conducted on silica gel 60 F$_{254}$ plates.

2.2. Synthesis

1-Arylethanones **1** based on 2-methyl-1-benzothiophen and 2-heptyl-1-benzothiophen were obtained by their successive 3-acetylation [40]. 1-[4-(Dialkylamino)phenyl]ethanones were synthesized from commercial fluorobenzene by its 4-acetylation [41]



Scheme 1. DCPs containing dialkylamino groups in ethene "bridge" or in aryl moieties.

and subsequent efficient nucleophilic substitution of fluorine atom in water by corresponding secondary amine by earlier developed method [42].

β-Ketoesters **2** were prepared by previously described way [43] based on acylation of Meldrum's acid with corresponding arylacetic acids obtained in turn by the reduction of ethyl-2-(2-alkylbenzothiophene-3-yl)-2-oxoacetates with triethylsilane [44] or by Willgerodt–Kindler reaction [45] of 1-[4-(dialkylamino) phenyl]ethanones.

α-Bromoketones **3** were synthesized by 5-min refluxing of mixture of corresponding 1-arylethanone **1** (1.0 eq.) with copper (II) bromide (2.5 eq.) in methanol (the technique similar to that for 2,3-diarylcyclopent-2-en-1-ones bromination [30]).

2,3-Diarylcyclopent-2-en-1-ones **4** were obtained by alkylation of β-ketoesters **2** with bromoketones **3** [28] (Scheme 2) and arylmethylidenecyclopentenones **6** were prepared by the reactions of compound **4h** with benzaldehydes **5** [32] (Scheme 3), as following. The cyclopentenones **4h** [28], **4i** [28], **4j** [28], **4k** [46], **4l** [46] and **4m** [47] were synthesized from corresponding ketoester **2** and bromoketones **3** by the method used in Ref [28].

2.2.1. *Synthesis of diarylcyclopentenones (**4**) (general procedure)*

To a solution of ketoester **2** (10 mmol) in abs. benzene (30 mL) sodium (0.24 g, 10.5 mmol) was added, and the mixture was stirred for 3–4 h until sodium dissolved. To a cooled to 10 °C reaction mixture a solution of bromoketone **2** (10 mmol) in abs. benzene (15 mL) was added over 0.5 h. The solution was stirred overnight at room temperature, then poured into cold water (150 mL) and extracted with ethylacetate (3 × 50 mL). The combined organic phases were washed with water (100 mL), filtered through 1 cm layer of silica gel and evaporated. The intermediate – alkylated ketoester – was used further without additional purification.

A solution of KOH (0.84 g, 15 mmol) in water (11 mL) was added at once to a solution of crude alkylated ketoester (3 mmol) in ethanol (11 mL). The reaction mixture was refluxed for 4 h, then cooled, poured into water (10 mL) and extracted with ethyl acetate (3 × 20 mL). The combined extracts were washed with water (50 mL), dried with magnesium sulfate and evaporated in vacuum. The residue was purified by column chromatography eluting by petrol. ether/ethyl acetate 4:1 and recrystallized from ethanol. The physical and chemical properties including spectral characteristics of DCPs **4h**–**j** [28], **4k**,**l** [46] and **4m** [30,47] have been reported previously.

2.2.2. *2-(2-Methyl-1-benzothiophen-3-yl)-3-(4-pyrrolidin-1-ylphenyl)cyclopent-2-en-1-one (**4a**)*

Yield 0.50 g (45%), yellow powder, M.p. 80–82 °C (ethanol). ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.94–2.02 (m, 4H, CH_2^{pyrrol}), 2.28 (s, 3H, CH_3), 2.71–2.77 (m, 2H, $CH_2^{cyclopent}$), 3.18–3.31 (m, 6H, $2CH_2^{pyrrol}$, $CH_2^{cyclopent}$), 6.34 (d, 2H, H^{arom}, $J = 8.8$ Hz), 7.19–7.32 (m, 5H, H^{arom}), 7.76 (d, 1H, H^{arom}, $J = 7.7$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.82, 25.46, 28.89, 34.43, 47.46, 110.85, 111.32, 122.02, 122.58, 123.64, 124.05, 126.57, 129.50, 129.66, 137.89, 138.90, 139.25, 149.34, 170.12, 207.26 (C=O). Mass, *m/z* (%): 373 (100, $[M]^+$). HRMS: Calculated for $C_{24}H_{23}NOS$ ($M + H^+$): 374.1573. Found: 374.1572.

2.2.3. *2-(2-Methyl-1-benzothiophen-3-yl)-3-(4-piperidin-1-ylphenyl)cyclopent-2-en-1-one (**4b**)*

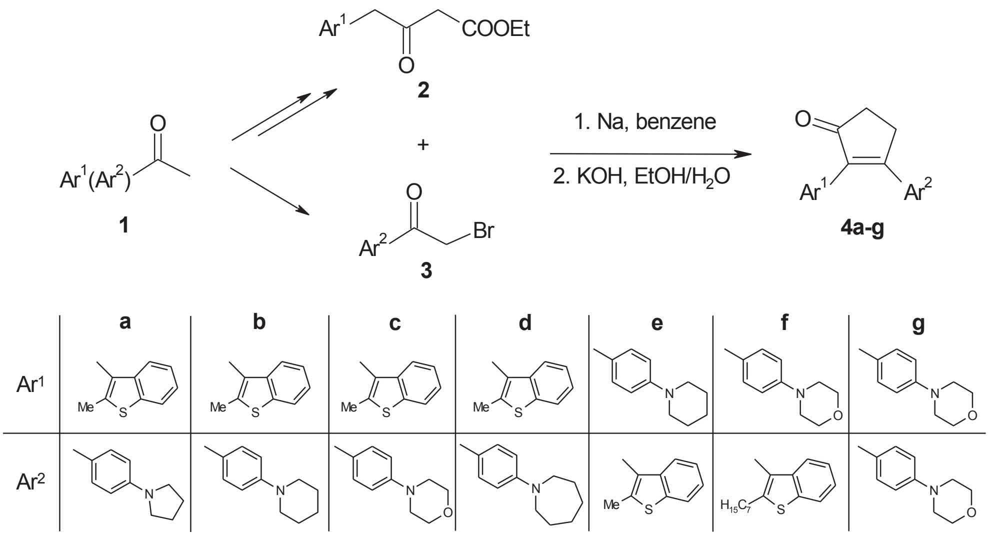
Yield 0.23 g (20%), red powder, M.p. 80–83 °C (ethanol). ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.52–1.65 (m, 6H, $3CH_2^{piper}$), 2.27 (s, 3H, CH_3), 2.71–2.78 (m, 2H, $CH_2^{cyclopent}$), 3.15–3.27 (m, 6H, $2CH_2^{piper}$, $CH_2^{cyclopent}$), 6.67 (d, 2H, H^{arom}, $J = 9.2$ Hz), 7.19–7.31 (m, 5H, H^{arom}), 7.76 (d, 1H, H^{arom}, $J = 7.0$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.82, 24.36, 25.43, 28.93, 34.45, 48.70, 113.06, 114.08, 121.24, 122.06, 122.52, 123.72, 123.95, 124.09, 129.43, 131.10, 138.90, 139.15, 152.75, 169.73, 207.44 (C=O). Mass, *m/z* (%): 387 (100, $[M]^+$). HRMS: Calculated for $C_{25}H_{25}NOS$ ($M + H^+$): 388.1730. Found: 388.1730.

