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

Irena Škorić, Ilijana Kikaš, Margit Kovács, Marija Šindler-Kulyk, Ottó Horváth

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 their physical properties [1,2], and because they are involved in numerous natural compounds [30], 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 single-state lifetime is also relatively short ($\tau_s < 0.3$ ns).

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chemical behavior was observed for 2,3-distyrylfuran derivatives (2 (R = H), 3 (R = CH₃)) [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 = CH₃) [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, CH₃) 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 = CH₃) [21].

2. Experimental

2.1. General

The ¹H and ¹³C 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 CDCl₃ 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; injector temperature: 300 °C; volume injected: 5 µL. Melting points were obtained using an Original Koffler Mikroseitizschen 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 F254 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-distyryfurans 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 arytriphenylphosphonium bromides (R = H, Cl, OCH₃, NO₂), the 3-styryl derivatives 4 [20] and 6a–c were synthesized, and formylated using N,N-dimethylformamide and POCl₃ 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.
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, OCH3 or benzene, R = NO2), 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 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, OCH3 or benzene, R = NO2), 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 washed with water. After removal of the solvent, the crude reaction mixture was purified and the mixture of 4 iso-somers 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 iso-mers. A mixture of isomers of 2a and 2c in benzene (∼4.0 × 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%; Rf 0.37 (petroleum ether/diethylether 10:0.1); yellow crystals; mp 129 °C; UV (EtOH) /NAK max (log ε) 384 (4.32, sh), 364 (4.47), 347 (4.37, sh), 284 (4.28), 276 (4.27, sh) nm; ¹H NMR (CDCl3, 600 MHz) ıH 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, Het), 7.07 (d, J = 15.8 Hz, 1H, Het), 7.03 (d, J = 15.8 Hz, 1H, Het), 6.86 (d, J = 15.8 Hz, 1H, Het), 6.69 (d, J = 1.7 Hz, 1H); ¹³C NMR (75 MHz, CDCl3) ıC 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), 117.72 (d), 114.30 (d), 108.90 (d); MS m/z (ESI) (%) 307 (M+, 100%); Anal. Calcd for C20H15ClO: 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%; Rf 0.37 (petroleum ether/diethylether 10:0.1); yellow crystals; mp 129 °C; UV (EtOH) /NAK max (log ε) 384 (4.32, sh), 364 (4.47), 347 (4.37, sh), 284 (4.28), 276 (4.27, sh) nm; ¹H NMR (CDCl3, 600 MHz) ıH 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, Het), 7.07 (d, J = 15.8 Hz, 1H, Het), 7.03 (d, J = 15.8 Hz, 1H, Het), 6.86 (d, J = 15.8 Hz, 1H, Het), 6.69 (d, J = 1.7 Hz, 1H); ¹³C NMR (75 MHz, CDCl3) ıC 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 C20H15ClO: C, 78.30; H, 4.93. Found: C, 78.21; H, 5.07.
dissolved in dimethylformamide (1 mL, 18.8 mmol). After adjusting the pH (6), 108.76 (d, C4f), 55.35 (q, OCH3); MS (ESI) m/z 127.25 (d), 126.20 (2d), 121.28 (s), 118.08 (d), 114.23 (2d), 111.95 = 16.2 Hz, 1H, Het), 7.13 (d, J = 8.8 Hz, 2H, Har), 6.94 (d, J = 16.2 Hz, 1H, H4f), 6.82 (d, J = 16.2 Hz, 1H, H2f), 6.67 (d, J = 1.9 Hz, 1H, H4f), 3.83 (s, 3H, OCH3); 13C NMR (75 MHz, CDCl3) δC: 159.45 (s), 150.48 (s), 142.19 (d, C 5f), 137.52 (s), 128.69 (12d), 285.12 (1d), 277.44 (2d), 127.39 (2d), 127.25 (d), 126.20 (2d), 121.84 (3s), 114.23 (2d), 111.95 (1d), 108.76 (d, C4f), 55.35 (q, OCH3); MS (ESI) m/z (%) 303 (M+, 100%); Anal. Calcd for C21H15NO3: C, 75.70; H, 4.76. Found: C, 75.44; H, 4.99.

