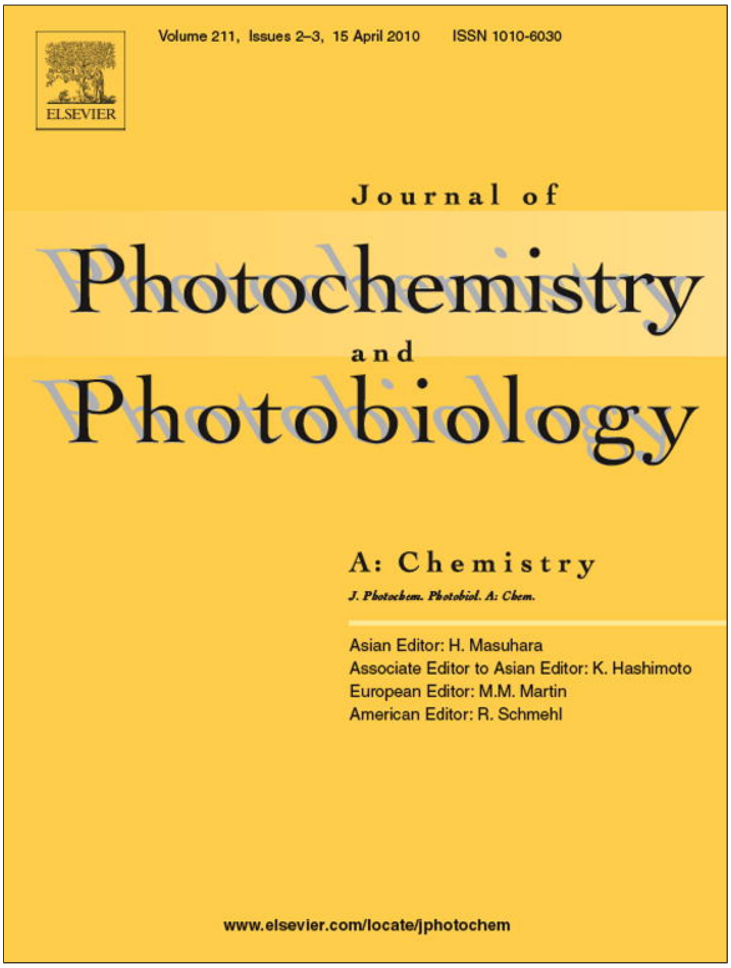

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Synthesis, spectroscopic characterization and photophysics of new functionalized 2,3-distyrylfurans: Substituent and solvent effects on their photobehavior

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ABSTRACT

Two new groups of *p*-chloro-, *p*-methoxy- and *p*-nitro-substituted derivatives of the *trans*,*trans*-isomers of 2,3-distyrylfuran have been synthesized by a sequence of reactions according to known methods. These new conjugated heterocyclic compounds along with the parent one and its methyl-derivative have been characterized spectrally, photophysically and photochemically. These compounds, except for the nitro-derivatives, display high fluorescence quantum yields in the non-polar *n*-hexane ($\Phi_F = 0.76–0.98$). In ethanol of high polarity, the lifetime of their singlet excited state increases from 1.31–2.59 ns to 2.01–4.77 ns, significantly enhancing the quantum yield of their photochemical reaction from 0.02–0.24 to 0.25–0.46, and diminishing their fluorescence efficiency ($\Phi_F = 0.26–0.64$). Deviating from the other compounds studied, the quantum yields for both the fluorescence and the photolysis of the nitro-derivatives are rather low ($\Phi_F < 10^{-4}$, $\Phi = 0.025–0.042$ in ethanol), probably due to an efficient intersystem crossing leading to a non-reactive triplet state. Accordingly, their singlet-state lifetime is also relatively short ($\tau_F < 0.3$ ns).

1. Introduction

Numerous types of heteropolycyclic compounds with conjugated bond structure play important roles in both natural and artificial systems due to their peculiar photochemical and photophysical properties [1,2]. While these kinds of molecules with nitrogen heterocycles such as porphyrins and diimines are involved in visible light-driven photoinduced processes predominantly as metal complexes [3–10], those with oxygen heterocycles undergo various photochemical reactions upon UV irradiation [11–15].

Furan derivatives are of great importance due to their role in organic chemistry as building blocks in various synthetic routes and because they are involved in numerous natural compounds [16,17]. Unsaturated furan and benzofuran derivatives containing furan rings connected through vinylene links are the starting materials for photochemical reactions [18–21]. These types of compounds offer potential applications as fluorescent probes in biology and medicine, in environmental and analytical sciences as well as in optoelectronics [22,23]. Besides, some 2,3-distyryl-substituted furan derivatives proved to be applicable in electrophotographic photoreceptors as charge transporting agents [24–26]. The special photoinduced properties of these molecules have drawn our attention to their design, synthesis and study.

Recently, synthesis, photophysical and photochemical study of some new furan and benzofuran derivatives have been realized [21,27–30]. In the case of 2,3-distyryl benzofurans **1** (Scheme 1), hexatriene systems with the central double bond incorporated into the furan ring, both the characteristic absorption and the emission bands proved to be significantly influenced by the substituent on the phenyl group connected to the furan ring through vinylene links [28]. Except for the nitro-substituted compound, they displayed efficient fluorescence with rather short lifetimes. However, solvent polarity significantly affected the photophysical properties of the nitro-derivative, while the corresponding behavior of the other compounds studied was slightly or moderately solvent-dependent. UV irradiation of these molecules did not result in trans–cis isomerization nor an intramolecular cycloaddition reaction. Instead, intermediary formation of polymeric cyclobutane structures was suggested on the basis of stilbene-like end-products. Conformation study of these benzofuran derivatives indicated that the conformations are not planar and those rotational isomers are energetically preferred in which the distance of the two vinyl links, and thus that of the phenyl groups, are larger [30]. This result confirms the lack or very low efficiency of photoinduced trans–cis isomerization and intramolecular cycloaddition reactions. Very similar photo-

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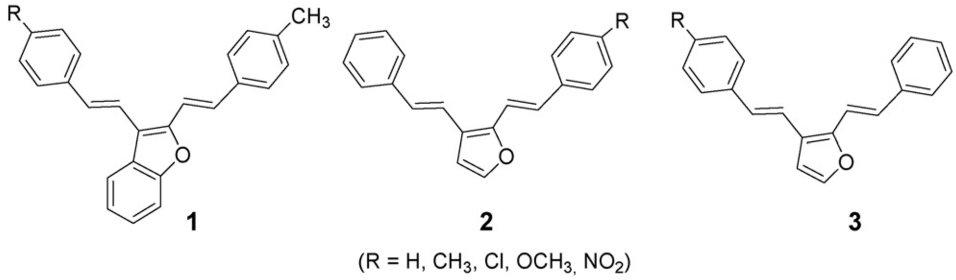


Scheme 1.

chemical behavior was observed for 2,3-distyrylfuran derivatives (**2** (R = H), **3** (R = CH_3)) [21].

Detailed photophysical and conformation studies were also made on unsubstituted 2,3- and 2,5-di(phenylethenyl)furan derivatives [27]. Similarly to the benzofuran derivatives **1**, for 2,3-distyrylfuran derivative **2** (R = H) the non-planar conformations are energetically favorable, and in the most stable rotamer the distance of the phenyl groups is the longest possible. The latter theoretical results are confirmed by the X-ray crystal structure of methyl-substituted 2,3-distyrylfuran derivative **3** (R = CH_3) [20]. However, for 2,5-distyrylfurans the planar conformations are preferred, and in the most stable rotamer the distance of the phenyl groups is the shortest possible. Since irradiation of these organic fluorophores resulted in a photoisomerization equilibrium totally shifted towards the *trans*,*trans*-isomers of these distyrylfuran compounds, only these isomers were studied from the viewpoints of conformation and photoinduced behavior [27]. Their absorption and emission spectra display a slight solvent-dependence, while their fluorescence lifetimes and quantum yields are significantly affected by the solvent polarity–non-polar solvents increase these parameters.

Deviating from the corresponding benzofuran compounds **1**, the substituted derivatives **2** and **3** (R ≠ H, CH_3) have not been prepared yet, although the study of the photoinduced properties of these fluorophores and the comparison with those of the previous molecules may reveal general tendencies and correlations of their characteristics, promoting their potential applicability in biological and analytical sciences.

Thus, as a natural continuation of our studies regarding 2,3-distyrylbenzofurans **1** and unsubstituted 2,3-distyrylfuran **2** and/or **3** (R = H), in this work we publish the synthesis of two new groups of *p*-chloro-, *p*-methoxy- and *p*-nitro-substituted derivatives **2** and **3** (having a substituent in the *p*-position on one of the benzene rings), their spectral characterization, and the detailed investigation of the photophysical behavior of these compounds. For comparison, the corresponding measurements were also carried out with the unsubstituted compound **2** (R = H) and the *p*-methyl-substituted derivative **3** (R = CH_3) [21].