2.2.4. *2-(2-Methyl-1-benzothiophen-3-yl)-3-(4-morpholin-4-ylphenyl)cyclopent-2-en-1-one (**4c**)*

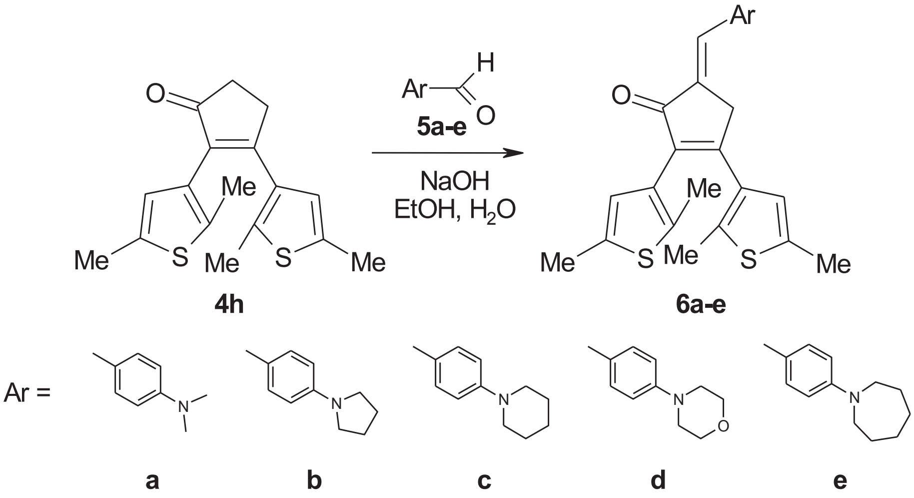
Yield 0.47 g (40%), brown powder, M.p. 75–77 °C (ethanol). ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.26 (s, 3H, CH_3), 2.73–2.79 (m, 2H, $CH_2^{cyclopent}$), 3.14–3.20 (m, 4H, $2CH_2^{morph}$), 3.20–3.26 (m, 2H, $CH_2^{cyclopent}$), 3.75–3.83 (m, 4H, $2CH_2^{morph}$), 6.68 (d, 2H, H^{arom}, $J = 8.9$ Hz), 7.17–7.25 (m, 5H, H^{arom}), 7.77 (d, 1H, H^{arom}, $J = 7.9$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.82, 29.76, 34.46, 47.67, 66.62, 113.39, 113.99, 122.06, 122.44, 123.75, 124.11, 129.27, 130.13, 138.14, 138.88, 139.04, 152.35, 169.34, 207.26 (C=O). Mass, *m/z* (%): 389 (47, $[M]^+$), 331 (17, $[M-C_3H_6O]^+$), 190 (100, $[C_{11}H_{10}OS]^+$), 148 (42, $[C_9H_8S]^+$), 132 (48, $[C_9H_{10}N]^+$). HRMS: Calculated for $C_{24}H_{23}NO_2S$ ($M + Na^+$): 412.1342. Found: 412.1338.

2.2.5. *3-(4-Azepan-1-ylphenyl)-2-(2-methyl-1-benzothiophen-3-yl)-2-en-1-one (**4d**)*

Yield 0.54 g (45%), red powder, M.p. 90–92 °C (ethanol). ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.42–1.75 (m, 8H, $4CH_2^{\text{азеп}}$), 2.26 (s, 3H,



Scheme 2. Synthetic route for the preparation of dialkylamino-containing DCPs **4a**–**g**.



Scheme 3. Condensation of dithienylcyclopentenone **4h** with substituted benzaldehydes **5a**–**e**.

CH$_3$), 2.67–2.77 (m, 2H, CH$_2^{\text{cyclopent}}$), 3.15–3.25 (m, 2H, CH$_2^{\text{cyclopent}}$), 3.32–3.44 (m, 4H, 2CH$_2^{\text{азеп}}$), 6.44 (d, 2H, H$^{\text{arom}}$, $J = 8.8$ Hz), 7.12–7.31 (m, 5H, H$^{\text{arom}}$), 7.74 (d, 1H, H$^{\text{arom}}$, $J = 7.7$ Hz). ^{13}C NMR (75 MHz, CDCl$_3$, δ, ppm): 14.83, 26.91, 27.44, 28.80, 34.41, 49.26, 110.74, 121.60, 122.02, 122.59, 123.56, 124.06, 126.61, 129.48, 129.85, 137.50, 138.90, 139.27, 150.62, 169.74, 207.24 (C=O). Mass, *m/z* (%): 401 (100, [M]$^+$). HRMS: Calculated for $C_{26}H_{27}NOS$ (M + Na$^+$): 424.1706. Found: 424.1710.

2.2.6. 3-(2-Methyl-1-benzothiophen-3-yl)-2-(4-piperidin-1-ylphenyl)cyclopent-2-en-1-one (4e)

Yield 0.35 g (30%), pale red powder, M.p. 146–149 °C (ethanol). ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 1.44–1.74 (m, 6H, 3CH$_2^{\text{piper}}$), 2.10 (s, 3H, CH$_3$), 2.65–2.77 (m, 2H, CH$_2^{\text{cyclopent}}$), 2.97–3.24 (m, 6H, 2CH$_2^{\text{piper}}$, CH$_2^{\text{cyclopent}}$), 6.70 (d, 2H, H$^{\text{arom}}$, $J = 8.4$ Hz), 7.11 (d, 2H, H$^{\text{arom}}$, $J = 8.4$ Hz), 7.29 (t, 2H, H$^{\text{arom}}$, $J = 3.7$ Hz), 7.48–7.56 (m, 1H, H$^{\text{arom}}$), 7.70–7.80 (m, 1H, H$^{\text{arom}}$). ^{13}C NMR (75 MHz, CDCl$_3$, δ, ppm): 14.77, 24.33, 25.67, 30.76, 35.53, 50.04, 115.63, 122.03, 122.28, 124.02, 124.52, 129.22, 129.90, 136.78, 138.75, 138.92, 142.09, 163.40, 207.97 (C=O). Mass, *m/z* (%): 387 (95, [M]$^+$). HRMS: Calculated for $C_{25}H_{25}NOS$ (M + H$^+$): 388.1730. Found: 388.1730.

