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Synthesis and spectral properties of fluorescent photochromic diarylethenes with 6,6a-dihydropentalene-2(1*H*)-one ethene "bridge"

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ABSTRACT

An alternative synthetic strategy for the preparation of 6,6a-dihydropentalene-2(1*H*)-one derivatives comprising the stage of the regioselective α-bromination of cyclopentenone system has been proposed. The method along with the bromination process includes the alkylation of ethyl 4-aryl-3-oxobutanoate with bromocyclopentenones and intramolecular carbocyclization reaction of alkylated product. The cyclization reaction has been studied in detail and it was found that the yields of the main and side products depend strongly on alkali concentration, and the method can be also used to design 8,8a-dihydrocyclopenta[a]inden-2(1H)-one unit. The spectral properties of the compounds obtained have been studied, and it was found that pentalenone derivatives as well as starting cyclopentenones, exhibit photochromic properties; in addition, the former, unlike the latter, are also fluorescent.

1. Introduction

The compounds containing cyclopent-2-en-1-one rings in their structures are of great importance because of the prevalence in natural products and other bioactive compounds as well as its applications in various aspects of science and medicine [1–5]. Thus, the jasmons (2,3-dialkylcyclopent-2-en-1-ones) are utilized in perfumes, cosmetics and as a food flavorings [6–9]; methylenomycins (2,3-dialkyl-5-methylenecyclopent-2-en-1-one) are known to be an antibiotics effective against both Gram-negative and Gram-positive bacteria [10–13]; 2,3-diarylcyclopent-2-en-1-ones (DCPs) were found to be useful for medicine as non-steroidal anti-inflammatory [5,14,15] and antitumor [1,16,17] agents.

5-, 6-, 7-Membered cycloalkenones annelated to a cyclopentene, cyclohexene, indanone and other similar rings are under extensive investigation in medicinal chemistry because of their high biological activity. For example, tetrahydrofluorenones due to its structural similarity to 17β-estradiol are a new class of estrogen receptor β-subtype selective ligands [18–21], while cyclopenta[*a*]inden-2-ones can be employed for the treatment of brain edema [22,23].

Recently, we have found that DCPs are a new promising class of photochromic diarylethenes with easily modifiable ethene "bridge" [3,24–26]. Thereby, our previous work devoted to the synthesis of DCPs by means of a convenient method for the cyclopent-2-en-1-one ring construction urged us to use the same technique to annelate the second cyclopent-2-en-1-one ring to DCPs molecules. The resulting compounds – 3,4,5-triaryl-6,6a-dihydropentalene-2(1*H*)-ones – could possess both above-mentioned biological and pharmacological activities and demonstrate new improved photochromic parameters.

2. Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer. 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. High resolution mass spectra were obtained on a Bruker maXis spectrometer.

Commercially available reagents and solvents were used. 2,3-Bis(2,5-dimethylthiophen-3-yl)cyclopent-2-en-1-one **1** [3] and 5-bromo-2,3-bis(2,5-dimethylthiophen-3-yl)cyclopent-2-en-1-one **2**

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[24] have been prepared by the previously reported methods. Column chromatography was performed using silica gel 60 (70–230 mesh); TLC analysis was conducted on silica gel 60 F_{254} plates.

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 (Acros) 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 6 W Vilber Lourmat (France) UV-lamp model VL-6.LC (365 nm light). The fluorescence quantum yields were determined by comparing with quinine bisulfate in 0.1 N H_2SO_4 ($\varphi_{em} = 0.55$) [27] 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 [3,28].

2.1. Alkylation of ethyl 4-aryl-3-oxobutanoates (3) with bromoketones (2 and 12) (general method)

To a solution of corresponding ethyl 4-aryl-3-oxobutanoate **3** (2.0 mmol) in abs. benzene (5 mL) metallic sodium (0.05 g, 2.05 mmol) was added and the mixture was stirred overnight (sodium dissolved entirely). To this solution under boiling point corresponding bromoketone (**2** or **12**) (0.38 g, 1.0 mmol) was added and reaction mixture was reflux for 5 h, then poured into cold water (100 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic phases were washed with water (40 mL), dried with magnesium sulfate and evaporated in vacuum. The residue was purified by column chromatography eluting by petrol. ester/ethyl acetate 8:1. Diketoester **13** was used in further synthesis without additional purification.

2.2. Ethyl 2-[3,4-bis(2,5-dimethylthiophene-3-yl)-2-oxocyclopent-3-en-1-yl]-4-(naphthalen-1-yl)-3-oxobutanoate (4a)

Yield 0.39 g (71%), grey powder, Mp 63–64.5 °C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.18, 1.22 (2t (keto-enol tautomers), J = 7.2 Hz, 3H, $CH_2\underline{CH_3}$), 1.88 (m, 6H, 2Me), 2.32–2.49 (m, 6H, 2Me), 2.90 (dd, J = 3.6, 18.2 Hz, ½$\underline{CH_2}$CH), 2.99–3.08 (m, 1.5H), 3.19–3.29 (m, 1H), 4.01–4.53 (m, 5H), 6.39–6.54 (m, 2H, H^{thioph}), 7.35–7.57 (m, 4H,H^{naph}), 7.79–8.01 (m, 3H, H^{naph}). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 13.67, 13.70, 13.79, 13.85, 14.34, 14.72, 14.76, 14.91, 35.19, 35.57, 44.87, 45.07, 48.26, 48.36, 56.10, 56.74, 61.29, 61.45, 123.74, 123.78, 124.75, 124.86, 125.15, 125.24, 125.51, 125.55, 126.15, 127.96, 128.02, 128.36, 128.44, 128.56, 128.59, 129.54, 129.72, 133.26, 133.51, 135.01, 135.08, 135.45, 135.57, 136.15, 136.33, 137.24, 164.04, 164.44, 167.66, 168.64, 201.66, 201.87, 205.85, 205.89. Mass, m/z (%): 556 (100, $[M]^+$), 387 (28, $[M-\ NaphCH_2C(O)]^+$), 301 (19, $[M-\ NaphCH_2C(O)CHC(O)OCH_2CH_3]^+$). HRMS Calcd for $C_{33}H_{32}O_4S_2$ ($M + Na^+$): 579.1634; Found: 579.1632.