trans,trans-2-[4-(Nitrophenyl)ethenyl]furan (trans,trans-2c) was isolated as the main product. Yield 12.6%; according to 1HNMR spectroscopy, a mixture of 55% cis- and 45% trans-isomer.

cis-6a: Rf 0.27 (petroleum ether); colorless oil; UV (EtOH) λmax (log ε) 276 (4.08) nm; 1H NMR (CDCl3, 600 MHz) δH: 7.36–7.37 (m, 1H, H5f), 7.24–7.31 (m, 5H, 4H4f, 1H4g); 6.47 (d, J = 11.7 Hz, 1H, H4f), 6.39 (d, J = 11.7 Hz, 1H, H4f), 6.11 (dd, J = 1.6; 0.5 Hz, 1H, H5f); 13C NMR (150 MHz, CDCl3) δC: 142.24 (d, C2f/5f), 141.73 (d, C5f), 135.80 (3s), 132.38 (2s), 129.59 (2d), 129.76 (2d), 126.61 (1H, H3f), 120.29 (d, C4f), 110.58 (d, C5f); MS z/EI (204/206) (M+, 100%).

cis-6a: Rf 0.15 (petroleum ether); white crystals; mp 94 °C; UV (EtOH) λmax (log ε) 276 (4.08) nm; 1H NMR (CDCl3, 600 MHz) δH: 7.36–7.37 (m, 1H, H5f), 7.24–7.31 (m, 5H, 4H4f, 1H4g); 6.47 (d, J = 11.7 Hz, 1H, H4f), 6.39 (d, J = 11.7 Hz, 1H, H4f), 6.11 (dd, J = 1.6; 0.5 Hz, 1H, H5f); 13C NMR (150 MHz, CDCl3) δC: 142.24 (d, C2f/5f), 141.73 (d, C5f), 135.80 (3s), 132.38 (2s), 129.59 (2d), 129.76 (2d), 126.61 (1H, H3f), 120.29 (d, C4f), 110.58 (d, C5f); MS z/EI (204/206) (M+, 100%).

2,3-distyrylfuran derivatives 3a–c were prepared by Wittig reaction. To a stirred solution of furan-3-carbaldehyde (0.5 g, 5.21 mmol) and the phosphorus trioxide (0.34 g, 2.68 mmol) in benzene (10 mL) and the 4 isomers of trans-2,3-distyrylfuran derivatives 3a–c were used in a Wittig reaction to prepare 2,3-distyrylfuran derivatives 7a–c (as a mixture of cis- and trans-isomer) were prepared by Wittig reaction to prepare 2,3-distyrylfuran derivatives 7a–c. To a stirred solution of benzyltrimethylphosphonium salt (0.113 g, 0.26 mmol) and formyl derivatives 7a–c (0.26 mmol) in absolute ethanol (30 mL) a solution of sodium hydroxide (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 washed 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/diethyl ether (10–50%) 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 x 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/diethyl ether (0–5%) mixture as eluent. The photochemical isomerization was followed by NMR measurements. Isomers of 3b,c were separated by TLC using petroleum ether/diethyl ether (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 1HNMR spectroscopy, a mixture of 55% cis- and 45% trans-isomer.

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600 MHz) δ 8.93 (s, 1H, CHO), 7.44 (d, J = 1.8 Hz, 1H, Hg), 7.29 (d, J = 8.5 Hz, 2H, Hg), 7.22 (d, J = 8.5 Hz, 2H, Hg), 6.93 (d, J = 12.1 Hz, 1H, Hg), 6.82 (d, J = 1.7 Hz, 1H, Hg), 6.72 (d, J = 1.8 Hz, 1H, Hg); 13C NMR (75 MHz, CDCl3) δc 178.45 (d, CHO), 145.37 (s, C1), 146.92 (d, C15), 134.97 (s), 134.57 (d), 137.79 (s), 130.12 (2d), 128.71 (2d), 119.42 (d), 117.03 (s), 112.78 (d, C 4f); MS m/z (EI) 232/234 (M+- 100%).