2.2.7. 3-(2-Heptyl-1-benzothiophen-3-yl)-2-(4-morpholin-4-ylphenyl)cyclopent-2-en-1-one (4f)

Yield 0.35 g (25%), gray powder, M.p. 160–163 °C (ethanol). ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 0.84–0.94 (m, 3H, CH$_3$), 1.16–1.32 (m, 10H, 5CH$_2$), 2.37–2.63 (m, 2H, CH$_2$), 2.76–2.81 (m, 2H, CH$_2^{\text{cyclopent}}$), 3.05–3.12 (m, 4H, 2CH$_2^{\text{morph}}$), 3.14–3.25 (m, 2H, CH$_2^{\text{cyclopent}}$), 3.77–3.84 (m, 4H, 2CH$_2^{\text{morph}}$), 6.70 (d, 2H, H$^{\text{arom}}$, $J = 8.9$ Hz), 7.16 (d, 2H, H$^{\text{arom}}$, $J = 8.9$ Hz), 7.30–7.38 (m, 2H, H$^{\text{arom}}$), 7.49–7.56 (m, 1H, H$^{\text{arom}}$), 7.78–7.84 (m, 1H, H$^{\text{arom}}$). ^{13}C NMR (75 MHz, CDCl$_3$, δ, ppm): 14.14, 22.70, 29.09, 29.41, 29.45, 30.95, 31.25, 31.75, 35.53, 48.86, 66.86, 114.99, 122.01, 122.46, 122.76, 124.05, 124.54, 129.11, 129.47, 138.65, 138.96, 142.00, 142.84, 150.73, 164.40, 207.89 (C=O). Mass, *m/z* (%): 473 (100, [M]$^+$), 388 (10, [M–C$_6$H$_{13}$]$^+$). Calculated for $C_{30}H_{35}NO_2S$, %: C, 76.07, H, 7.45. Найдено, %: C, 73.15, H, 7.48.

2.2.8. 2,3-Bis(4-morpholin-4-ylphenyl)cyclopent-2-en-1-one (4g)

Yield 0.38 g (32%), yellow powder, M.p. 224–224.5 °C (ethanol). ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 2.61–2.69 (m, 2H, CH$_2^{\text{cyclopent}}$), 2.95–3.04 (m, 2H, CH$_2^{\text{cyclopent}}$), 3.14–3.27 (m, 4H, N(CH$_2$)$_2^{\text{morph}}$), 3.80–3.93 (m, 4H, O(CH$_2$)$_2^{\text{morph}}$), 6.76 (d, 2H, H$^{\text{phenyl}}$, $J = 8.8$ Hz), 6.91 (d, 2H, H$^{\text{phenyl}}$, $J = 8.8$ Hz), 7.18 (d, 2H, H$^{\text{phenyl}}$, $J = 8.8$ Hz), 7.37 (d, 2H, H$^{\text{phenyl}}$, $J = 8.8$ Hz). ^{13}C NMR (75 MHz, CDCl$_3$, δ, ppm): 28.92, 29.68, 47.94 (N(CH$_2$)$_2^{\text{morph}}$), 49.06 (N(CH$_2$)$_2^{\text{morph}}$), 66.65 (O(CH$_2$)$_2^{\text{morph}}$), 66.91 (O(CH$_2$)$_2^{\text{morph}}$), 113.96, 115.50, 124.48, 126.41, 129.57, 130.39, 137.34, 150.48, 150.86, 166.17, 208.80 (C=O). Mass, *m/z* (%): 404 (93, [M]$^+$). Calculated for $C_{25}H_{28}N_2O_3$, %: C, 74.23, H, 6.98, N, 6.93. Найдено, %: C, 73.85, H, 7.05, N, 6.98.

2.2.9. Synthesis of 5-arylmethylidenecyclopent-2-en-1-ones (6) (general method)

(Scheme 3). The mixture of dithienylcyclopentenone **4h** (0.33 mmol) and corresponding aldehyde **5** (0.43 mmol) in mixture of ethanol (1 mL) and 10%-solution of NaOH in water (1 mL) was refluxed for 1–3 h to maximal conversion of initial cyclopentenone **4h** (TLC-control) and poured into ice-water (60 mL). The residue was filtered off, washed with water (2 × 20 mL), petrol ether (2 × 20 mL) and recrystallized from ethanol.

2.2.10. 2,3-Bis(2,5-dimethylthiophen-3-yl)-5-{[4-(dimethylamino)phenyl]methylidene} cyclopent-2-en-1-one (6a)

Yield 0.13 g (91%), yellow powder, M.p. 198–199 °C (ethanol). ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 1.92 (s, 3H, Me), 1.95 (s, 3H, Me), 2.40 (s, 3H, Me), 2.43 (s, 3H, Me), 3.04 (s, 6H, 2NCH$_3$), 3.81 (s, 2H, CH$_2^{\text{cyclopent}}$), 6.58 (s, 1H, H$^{\text{thioph}}$), 6.66 (s, 1H, H$^{\text{thioph}}$), 6.74 (d, $J = 8.4$ Hz, 2H, H$^{\text{phenyl}}$), 7.47 (s, 1H, CH$^{\text{aldeh}}$), 7.55 (d, $J = 8.4$ Hz, 2H, H$^{\text{phenyl}}$). ^{13}C NMR (75 MHz, CDCl$_3$, δ, ppm): 14.35, 14.68, 15.24, 15.35, 37.62 (CH$_2^{\text{cyclopent}}$), 40.19 (2NCH$_3$), 112.09, 123.57, 125.27, 126.94, 128.68, 129.90, 132.16, 132.38, 133.89, 135.07, 135.60, 136.69, 136.97, 137.50, 151.05, 157.48, 195.54 (C=O). Mass, *m/z* (%): 433 (85, [M]$^+$), 418 (100, [M–CH$_3$]$^+$), 390 (32, [M– N(CH$_3$)$_2$]$^+$). HRMS: Calculated for $C_{26}H_{27}NOS_2$ (M + H)$^+$: 434.1607. Found: 434.1601. IR (KBr), cm^{-1}: 2951 (C–H$^{\text{arom}}$), 2914 (C–H$^{\text{arom}}$), 2864 (C–H$^{\text{arom}}$), 1676 (C=O), 1600, 1526, 1443, 1371, 1291 (C$^{\text{arom}}$–N), 1189 (C$^{\text{aliph}}$–N), 1139, 815 (C–H$^{\text{phenyl}}$), 528.