2.3. Ethyl 2-[3,4-bis(2,5-dimethylthiophene-3-yl)-2-oxocyclopent-3-en-1-yl]-4-(1-dimethylthiophen-3-yl)-3-oxobutanoate (4b)

Yield 0.33 g (61%), grey powder, Mp 54–55 °C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.22, 1.30 (2t (keto-enol tautomers), J = 7.2 Hz, 3H, $CH_2\underline{CH_3}$), 1.88–1.95 (m, 6H, 2Me), 2.23–2.43 (m, 12H, 4Me), 2.94 (dd, J = 3.3, 18.0 Hz, ½$\underline{CH_2}$CH), 3.01–3.12 (m, 1.5H), 3.16–3.23 (m, 1H), 3.69 (d, J = 4.0 Hz, 1H), 3.85 (s, 1H), 4.08–4.16, 4.17–4.29 (2 m, 3H), 6.45 (s, 1H, H^{thioph}), 6.47–6.60 (m, 2H, H^{thioph}). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 13.02, 13.07, 14.11, 14.17, 14.69, 15.10, 15.14, 15.16, 15.23, 15.24, 35.52, 35.84, 43.03, 44.98, 45.27, 56.63, 57.14, 61.59, 61.75, 125.07, 125.17, 126.45, 127.38, 127.42, 128.12, 128.24, 128.89, 128.94, 133.62, 133.66, 133.80, 133.93, 134.59, 134.74, 135.30, 135.36, 135.79, 135.87, 135.90, 136.56, 136.68, 137.49, 137.54, 164.40, 164.47, 168.00, 168.98, 201.55, 201.84, 206.08, 206.11. Mass, m/z (%): 540 (98, $[M]^+$), 387 (100, $[M-\ ThCH_2C(O)]^+$), 301 (83, $[M-\ ThCH_2C(O)CHC(O)OCH_2CH_3]^+$). HRMS Calcd for $C_{29}H_{32}O_4S_3$ ($M + Na^+$): 563.1355; Found: 563.1349.

2.4. 3,4,5-Triaryl-6,6a-dihydropentalene-2(1H)-ones (5) and 3-(2,5-dimethylthiophen-3-yl)-8,8a-dihydrocyclopenta[a]inden-2(1H)-one 14 (general method)

A 13%-solution of KOH (1.5 g, 26.8 mmol) in water (10 mL) was added at once to a solution of corresponding diketoesters (**4** or **13**) (0.4 mmol) in ethanol (10 mL). The reaction mixture was refluxed for 2 h, then cooled, poured into water (100 mL) and extracted with ethyl acetate (3 × 30 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. ester/ethyl acetate 6:1 and recrystallized from hexane. When 2%-solution of KOH (0.2 g, 4.00 mmol) in water (10 mL) was used in this reaction by-products **8** and **10** were also isolated.

2.5. 4,5-Bis(2,5-dimethylthiophene-3-yl)-3-(naphthalen-1-yl)-6,6a-dihydropentalen-2(1H)-one (5a)

Yield 0.05 g (27%), brown powder, Mp 74–76 °C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.57 (s, 3H, Me), 1.80 (s, 3H, Me), 1.97 (s, 3H, Me), 2.39 (s, 3H, Me), 2.76 (td, J = 4.5, 18.8 Hz, 1H, ½CH_2C(O)), 2.92–3.17 (m, 3H, ½CH_2C(O), CH_2C–Th), 3.73–3.91 (m, 1H, $CH_2\underline{CH}CH_2$), 6.53–6.67 (m, 2H, H^{thioph}), 7.19–7.32 (m, 2H, H^{Naph}), 7.36–7.50 (m, 2H, H^{Naph}), 7.62–7.71 (m, 2H, H^{Naph}), 7.77–7.84 (m, 1H, H^{Naph}). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 13.94, 14.42, 14.93, 15.13, 42.26, 42.51, 45.32, 124.60, 124.73, 124.93, 125.28, 125.41, 125.54, 125.66, 126.07, 126.50, 127.39, 127.66, 127.96, 129.45, 129.87, 131.86, 132.15, 133.28, 134.83, 136.08, 136.87, 185.50, 207.64 (C=O). Mass, m/z (%): 466 (100, $[M]^+$), 451 (55, $[M-CH_3]^+$). HRMS Calcd for $C_{30}H_{26}OS_2$ ($M + Na^+$): 489.1317; Found: 489.1303.

2.6. 3,4,5-Tris(2,5-dimethylthiophene-3-yl)-6,6a-dihydropentalen-2(1H)-one (5b)

Yield 0.04 g (19%), amorphous brown powder. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.77 (s, 3H, Me), 1.96 (s, 3H, Me), 2.02 (s, 3H, Me), 2.19 (s, 6H, 2Me), 2.34 (s, 3H, Me), 2.52 (dd, J = 4.8, 17.2 Hz, 1H, ½$\underline{CH_2}$C(O)), 2.78 (dd, J = 6.6, 17.2 Hz, 1H, ½$\underline{CH_2}$C(O)), 2.86 (dd, J = 6.2, 15.8 Hz, 1H, ½$\underline{CH_2}$C–Th), 3.00 (dd, J = 7.3, 15.8 Hz, 1H, ½$\underline{CH_2}$C–Th), 3.57–3.67 (m, 1H, $CH_2\underline{CH}CH_2$), 5.90 (s, 1H, H^{thioph}), 5.96 (s, 1H, H^{thioph}), 6.45 (s, H, H^{thioph}). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 13.71, 14.01, 14.86, 14.93, 14.97, 15.19, 41.77, 42.23, 45.27, 125.12, 125.69, 126.55, 126.67, 126.94, 126.99, 127.79, 130.78, 132.16, 134.09, 134.48, 134.91, 136.11, 136.63, 137.47, 151.71, 207.30 (C=O). Mass, m/z (%): 450 (100, $[M]^+$), 435 (65, $[M-CH_3]^+$). HRMS Calcd for $C_{26}H_{26}OS_3$ ($M + Na^+$): 473.1038; Found: 473.1033.