cis-7c: Rf 0.15 (petroleum ether/diethyl ether 10:1); white crystals; mp 68 °C; UV (EtOH) λmax (log ε) 344 (4.32), 277 (4.30) nm; 1H NMR (CDCl3, 600 MHz) δ 8.91 (s, 1H, CHO), 7.57 (d, J = 1.7 Hz, 1H, Hg), 7.49 (d, J = 8.5 Hz, 2H, Hg), 7.46 (d, J = 16.2 Hz, 1H, Hg), 7.09 (d, J = 16.2 Hz, 1H, Hg), 6.91 (d, J = 8.5 Hz, 2H, Hg), 6.83 (d, J = 17.1 Hz, 1H, Hg), 3.81 (s, 3H, OCH3); MS m/z (EI) 228 (M+ 100%).

cis-7b: Rf 0.08 (petroleum ether/diethyl ether 10:1); yellow crystals; mp 93 °C; UV (EtOH) λmax (log ε) 340 (4.32), 277 (4.30) nm; 1H NMR (CDCl3, 600 MHz) δ 8.91 (s, 1H, CHO), 7.57 (d, J = 1.7 Hz, 1H, Hg), 7.49 (d, J = 8.5 Hz, 2H, Hg), 7.46 (d, J = 16.2 Hz, 1H, Hg), 7.09 (d, J = 16.2 Hz, 1H, Hg), 6.91 (d, J = 8.5 Hz, 2H, Hg), 6.83 (d, J = 17.1 Hz, 1H, Hg), 3.82 (s, 3H, OCH3); MS m/z (EI) 228 (M+ 100%).

cis-7c: Rf 0.40 (petroleum ether/diethyl ether 10:0.5); mp 82–83 °C; UV (EtOH) λmax (log ε) 322 (4.19) nm; 1H NMR (CDCl3, 600 MHz) δ 9.96 (s, 1H, CHO), 8.18 (d, J = 8.7 Hz, 2H, Hg), 7.47 (d, J = 1.8 Hz, 1H, Hg), 7.46 (d, J = 8.7 Hz, 2H, Hg), 7.11 (d, J = 12.2 Hz, 1H, Hg), 6.83 (d, J = 12.2 Hz, 1H, Hg), 6.16 (d, J = 1.8 Hz, 1H, Hg); MS m/z (EI) 243 (M+ 100%).

cis-7c: Rf 0.35 (petroleum ether/diethyl ether 10:0.5); mp 122–123 °C; UV (EtOH) λmax (log ε) 345 (4.41) nm; 1H NMR (CDCl3, 600 MHz) δ 9.95 (s, 1H, CHO), 8.24 (d, J = 8.7 Hz, 2H, Hg), 7.82 (d, J = 16.3 Hz, 1H, Hg), 7.68 (d, J = 8.7 Hz, 2H, Hg), 7.63 (d, J = 1.6 Hz, 1H, Hg), 7.18 (d, J = 16.3 Hz, 1H, Hg), 6.89 (d, J = 1.9 Hz, 1H, Hg); MS m/z (EI) 243 (M+ 100%).

cis-trans-2-(2-Phenylethyl)-3-[2-(4-

2.3. Photochemical and photophysical experiments

Typically, the irradiations were carried out with 3.5-cm3 solutions in 1-cm cells at room temperature. HPLC grade ethanol and n-hexane were used as solvents in these experiments. During the photoyses 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 ferroxylic actinometer [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 at which the products did not absorb. Emission spectra were measured on a PerkinElmer LS50B spectrometer. Ru(bpy)3Cl2 [35], quinine bisulfate (in 0.5 M H2SO4), and 9,10-diphenylanthracene [36] were utilized as references for determination of the fluorescence quantum yields. Each 2,3-distyrylphenyl 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 2d [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 photographic 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 distyrylphenyl compounds 2a-d and 3a-d were photochemically

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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 compound the longest-wavelength absorption band gradually 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. The nitro-substituted derivatives (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, despite the solvent polarity.

The nitro-substituted derivatives (2c and 3c) display much lower efficiencies for the photolysis, besides the effects of the solvent polarity in these cases are opposite to those of the other compounds studied. This phenomenon 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 S1 \rightarrow T1 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-