2.2.11. 2,3-Bis(2,5-dimethylthiophen-3-yl)-5-[(4-pyrrolidin-1-ylphenyl)methylidene]cyclopent-2-en-1-one (6b)

Yield 0.13 g (90%), yellow powder, M.p. 160–163 °C (ethanol). ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 1.91 (s, 3H, CH$_3$); 1.95 (s, 3H, CH$_3$); 2.00–2.13 (m, 4H, CH$_2$); 2.40 (s, 3H, CH$_3$); 2.43 (s, 3H, CH$_3$); 3.23–3.34 (m, 4H, CH$_2$); 3.80 (s, 2H, CH$_2$); 6.55–6.64 (s, 1H, 1H$^{\text{thioph}}$, д, 2H, H$^{\text{phenyl}}$, $J = 6.9$ Hz); 6.66 (s, 1H, H$^{\text{thioph}}$); 7.47 (s, 1H, CH$^{\text{aldeh}}$); 7.54 (d, 2H, H$^{\text{phenyl}}$, $J = 6.9$ Hz). ^{13}C ЯМР (75 MHz, CDCl$_3$, δ, ppm): 14.31, 14.64, 15.20, 15.31, 25.54 (CH$_2$), 37.66 (CH$_2$), 47.60 (2CH$_2$), 111.89, 122.87, 125.25, 126.91, 128.00, 129.93, 132.22, 132.55, 133.89, 134.99, 135.51, 136.61, 136.83, 137.47, 148.59, 157.28, 195.52 (C=O). Mass, *m/z* (%): 459 (100, $[M]^+$); 444 (96, $[M-CH_3]^+$). HRMS: Calculated for $C_{28}H_{29}NOS_2$ $(M+H)^+$: 460.1763. Found: 460.1749. IR (KBr), cm^{-1}: 2965 ($C-H^{arom}$), 2914 (CH_3, $C-H^{arom}$), 2841 (CH_3, $C-H^{arom}$), 1678 (C=O), 1601 (C=C), 1526, 1444, 1390, 1292 ($C_{arom}-N$), 1185 ($C^{aliph}-N$), 1140, 808 ($C-H^{phenyl}$).

*2.2.12. 2,3-Bis(2,5-dimethylthiophen-3-yl)-5-[(4-piperidin-1-ylphenyl)methylidene]cyclopent-2-en-1-one (**6c**)*

Yield 62 Мг (40%), yellow powder, M.p. 156–158 °C (ethanol). ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.58–1.77 (m, 6H, CH_2), 1.91 (s, 3H, CH_3), 1.94 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 3.27–3.67 (m, 4H, CH_2), 3.81 (s, 2H, CH_2), 6.58 (s, 1H, H^{thioph}), 6.66 (s, 1H, H^{thioph}), 6.92 (d, 2H, H^{phenyl}, $J = 8.2$), 7.46 (s, 1H, CH^{aldeh}), 7.54 (d, 2H, H^{phenyl}, $J = 8.2$). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.32, 14.66, 15.21, 15.32, 24.42 (CH_2), 25.57 ($2CH_2$), 37.51 (CH_2), 49.17 ($2CH_2$), 115.01, 125.19, 125.27, 126.85, 129.39, 129.78, 131.78, 132.20, 133.79, 135.08, 135.61, 136.70, 137.04, 137.42, 152.16, 157.67, 195.54 (C=O). Mass, *m/z* (%): 473 (100, $[M]^+$); 458 (27, $[M-CH_3]^+$). HRMS: Calculated for $C_{29}H_{31}NOS_2$ $(M+H)^+$: 474.1920. Found: 474.1910. IR (KBr), cm^{-1}: 2966 ($C-H^{arom}$), 2935 ($C-H^{arom}$), 2915 (CH_3, $C-H^{arom}$), 2854 (CH_3, $C-H^{arom}$), 2822 ($C-H^{arom}$), 1682 (C=O), 1635, 1603 (C=C), 1519, 1443, 1385, 1291 ($C^{arom}-N$), 1252, 1223, 1190 ($C^{aliph}-N$), 1140, 1125, 923, 883, 815 ($C-H^{phenyl}$).

*2.2.13. 2,3-Bis(2,5-dimethylthiophen-3-yl)-5-[(4-morpholin-4-ylphenyl)methylidene] cyclopent-2-en-1-one (**6d**)*

Yield 0.10 g (82%), yellow powder, M.p. 211–213 °C (ethanol). ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.88 (s, 3H, Me), 1.92 (s, 3H, Me), 2.37 (s, 3H, Me), 2.40 (s, 3H, Me), 3.24 (s, 4H, $2CH_2^{morph}$), 3.78 (s, 2H, $CH_2^{cyclopent}$), 3.84 (s, 4H, $2CH_2^{morph}$), 6.54 (s, 1H, H^{thioph}), 6.63 (s, 1H, H^{thioph}), 6.89 (d, $J = 8.1$ Hz, 2H, H^{phenyl}), 7.43 (s, 1H, CH^{aldeh}), 7.53 (d, $J = 8.1$ Hz, 2H, H^{phenyl}). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.23, 14.59, 15.12, 15.22, 37.34 ($CH_2^{cyclopent}$), 48.06 (CH_2^{morph}), 66.66 (CH_2^{morph}), 114.73, 125.06, 126.60, 126.72, 129.58, 130.13, 131.28, 131.99, 133.61, 135.05, 135.58, 136.69, 137.10, 137.29, 151.58, 157.81, 195.37 (C=O). Mass, *m/z* (%): 475 (100, $[M-H]^+$), 460 (55, $[M-CH_3]^+$). HRMS: Calculated for $C_{28}H_{29}NO_2S_2$ $(M+H)^+$: 476.1712. Found: 476.1709. IR (KBr), cm^{-1}: 2984 ($C-H^{arom}$), 2908 ($C-H^{arom}$), 2856 ($C-H^{arom}$), 1680 (C=O), 1636, 1596, 1520, 1448, 1296 ($C^{arom}-N$), 1244, 1188 ($C^{aliph}-N$), 1124, 1112, 928, 836, 820 ($C-H^{phenyl}$).

*2.2.14. 5-[(4-Azepan-1-ylphenyl)methylidene]-2,3-bis(2,5-dimethylthiophen-3-yl)cyclopent-2-en-1-one (**6e**)*

Yield 0.13 g (84%), brown powder, M.p. 166–168 °C (ethanol). ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.50–1.61 (m, 8H, CH_2), 1.92 (s, 3H, CH_3), 1.94 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 3.49–3.58 (m, 4H, CH_2), 3.80 (s, 2H, CH_2), 6.58 (s, 1H, H^{thioph}), 6.65 (s, 1H, H^{thioph}), 6.72 (d, 2H, H^{phenyl}, $J = 8.8$ Hz), 7.45 (s, 1H, CH^{aldeh}), 7.52 (d, 2H, H^{phenyl}, $J = 8.8$ Hz). ЯМР ^{13}C (75 MHz, $CDCl_3$, δ, ppm): 14.32, 14.66, 15.22, 15.33, 27.01 ($2CH_2$), 27.59 ($2CH_2$), 37.64 (CH_2), 49.62 ($2CH_2$), 111.35, 122.76, 125.25, 126.91, 128.04, 129.92, 132.27, 132.70, 133.89, 134.99, 135.53, 136.60, 136.85, 137.47, 149.79, 157.24, 195.55 (C=O). Mass, *m/z* (%): 487 (100, $[M]^+$); 472 (20, $[M-CH_3]^+$). HRMS: Calculated for $C_{30}H_{33}NOS_2$ $(M+H)^+$: 488.2076. Found: 488.2062. IR (KBr), cm^{-1}: 2930 ($C-H^{arom}$), 2854 (CH_3, $C-H^{arom}$), 1676 (C=O), 1579 (C=C), 1520, 1469, 1397, 1291 ($C^{arom}-N$), 1260, 1186 ($C^{aliph}-N$), 1165, 1111, 917, 811 ($C-H^{phenyl}$).