2. Experimental

2.1. General

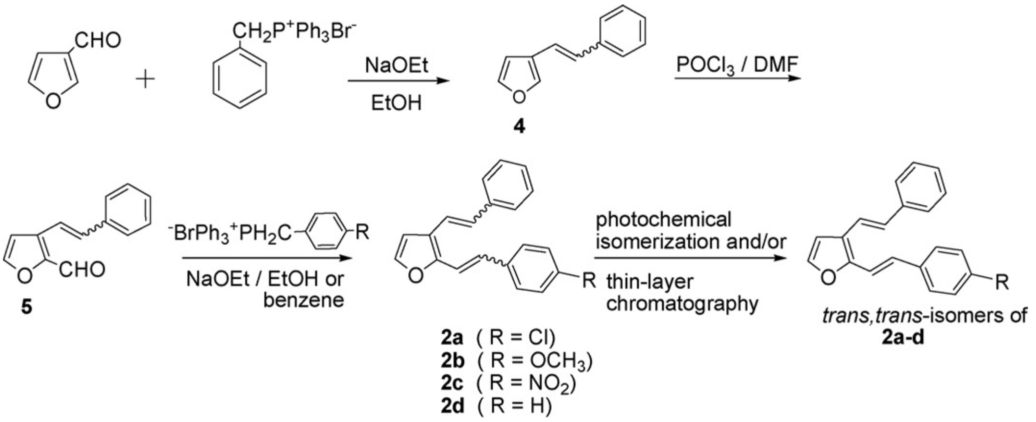
The ^1H and ^{13}C NMR spectra were recorded on a Bruker AV-600 Spectrometer at 300 and 600 MHz and 75 or 150 MHz, respectively. All NMR spectra were measured in $CDCl_3$ using tetramethylsilane as reference. UV spectra were measured on a Varian Cary 50 UV/VIS Spectrophotometer and a SPECORD S-100 diode array spectrophotometer. For the measurement of fluorescence and excitation spectra a PerkinElmer LS50B spectrofluorimeter was applied. Luminescence lifetime measurements were performed using a laser flash photolysis system previously described [31]. A Quantel Brilliant Nd:YAG laser yielding 355-nm pulses of about 5 ns duration served as a light source. All the new compounds were identified and proved by GC–MS system getting chromatograms and mass spectra. The GC–MS analyses were performed on a Varian CP-3800 Gas Chromatograph-Varian Saturn 2200 equipped with FactorFour Capillary Column VF-5ms, 30 m × 0.25 mm i.d.; GC operating conditions for all experiments: column temperature programmed from 110 °C to 300 °C (6 min isothermal) at a rate of 33 °C min^{-1}; carrier gas: helium; flow rate: 1 mL min^{-1}; injector temperature: 300 °C; volume injected: 5 μL. Melting points were obtained using an Original Kofler Mikroheitztisch apparatus (Reichert, Wien) and are uncorrected. Elemental analyses were carried out on PerkinElmer, Series II, CHNS Analyzer 2400. Silica gel (Merck 0.063–0.2 mm) was used for chromatographic purifications. Thin-layer chromatography (TLC) was performed on Merck precoated silica gel 60 F_{254} plates. Solvents were purified by distillation. Boiling range of petroleum ether, used for chromatographic separation, was 40–70 °C. Furan-3-carboxaldehyde was obtained from a commercial source (Aldrich). Benzyltriphenylphosphonium bromide, and *p*-chloro-, *p*-methoxy- and *p*-nitrobenzyltriphenylphosphonium bromides were synthesized from the corresponding bromides and triphenylphosphine in benzene solution.

2.2. Preparation of ***2a–c*** and ***3a–c***

The new functionalized 2,3-distyrylfurans **2a–c** and **3a–c** were prepared *via* three-step synthesis according to known methods (Schemes 2 and 3). In the first step by Wittig reaction from furan-3-carboxaldehyde and corresponding aryltriphenylphosphonium bromides (R = H, Cl, OCH_3, NO_2), the 3-styryl derivatives **4** [20] and **6a–c** were synthesized, and formylated using *N*,*N*-dimethylformamide and $POCl_3$ producing the corresponding formyl derivatives **5** and **7a–c**. These products were the starting compounds for the second Wittig reaction with the other respective triphenylphosphonium salts resulting in 2,3-divinylfuran derivatives **2a–c** and **3a–c** as mixtures of configurational isomers. The *trans*,*trans*-isomers **2a–c** and **3a–c** were isolated combining thin-layer and column chromatography and/or photochemical isomerization (Schemes 2 and 3). Related derivatives *trans*,*trans*-**2d** and *trans*,*trans*-**3d**, parent one and its methyl-derivative, have been already characterized spectrally earlier [20,27], and here their photophysically and photochemically characterization is broadened for comparison with the new compounds.

2.2.1. Preparation of ***2a–c***

Compounds **2a–c** were prepared in three steps by two Wittig reactions and Vilsmeier formylation (Scheme 2). In the first step 3-styrylfuran **4** was prepared by Wittig reaction from benzyltriphenylphosphonium bromide and freshly distilled furan-3-carboxaldehyde. To a stirred solution of benzyltriphenylphosphonium bromide (7.85 g, 18.1 mmol) and furan-3-carboxaldehyde (1.74 g, 18.1 mmol) in absolute ethanol (100 mL) a solution of sodium ethoxide (0.442 g, 19.2 mmol in 20 mL ethanol) was added dropwise. Stirring was continued under a stream of nitrogen for

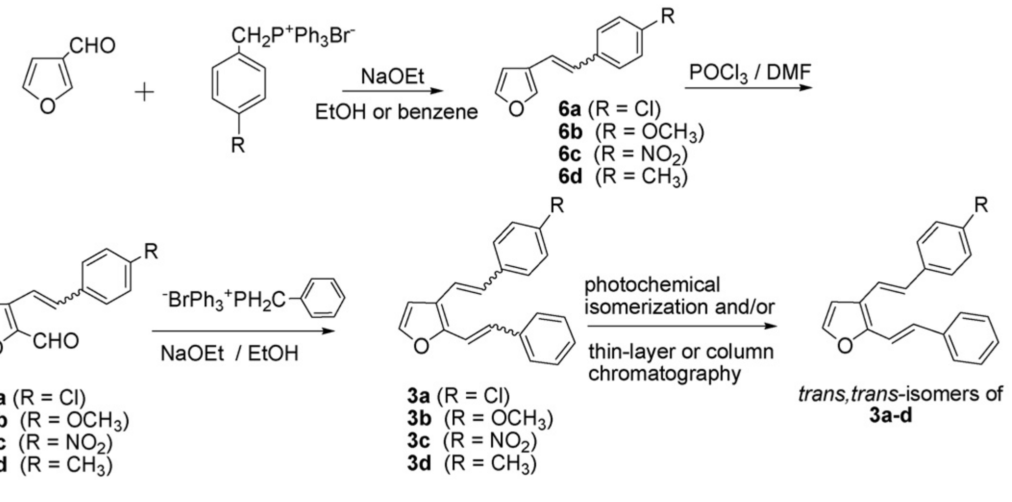


Scheme 2.

3 h at RT. After removal of the solvent, the residue was worked up with water and benzene. The benzene extracts were dried and concentrated. The crude reaction mixture was purified by column chromatography on silica gel using petroleum ether as eluent. Vilsmeier formylation was carried out from 3-styrylfuran **4** (0.99 g, 5.8 mmol) dissolved in dimethylformamide (1 mL, 18.8 mmol). After adjusting the temperature at ∼12 °C, phosphorus-oxychloride (0.89 g, 5.8 mmol) was added and the reaction mixture was allowed gradually to warm up to room temperature and stirred for 24 h. The reaction mixture was decomposed by the continuous addition (with cooling) of sodium hydroxide solution (10%) and the product was worked up with diethylether. The diethylether extracts were washed with water. After removal of the solvent, the crude reaction mixture of 2-formyl-3-styrylfuran **5** (as a mixture of *cis*- and *trans*-isomer) was used in a Wittig reaction to prepare 2,3-distyrylfuran derivatives **2a–c**. To a stirred solution of formyl derivative **5** (0.106 g, 0.52 mmol) and the phosphonium salts (0.52 mmol in 50 mL of: absolute ethanol, R = Cl, OCH_3 or benzene, R = NO_2), sodium ethoxide (0.014 g, 0.61 mmol in 10 mL ethanol) was added. Stirring was continued under a stream of nitrogen for 1 day at RT. After removal of the solvent, the residue was worked up with water and benzene. The benzene extracts were dried and concentrated. The crude reaction mixture was purified and the mixture of 4 isomers of **2a–c** was isolated by column chromatography on silica gel using petroleum ether/diethylether (0–5%) as eluent. After the photochemical isomerization of the photomixtures of **2a** and **2c** the *trans*,*trans*-isomers of **2a** and **2c** were isolated as the main isomers. A mixture of isomers of **2a** and **2c** in benzene ($\sim 4.0 \times 10^{-3}$ M) was purged with argon for 15 min and irradiated at 350 nm in a Rayonet reactor in a quartz tube. After 20 min the reaction mixture of **2a** contained 90% of the *trans*,*trans*-isomer. The solvent was removed in vacuum and the oily residue chromatographed on silica gel using petroleum ether to isolate pure *trans*,*trans*-**2a** in the last fractions. Reaction mixture of **2c** was completely isomerised to *trans*,*trans*-isomer of **2c** after 90 min of irradiation. The photochemical isomerization was followed by NMR measurements with time. Isomers of **2b** were separated by repeated thin-layer chromatography using petroleum ether/diethylether (3–7%) mixture as eluent. Characterization data of the new compounds *trans*,*trans*-**2a–c** are given below.

trans,*trans*-2-[2-(4-Chlorophenyl)ethenyl]-3-(2-phenylethenyl)furan (*trans*,*trans*-**2a**): Yield 66%; R_f 0.37 (petroleum ether/diethylether 10:0.1); yellow crystals; mp 129 °C; UV (EtOH) λ_{max} (log ε) 384 (4.32, sh), 364 (4.47), 347 (4.37, sh), 284 (4.28), 276 (4.27, sh) nm; ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 7.51 (d, *J* = 8.0, 2H), 7.44 (d, *J* = 8.40 Hz, 2H), 7.38 (d, *J* = 1.7 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.25–7.28 (m, 1H), 7.11 (d, *J* = 15.8 Hz, 1H, H_{et}), 7.07 (d, *J* = 15.8 Hz, 1H, H_{et}), 7.03 (d, *J* = 15.8 Hz, 1H, H_{et}), 6.86 (d, *J* = 15.8 Hz, 1H, H_{et}), 6.69 (d, *J* = 1.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 149.79 (s), 142.5 (d), 137.31 (s), 135.62 (s), 134.84 (s), 133.23 (s), 129.24 (d), 128.91 (2d), 128.72 (2d), 127.59 (d), 127.57 (2d), 126.27 (2d), 126.07 (d), 117.72 (d), 114.30 (d), 108.90 (d); MS *m*/*z* (ESI) (%) 307 (M^+, 100%); Anal. Calcd for $C_{20}H_{15}ClO$: C, 78.30; H, 4.93. Found: C, 78.21; H, 5.07.

trans,*trans*-2-[2-(4-Methoxyphenyl)ethenyl]-3-(2-phenylethenyl)furan (*trans*,*trans*-**2b**): Yield 80%; R_f 0.50



Scheme 3.