<table>
<thead>
<tr>
<th>R (code)</th>
<th>( \Phi ) (in n-hexane)</th>
<th>( \Phi ) (in ethanol)</th>
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<td>Cl (2a)</td>
<td>0.09</td>
<td>0.30</td>
</tr>
<tr>
<td>OCH3 (2b)</td>
<td>0.14</td>
<td>0.25</td>
</tr>
<tr>
<td>NO2 (2c)</td>
<td>0.07</td>
<td>0.025</td>
</tr>
<tr>
<td>H (2d)</td>
<td>0.02</td>
<td>0.38</td>
</tr>
<tr>
<td>CI (3a)</td>
<td>0.24</td>
<td>0.46</td>
</tr>
<tr>
<td>OCH3 (3b)</td>
<td>0.07</td>
<td>0.33</td>
</tr>
<tr>
<td>NO2 (3c)</td>
<td>0.16</td>
<td>0.042</td>
</tr>
<tr>
<td>CH3 (3d)</td>
<td>0.03</td>
<td>0.35</td>
</tr>
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</table>

a Standard deviation: ±7%.
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 (λω = 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 (λω = 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 (λω = 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 (λω = 366 nm, ℓ = 1 cm).
Table 2
Spectral behavior of 2,3-distyrylfuran derivatives in n-hexane at room temperature.

<table>
<thead>
<tr>
<th>R (code)</th>
<th>(\lambda_{\text{max}}^{\text{nm}}/\text{nm}^2 (\log \varepsilon))</th>
<th>(\Delta\nu_{\text{abs}}/\text{cm}^{-1})</th>
<th>(\lambda_{\text{max}}^e/\text{nm})</th>
<th>(\Delta\nu^e/\text{cm}^{-1})</th>
<th>(\Delta\nu_{\text{max}}/\text{cm}^{-1})</th>
<th>(\Delta\nu_{100}/\text{cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl (2a)</td>
<td>344,362,382 (4.65), 382 (4.65)</td>
<td>1450</td>
<td>400,425,450</td>
<td>1470</td>
<td>4090</td>
<td>1180</td>
</tr>
<tr>
<td>OCH3 (2b)</td>
<td>346,364,384 (4.34), 387 (4.34)</td>
<td>1630</td>
<td>401,426,450</td>
<td>1460</td>
<td>4000</td>
<td>902</td>
</tr>
<tr>
<td>NO2 (2c)</td>
<td>386,405 (4.51), 429</td>
<td>1380</td>
<td>451,472,508</td>
<td>1210</td>
<td>3730</td>
<td>1290</td>
</tr>
<tr>
<td>H (2d)</td>
<td>343,358 (4.48), 379 (4.48)</td>
<td>1550</td>
<td>398,422,445</td>
<td>1430</td>
<td>4240</td>
<td>1260</td>
</tr>
<tr>
<td>Cl (3a)</td>
<td>344,362,383 (4.23), 383 (4.23)</td>
<td>1670</td>
<td>397,421,446</td>
<td>1440</td>
<td>4020</td>
<td>920</td>
</tr>
<tr>
<td>OCH3 (3b)</td>
<td>345,362,384 (4.46), 380 (4.46)</td>
<td>1310</td>
<td>403,427,451</td>
<td>1390</td>
<td>4210</td>
<td>1500</td>
</tr>
<tr>
<td>NO2 (3c)</td>
<td>382,405 (4.51), 425</td>
<td>1470</td>
<td>447,470,500</td>
<td>1090</td>
<td>3720</td>
<td>1160</td>
</tr>
<tr>
<td>CH3 (3d)</td>
<td>343,358,384 (4.51), 380 (4.51)</td>
<td>1620</td>
<td>398,422,446</td>
<td>1430</td>
<td>4240</td>
<td>1190</td>
</tr>
</tbody>
</table>

* The main maximum is underlined.