3. Results and discussion

The photochromic characteristics of diarylethenes have been measured in acetonitrile solutions at 293 K with alternating irradiation by UV light (λ^{ir} = 365 nm) and visible light ($\lambda^{ir} > 400$ nm) and are summarized in Table 1. Upon UV-irradiation, the colorless solutions of DCPs **4** and **6** were converted into colored ones and bleached back to colorless under visible light that is due to the reversible electrocyclic reaction of hexatriene system from colorless form **A** to cyclic (colored) form **B** (Scheme 4).

Analyzing the data in Table 1 one can see that the properties of DCPs **4a**–**g** and **6a**–**e** containing electron donating dialkylamino-groups depend considerably on their structures. Some correlations between diarylethenes structures and its fluorescent and photochromic parameters have been revealed.

3.1. Photochromic properties of DCPs

From the structures of the DCPs synthesized one can see that the compounds **4a**–**d**,**g** and **6a**–**e** are bichromophoric, with a merocyanine system fused to a photochromic one. While in DCPs **4a**–**d**,**g** these systems intersect, in compounds **6a**–**e** they are separated; compounds **4e**,**f** in the same time lack merocyanine system at all (Scheme 1). The structural differences are certain to affect the photochromic properties of DCPs.

As to the values of absorption bands maxima of open-ring isomers **A** of DCPs it should be noticed that the presence of dialkylamino groups in the molecules causes, as a rule, the appearance of the bands of forms **A** in the fields of long wave UV light and/or visible light (Table 1). For example, for DCPs **4a**–**d**,**g** the maxima are ranged in the 344–380 nm, while for compounds **6a**–**e** they are strongly shifted up to the 386–422 nm (in contrast with parent dithienyl-derivative **4h**: the most long-wavelength band is only at 309 nm). Only in case of DCPs **4e**,**f** absorption bands of colorless forms **A** were observed in the fields of short wave UV light (at 261–262 nm). It is of interest to see that these observations correlate with the above-mentioned structural features of compounds: thus, it seems to be merocyanine system in the initial forms **A** of DCPs **4a**–**d**,**g**, **6a**–**e** which induces the appearance of absorption bands in long wave UV or visible region; and on the contrary, DCPs **4e**,**f** (without merocyanine system) lack long wavelength absorption bands. The absorption bands shifts towards visible spectrum region (like in case of DCPs **6a**–**e**) is known to be a promising feature of compounds as for different practical applications it is significant to handle diarylethenes which can be processed by less destructive visible light rather than UV [48].

Absorption bands maxima of photoinduced isomers **B** of DCPs **4a**–**d** are ranged in the 455–504 nm. The introduction of dialkylamino groups into the ethene “bridge” leads to bathochromic shifts of the bands of colored forms **B**: from 547 nm for compound **4h** to 568–580 nm region for its derivatives **6a**–**e**. Talking about compounds **4** it is worthwhile to notice the entire absence of photochromic properties of DCPs **4e**–**g**; one might try to explain the observation by the above-mentioned lack of merocyanine system in the diarylethenes structures.

However then it was determined that this effect is not due to the presence or absence of dialkylamino groups in DCPs molecules but caused by the presence of the phenyl moiety in the structures. It was shown by the several examples (Chart 1) that when phenyl ring is in the 3rd position of ethene “bridge”, DCPs (compounds **4b**,**h**,**i**,**k**) are basically photochromic diarylethenes but when phenyl group is attached to the second position, DCPs (compounds **4e**,**g**,**j**,**l**,**m**) do not undergo photocyclization at all. It should be emphasized that the nature of the second aryl group (thienyl, benzothienyl or oxazolyl) in the structures as well as the presence or absence of substituents in phenyl ring does not matter: this regularity is valid for DCPs with different kind of aryl moieties (Chart 1).

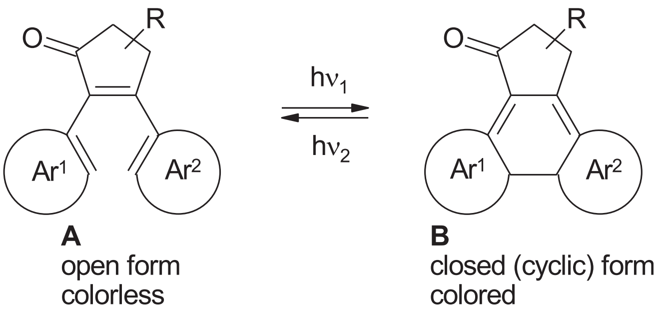
The reason for the lack of photochromic activity may be different, including competition between photochromic properties

Table 1
Photochromic and fluorescent characteristics of DCPs synthesized in acetonitrile ($C = 2\cdot10^{-5}$ mol L^{-1}) at 293 K in air.