(petroleum ether/diethylether 10:0.4); yellow–orange crystals; mp 158 °C; UV (EtOH) λ_{max} (log ε) 388 (4.15, sh), 366 (4.34), 352 (4.28, sh), 284 (4.16), 275 (4.13, sh) nm; ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.44–7.53 (m, 5H, H_{ar}), 7.32–7.39 (m, 3H, 2H_{ar}, H_{5f}), 7.12 (d, J = 15.9 Hz, 1H, H_{et}), 7.06 (d, J = 16.2 Hz, 1H, H_{et}), 6.97 (d, J = 15.9 Hz, 1H, H_{et}), 6.90 (d, J = 8.9 Hz, 2H, H_{ar}), 6.82 (d, J = 16.2 Hz, 1H, H_{et}), 6.67 (d, J = 1.9 Hz, 1H, H_{4f}), 3.83 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C: 159.45 (s), 150.48 (s), 142.19 (d, C_{5f}), 137.52 (s), 129.93(s), 128.69 (2d), 128.51 (d), 127.74 (2d), 127.39 (d), 127.25 (d), 126.20 (2d), 121.28 (s), 118.08 (d), 114.23 (2d), 111.95 (d), 108.76 (d, C_{4f}), 55.35(q, OCH_3); MS (ESI) *m*/*z* (%) 303 (M^+, 100%); Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.21; H, 6.26.

trans,*trans*-2-[2-(4-Nitrophenyl)ethenyl]-3-(2-phenylethenyl)furan (*trans*,*trans*-**2c**): Yield 31%; R_f 0.34 (petroleum ether/diethylether 10:0.5); orange crystals; mp 195–196 °C; UV (EtOH) λ_{max} (log ε) 415 (4.31), 311 (4.19), 283 (4.17), 284 (4.28) nm; ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 8.24 (d, J = 8.8 Hz, 2H, H_{ar}), 7.65 (d, J = 8.8 Hz, 2H, H_{ar}), 7.55 (d, J = 8.0 Hz, 2H, H_{ar}), 7.46 (d, J = 2.0 Hz, 1H, H_{5f}), 7.40 (t, J = 7.7 Hz, 2H, H_{ar}), 7.25–7.34 (m, 2H, H_{ar}, H_{et}), 7.15 (d, J = 16.2 Hz, 1H, H_{et}), 7.13 (d, J = 16.2 Hz, 1H, H_{et}), 6.39 (d, J = 16.2 Hz, 1H, H_{et}), 6.76 (d, J = 2.0 Hz, 1H, H_{4f}); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 148.64 (s), 143.20 (d, C_{5f}), 143.17 (s), 136.52 (s), 129.89 (d), 128.29 (2d), 127.43 (d), 126.18 (2d), 125.90 (2d), 124.08 (d), 123.74 (2d), 117.15 (d), 116.73 (d), 108.71 (d, C_{4f}); too small quantity to see two remaining singlets; MS (ESI) *m*/*z* (%) 318 (M^+, 100%); Anal. Calcd for $C_{20}H_{15}NO_3$: C, 75.70; H, 4.76. Found: C, 75.44; H, 4.99.

2.2.2. Preparation of **3a–c**

Compounds **3a–c** were prepared in three steps by a Wittig reaction and Vilsmeier formylation (Scheme 3). In the first step 3-styrylfurans **6a–c** were prepared by Wittig reaction. To a stirred solution of furan-3-carbaldehyde (0.5 g, 5.21 mmol) and the phosphonium salts (5.21 mmol in 50 mL of: absolute ethanol, R = Cl, OCH_3 or benzene, R = NO_2), sodium ethoxide (0.15 g, 6.5 mmol in 20 mL ethanol) was added. Stirring was continued under stream of nitrogen for 1 day at RT. After removal of the solvent the residue was worked up with water and benzene. The benzene extracts were dried and concentrated. The crude reaction mixture was purified and the *cis*- and *trans*-isomers were separated by TLC using petroleum ether/diethylether (0–10%) mixture as eluent. Vilsmeier formylation was carried out from 3-styrylfurans **6a–c** (2.68 mmol) dissolved in dimethylformamide (1 mL, 18.8 mmol). After adjusting the temperature at ~11 °C, phosphorus-oxychloride (0.41 g, 2.68 mmol) was added and the reaction mixture was allowed gradually to worm up to room temperature and stirred for 24 h. The reaction mixture was decomposed by the continuous addition (with cooling) of 10% sodium hydroxide solution and the product was worked up with diethylether. The diethylether extracts were washed with water. After removal of the solvent, the crude reaction mixtures of 2-formyl-3-styrylfuran **7a–c** (as a mixture of *cis*- and *trans*-isomer) were used in a Wittig reaction to prepare 2,3-distyrylfuran derivatives **3a–c**. To a stirred solution of benzyltriphenylphosphonium salt (0.113 g, 0.26 mmol) and formyl derivatives **7a–c** (0.26 mmol) in absolute ethanol (50 mL) a solution of sodium ethoxide (0.013 g, 0.57 mmol in 10 mL ethanol) was added dropwise. Stirring was continued under a stream of nitrogen for 1 day at RT. After removal of the solvent, the residue was worked up with water and benzene. The benzene extracts were dried and concentrated. The crude reaction mixture was purified and the 4 isomers of **3a-c** were isolated by column chromatography on silica gel using petroleum ether/diethylether (0–10%) mixture as eluent. After the photochemical isomerization of the mixture of four isomers of **3a** the *trans*,*trans*-**3a** was isolated as the main isomer. A mixture of isomers of **3a** in benzene (~3.5×10^{-3} M) was purged with argon for 15 min and irradiated at 350 nm in a Rayonet reactor in a quartz tube. After 40 min the reaction mixture contained 80% of the *trans*,*trans*-**3a** which was isolated by thin-layer chromatography using petroleum ether/diethylether (0–5%) mixture as eluent. The photochemical isomerization was followed by NMR measurements. Isomers of **3b,c** were separated by TLC using petroleum ether/diethylether (1.5–2.5%) as eluent. Characterization data of the new compounds **6a–c**, **7a–c** and *trans*,*trans*-**3a–c** are given below.

3-(p-Chlorostyryl)furan (**6a**). Yield 12.6%; according to ^{1}H NMR spectroscopy, a mixture of 55% *cis*- and 45% *trans*-isomer.

cis-**6a**: R_f 0.27 (petroleum ether); colorless oil; UV (EtOH) λ_{max} (log ε) 276 (4.08) nm; ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 7.36–7.37 (m, 1H, H_{5f}), 7.24–7.31 (m, 5H, 4H_{ar}, H_{2f}), 6.47 (d, J = 11.7 Hz, 1H, H_{et}), 6.39 (d, J = 11,7 Hz, 1H, H_{et}), 6.11 (dd, J = 1.6; 0.5 Hz, 1H, H_{4f}); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 142.24 (d, $C_{2f/5f}$), 141.73 (d, $C_{2f/5f}$), 135.80 (s), 132.38 (s), 129.59 (2d), 127.96 (2d), 127.61 (d), 121.51 (s), 120.29 (d), 109.58 (d, C_{4f}); MS *m*/*z* (EI) 204/206 (M^+, 100%).

trans-**6a**: R_f 0.15 (petroleum ether); white crystals; mp 94 °C; UV (EtOH) λ_{max} (log ε) 317 (4.00, sh), 293 (4.26), 285 (4.25, sh) nm; ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.53 (bs, 1H, $H_{2f/5f}$), 7.40–7.42 (m, 1H, $H_{2f/5f}$), 7.37 (d, J = 8.6 Hz, 2H, H_{ar}), 7.29 (d, J = 8.6 Hz, 2H, H_{ar}), 6.94 (d, J = 16.2 Hz, 1H, H_{et}), 6.75 (d, J = 16.2 Hz, 1H, H_{et}), 6.63–6.65 (m, 1H, H_{4f}); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 143.33 (d, $C_{2f/5f}$), 140.68 (d, $C_{2f/5f}$), 135.38 (s), 132.35 (s), 128.30 (2d), 126.77 (2d), 126.60 (d), 123.82 (s), 118.56 (d), 106.79 (d, C_{4f}); MS *m*/*z* (EI) 204/206 (M^+, 100%).