2.7. 2,3-Bis(2,5-dimethylthiophene-3-yl)-5-[3-(naphthalen-1-yl)-2-oxopropyl]cyclopent-2-en-1-one (8a)

Yield 0.06 g (32%), dark brown powder, Mp 35–36 °C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.86 (s, 3H, Me), 1.88 (s, 3H, Me), 2.37 (s, 6H, 2Me), 2.39–2.48 (m, 1H, ½$\underline{CH_2}$C–Th), 2.66 (dd, J = 8.7, 17.7 Hz, 1H, ½$CH\underline{CH_2}$), 2.90–3.02 (m, 1H, $CH_2\underline{CH}CH_2$), 3.11 (d, J = 17.7 Hz, 1H, ½$CH\underline{CH_2}$), 3.15 (dd, J = 2.4, 17.7 Hz, 1H, ½$\underline{CH_2}$C–Th), 4.20 (s, 2H, CH_2^{Naph}), 6.45 (s, 2H, $2H^{thioph}$), 7.39–7.57 (m, 4H, H^{Naph}), 7.80-7.96 (m, 3H, H^{Naph}). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.17, 14.69, 15.09, 15.23, 38.34, 41.31, 42.86, 48.66, 123.90, 125.13, 125.54,

125.91, 126.00, 126.56, 126.69, 128.84, 128.88, 129.05, 130.75, 132.28, 133.67, 134.02, 134.69, 135.22, 135.77, 136.54, 137.44, 164.18, 207.14 (C=O), 208.42 (C=O). Mass, *m/z* (%): 484 (100, $[M]^+$), 343 (37, $[M-NaphCH_2]^+$). HRMS Calcd for $C_{26}H_{28}O_2S_3$ ($M + Na^+$): 507.1423; Found: 507.1417.

2.8. 2,3-Bis(2,5-dimethylthiophene-3-yl)-5-[3-(2,5-dimethylthiophene-3-yl)-2-oxopropyl]cyclopent-2-en-1-one (8b)

Yield 0.02 g (10%), dark brown powder, Mp 65–67 °C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.87 (s, 3H, Me), 1.88 (C, 3H, Me), 2.28 (C, 3H, Me), 2.35(s, 6H, 2Me), 2.36(s, 3H, Me), 2.49 (dd, $J = 2.9$, 18.0 Hz, 1H, ½CH_2C–Th), 2.60 (dd, $J = 9.2$, 18.0 Hz, 1H, ½$CHCH_2$), 2.87–2.95 (m, 1H, CH_2CHCH_2), 3.06 (dd, $J = 3.7$, 17.6 Hz, 1H, ½CH_2C–Th), 3.15 (dd, $J = 7.2$, 18.2 Hz, 1H, ½$CHCH_2$), 3.55 (s, 2H, CH_2Th), 6.43 (s, 1H, H^{thioph}), 6.46 (s, 1H, H^{thioph}), 6.48 (s, H, H^{thioph}). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 13.11, 14.19, 14.72, 15.12, 15.16, 15.25, 38.40, 41.27, 43.06, 43.08, 125.08, 126.50, 127.14, 128.88, 129.02, 133.17, 133.68, 134.65, 135.18, 135.80, 136.09, 136.60, 137.41, 164.12, 206.37 (C=O), 208.42 (C=O). Mass, m/z (%): 468 (47, $[M]^+$), 343 (45, $[M- ThCH_2]^+$), 315 (100, $[M- ThCH_2C(O)]^+$). HRMS Calcd for $C_{26}H_{28}O_2S_3$ ($M + Na^+$): 491.1144; Found: 491.1146.

2.9. [2-Oxo-3,4-bis(2,5-dimethylthiophene-3-yl)cyclopent-3-en-1-yl]acetic acid (10a)

Yield 0.08 g (54%), dark gray powder, Mp 97–98.5 °C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.90 (s, 3H, Me), 1.91 (s, 3H, Me), 2.37 (s, 3H, Me), 2.38 (s, 3H, Me), 2.62 (dd, $J = 7.5$, 15.9 Hz, 1H, ½CH_2COOH), 2.77 (d, $J = 18.3$ Hz, 1H, ½CH_2COOH), 2.93–3.01 (m, 1.5H, CH_2CHCH_2, ¼CH_2C–Th), 3.04 (d, $J = 4.1$ Hz, 0.5H, ¼CH_2C–Th), 3.23 (dd, $J = 6.6$, 18.0 Hz, 1H, ½CH_2C–Th), 6.46 (s, 1H, H^{thioph}), 6.56 (s, 1H, H^{thioph}), 9.29 (br. s, 1H, COOH). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 13.92, 14.52, 14.90, 15.02, 35.31, 37.86, 41.29, 124.84, 126.29, 128.90, 133.36, 134.55, 135.16, 135.70, 136.58, 137.50, 164.25, 177.47 (COOH), 207.59 (C=O). Mass, *m/z* (%): 360 (100, $[M]^+$), 345 (60, $[M-CH_3]^+$), 327 (87, $[M-CH_3-H_2O]^+$), 299 (36, $[M-CH_3-HCOOH]^+$). HRMS Calcd for $C_{19}H_{20}O_3S_2$ ($M + Na^+$): 383.0746; Found: 383.0751.

2.10. 3-(2,5-Dimethylthiophene-3-yl)-8,8a-dihydrocyclopenta[a]inden-2(1H)-one (14)

Yield 0.03 g (22%, calculated from initial bromoketone **12**), amorphous brown powder. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.32 (s, 3H, Me), 2.39 (s, 3H, Me), 2.57 (dd, $J = 4.4$, 16.1 Hz, 1H, ½CH_2C(O)), 2.81 (dd, $J = 8.1$, 17.1 Hz, 1H, ½CH_2C(O)), 2.93 (dd, $J = 6.6$, 17.6 Hz, 1H, ½CH_2-Ph), 3.36 (dd, $J = 8.5$, 16.1 Hz, 1H, ½CH_2-Ph), 3.62–3.77 (m, 1H, CH_2CHCH_2), 6.49 (s, 1H, H^{thioph}), 7.11–7.33 (m, 3H, H^{arom}), 7.38–7.44 (m, 1H, H^{arom}). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 15.17, 15.33, 38.11, 42.54, 45.66, 124.98, 125.91, 126.72, 127.35, 127.50, 128.68, 128.98, 131.74, 132.39, 133.65, 136.21, 149.23, 208.02 (C=O). Mass, *m/z* (%): 280 (2, $[M]^+$), 170 (65, $[M-$ thiophene$]^+$). HRMS Calcd for $C_{18}H_{16}OS$ ($M + H^+$): 281.0995; Found: 281.0999.