Entry	Photochromism					Fluorescence			
	Compound	λ_A[a], nm (ε, $L\cdot mol^{-1}\cdot cm^{-1}$)	λ_B[b], nm (ε, $L\cdot mol^{-1}\cdot cm^{-1}$)	$\varphi_{A\to B}$[c]	$\varphi_{B\to A}$[d]	λ_{ex}[e], nm	λ_{em}[f], nm	φ_{em}^{open}[g]	φ^{UV}[h]
1	**4a**	238 ($7.31\cdot10^4$) 378 ($4.50\cdot10^4$)	504 ($1.53\cdot10^4$)	0.27	0.001	378	464	0.13	–
2	**4b**	235 ($6.34\cdot10^4$) 355 ($3.62\cdot10^4$)	478 ($1.13\cdot10^4$)	0.11	0.001	350	456	0.13	–
3	**4c**	238 ($7.84\cdot10^4$) 344 ($3.63\cdot10^4$)	455 ($5.52\cdot10^3$)	0.16	0.001	350	443	0.30	–
4	**4c** + **HCl**	230 ($4.57\cdot10^4$) 356 ($6.65\cdot10^3$)	398 ($2.55\cdot10^4$), 545 ($2.40\cdot10^4$)	0.07	0.003			~$5\cdot10^{-3}$	–
5	**4d**	234 ($6.50\cdot10^4$) 380 ($4.08\cdot10^4$)	494 ($1.38\cdot10^4$)	0.15	0.001	380	449	0.17	–
6	**4e**	262 ($5.12\cdot10^4$)	Non photochromic			261	539	0.09	–
7	**4f**	261 ($2.64\cdot10^4$)	Non photochromic			261	538	0.15	–
8	**4f** + **HCl**	361 ($3.55\cdot10^4$)	Non photochromic					~$3\cdot10^{-3}$	–
9	**4g**	254 ($3.45\cdot10^4$) 348 ($3.10\cdot10^4$)	Non photochromic			348	549	0.09	–
10	**4g** + **HCl**	283 ($3.03\cdot10^4$)	Non photochromic					~$2\cdot10^{-3}$	–
11	**4h**	208 ($1.64\cdot10^4$), 245 ($1.46\cdot10^4$), 309 ($6.43\cdot10^3$)	547 ($1.11\cdot10^4$)	0.27	0.065	Non fluorescent			
12	**6a**	233 ($6.48\cdot10^4$) 411 ($3.93\cdot10^4$)	577 (*br.*) ($2.65\cdot10^4$)	0.01	0.001	411	542	0.34	0.17
13	**6a** + **HCl**	296 ($5.02\cdot10^4$)	605 ($1.00\cdot10^4$)	0.31	0.010			~$2\cdot10^{-3}$	$<2\cdot10^{-3}$
14	**6b**	341 ($3.75\cdot10^4$) 421 ($2.88\cdot10^4$)	578 (*br.*) ($2.12\cdot10^4$)	0.005	0.0003	421	548	0.24	0.15
15	**6b** + **HCl**	372 ($1.25\cdot10^5$)	602 ($3.80\cdot10^4$)	0.005	0.0003			~$1\cdot10^{-3}$	$<1\cdot10^{-3}$
16	**6c**	240 ($4.51\cdot10^4$) 402 ($2.83\cdot10^4$)	580 ($4.45\cdot10^4$)	0.01	0.001	402	552	0.17	0.05
17	**6c** + **HCl**	367 ($1.86\cdot10^5$)	590 ($2.25\cdot10^4$)	0.02	0.001			~$1\cdot10^{-3}$	$<1\cdot10^{-3}$
18	**6d**	252 ($1.90\cdot10^4$) 386 ($1.62\cdot10^4$)	571 ($7.90\cdot10^3$)	0.04	0.004	386	537	0.16	0.04
19	**6d** + **HCl**	311 ($3.15\cdot10^4$), 359 ($2.23\cdot10^4$)	604 ($1.53\cdot10^4$)	0.11	0.004			$1\cdot10^{-3}$	$<1\cdot10^{-3}$
20	**6e**	341 ($3.75\cdot10^4$) 422 ($1.98\cdot10^4$)	568 (*br.*) ($2.45\cdot10^4$)	0.005	0.0001	421	543	0.33	0.22
21	**6e** + **HCl**	308 ($1.04\cdot10^5$), 357 ($3.90\cdot10^4$)	583 ($4.00\cdot10^4$)	0.003	0.001			~$1\cdot10^{-3}$	$<1\cdot10^{-3}$

[a] Absorption maxima (extinction coefficients) of open-ring isomers of DCPs.
[b] Absorption maxima (extinction coefficients) of closed-ring isomers DCPs.
[c] Quantum yields of ring-closure reactions of DCPs.
[d] Quantum yields of ring-opening reactions of DCPs.
[e] Emission excitation wavelengths of DCPs.
[f] Emission maxima wavelengths of DCPs.
[g] Fluorescence quantum yields of ring-open isomers of DCPs.
[h] Fluorescence quantum yields of DCPs after 2-Min UV-irradiation ($\lambda^{ir} = 365$ nm).

and fluorescence emission; moreover, in some cases the latter can completely suppress the photoswitching process. Another possible reason may be an intermolecular charge transfer with the formation of TICT (twisted intermolecular charge transfer interaction) states, which, according to the literature, often leads to the complete disappearance of photochromic properties [49,50]. The possibility of such an effect could be related with the conjugation between an electron-acceptor carbonyl and electron-donor dialkylamino groups of diarylethene molecule. Other factors may also contribute to lack of photochromism. So, we have recently found that diarylethenes comprising oxazole and phenyl rings as aryl moieties under UV-irradiation (λ = 365 nm) undergo photoisomerization with skeletal rearrangement, giving the naphthalene derivatives (Scheme 5) [46]. This photoreaction proceeds also through the formation of cyclic form, although in the case of 2-phenyl-substituted diarylcyclopentenone (compound **4l**) the formation of the cyclic form is also unable to register, but the change of the absorption spectrum in the UV region is observed (see Ref. [46] where this phenomenon has been described in detail).



Scheme 4. Photochromic reactions of DCPs.

In the case of benzothiophene derivative **4e** the photochromic transformation has not also been observed but in contrast of compounds **4g,m** it is observed the absorption spectra change in the UV-region without the appearance of the absorption band in the visible region (Scheme 6 and Fig. 1). For this reaction the product structure has not yet been proved, but the reaction most likely proceeds with the opening of the benzothiophene ring, similar to that described most recently by Kawai et al. [51].

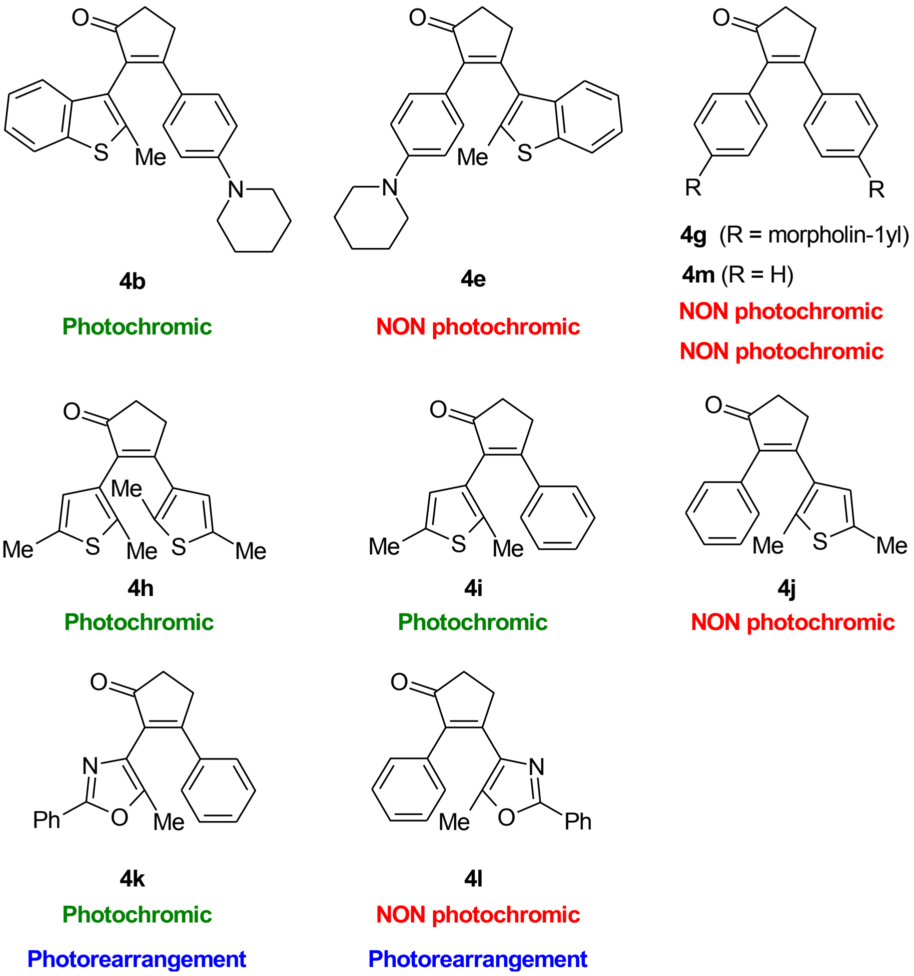
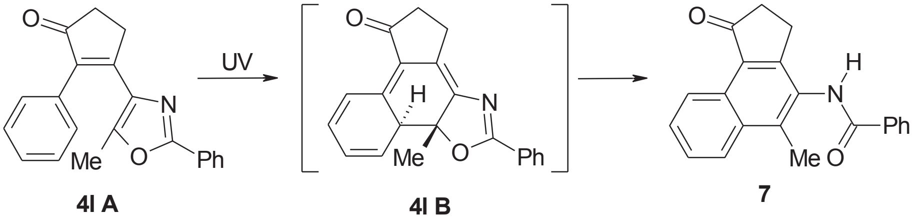