3-(p-Methoxystyryl)furan (**6b**). Yield 54.2%; according to ^{1}H NMR spectroscopy, a mixture of 47% *cis*- and 53% *trans*-isomer.

cis-**6b**: R_f 0.30 (petroleum ether/diethylether 10:0.3); yellow oil; UV (EtOH) λ_{max} (log ε) 278 (3.02) nm; ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 7.36 (bs, 1H, $H_{2f/5f}$), 7.26 (d, J = 8.6 Hz, 2H, H_{ar}), 7.24–7.25 (m, 1H, $H_{2f/5f}$), 6.84 (d, J = 8.6 Hz, 2H, H_{ar}), 6.48 (d, J = 11.8 Hz, 1H, H_{et}), 6.30 (d, J = 11.8 Hz, 1H, H_{et}), 6.18 (d, J = 1.5 Hz, 1H, H_{4f}), 3.81 (s, 3H, OCH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 155.24 (s), 141.33 (d, $C_{2f/5f}$), 133.73 (d, $C_{2f/5f}$), 125.80 (s), 123.38 (s), 124.57 (d), 123.38 (2d), 114.82 (d), 112.33 (s), 111.88 (2d), 105.96 (d, C_{4f}), 51.97 (q); MS *m*/*z* (EI) 200 (M^+, 100%).

trans-**6b**: R_f 0.20 (petroleum ether/diethylether 10:0.3); white crystals; mp 101 °C; UV (EtOH) λ_{max} (log ε) 293 (4.04), 286 (4.05, sh) nm; ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 7.49 (bs, 1H, $H_{2f/5f}$), 7.38–7.39 (m, 1H, $H_{2f/5f}$), 7.38 (d, J = 8.6 Hz, 2H, H_{ar}), 6.87 (d, J = 8.6 Hz, 2H, H_{ar}), 6.83 (d, J = 16.2 Hz, 1H, H_{et}), 6.76 (d, J = 16.2 Hz, 1H, H_{et}), 6.64 (d, J = 2.0 Hz, 1H, H_{4f}), 3.81 (s, 3H, OCH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 158.57 (s), 143.10 (d, $C_{2f/5f}$), 138.84 (d, $C_{2f/5f}$), 128.68 (s), 127.47 (d), 126.78 (2d), 115.84 (d), 113.58 (s), 113.60 (2d), 106.86 (d, C_{4f}), 54.81 (q); MS *m*/*z* (EI) 200 (M^+, 100%).

3-(p-Nitrostyryl)furan (**6c**). Yield 64.8%; according to ^{1}H NMR spectroscopy, a mixture of 33% *cis*- and 67% *trans*-isomer.

cis-**6c**: R_f 0.55 (petroleum ether/diethylether 10:0.2); yellow oil; UV (EtOH) λ_{max} (log ε) 285 (4.11) nm; ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 8.15 (d, J = 8.8 Hz, 2H, H_{ar}), 7.49 (d, J = 8.8 Hz, 2H, H_{ar}), 7.40 (d, J = 0.6 Hz, 1H, H_{2f}), 7.27 (dd, J = 1.5; 0.6 Hz, 1H, H_{5f}), 6.56 (d, J = 12.1 Hz, 1H, H_{et}), 6.52 (d, J = 12.1 Hz, 1H, H_{et}), 6.09 (d, J = 1.5 Hz, 1H, H_{4f}); MS *m*/*z* (EI) 215 (M^+, 100%).

trans-**6c**: R_f 0.27 (petroleum ether/diethylether 10:0.2); orange crystals; mp 117 °C; UV (EtOH) λ_{max} (log ε) 325 (4.07) nm; ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 8.20 (d, J = 8.8 Hz, 1H, H_{ar}), 7.62 (s, 1H, H_{2f}), 7.57 (d, J = 8.8 Hz, 1H, H_{ar}), 7.46 (d, J = 1.4 Hz, 1H, H_{5f}), 7.16 (d, J = 16.2 Hz, 1H, H_{et}), 6.85 (d, J = 16.2 Hz, 1H, H_{et}), 6.69 (d, J = 1.4 Hz, 1H, H_{4f}); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 144.33 (d, $C_{2f/5f}$), 144.08 (s), 142.54 (d, $C_{2f/5f}$), 126.57 (2d), 126.17 (d), 124.28 (2d), 124.14 (s), 123.26 (d), 107.31 (d, C_{4f}), 1 singlet is overlapped; MS *m*/*z* (EI) 215 (M^+, 100%).

2-Formyl-3-(p-chlorostyryl)furan (**7a**). Yield 47%; according to ^{1}H NMR spectroscopy, a mixture of 57% *cis*- and 43% *trans*-isomer.

cis-**7a**: R_f 0.37 (petroleum ether/diethylether 10:1); yellow oil; UV (EtOH) λ_{max} (log ε) 305 (4.13), 261 (3.88) nm; ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 9.83 (s, 1H, CHO), 7.44 (d, J = 1.8 Hz, 1H, H_{5f}), 7.29 (d, J = 8.5 Hz, 2H, H_{ar}), 7.22 (d, J = 8.5 Hz, 2H, H_{ar}), 6.93 (d, J = 12.1 Hz, 1H, H_{et}), 6.82 (d, J = 12.1 Hz, 1H, H_{et}), 6.22 (d, J = 1.8 Hz, 1H, H_{4f}); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 178.45 (d, CHO), 148.57 (s, C_{2f}), 146.92 (d, C_{5f}), 134.99 (s), 134.15 (d), 133.79 (s), 130.12 (2d), 128.71 (2d), 118.92 (d), 117.03 (s), 112.78 (d, C_{4f}); MS m/z (EI) 232/234 (M^+, 100%).

trans-**7a**: R_f 0.24 (petroleum ether/diethylether 10:1); white crystals; mp 78 °C; UV (EtOH) λ_{max} ($\log \varepsilon$) 331 (4.35), 265 (4.31) nm; ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 9.92 (s, 1H, CHO), 7.59 (d, J = 16.2 Hz, 1H, H_{et}), 7.60 (d, J = 1.7 Hz, 1H, H_{5f}), 7.48 (d, J = 8.5 Hz, 2H, H_{ar}), 7.35 (d, J = 8.5 Hz, 2H, H_{ar}), 7.08 (d, J = 16.2 Hz, 1H, H_{et}), 6.85 (d, J = 1.7 Hz, 1H, H_{4f}); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 178.89 (d, CHO), 154.11 (s), 147.52 (d, C_{5f}), 134.73 (s), 133.79 (d), 133.0 (s), 129.03 (2d), 128.16 (2d), 119.0 (s), 117.40 (d), 109.65 (d, C_{4f}); MS m/z (EI) 232/234 (M^+, 100%).

2-Formyl-3-(p-methoxystyryl)furan (**7b**). Yield 30%; according to ^{1}H NMR spectroscopy, a mixture of 26% *cis*- and 74% *trans*-isomer.

cis-**7b**: R_f 0.15 (petroleum ether/diethylether 10:1); white crystals; mp 68 °C; UV (EtOH) λ_{max} (ε) 313 (4.15), 271 (3.93) nm; ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 9.81 (s, 1H, CHO), 7.44 (d, J = 1.8 Hz, 1H, H_{5f}), 7.23 (d, J = 8.7 Hz, 2H, H_{ar}), 6.84 (d, J = 8.7 Hz, 2H, H_{ar}), 6.83 (d, J = 11.9 Hz, 1H, H_{et}), 6.79 (d, J = 11.9 Hz, 1H, H_{et}), 6.31 (d, J = 1.8 Hz, 1H, H_{4f}), 3.82 (s, 3H, OCH_3); MS m/z (EI) 228 (M^+, 100%).

trans-**7b**: R_f 0.08 (petroleum ether/diethylether 10:1); yellow crystals; mp 93 °C; UV (EtOH) λ_{max} ($\log \varepsilon$) 340 (4.32), 277 (4.30) nm; ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 9.91 (s, 1H, CHO), 7.57 (d, J = 1.7 Hz, 1H, H_{5f}), 7.49 (d, J = 8.5 Hz, 2H, H_{ar}), 7.46 (d, J = 16.2 Hz, 1H, H_{et}), 7.09 (d, J = 16.2 Hz, 1H, H_{et}), 6.91 (d, J = 8.5 Hz, 2H, H_{ar}), 6.83 (d, J = 1.7 Hz, 1H, H_{4f}), 3.82 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 179.86 (d, CHO), 150.69 (s), 147.93 (d, C_{5f}), 134.46 (d), 128.48 (s), 127.99 (2d), 114.03 (s), 113.53 (2d), 109.21 (d), 54.90 (d), too small quantity to see one remaining singlet; MS m/z (EI) 228 (M^+, 100%).