2.11. Bromination of 3,4,5-triaryl-6,6a-dihydropentalene-2(1H)-one (5a)

The mixture of ketone **5a** (0.1 g, 0.2 mmol) and cupric bromide (0.11 g, 0.5 mmol) in methanol (5 mL) was stirred for 4 h under room temperature, then 3 h under 40 °C and eventually under refluxing to maximal conversion of starting material (TLC-analysis). The reaction mixture was poured into ice-water (50 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic phases were washed with water (20 mL), filtered through 1 cm layer of silica gel and evaporated. The residue was purified by column chromatography eluting by petrol. Ester/ethyl acetate 11:1 → 5:1 and compounds **15a-d** were isolated.

2.12. 1-Bromo-4,5-bis(2,5-dimethylthiophene-3-yl)-3-(naphthalen-1-yl)-6,6a-dihydropentalen-2(1H)-one (15a)

Yield 0.02 g (17%), brown powder, Mp 73–75 °C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.58 (s, 3H, Me), 1.78 (s, 3H, Me), 1.96 (s, 3H, Me), 2.34 (s, 3H, Me), 3.19–3.46 (m, 2H, CH_2), 4.03–4.19 (m, 1H, $CH_2CHCH(Br)$), 4.87 (dd, 1H, $J = 4.9$, 30.4 Hz, CHBr), 6.48–6.63 (m, 2H, H^{thioph}), 7.19–7.31 (m, 2H, H^{Naph}), 7.38–7.51 (m, 2H, H^{Naph}), 7.62–7.69 (m, 2H, H^{Naph}), 7.72–7.85 (m, 1H, H^{Naph}). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.00, 14.41, 15.05, 15.13, 40.99, 52.34, 55.91, 124.49, 124.65, 124.90, 125.09, 125.22, 125.53, 125.77, 125.94, 126.27, 126.52, 127.13, 127.76, 127.94, 128.17, 128.90, 131.42, 132.08, 133.26, 134.65, 136.35, 137.95, 181.49, 198.73 (C=O). Mass, m/z (%): 544, 546 (76, $[M]^+$), 466 (29, $[M-Br]^+$). HRMS Calcd for $C_{30}H_{25}BrOS_2$ ($M + H^+$): 547.0583; Found: 547.0588.

2.13. 4,5-Bis(2,5-dimethylthiophene-3-yl)-1-methoxy-3-(naphthalen-1-yl)-6,6a-dihydropentalen-2(1H)-one (15b)

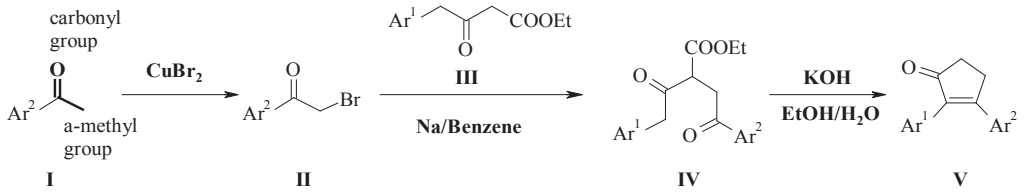
Yield 0.007 g (7%), yellow powder, Mp 66–67 °C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.95 (s, 6H, 2Me), 2.36 (s, 6H, 2Me), 3.21–3.33 (m, 3H, CH_2CH), 3.74 (s, 3H, OCH_3), 4.43 (dd, $J = 4.8$, 29.3 Hz, 1H, CHOMe), 6.50 (s, 2H, H^{thioph}), 7.29–7.48 (m, 3H, H^{naph}), 7.62–7.83 (m, 4H, H^{naph}). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 13.97, 14.41, 14.99, 15.14, 37.44, 48.82, 58.23, 76.50, 124.54, 124.70, 125.07, 125.12, 125.55, 125.75, 126.27, 126.33, 126.51, 127.81, 128.71, 130.01, 130.11, 133.50, 133.65, 134.42, 134.95, 136.11, 136.40, 136.54, 137.32, 160.68, 207.19 (C=O). Mass, *m/z* (%): 496 (100, $[M]^+$), 466 (65, $[M-OMe]^+$). HRMS Calcd for $C_{31}H_{28}O_2S_2$ ($M + Na^+$): 519.1422; Found: 519.1430.

2.14. 1,6a-Dibromo-4,5-bis(2,5-dimethylthiophene-3-yl)-3-(naphthalen-1-yl)-6,6a-dihydropentalen-2(1H)-one (15c)

Yield 0.006 g (5%), black powder, Mp 101–102 °C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.65 (s, 3H, Me), 1.73 (s, 3H, Me), 2.08 (s, 3H, Me), 2.35 (s, 3H, Me), 3.50 (d, 2H, $J = 7.0$ Hz, CH_2), 5.41 (s, 1H, CHBr), 6.37 (s, 1H, H^{thioph}), 6.49 (s, 1H, H^{thioph}), 7.31–7.57 (m, 4H, H^{Naph}), 7.74–7.85 (m, 3H, H^{Naph}), 10.41 (s, enolic OH). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 13.73, 14.46, 14.96, 15.31, 29.76, 35.34, 120.61, 123.11, 124.61, 124.94, 125.70, 126.14, 126.81, 127.03, 127.72, 128.24, 128.41, 128.53, 129.20, 130.95, 131.61, 133.22, 133.58, 134.30, 135.99, 136.91, 137.15, 148.17, 205.53 (C=O). Mass, m/z (%): 622, 624, 626 (5, $[M]^+$), 543, 545 (6, $[M-Br]^+$), 464 (100, $[M-2Br]^+$). HRMS Calcd for $C_{30}H_{25}BrOS_2$ ($M + H^+$): 622.9708; Found: 622.9709.

2.15. 1-Bromo-4,5-bis(2,5-dimethylthiophene-3-yl)-6a-methoxy-3-(naphthalen-1-yl)-6,6a-dihydropentalen-2(1H)-one (15d)

Yield 0.02 g (20%), black powder, Mp 71–72 °C (ethanol). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.64 (s, 3H, Me^{thioph}), 1.74 (s, 3H, Me^{thioph}), 1.98 (dd, 1H, $J = 3.3$, 13.9 Hz, ½CH_2), 2.09 (s, 3H, Me^{thioph}), 2.35 (s, 3H, Me^{thioph}), 2.36–2.43 (m, 1H, ½CH_2), 3.74 (s, 3H, OCH_3), 5.42 (s, 1H, CHBr), 6.50 (s, 1H, H^{thioph}), 6.73 (s, 1H, H^{thioph}), 7.32–7.55 (m, 4H, H^{Naph}), 7.69–7.85 (m, 3H, H^{Naph}). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 13.71, 14.48, 14.99, 15.18, 29.77, 50.70, 75.44, 121.35, 124.54, 124.68, 125.55, 125.79, 126.15, 126.77, 127.74, 127.96, 128.72, 129.55, 130.61, 133.21, 133.35, 133.55, 134.60, 136.24, 137.46, 137.52, 149.00, 168.15, 203.28 (C=O). Mass, *m/z* (%): 574, 576 (11, $[M]^+$), 544 (7,



Scheme 1. Photochromic 2,3-diarylcyclopent-2-en-1-ones **V** synthesis.