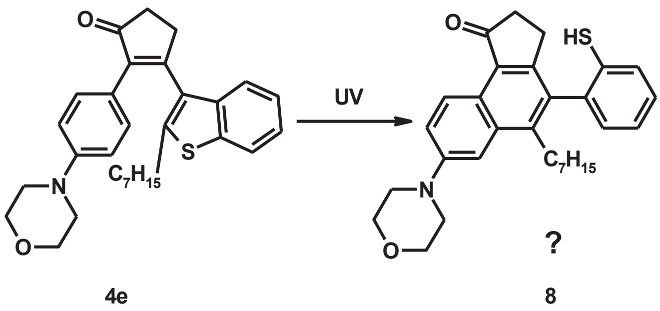
Chart 1. The influence of non-symmetry of DCPs molecules on its photochromic properties (presence or absence of photochromism).



Scheme 5. Photorearrangement of diarylethene **4l**.

For each of these compounds it is required further more detailed study, but in this work we have investigated the patterns of the influence of dialkylamino group at the different positions of photochromic molecules on spectral and kinetic characteristics.

Among the "structure-property" relationships the influence of dialkylamino groups introduction on the quantum yields of photoreactions could also be mentioned. The typical changes observed in the absorption spectra of the photochromic reactions of diarylethenes (for compound **6e**) in acetonitrile are shown in Fig. 2. The spectral characteristics and quantum yields of the photoreactions are summarized in Table 1. One can see that the most significant effect is observed in case of transition from DCP **4h** to its derivatives **6a**–**e**. Such ethene "bridge" modification (introduction of additional π-system with electron donating dialkylamino groups and therefore creation of merocyanine system in the molecule) results



Scheme 6. Photoreaction of diarylethene **4e** and possible structure of photoproduct **8**.

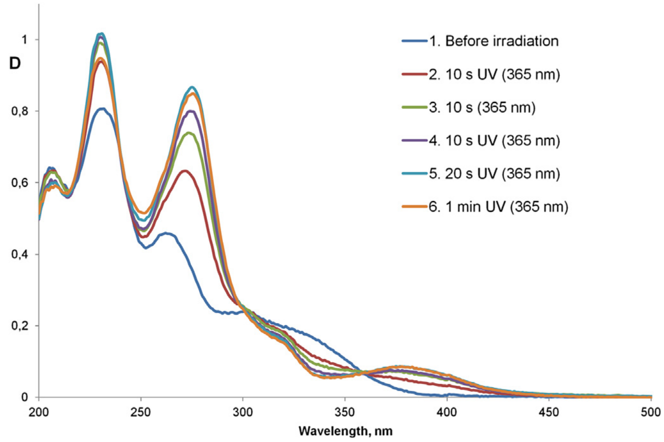


Fig. 1. Absorption spectra changes of diarylethene **4e** in acetonitrile solution ($C \approx 2*10^{-5}$ M) before and after irradiation with UV (365 nm).

in the essential decrease of photocyclization efficiency: photocoloration quantum yield is diminished from 0.27 for diarylethene **4h** to 0.005–0.04 for compounds **6a**–**e**. Diarylethenes **6a**–**e** are fluorescent substances (in contrast to **4h**, see below) and their photocyclization quantum yields reduction therefore can be explained by the competition between photochromic and emission processes, which leads to essential suppression of the former.

For several DCPs synthesized thermal stability of its photoinduced forms **B** has been estimated by calculation of rate constants of thermal cycloreversion reaction and half-lifes of the ring-closed isomers **B** in the dark (Table 2). Compounds **4a**,**b**,**d** containing phenyl moieties in the structures were assumed to be actually thermally unstable: their colored isomers became colorless in the dark during as little as 6.2–12 h. The insertion of merocyanine system into ethene "bridge" of DCP **4h** proved to lead as a rule to slight decrease of stability of cyclic forms **B** from 939 h for compound **4h** to 520–585 h for DCPs **6b**–**e**. Only in case of dimethylamino-derivative **6a** 3-fold increase of stability was detected.

3.2. Fluorescent properties of DCPs

In the paper fluorescent properties of DCPs synthesized have also been studied; such characteristics as wavelengths of emission bands maxima and fluorescence quantum yields were measured and are represented in Table 1.

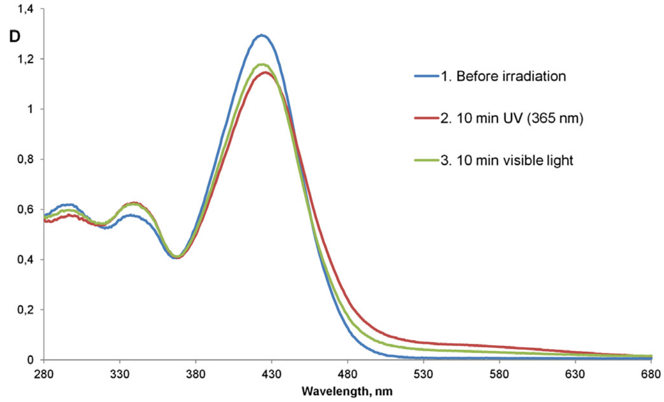


Fig. 2. Absorption spectra changes of diarylethene **6e** in acetonitrile solution ($C \approx 2*10^{-5}$ M) before and after irradiation with UV (365 nm) and visible light.

Table 2
Kinetic data of thermal bleaching reactions of DCPs synthesized (acetonitrile solutions, $C = 2\cdot10^{-5}$ mol L^{-1} at 293 K in air).