2-Formyl-3-(p-nitrostyryl)furan (**7c**). Yield 61%; according to ^{1}H NMR spectroscopy, a mixture of 27% *cis*- and 73% *trans*-isomer.

cis-**7c**: R_f 0.40 (petroleum ether/diethylether 10:0.5); mp 82–83 °C; UV (EtOH) λ_{max} (ε) 322 (4.19) nm; ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 9.86 (s, 1H, CHO), 8.18 (d, J = 8.7 Hz, 2H, H_{ar}), 7.47 (d, J = 1.8 Hz, 1H, H_{5f}), 7.46 (d, J = 8.7 Hz, 2H, H_{ar}), 7.11 (d, J = 12.2 Hz, 1H, H_{et}), 6.88 (d, J = 12.2 Hz, 1H, H_{et}), 6.16 (d, J = 1.8 Hz, 1H, H_{4f}); MS m/z (EI) 243 (M^+, 100%).

trans-**7c**: R_f 0.35 (petroleum ether/diethylether 10:0.5); mp 122 °C; UV (EtOH) λ_{max} ($\log \varepsilon$) 345 (4.41) nm; ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 9.95 (s, 1H, CHO), 8.24 (d, J = 8.7 Hz, 2H, H_{ar}), 7.82 (d, J = 16.3 Hz, 1H, H_{et}), 7.68 (d, J = 8.7 Hz, 2H, H_{ar}), 7.63 (d, J = 1.6 Hz, 1H, H_{5f}), 7.18 (d, J = 16.3 Hz, 1H, H_{et}), 6.89 (d, J = 1.9 Hz, 1H, H_{4f}); MS m/z (EI) 243 (M^+, 100%).

trans,trans-2-(2-Phenylethenyl)-3-[2-(4-chlorophenyl)ethenyl]furan (*trans,trans*-**3a**): Yield 57%; R_f 0.40 (petroleum ether/diethylether 10:0.4); yellow crystals; mp 130–131 °C; UV (EtOH) λ_{max} ($\log \varepsilon$) 362 (4.23), 347 (4.20, sh), 327(4.12, sh), 284 (4.22), 277 (4.20) nm; ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.52 (d, J = 7.5 Hz, 2H, H_{ar}), 7.23–7.45 (m, 8H, $6H_{ar}$, H_{5f}), 7.06–7.13 (m, 3H, H_{ar}), 6.77 (d, J = 16.1 Hz, 1H, H_{et}), 6.66 (d, J = 1.8 Hz, 1H, H_{4f}); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 150.36 (s), 142.63 (d, C_{5f}), 137.00 (s), 135.94 (s), 133.00 (s), 128.87 (2d), 128.76 (2d), 127.83 (d), 127.52 (d), 127.39 (2d), 126.49 (2d), 121.83 (s), 118.52 (d), 113.67 (d), 108.72 (d, C_{4f}); MS m/z (ESI) 307/305 (M^+, 100%); Anal. Calcd for $C_{20}H_{15}ClO$: C, 78.30; H, 4.93. Found: C, 78.55; H, 4.67.

trans,trans-2-(2-Phenylethenyl)-3-[2-(4-methoxyphenyl)ethenyl]furan (*trans,trans*-**3b**): Yield 52%; R_f 0.60 (petroleum ether/diethylether 10:0.6); yellow crystals; mp 187–188 °C; UV (EtOH) λ_{max} ($\log \varepsilon$) 380 (4.38, sh), 366 (4.50), 347 (4.42, sh), 286 (4.39), 278 (4.33, sh); ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 7.53 (d, J = 7.3 Hz, 2H, H_{ar}), 7.45 (d, J = 8.6 Hz, 2H, H_{ar}), 7.37 (t, J = 7.3 Hz, 2H, H_{ar}), 7.36 (d, J = 1.9 Hz, 1H, H_{5f}), 7.26 (t, J = 7.3 Hz, 1H, H_{ar}), 7.11 (d, J = 15.8 Hz, 1H, H_{et}), 7.08 (d, J = 15.8 Hz, 1H, H_{et}), 7.00 (d, J = 16.0 Hz, 1H, H_{et}), 6.91 (d, J = 8.6 Hz, 2H, H_{ar}), 6.81 (d, J = 16.0 Hz, 1H, H_{et}), 6.67 (d, J = 1.9 Hz, 1H, H_{4f}), 3.84 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 150.11 (s), 144.15 (d, C_{5f}), 143.09 (s), 137.25 (s), 129.18 (d), 128.77 (2d), 127.97 (d), 125.79 (2d), 124.99 (2d), 124.38 (d), 122.94 (2d), 118.36 (d), 117.77 (d), 107.97 (d, C_{4f}); two singlets are missing; MS m/z (ESI) 302 (M^+, 100%); Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.18; H, 6.35.

trans,trans-2-(2-Phenylethenyl)-3-[2-(4-nitrophenyl)ethenyl]furan (*trans,trans*-**3c**): Yield 50%; R_f 0.20 (petroleum ether/diethylether 10:0.2); orange crystals; mp 213 °C; UV (EtOH) λ_{max} ($\log \varepsilon$) 403 (4.33), 324 (4.34); ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 8.21 (d, J = 8.8 Hz, 2H, H_{ar}), 7.61 (d, J = 8.8 Hz, 2H, H_{ar}), 7.54 (d, J = 7.8 Hz, 2H, H_{ar}), 7.24–7.43 (m, 5H, $3H_{ar}$, H_{et}, H_{5f}), 7.18 (d, J = 16.0 Hz, 1H, H_{et}), 7.09 (d, J = 16.0 Hz, 1H, H_{et}), 6.86 (d, J = 15.9 Hz, 1H, H_{et}), 6.70 (d, J = 1.6 Hz, 1H, H_{4f}); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 151.60 (s), 146.55 (s), 143.97 (s), 142.93 (d, C_{5f}), 136.71 (s), 129.04 (d), 128.82 (2d), 128.16 (d), 126.63 (2d), 126.51 (2d), 126.23 (d), 124.21 (2d), 122.49 (d), 121.33 (s), 113.25 (d), 108.58 (d, C_{4f}); (ESI) 317 (M^+, 100%); Anal. Calcd for $C_{20}H_{15}NO_3$: C, 75.70; H, 4.76. Found: C, 75.87; H, 4.49.

2.3. Photochemical and photophysical experiments

Typically, the irradiations were carried out with 3.5-cm^3 solutions in 1-cm cells at room temperature. HPLC grade ethanol and *n*-hexane were used as solvents in these experiments. During the photolyses the reaction mixtures were continuously homogenized by magnetic stirring. For photochemical reactions under continuous irradiation at 366 nm, an AMKO LTI photolysis equipment, containing a 200 W Xe–Hg-lamp and a monochromator was used [32]. Incident light intensity was determined with a thermopile calibrated by ferrioxalate actinometry [33,34]. Quantum yield measurements were carried out with samples of nearly 100% light absorption. Following the change of the absorption spectrum of the solution photolyzed, the quantum yield for the photochemical transformation of the starting material was determined from the initial rate calculated from the absorbance vs. time plot at a characteristic wavelength where the products did not absorb.

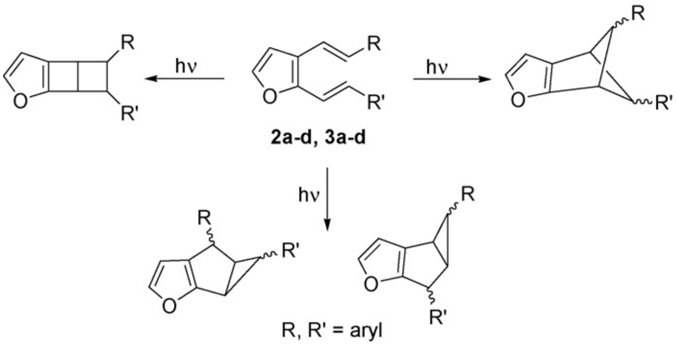
Emission spectra were measured on a PerkinElmer LS50B spectrofluorimeter. $Ru(bpy)_3Cl_2$ [35], quinine bisulphate (in 0.5 M H_2SO_4), and 9,10-diphenyl-anthracene [36] were utilized as references for determination of the fluorescence quantum yields. Each 2,3-distyrylfuran derivative studied was excited at the wavelength of its absorption maximum. Luminescence spectra were corrected for the detector sensitivity.

Fluorescence lifetimes were measured by a kinetic laser system utilizing a Quantel Brilliant Nd:YAG laser with a Tektronix DPO 4034 digital oscilloscope. Since the fluorescence lifetimes of the compounds studied are comparable with the laser half-width, a deconvolution method was applied for their determination [37].

To compare the photochemical behavior of **2a–c** and **3a–c** with that of the analogous **2d** and **3d** [21], solutions of *trans,trans*-**2a–c** and *trans,trans*-**3a–c** in deuterated benzene (e.g. 7×10^{-2} M) were irradiated in NMR tubes in a Rayonet RPR-100 photochemical reactor at 366 nm and the reaction course was followed by H NMR until the complete conversion.

3. Results and discussion

For the sake of comparability with the previous results [21,28] and due to their thermodynamic stability in the photoisomerization equilibrium, exclusively the *trans,trans*-isomers of the distyrylfuran compounds **2a–d** and **3a–d** were photophysically



Scheme 4. Possible intramolecular photochemical reactions of the ethylenic bonds of **2a–d** and **3a–d**.

and photochemically studied in this work. Thus, in the following, the codes **2a–d** and **3a–d** refer to the corresponding *trans*,*trans*-isomers.

3.1. Photochemical experiments

Irradiation experiments with each new substituted 2,3-distyrylfuran derivative (**2a–c** and **3a–c**) were carried out in both ethanol and *n*-hexane in order to get some information regarding the effect of the solvent polarity. For comparison, solutions of one methyl-substituted (**3d**) and the unsubstituted 2,3-distyrylfuran derivatives (**2d**), as known compounds [21], were also irradiated to study how the substituents influence the efficiency of the photolysis. The systems were argon-saturated for avoiding the photoinduced oxidation of the excited molecules. The concentration of the starting compounds was in the order of 10^{-4} M. The excitation wavelength of 366 nm was applied for each photolysis.