[M− OMe]$^+$), 495 (82, [M−Br]$^+$), 480 (15, [M−Br − Me]$^+$). HRMS Calcd for $C_{31}H_{27}BrO_2S_2$ (M + K$^+$): 613.0267; Found: 613.0259.

3. Results and discussion

3.1. Synthesis

Cyclopentenones are useful synthons for the preparation of various cyclopentyl compounds due to the versatility of their functionality. Cyclopent-2-en-1-one ring or cycloalkenones annelated onto indanone cycle is known to be constructed by a various ways including the ring-closing metathesis followed by the allylic oxidative rearrangement [20,21], by Pauson–Khand reaction [29–34] as well as by different methods based on the cyclization of 1,4-dicarbonyl compounds [1,18,23,35,36] similar to the Robinson annelation reaction [37]. But the techniques in most cases involve peculiar and inconvenient processes or require the utilization of reagents difficult of access or lithium and boron organic compounds and, therefore, low temperatures. So, despite of above mentioned practical importance of the cycloalkenones annelated onto a cyclopentene, cyclohexene and indanone rings, there is no convenient and effective method for its preparation.

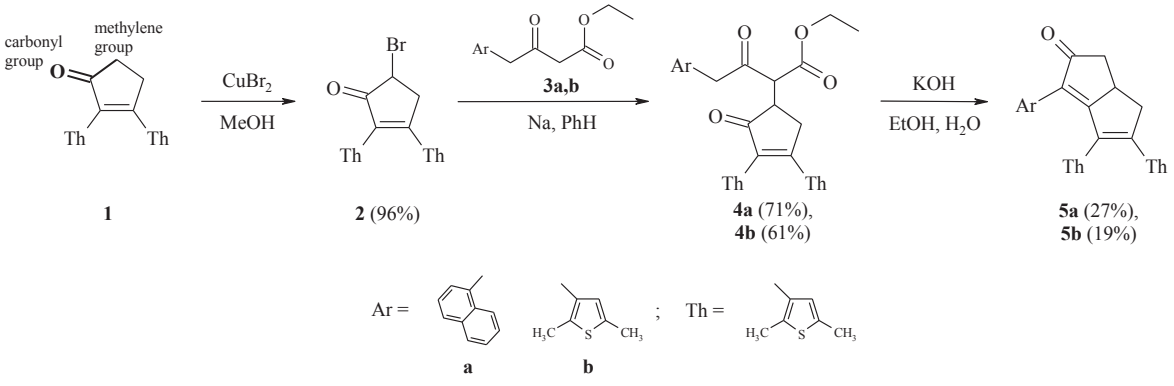
At the same time the recently proposed technique for DCPs synthesis [3] on the basis of ketones **I** pretends to be a convenient way to the cyclopent-2-en-1-one ring construction. It includes the alkylation of ethyl 4-aryl-3-ketobutanoates **III** [38] by α-bromoketones **II** as a key stage followed by the cyclization of intermediate **IV** with potassium hydroxide in aqueous ethanol solution to form DCPs **V** (Scheme 1). This method seems to be useful for cyclopentenone ring building based actually on any compounds containing in its structure (like in the structure of compound **I**) the carbonyl function and methyl (or methylene) group in α-position.

As DCPs **V** contain the carbonyl and methylene groups in its structure, it was then decided to extend this strategy to annelate the second cyclopenten-2-en-1-one ring to ethene "bridge" of DCPs **V**. 2,3-Bis(2,5-dimethylthiophen-3-yl)cyclopent-2-en-1-one **1** was chosen as a starting material for the development of this method (Scheme 2), and at the first step the 5-bromoketone **2** has been prepared by the previously reported technique [24] for the DCPs regioselective bromination with copper (II) bromide.

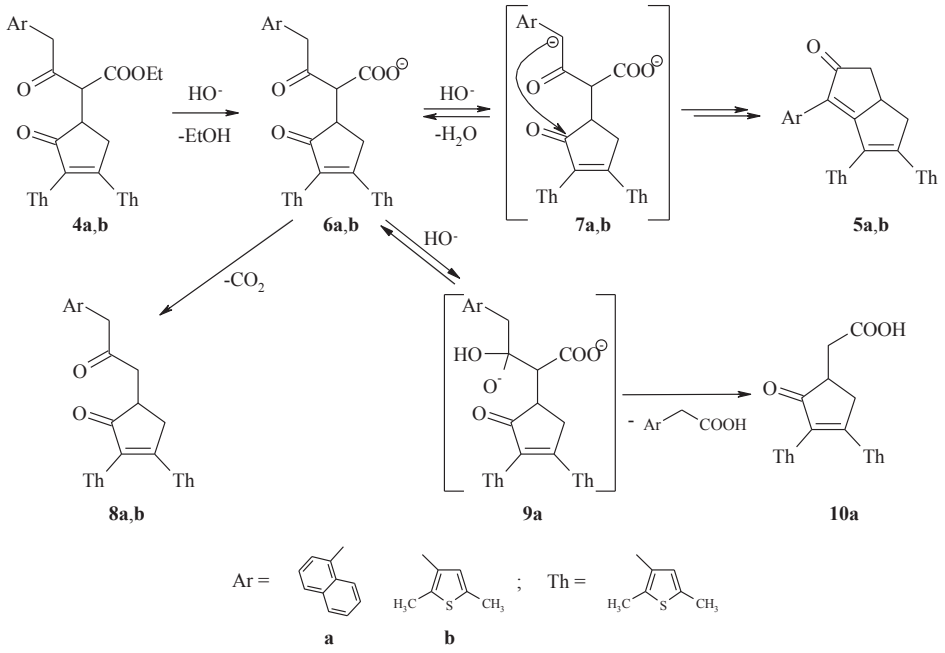
The alkylation of ethyl 4-aryl-3-ketobutanoates **3** with 5-bromoketones **2** in the presence of metallic sodium proved to be different from the similar reaction in DCPs synthesis. Thus, in contrast with the reaction between **II** and **III** (Scheme 1) which have been shown [3] to occur at room temperature, the reaction between compounds **2** and **3** does not proceed in these mild conditions. The fact is likely to be explained by the secondary bromine atom in bromide **2** instead of primary one in bromides **II**, which provides the steric hindrance for attack of the nucleophile. The studies of the alkylation reaction resulted in the optimal conditions, namely, the use of 2-fold excess of ketoesters **3** and the reaction carrying out at the boiling point. Under these conditions the intermediate compounds **4** are obtained with 71% (for **4a**) and 61% (for **4b**) yields after column chromatography, but it was also found that diketoesters **4** can be involved in the subsequent cyclization reaction without additional purification.