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

<table>
<thead>
<tr>
<th>R (code)</th>
<th>(\lambda_{\text{max}}^{\text{nm}}/\text{nm}^2 (\log \varepsilon))</th>
<th>(\Delta\nu_{\text{abs}}/\text{cm}^{-1})</th>
<th>(\lambda_{\text{max}}^e/\text{nm})</th>
<th>(\Delta\nu^e/\text{cm}^{-1})</th>
<th>(\Delta\nu_{\text{max}}/\text{cm}^{-1})</th>
<th>(\Delta\nu_{100}/\text{cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl (2a)</td>
<td>347,362 (4.47), 382 (4.47)</td>
<td>1450</td>
<td>405,429,454</td>
<td>1380</td>
<td>4310</td>
<td>1490</td>
</tr>
<tr>
<td>OCH3 (2b)</td>
<td>349,364 (4.34), 387 (4.34)</td>
<td>1630</td>
<td>407,431,452</td>
<td>1370</td>
<td>4270</td>
<td>1270</td>
</tr>
<tr>
<td>NO2 (2c)</td>
<td>414 (4.31)</td>
<td>-</td>
<td>571</td>
<td>-</td>
<td>6640</td>
<td>-</td>
</tr>
<tr>
<td>H (2d)</td>
<td>342,359 (4.51), 380 (4.51)</td>
<td>1540</td>
<td>404,426,452</td>
<td>1280</td>
<td>4380</td>
<td>1560</td>
</tr>
<tr>
<td>Cl (3a)</td>
<td>327,347,362 (4.23), 384 (4.23)</td>
<td>1580</td>
<td>403,426,453</td>
<td>1340</td>
<td>4150</td>
<td>1230</td>
</tr>
<tr>
<td>OCH3 (3b)</td>
<td>345,362 (4.50), 382 (4.50)</td>
<td>1450</td>
<td>412,434,458</td>
<td>1230</td>
<td>4580</td>
<td>1900</td>
</tr>
<tr>
<td>NO2 (3c)</td>
<td>403 (4.33)</td>
<td>-</td>
<td>567</td>
<td>-</td>
<td>7180</td>
<td>-</td>
</tr>
<tr>
<td>CH3 (3d)</td>
<td>344,359 (4.51), 380 (4.51)</td>
<td>1540</td>
<td>403,426,453</td>
<td>1340</td>
<td>4380</td>
<td>1500</td>
</tr>
</tbody>
</table>

* 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 (\(\Delta\nu_{\text{max}}\)) and the 0–0 transition (\(\Delta\nu_{100}\)). For the derivatives with R=H, Cl, and OCH3 (on either styryl group) as well as CH3 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 derivatives (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 \(\pi\) 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 CI and OCH3 derivatives of both types of compounds (2a, 3a and 2b, 3b) in n-hexane. The substituents on the styryl group in position 3 result in smaller shifts (2 nm for Cl (3a) and 4 nm for OCH3 (3b)) than on the styryl group in position 2 (4 nm for Cl (2a) and 6 nm for OCH3 (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 vibronic structure with maxima corresponding to the transition from the vibrational level \(v=0\) of the ground state to the \(v'=2\) 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 (\(\Delta\nu_{\text{max}}\)). 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 \(S_0 \rightarrow S_1\) 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 \(\pi\) 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. This 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 ($\Delta \nu_{00}$) 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 $\Delta \nu_{02} = 1210$ 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 2 and 3, 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 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 all the competitive ways of decay of the excited 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.
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 quan-

tum 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 inefficient intersystem crossing (S1 → T1) 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.

Acknowledgements

This work was supported by grants from the Ministry of Science, and photochemistry of styryl substituted annelated furan derivatives, Hetero-
[15] I. Škorić, M. Šindler-Kulyk, Synthesis and photochemistry of styryl substituted annelated furan derivatives. IV. Concentration directed intramolec-
[17] I. Škorić, N. Basarić, Z. Marinić, A. Višnjevac, B. Kojić-Prodić, M. Šindler-
gapore, 2006.
[22] V. Vulgolina, M.E. Garst, A.S. Chandraratna, Stereoselective synthesis and repro-
ducibility of conformationally defined retinoic X receptor selective lig-
[23] I. Baraldi, E. Benassi, S. Ciorba, M. Šindler-Kulyk, I. Škorić, A. Spalletti, Struc-
gapore, 2006.
[27] Y. Yokoyama, M. Takashima, C. Higaki, K. Shidori, S. Moriguchi, C. Ando, Y. Murakami, Synthetic studies of indoles and related compounds. 32. An inter-
[28] V. Vulgolina, M.E. Garst, A.S. Chandraratna, Stereoselective synthesis and repro-
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[29] I. Baraldi, E. Benassi, S. Ciorba, M. Šindler-Kulyk, I. Škorić, A. Spalletti, Struc-
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[35] I. Baraldi, E. Benassi, S. Ciorba, M. Šindler-Kulyk, I. Škorić, A. Spalletti, Struc-
gapore, 2006.
[40] V. Vulgolina, M.E. Garst, A.S. Chandraratna, Stereoselective synthesis and repro-
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