Regardless of the substituent, upon irradiation of each compound the longest-wavelength absorption band gradually disappeared (see Figs. 1–4), while the band (or the double band of the nitro-derivatives) at about 270 nm significantly decreased and in some cases slightly shifted. These spectral changes indicate that the long-range conjugation between the two phenyl groups *via* the hexatriene link has been ceased by the photolysis, and the electronic system of the aromatic rings became isolated in the case of all derivatives. This phenomenon also suggests that neither trans–cis isomerization nor an intramolecular cycloaddition reaction plays a considerable role in the photolysis of these compounds. Instead, as it was observed previously in the case of the photolysis of the distyrylfuran [21] and benzofuran derivatives [28], stilbene-like end-products may form *via* intermediate cyclobutane structures. The NMR spectra of all photomixtures after irradiation of **2a–c** and **3a–c** did not show any characteristic signal either for the aliphatic protons of hypothetic bicyclic structures (Scheme 4) or for cyclobutane dimeric structures. No intramolecular heteropolycyclic cycloaddition products were detected, confirming the similarity of the photochemical behavior to that of analogous compounds.

Table 1
Quantum yields for the photolysis of 2,3-distyrylfuran derivatives in argon-saturated *n*-hexane and ethanol (λ_{ir} = 366 nm).[a]

R (code)	Φ (in *n*-hexane)	Φ (in ethanol)
Cl (**2a**)	0.09	0.30
OCH_3 (**2b**)	0.14	0.25
NO_2 (**2c**)	0.07	0.025
H (**2d**)	0.02	0.38
Cl (**3a**)	0.24	0.46
OCH_3 (**3b**)	0.07	0.33
NO_2 (**3c**)	0.16	0.042
CH_3 (**3d**)	0.03	0.35

[a] Standard deviation: ±7%.

Since these photochemical results implied that the 2,3-distyrylfurans **2a–d** and **3a–d** do not give interesting heteropolycyclic compounds (Scheme 4) as intramolecular cycloaddition products, further intention was the study of substituent and solvent effects on their photoactivity.

The quantum yields of the photoinduced disappearence of the starting molecules in both solvents are summarized in Table 1.

As the data show a very strong solvent effect can be observed in the case of the unsubstituted 2,3-distyrylfuran (**2d**). In the non-polar *n*-hexane the quantum yield is a bit more than one order of magnitude lower than in the polar ethanol. This phenomenon indicates that the transition state of the reaction reached upon excitation is more polar than the initial (ground) state. An increase in polarity of solvent will stabilize the transition state relative to the initial state and, thus, lead to an increase in reaction rate, i.e. quantum yield [38]. A similarly strong effect is found for the methyl-substituted derivative (**3d**), suggesting that a simple electron-donating group without lone pairs does not influence the effect of the solvent polarity.

For the chloro- (**2a** and **3a**) and methoxy-substituted (**2b** and **3b**) derivatives, the quantum yields in ethanol are as similarly high as for the unsubstituted and methyl-substituted compounds. In all these cases this phenomenon can be accounted for the phenyl groups connected to the styryl links, promoting their reactivity for intermolecular [2 + 2]-photocycloaddition which results in the intermediate cyclobutane structures suggested. In ethanol the photolysis quantum yields are appreciably higher for the isomers with the substituent on the styryl group of position 3 than for the corresponding ones of position 2. Besides, a less strong but still significant solvent effect of the same type is also shown in these cases, no matter on which phenyl group are these substituents. This moderate decrease in the solvent effect may be attributed to the fact that both the chlorine and the oxygen atoms directly connected to the aromatic ring possess lone pairs, which can be involved in the conjugation of the whole bond system. Hence they can slightly increase the stability of the excited state in the non-polar solvent compared to the case of the unsubstituted and methyl-substituted compounds.

The nitro-substituted derivatives (**2c** and **3c**) display much less efficiencies for the photolysis, besides the effects of the solvent polarity in these cases are opposite to those of the other compounds studied. Both phenomena can be attributed to the strong electron-withdrawing effect of the nitro group. This substituent in para position significantly decreases the electron density on the styryl link, diminishing the chance for the intermolecular [2 + 2]-photocycloaddition, which is apparently the key step of the photolysis. Thus, the corresponding quantum yields in ethanol are one order of magnitude lower than those for the other compounds studied. The opposite solvent effect indicates that in the case of the nitro-derivatives another way of decay of the excited state becomes more efficient in ethanol than in *n*-hexane in competition with the photochemical reaction. Since, as it is shown later (see in Section 3.2.2), also the corresponding fluorescence quantum yields are lower in the solvent of higher polarity, an efficient $S_1 \rightarrow T_1$ intersystem crossing leading to a non-reactive may be the competitive way of decay. This conclusion is in accordance with the results published on the nitro-derivative of the analogous benzofuran compound [28,30].

3.2. Photophysics

3.2.1. UV–vis absorption spectra

Figs. 5 and 6 display the UV–vis absorption and fluorescence emission spectra of **3c** and **3d** (as examples) in ethanol and *n*-

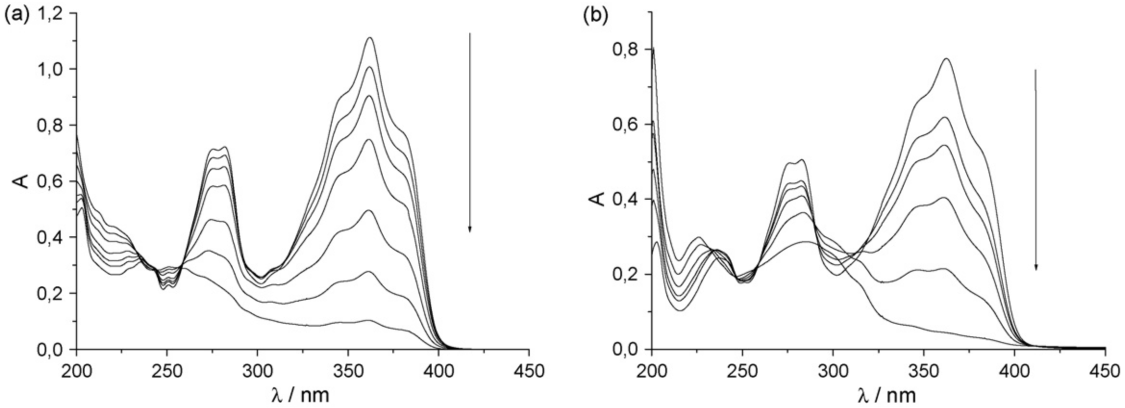


Fig. 1. Spectral change during the irradiation of **2a** in *n*-hexane (a) after 0, 2, 4, 8, 16, 32, 64 min, and in ethanol (b) after 0, 1, 2, 4, 8, 16 min (λ_{ir} = 366 nm, ℓ = 1 cm).

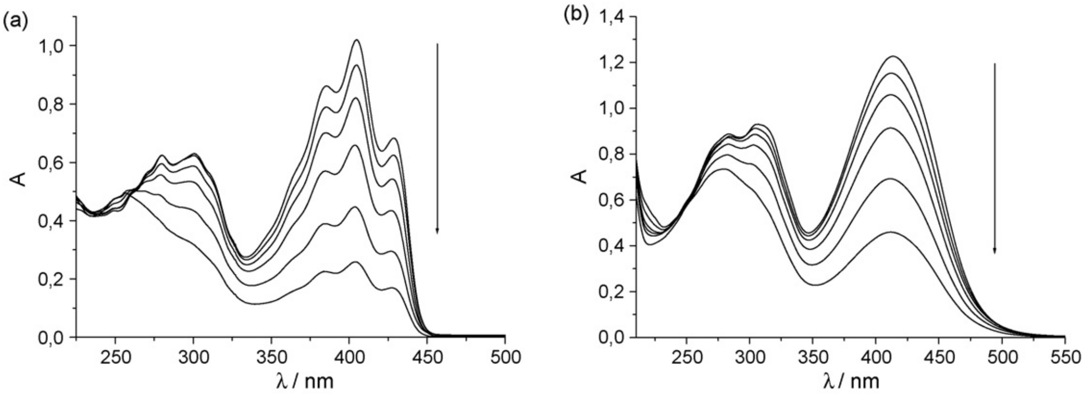


Fig. 2. Spectral change during the irradiation of **2c** in *n*-hexane (a) after 0, 4, 8, 16, 32, 64 min, and in ethanol (b) after 0, 8, 16, 32, 64, 128 min (λ_{ir} = 366 nm, ℓ = 1 cm).

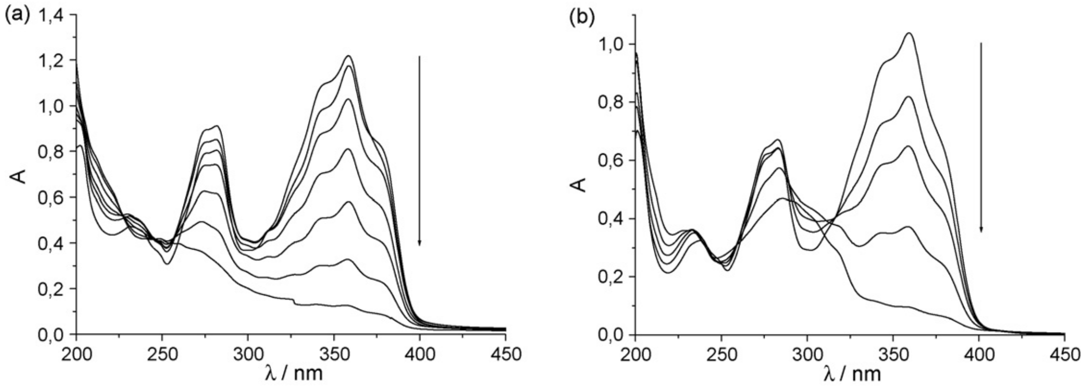


Fig. 3. Spectral change during the irradiation of **2d** in *n*-hexane (a) after 0, 2, 4, 8, 16, 32, 64 min, and in ethanol (b) after 0, 1, 2, 4, 8 min (λ_{ir} = 366 nm, ℓ = 1 cm).