As expected, the reaction of the cyclization of compounds **4** with potassium hydroxide in aqueous ethanol solution is not a simple process but is accompanied by different side reactions (Scheme 3). The way of the cyclopentenone ring formation (compounds **5**) includes the initial hydrolysis of esters **4** to form the salts **6** followed by the dianions **7** formation under the alkali action. But the compounds **6** turned out to participate also in other reactions. So, on the one hand the decarboxylation of salt **6** can lead to diketone **8** while the nucleophilic addition of hydroxide anion to carbonyl function of **6** seems to be a way resulting in acid **10a** *via* dianion **9a**. These side reactions were observed when low excess (5–10 eq.) of potassium hydroxide was used. The reaction conditions optimal for ketones **5** synthesis are the following: the use of 13% water solution of KOH (72 eq.) in ethanol, with the ratio of EtOH/H_2O being 1:1. It allows carrying out the cyclization of compounds **4** with the yields of ketones **5a** and **5b** 27% and 19%, respectively.

To show that the proposed method for cyclopent-2-en-1-one ring annelation can be useful not only in case of 2,3-



Scheme 2. Synthetic route for the preparation of 3,4,5-triaryl-6,6a-dihydropentalene-2(1*H*)-ones **5**.



Scheme 3. The ways of formation of 3,4,5-triaryl-6,6a-dihydropentalene-2(1*H*)-ones **5** and by-products **8** and **10**.

diarylcyclopentenones **1**, the technique was extended to indanone **6** (Scheme 4). The bromoketone **11** was prepared by reported method [39] and was employed for 4-(2,5-dimethylthiophen-3-yl)-3-ketobutanoates **3b** alkylation in the optimal conditions mentioned above. The compound **14** has been obtained with total 22% yield by cyclization of diketoester **13**.

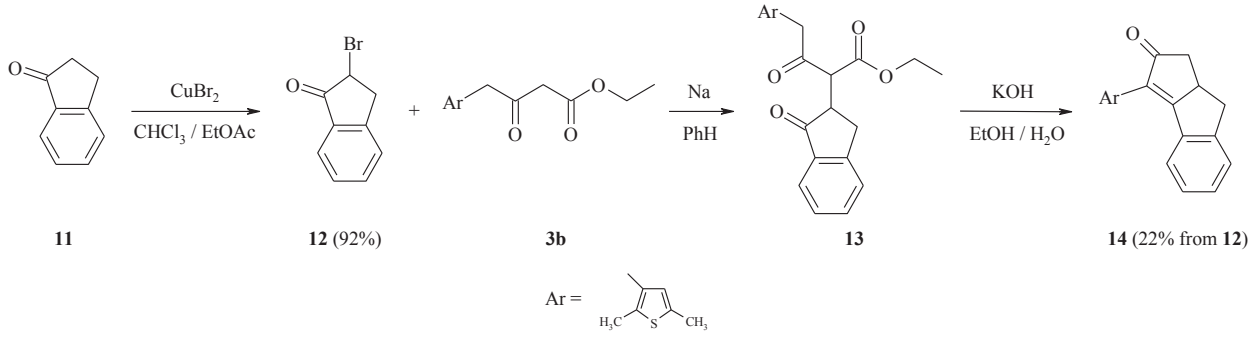
Next, it would very attractive to continue the strategy proposed and to annelate the third cyclopentenone ring to the molecules of compounds **5**, thus, obtaining previously undescribed compounds with three condensed cyclopentene cycles and a carbonyl group. Triaryldihydropentaleneone **5a** was chosen for this way realization and the first step on this way should be the bromination of ketone **5a** into the α-position to carbonyl function (compound **15a**, Scheme 5). However the limiting stage of this synthetic strategy has proved bromination reaction. The same conditions (copper (II) bromide in methanol) were used that have been applied for bromoketone **2** synthesis but as compared with ketones **1** bromination a range of by-products **15b-d** was formed and the conversion of starting material **5a** was not full. All these resulted in desired bromide **15a** with only 17% yield and did not allow synthesizing the substances with three condensed cyclopentene cycles. The main problem in this case seems to be the existence of protone in 6a-position of dihydropentaleneone molecule (shown in bold in structure **5a**, Scheme 5) which leads to the dibromo- **15c** and then to bromo-methoxy- **15d** by-products. The utilization of other brominating reagents such as bromine and *N*-bromosuccinimide resulted in complex mixture of compounds.

3.2. Spectral properties

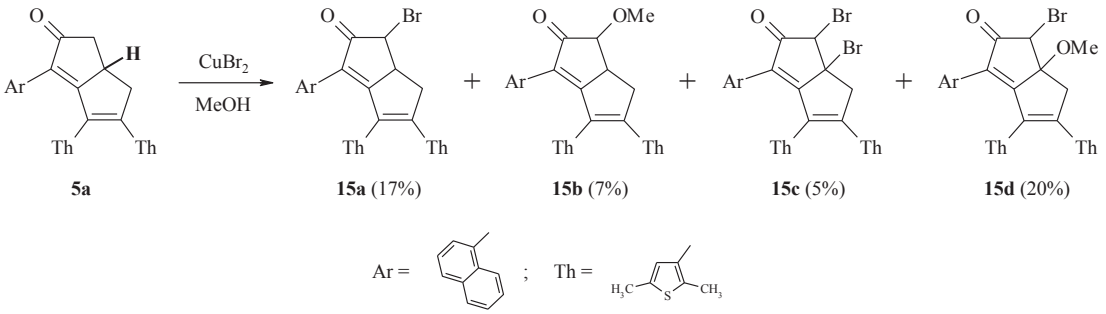
3.2.1. Photochromic properties of diarylethenes

The photochromic characteristics of diarylethenes have been measured in acetonitrile solutions at 293 K with alternating irradiation by UV light ($\lambda^{ir} = 365$ nm) and visible light ($\lambda^{ir} > 400$ nm) and are summarized in Table 1. Upon UV-irradiation, the colorless solutions of DCPs **1** and **5a**,**b** were converted into colored ones and bleached back to colorless under visible light that is due to the reversible electrocyclic reaction of hexatriene system (Scheme 6).