Entry	Compound	$kB\rightarrow A$therm[a], s^{-1}	$\tau_{1/2\ therm}^{B\rightarrow A}$ [b], h
1	**4a**	$2.69\cdot10^{-5}$	7.2
2	**4b**	$3.11\cdot10^{-5}$	6.2
3	**4d**	$1.63\cdot10^{-5}$	12
4	**4h**	$2.05\cdot10^{-7}$	939
5	**6a**	$6.84\cdot10^{-8}$	2810
6	**6b**	$3.29\cdot10^{-7}$	585
7	**6c**	$3.39\cdot10^{-7}$	568
8	**6d**	$3.61\cdot10^{-7}$	533
9	**6e**	$3.70\cdot10^{-7}$	520

[a] Thermal cycloreversion reaction rate constants (obtained from kinetic curves).
[b] Half-lifes of the ring-closed isomers in the dark.

It was found that all compounds containing dialkylamino groups (in aryl moieties or in ethene "bridge") are capable of emitting fluorescence under UV-light excitation. The emission parameters depend strong on the compounds structure. So, among DCPs **4a**–**g** the influence of the molecules non-symmetry should be again mentioned: compounds **4a**–**d** (with merocyanine system in open forms **A**) emit in violet-blue region of spectrum (443–464 nm) while in case of non-photochromic DCPs **4e**–**g** (no merocyanine system) the fluorescence bands are bathochromically shifted to green spectrum region (538–549 nm). The introduction of merocyanine system into cyclopentenone "bridge" of DCPs turned out to be the efficient way to obtain fluorescent diarylethenes: while parent compound **4h** is non-fluorescent its derivatives **6a**–**e** possess emission at the 537–552 nm region.

The dialkylamino group influence on this property is not entirely obvious. It is only could be mentioned that in a series of DCPs **4a**–**d**,**g** (with merocyanine system in colorless form **A**) and **4e**,**f** (without merocyanine system) the highest fluorescence quantum yields are observed for morpholine-containing compounds **4c** (0.30) and **4f** (0.17) correspondingly, although the quantum yield of bis(morpholinophenyl) derivatives (DCP **4g**) is as little as 0.09.

The fluorescence of compounds **6a**–**e** was shown to be light-sensitive, with emission decaying (its quantum yields decrease) under UV-irradiation (Table 1 and Fig. 3). It is worthwhile to note that the emission reduction is reversible and under irradiation with visible light the emission is revived again. The photosensitivity of fluorescence of DCPs **4** was not studied because of low fatigue resistance of the substances.

3.3. Acidochromism of DCPs

The addition of acid to the solutions of dialkylamino-containing DCPs was expected to induce essential changes both in photochromic and in fluorescent properties of compounds. The acidification of solutions was carried out by the passing high excess of hydrogen chloride by means of syringe.

It was already noted above that the introduction of merocyanine system into the ethene "bridge" of the molecules leads to the appearance of the absorption bands of DCPs isomers **A** in range of visible light (compounds **6a**–**e**). Therefore it is not surprising to see that the passing HCl through acetonitrile solutions of these diarylethenes results in vanishing of the long-wavelength bands because of dimethylamino group protonation, which destroys its electron donating ability and break down the merocyanine system on the whole (compare data for colorless forms **A** of pure compounds **6** and after addition of HCl_g in Table 1 and Fig. 3). In case of DCPs **4** the influence of acid addition on initial isomers **A** properties is more complex: in case of compounds **4c** (with merocyanine system in the

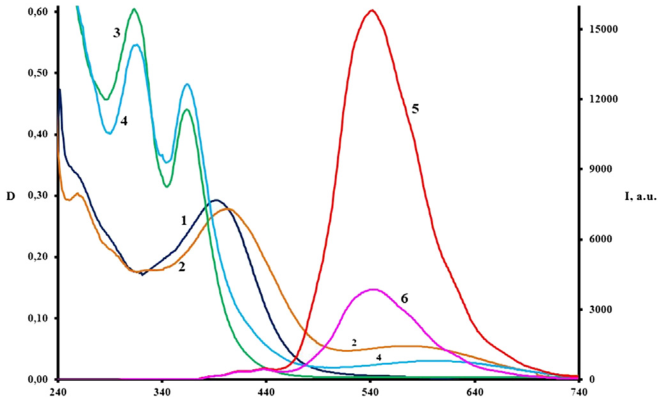


Fig. 3. Spectral changes of fluorescent switch **6d** under UV-irradiation. Absorption spectra (left axis) of DCP **6d** ($C = 2.0 \times 10^{-5}$ mol L^{-1} in CH_3CN) at 293 K: before irradiation (curve **1**), after 2 Min UV irradiation ($\lambda^{ir} = 365$ nm, curve **2**), with HCl_g passing through before irradiation (curve **3**) and with HCl_{gas} passing through after 20s UV irradiation ($\lambda^{ir} = 365$ nm, curve **4**). Emission spectra (right axis) of DCP **6d** ($C = 2.0 \times 10^{-6}$ mol L^{-1} in CH_3CN) at 293 K with emission excitation at $\lambda_{ex} = 386$ nm: before irradiation (curve **5**) and after 2 Min UV irradiation ($\lambda^{ir} = 365$ nm, curve **6**).

structure) and **4f** (without merocyanine system) its absorption bands are shifted bathochromically, while for DCP **4g** hypsochromic shift is observed (Table 1). Such ambiguity may be explained by the fact that photochromic and merocyanine systems in diarylethenes **4** are not separated (as in the compounds **6**) but overlapped and it is likely observed the strong electron withdrawing effect of protonated nitrogen atom on the position of absorption band.

As to sensitivity of fluorescent parameters of diarylethenes synthesized to pH of media, it should be mentioned that for all dialkylamino-containing DCPs **4**–**6** actually complete quenching of emission is occurred (no matter the compounds contain the merocyanine system or not). This effect is attributed to the protonation of nitrogen atom and witnesses that electron donating dialkylamino groups in the structures are responsible to the presence of fluorescent properties of the molecules.

It should be emphasized that the protonation of nitrogen atom and its consequences (changes of photochromic and fluorescent properties) are reversible. So, subsequent addition of DBU or ammonia to acidified solutions returns their properties back to the initial values.

4. Conclusion

A series of new fluorescent diarylethenes with cyclopentenone ethene "bridge" containing electron donating dialkylamino groups in ethene fragment or in aryl moieties of 2,3-diarylcyclopent-2-en-1-ones have been synthesized. It was shown that the compounds possess three types of activities – photochromic, fluorescent, acidochromic – which leads to photo- and pH-switchable emission of these diarylethenes. It has been that the most promising fluorescent switches can be obtained based on 2,3-diarylcyclopent-2-en-1-ones with dialkylamino groups incorporated in ethene "bridge" due to their thermal stability and sensitivity to visible light. It has been established that the introduction at the second position of the cyclopentenone ring the benzene residue leads to the disappearance of the photochromic properties.

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