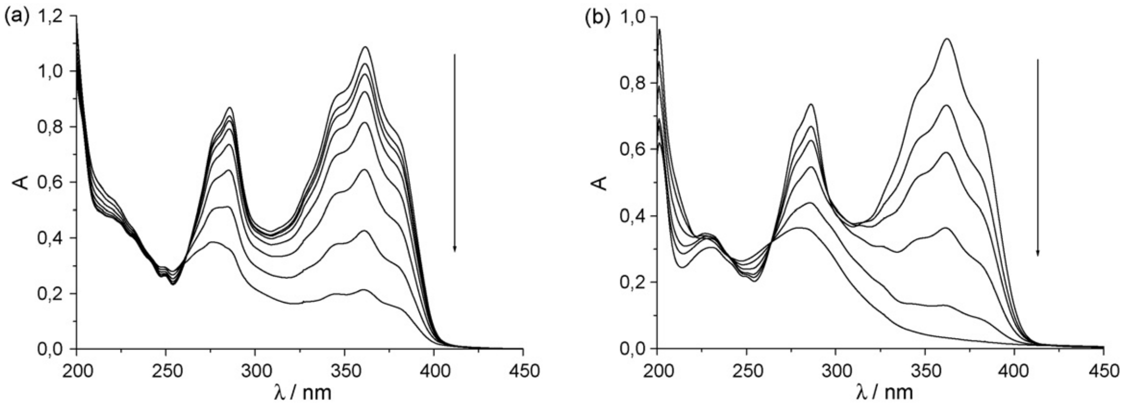


Fig. 4. Spectral change during the irradiation of **3b** in *n*-hexane (a) after 0, 1, 2, 4, 8, 16, 32, 64 min, and in ethanol (b) after 0, 1, 2, 4, 8, 16 min (λ_{ir} = 366 nm, ℓ = 1 cm).

Table 2
Spectral behavior of 2,3-distyrylfuran derivatives in *n*-hexane at room temperature.

R (code)	$\lambda_{\mathrm{abs}}^{\mathrm{max}}$/nm[a] ($\log\varepsilon$)	$\Delta\tilde{\nu}_{\mathrm{abs}}$/cm^{-1}	$\lambda_{F}^{\mathrm{max}}$/nm	$\Delta\tilde{\nu}_{F}$/cm^{-1}	$\Delta\tilde{\nu}_{S,\mathrm{max}}$/cm^{-1}	$\Delta\tilde{\nu}_{S,00}$/cm^{-1}
Cl (**2a**)	344^{sh}, $\underline{362}$ (4.65), 382^{sh}	1450	400, $\underline{425}$, 450	1470	4090	1180
OCH_3 (**2b**)	346^{sh}, $\underline{364}$ (4.34), 387^{sh}	1630	401, $\underline{426}$, 450	1460	4000	902
NO_2 (**2c**)	386, $\underline{405}$ (4.51), 429	1380	451, $\underline{477}$, 508	1210	3730	1140
H (**2d**)	343^{sh}, $\underline{358}$ (4.48), 379^{sh}	1550	398, $\underline{422}$, 445	1430	4240	1260
Cl (**3a**)	344^{sh}, $\underline{360}$ (4.23), 383^{sh}	1670	397, $\underline{421}$, 446	1440	4020	920
OCH_3 (**3b**)	345^{sh}, $\underline{362}$ (4.46), 380^{sh}	1310	403, $\underline{427}$, 451	1390	4210	1500
NO_2 (**3c**)	382, $\underline{400}$ (4.45), 425	1470	447, $\underline{470}$, 500	1090	3720	1160
CH_3 (**3d**)	343^{sh}, $\underline{358}$ (4.61), 380^{sh}	1620	398, $\underline{422}$, 446	1430	4240	1190

[a] The main maximum is underlined.

Table 3
Spectral behavior of 2,3-distyrylfuran derivatives in ethanol at room temperature.

R (code)	$\lambda_{\mathrm{abs}}^{\mathrm{max}}$/nm[a] ($\log\varepsilon$)	$\Delta\tilde{\nu}_{\mathrm{abs}}$/cm^{-1}	$\lambda_{F}^{\mathrm{max}}$/nm	$\Delta\tilde{\nu}_{F}$/cm^{-1}	$\Delta\tilde{\nu}_{S,\mathrm{max}}$/cm^{-1}	$\Delta\tilde{\nu}_{S,00}$/cm^{-1}
Cl (**2a**)	347^{sh}, $\underline{362}$ (4.47), 382^{sh}	1450	405, $\underline{429}$, 454	1380	4310	1490
OCH_3 (**2b**)	349^{sh}, $\underline{364}$ (4.34), 387^{sh}	1630	407, $\underline{431}$, 452	1370	4270	1270
NO_2 (**2c**)	$\underline{414}$ (4.31)	–	$\underline{571}$	–	6640	–
H (**2d**)	342^{sh}, $\underline{359}$ (4.51), 380^{sh}	1540	404, $\underline{426}$, 452	1280	4380	1560
Cl (**3a**)	327^{sh}, 347^{sh}, $\underline{362}$ (4.23), 384^{sh}	1580	403, $\underline{426}$, 452	1340	4150	1230
OCH_3 (**3b**)	345^{sh},$\underline{362}$ (4.50), 382^{sh}	1450	412, $\underline{434}$, 458	1230	4580	1900
NO_2 (**3c**)	$\underline{403}$ (4.33)	–	$\underline{567}$	–	7180	–
CH_3 (**3d**)	344^{sh}, $\underline{359}$ (4.51), 380^{sh}	1540	403, $\underline{426}$, 453	1340	4380	1500

[a] The main maximum is underlined.

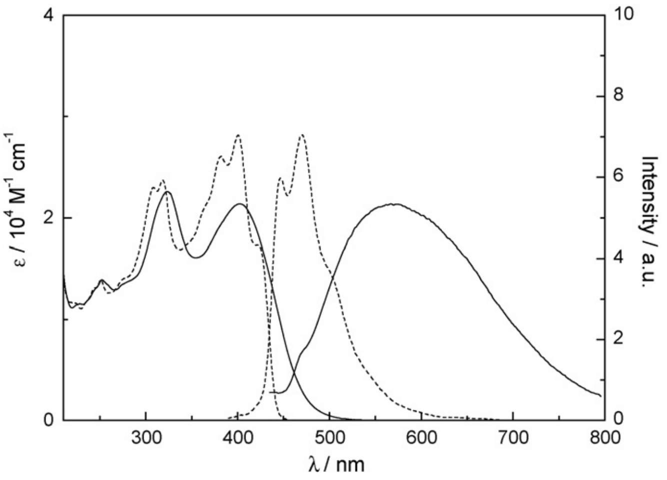


Fig. 5. UV–vis absorption and fluorescence emission spectra of **3c** in *n*-hexane (dashed line) and ethanol (solid line).

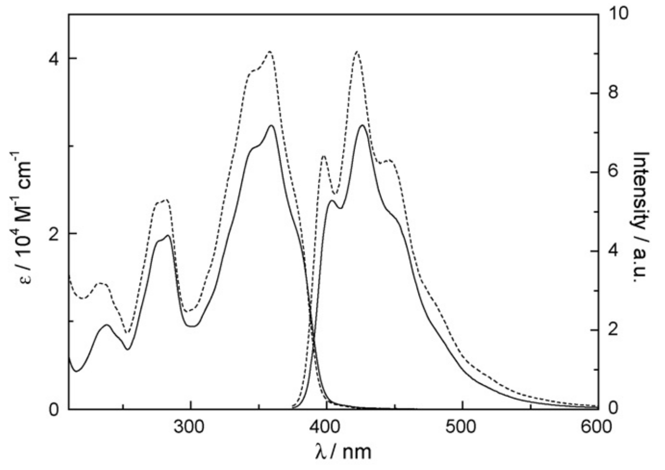


Fig. 6. UV–vis absorption and fluorescence emission spectra of **3d** in *n*-hexane (dashed line) and ethanol (solid line).

hexane at room temperature and Tables 2 and 3 summarize the characteristic spectral data (maxima wavelengths and vibronic progressions of the absorption and emission spectra and the Stokes-shifts) of the compounds studied in ethanol and *n*-hexane, respectively. Stokes-shifts were calculated for both the maxima ($\Delta\tilde{\nu}_{S,\mathrm{max}}$) and the 0–0 transition ($\Delta\tilde{\nu}_{S,00}$).

For the derivatives with R = H, Cl, and OCH_3 (on either styryl group) as well as CH_3 on styryl group in position 3, band absorption maxima are found in the range of 358–364 nm, and assigned to the $S_0 \rightarrow S_1$ transition of essentially $\pi \rightarrow \pi^*$ nature. Compared to the corresponding benzofuran derivates (2-(4′-methyl-styryl),3-(4′-R-styryl)benzofuran) [30], this band is 12–13 nm blue-shifted. This phenomenon can be attributed to the less extended conjugated π bond system in the case of the furan derivatives. However, the effects of the substituents are the same regarding the shift compared to the unsubstituted derivative. Thus, very slight (2–6 nm) red shifts were observed for the Cl and OCH_3 derivatives of both types of compounds (**2a**, **3a** and **2b**, **3b**) in *n*-hexane. The substiuents on the styryl group in position 3 result in smaller shifts (2 nm for Cl (**3a**) and 4 nm for OCH_3 (**3b**)) than on the styryl group in position 2 (4 nm for Cl (**2a**) and 6 nm for OCH_3 (**2b**)). The methyl substituent on the furan compound (**3d**) does not cause any shift. In ethanol the same tendencies can be observed, and the solvent polarity does not affect the position of the main absorption band of these furan derivatives.