Analyzing the data in Table 1 one can see that the introduction of extended π-system into the ethene "bridge" of DCP **1** considerably influences their properties. As to the spectral parameters of open-ring isomers **A** it should be noted that the transition from DCPs to corresponding dihydropentalenones results in the shift of the absorption band of form **A** to the higher wavelengths region. Whereas the highest value of absorption maximum wavelength of the DCP **1** is detected at 309 nm, for compounds **5a** and **5b** it is red-shifted to 347 nm and 351 nm respectively. Such absorption bands shift towards the visible spectrum region is known to be a



Scheme 4. The preparation of 3-(2,5-dimethylthiophen-3-yl)-8,8a-dihydrocyclopenta[*a*]inden-2(1*H*)-one **14**.



Scheme 5. The bromination of triaryldihydropentaleneones **5a** with copper (II) bromide.

Table 1
Spectral characteristics of initial and photoinduced forms of diarylcyclopentenones **1**, **5** in acetonitrile ($C = 2 \cdot 10^{-5}$ mol L^{-1}) at 293 K.

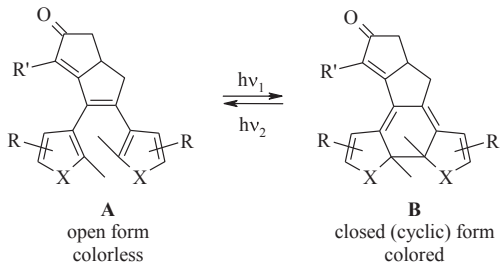
Entry	Photochromism					Fluorescence			
	Compound	λ_A[a], nm (ε, L mol^{-1} cm^{-1})	λ_B[b], nm (ε, L mol^{-1} cm^{-1})	$\varphi_{A \rightarrow B}$[c]	$\varphi_{B \rightarrow A}$[d]	λ_{ex}[e], nm	λ_{em}[f], nm	φ_{em}^{open}[g]	φ^{UV}[h]
1	**1**	208 ($1.64 \cdot 10^4$), 245 ($1.46 \cdot 10^4$), 309 ($6.43 \cdot 10^3$)	547 ($1.11 \cdot 10^4$)	0.27	0.065	Non fluorescent			
2	**5a**	278 ($5.04 \cdot 10^4$), 347 ($1.48 \cdot 10^4$)	522 ($2.95 \cdot 10^4$)	0.03	0.001	347	503	0.26	0.04
3	**5b**	251 ($2.18 \cdot 10^4$), 351 ($1.33 \cdot 10^4$)	523 ($6.40 \cdot 10^4$)	0.07	0.001	351	509	0.17	0.03

[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 (for compound **5a**) or 3-Min (for compound **5b**) UV-irradiation ($\lambda^{ir} = 365$ nm).

promising feature of compounds, as for different practical applications (for example for optical memories and fluorescent switches [40] or medicine diagnostics [41,42]) it is significant to handle diarylethenes which can be processed by visible rather than UV light, because the higher the wavelength of light the lower its energy and hence the less destructive it is.

The spectral properties of closed-ring isomers **B** of diarylethenes synthesized were found to be also influenced by the ethene "bridge" structure. First, the data in Table 1 witness that the "bridge" π-system elongation leads to essential hypsochromic shift of the absorption bands of colored forms **B** (from 547 nm for DCP **1**–522 nm or 523 nm for compounds **5a** and **5b** correspondingly). On the other hand, the presence of extended π-system in ethene "bridge" was found to lead to the increase of molar extinction coefficients of diarylethenes. And high values of extinction coefficients are known to be responsible to high sensitivity of photochromic substances and materials [40].

The compounds with the extended π-system located in the aryl groups are well-known from the literature [43–47] and it would be



Scheme 6. Photochromic reactions of diarylethenes.

of interest to compare their properties with those of diarylethenes **5**. First, it should be mentioned that the elongation of π-system *via* double bonds both in aryl moieties and in ethene "bridge" leads to the same effect namely, bathochromic shift of absorption bands of initial forms **A** of diarylethenes. As to photoinduced forms **B** the influence of π-system elongation is different: the elongation in aryl moieties results in bathochromic shift of the absorption bands rather than hypsochromic one as in the case of ethene "bridge".

As for quantum yields of photochromic cyclization and cycloreversion reactions, their values are also significantly affected by the compounds structure. Namely, the introduction of extended π-system into the ethene "bridge" of DCP **1** is seen from Table 1 to induce the reduction of cyclization and recyclization quantum yields (compounds **5a**,**b**). Diarylethenes **5a**,**b** are fluorescent substances (see Section 2.3 below) and their quantum yields reduction therefore can be explained by the competition between photochromism and fluorescence processes: light energy absorbed is spent both to photochromic reactions and to emission, which leads to essential suppression of the firsts [48]. In contrary, in case of non-fluorescent DCP **1** more light energy participates in photochromic reactions, thus, its quantum yields are higher than those of compounds **5a**,**b**.

3.2.2. Thermal stability and fatigue resistance of diarylethenes

The thermal stability and fatigue resistance of diarylethenes synthesized were measured in acetonitrile solutions ($C = 2 \cdot 10^{-5}$ mol L^{-1}) at 293 K in air and its values are summarized in Table 2.

It turned out that the synthesis of dihydropentaleneones **5a**,**b** is promising transformation of ethene "bridge" of DCP **1** which leads to the improvement of both fatigue resistance of compounds and its

Table 2
Fatigue resistance and thermal stability of diarylcyclopentenone **1** and its derivatives **5a**,**b**.