In both solvents this rather strong band shows a reduced vibrational structure with maxima corresponding to the transition from the vibrational level $\nu = 0$ of the ground state to the $\nu' = 2$ level of the first excited singlet state (S_1). Its vibronic progression depends on the substituents in the range of 1450–1670 cm^{-1}. This electronic excitation probably causes an appreciable change in the molecular geometry as indicated by the relatively large Stokes-shifts ($\Delta\tilde{\nu}_{S,\mathrm{max}}$). Beside the principal absorption band, the data of which are summarized in Tables 2 and 3, a second absorption band of similar intensity is displayed by these distyrylfuran compounds at shorter wavelengths. This band of two maxima, assigned to the $S_0 \rightarrow S_2$ transition (of also $\pi \rightarrow \pi^*$ nature), shows more significant blue shifts with respect to that observed for the corresponding benzofuran derivatives (20–23 nm) than the principal band does. This phenomenon suggests that the stabilization effect of the more extended conjugated π bond system in the case of the benzofuran derivatives compared to that of the corresponding furan compounds is stronger for the second singlet excited state (S_2) than for the first one (S_1).

Deviating from the previously discussed substituents, NO_2 (on either styryl group, i.e., **2c**, **3c**) results in significant red shifts (32–41 nm) in both solvents, compared to the absorption bands of the unsubstituted compound. Similar phenomenon was observed with the corresponding benzofuran derivative [30]. This effect may be the consequence of the more than doubled dipole moment of the nitro-derivatives in this excited state than in the ground state. The significantly larger dipole moments of the nitro compounds in the excited state are in accordance with the appreciable red shifts (3–9 nm) of the main band in ethanol compared to its position in the non-polar *n*-hexane, deviating from the other derivatives. The excited state of larger dipole moment is more strongly stabilized in polar solvent [39]. While in *n*-hexane the main band shows a vibrational structure with much better resolution than in the case of the other substituents, in ethanol this character completely vanishes due to the strong interaction with the solvent of high polarity (Fig. 5). Hence, in ethanol the Stokes-shift for the 0–0 transition ($\Delta\tilde{\nu}_{S,00}$) cannot be calculated (Table 3). Similarly to the other derivatives studied, also in this case, the second, strong absorption band displays two maxima and more significant blue shifts compared to that observed for the corresponding benzofuran derivative (16–33 nm) than the principal band does.

3.2.2. Fluorescence emission spectra and photophysics

The comparison of the emission and the absorption spectra of the compounds studied (see Figs. 5 and 6 and Tables 2 and 3) reveals some interesting features. Generally, for these compounds the vibrational structure of the fluorescence band is much better than that of the absorption bands. This kind of spectral behavior indicates a larger rigidity and planarity of the geometry of the emitting state (S_1) compared to that of the ground state (S_0). The fluorescence spectra do not depend on the excitation wavelength, and the excitation spectrum well overlaps with the absorption spectrum for all the compounds studied. The maximum emission band corresponds to the transition from the vibrational level $\nu = 0$ of the first excited singlet state (S_1) to the $\nu' = 2$ level of the ground state. The progression of the vibronic bands in *n*-hexane is about 1390–1470 cm^{-1}, slightly depending on the substituent and its position. The only exception is the nitro group, in the case of which $\Delta\tilde{\nu}_F = 1210\,cm^{-1}$ for position 2 and 1090 cm^{-1} for position 3. In ethanol no vibrational structure can be observed for the nitro-derivatives, similarly to the absorption bands, due to the high polarity of the solvent, while for the other compounds studied the vibronic progressions (1230–1380 cm^{-1}) are smaller than the corresponding ones in *n*-hexane. No such solvent effect was observed on the vibronic progressions of the main absorption bands.

Compared to the unsubstituted compound, methyl group does not result in any shift of the main fluorescence emission band, neither in ethanol nor in *n*-hexane. The Cl and OCH_3 substituents (**2a**, **3a** and **2b**, **3b**) cause a slight red shift in both ethanol (3–8 nm) and *n*-hexane (3–5 nm). However, the measure of the red shift for the nitro-derivatives (**2c** and **3c**) is rather large; 48 and 55 nm in *n*-hexane, while 141 and 145 nm in ethanol for position 3 and 2, respectively. This dramatic effect of the NO_2 group can be attributed to its strong electron-withdrawing property and the lack of the non-bonding electron pair on nitrogen, changing the geometry and polarity in both the ground and the excited state.

In ethanol the main emission band shows a slight red shift with respect to its wavelength in *n*-hexane for all the compounds studied with the exception of the nitro-derivatives, in the case of which a very strong red shift can be observed. The latter phenomenon is in accordance with the slight red shift of the corresponding absorption band, indicating that for the nitro-derivatives the change in the geometry upon excitation is much stronger in ethanol than in non-polar solvent. This is in accordance with the observations of the analogous benzofuran derivative, in the case of which an appreciable increase (more than doubling) of the dipole moment was calculated for the $S_0 \rightarrow S_2$ transition [30]. Thus, the stabilization effect of ethanol for excited state of the nitro compounds is very strong, resulting in increased Stokes-shifts compared to the other derivatives.

Table 4
Fluorimetric parameters of 2,3-distyrylfuran derivatives in *n*-hexane and ethanol.

R (code)	*n*-Hexane		Ethanol	
	Φ_F[a]	τ_F/ns[b]	Φ_F[a]	τ_F/ns[b]
Cl (**2a**)	0.91	1.79	0.44	3.61
OCH_3 (**2b**)	0.86	1.31	0.26	2.06
NO_2 (**2c**)	0.03	<0.3	$<10^{-4}$	<0.3
H (**2d**)	0.98	2.59	0.64	3.48
Cl (**3a**)	0.76	2.10	0.27	2.01
OCH_3 (**3b**)	0.93	1.79	0.63	4.77
NO_2 (**3c**)	0.016	<0.3	$<10^{-4}$	<0.3
CH_3 (**3d**)	0.89	2.05	0.59	2.44

[a] Standard deviation: ±7%.
[b] ±4%.

Table 4 summarizes the quantum yield and lifetime data for the fluorescence of the compounds studied in both solvents. Their fluorescence intensities display monoexponential decays. This indicates that the all the competitive ways of decay of the excitation state are of first order kinetics. Due to the rather short fluorescence lifetimes, practically no emission quenching by oxygen was observed in these cases.

Except for the nitro-derivatives, the fluorescent emission quantum yields in *n*-hexane are rather high, in several cases close to one. This indicates that the main relaxation route of the S_1 excited state in non-polar solvent is fluorescence. Generally, the sum of the quantum yields of the photolysis and the fluorescence for these compounds is about one, thus these two ways of decay used up the total energy of the excited state. In the case of the nitro-derivatives both the fluorescence and the photolysis quantum yields are rather low, and the emission lifetimes are much shorter than those observed for the other compounds studied. These phenomena indicate that another way of decay of the excited state is more efficient for the nitro-substituted compounds (**2c** and **3c**). This is probably an intersystem crossing ($S_1 \rightarrow T_1$) leading to a non-reactive triplet state. Similar phenomena were observed in the case of analogous benzofuran compound, and the formation of the triplet state was proved by the efficient formation singlet oxygen [28,30].

In ethanol the fluorescence quantum yields are significantly lower than in *n*-hexane (Table 4), indicating that the efficient stabilization of the polar excited state increases the probability of the photochemical conversion in competition with the emission as it was observed in the photolysis quantum yields (Table 1). This explanation is supported by the longer lifetimes of the emitting excited states in ethanol than in *n*-hexane. While even in ethanol, in several cases, the sum of the quantum yields of fluorescence and photolysis is close to one, in similar number of instants it is much below one, indicating that a third route, e.g., internal conversion or intersystem crossing can play a significant role in the decay of the excited state in this solvent.

4. Conclusion

The new 2,3-distyrylfuran derivatives, *trans*,*trans*-**2a–c** and *trans*,*trans*-**3a–c**, along with the previously synthesized *trans*,*trans*-**2d** and *trans*,*trans*-**3d** compounds, display interesting photoinduced properties, which promote their application as, e.g., potential fluorescence probes. Their fluorescence quantum yields are very sensitive to the solvent polarity, indicating that the emitting excited states are of higher dipole moment compared to the corresponding ground states. Hence, in non-polar *n*-hexane the fluorescence quantum yields in most cases are rather high, for some compounds close to one. The polar ethanol stabilizes these excited states, increasing their lifetime, thus promoting their decay *via* photochemical reaction of significant efficiency. The sum of the fluorescence and photolysis quantum yields is about one for some compounds in both solvents, indicating that these two ways of decay use up the energy of their excited state.

Deviating from the other compounds studied, the quantum yields for both the fluorescence and the photolysis of the nitro-derivatives **2c** and **3c** are rather low, probably due to an efficient intersystem crossing ($S_1 \rightarrow T_1$) leading to a non-reactive triplet state. The strong electron-withdrawing effect of the nitro group also results in significant red shifts in both the absorption and the emission bands compared to those of the unsubstituted compound. Due to the effect of the solvent polarity, even stronger red shifts of the fluorescence bands are caused by the nitro group in ethanol. This is manifested in the large Stokes-shifts indicating a significant change in the molecular geometry upon excitation.

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