Entry	Compound	Fatigue resistance (number of switching cycles)[a]	Thermal stability $\left(\tau_{1/2}{}^{B\rightarrow A}_{\text{therm}}, h\right)$#[b]
1	**1**	50	939
2	**5a**	100	3051
3	**5b**	75	2657

[a] Measured in air at 293 K under alternative irradiation with UV- ($\lambda^{ir} = 365$ nm) and visible ($\lambda^{ir} > 400$ nm) light.
[b] Half-lifes of the closed-ring isomers measured in air at 293 K in the dark after exposure of compounds to UV-light ($\lambda^{ir} = 365$ nm) (values obtained by kinetic data processing).

thermal stability. So, the transition from compound **1** to compounds **5a**,**b** results to the 1.5÷2-fold increasing of switching cycles number while the half-lifes of the closed-ring isomers **B** grow from 939 h (for DCP **1**) up to approximately 3000 h for dihydropentaleneones **5a**,**b**.

As high thermal stability and fatigue resistance are two main properties of photochromic compounds essential for its various applications [40] the synthesis of dihydropentaleneones can serve as one of the ways of the improvement of these characteristics.

3.2.3. *Fluorescent properties of diarylethenes and emission switching under UV/visible light*

Dihydropentaleneones **5a**,**b** with extended π-system in ethene "bridge" turned out to possess the emission. The fluorescence of these compounds might be explained not only by the extended π-system but also by the transfer of absorbed energy to the side aryl group (thienyl or naphthyl moiety). Their fluorescent properties have been examined in acetonitrile solutions at 293 K and the switching parameters have been measured under alternating UV ($\lambda^{ir} = 365$ nm) and visible light ($\lambda^{ir} > 400$ nm) irradiation (Table 1 and Figure 1), with the excitation wavelengths (λ_{ex}) being at maxima of corresponding excitation spectra.

Considering the data in Table 1 and Fig. 1, first of all one can see that the emission bands of diarylethenes **5** have a good matching

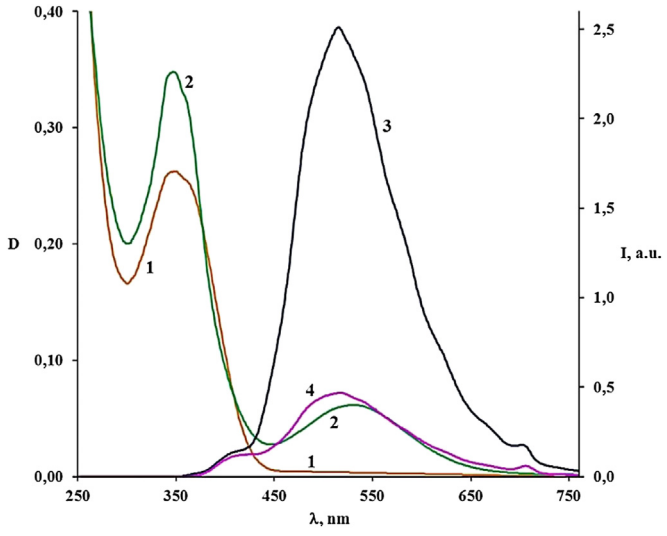


Fig. 1. Spectral changes of fluorescent switch **5b** under UV-irradiation. Absorption spectra (left axis) of DCP **5b** ($C = 2.0 \times 10^{-5}$ mol L^{-1} in CH_3CN) at 293 K: before irradiation (curve **1**) and after 3-Min UV irradiation ($\lambda^{ir} = 365$ nm, curve **2**). Emission spectra (right axis) of DCP **5b** ($C = 2.0 \times 10^{-6}$ mol L^{-1} in CH_3CN) at 293 K with emission excitation at $\lambda_{ex} = 351$ nm: before irradiation (curve **3**) and after 3-Min UV irradiation ($\lambda^{ir} = 365$ nm, curve **4**).

with their bands of absorption: the difference between λ_B and λ_{em} are as little as 19 nm for compound **5a** and 14 nm for compound **5b**. These effective overlaps are known to be an essential factor for the design of switches capable of fluorescence modulation.

The fluorescence quantum yields of diarylethenes **5** (φ_{em}^{open}) were measured using quinine bisulfate in 0.1 N H_2SO_4 as a reference [25]. It was found that both the emission intensity and its quantum yields are sensitive to UV-light, namely, the parameters decrease under UV-irradiation. Moreover, this phenomenon is the reversible process and under visible light the emission of compounds **5** is revived. The mentioned-above is illustrated by Fig. 1 where absorption and emission spectra of diarylethene **5b** are depicted. One can clearly see that after UV-irradiation along with the appearance of the absorption band at visible spectrum region (523 nm, curve **2**) the 5-fold reduction in the fluorescence intensity is detected (from approx. 2.5 a.u. (curve **3**) to approx. 0.5 a.u. (curve **4**)).

Such UV-induced fluorescence quenching effect is likely to be explained by various aspects. First, considering that it is colorless isomers **A** of diarylethenes **5** which possess the emission and the closed-ring isomers **B** are non-fluorescent (at least have no emission bands at 503 nm for **5a** and 509 nm for **5b**), it can be assumed that UV-induced emission reduction is due to the decrease in the concentration of initial isomers **A** during the photocyclization. Other causes of compounds **5** fluorescence decay under UV-light can be the capture of the part of emission by colored isomers **B** (because of broad overlap between bands of emission and absorption of colored isomers **B**), or the absorption of excitation photons by forms **B**. All these processes are likely to proceed simultaneously leading eventually to the fluorescence quenching observed.

So, the reversible emission quenching under alternative UV and visible irradiations can be the basis for the molecular switches.

4. Conclusions

A novel synthetic protocol to synthesize 6,6a-dihydropentalene-2(1*H*)-one derivatives in three stages including the regioselective bromination at α-position of cyclopentenone ring, the alkylation of ethyl 4-aryl-3-oxobutanoate with bromocyclopentenones and intramolecular carbocyclization reaction of alkylated product has been proposed. The investigation of the cyclization reaction shown that the main and side products yields depend significantly on the concentration of alkali. It was shown that the method can also be used to design 8,8a-dihydrocyclopenta[a]inden-2(1*H*)-one unit. The photoswitching properties of the compounds obtained have been studied, and it was found that pentalenone derivatives as well as starting cyclopentenones, exhibit photochromic properties; in addition, the former, unlike the latter, are also fluorescent.

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