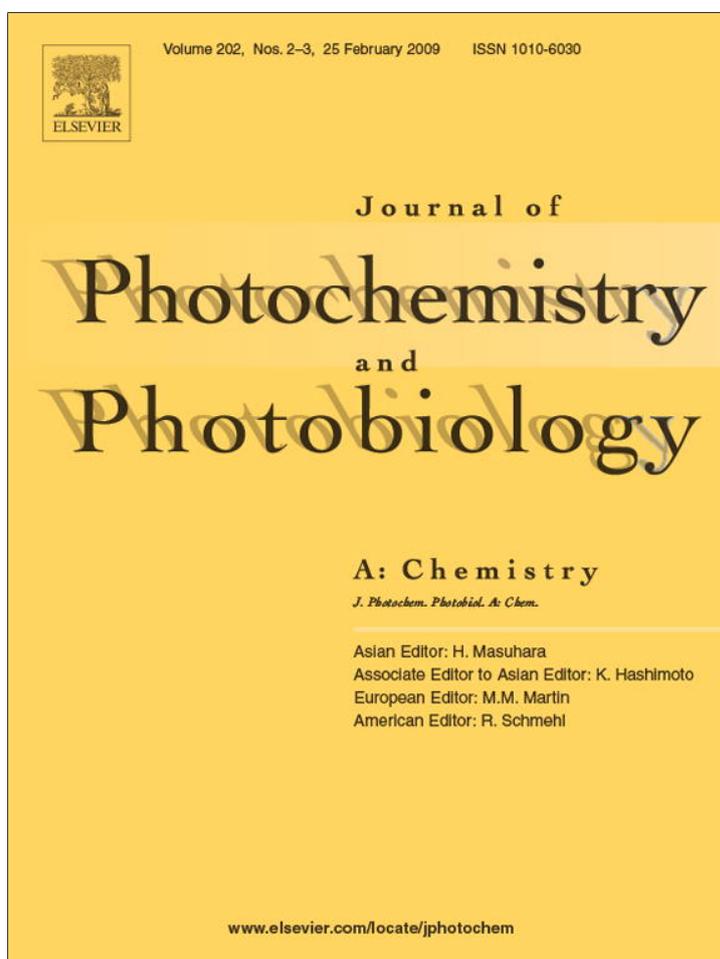


Provided for non-commercial research and education use.  
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

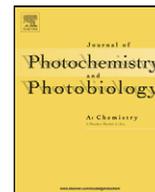
In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at ScienceDirect

# Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: [www.elsevier.com/locate/jphotochem](http://www.elsevier.com/locate/jphotochem)

## Novel conjugated $\omega,\omega'$ -diaryl hexatriene derivatives with the central double bond in the benzofuran ring and their photochemical and photophysical properties

Irena Škorić<sup>a</sup>, Serena Ciorba<sup>b</sup>, Anna Spalletti<sup>b,\*\*</sup>, Marija Šindler-Kulyk<sup>a,\*</sup><sup>a</sup> Department of Organic Chemistry, Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19, 10000 Zagreb, Croatia<sup>b</sup> Dipartimento di Chimica e Centro di Eccellenza Materiali Innovativi Nanostrutturati (CEMIN), Università di Perugia, 06123 Perugia, Italy

## ARTICLE INFO

## Article history:

Received 19 June 2008

Received in revised form

10 September 2008

Accepted 2 December 2008

Available online 11 December 2008

Dedicated to Professor Douglas C. Neckers on the occasion of his 70th birthday.

## Keywords:

Benzofuran

Fluorescence

Oxygen heterocycles

Photochemistry

Synthesis

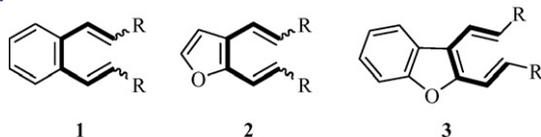
## ABSTRACT

The *trans,trans* isomers of 2-[2-(4-methylphenyl)ethenyl]-3-(2-phenylethenyl)benzo[*b*]furan and four derivatives have been synthesized by a sequence of reactions according to known methods. These new conjugated compounds have been characterized spectrally and photophysically. They practically do not react but decay by radiative relaxation. The high fluorescence quantum yields of these photostable compounds make them interesting as good fluorescent probes. The triplet behaviour of the NO<sub>2</sub>-derivative has been investigated by laser flash photolysis.

© 2008 Elsevier B.V. All rights reserved.

## 1. Introduction

The furan derivatives play an important role in organic chemistry as the building blocks in synthetic chemistry and have been found in many naturally occurring compounds [1,2]. Unsaturated furan derivatives, hetero-arylene compounds containing furylene rings connected through vinylene links (–CH=CH–) are especially interesting with regard to their electronic properties [3] and their potential applications in optoelectronics [4] as well as the starting materials for photochemical reactions [5–7]. Some distyryl substituted 2,3-furan derivatives have lately attracted the interest in electrophotographic photoreceptors as charge transporting agents [8–10].



\* Corresponding author. Tel.: +385 1 4597242; fax: +385 1 4597250.

\*\* Corresponding author. Tel.: +39 075 5855575; fax: +39 075 5855598.

E-mail addresses: [faby@unipg.it](mailto:faby@unipg.it) (A. Spalletti), [marija.sindler@fkit.hr](mailto:marija.sindler@fkit.hr) (M. Šindler-Kulyk).

In continuation of our study on photochemistry of furan conjugated system [11–21] with the central double bond placed in the benzene ring (**1**) we became interested in the hexatriene system in which the central double bond is a part of furan ring (**2**) [7] to explore the possibility of the synthesis of complicated fused furan-bicyclo structures. We have observed that this hexatriene system (**2**) behaves completely different from the hexatriene system with the central double bond incorporated in benzene ring (**1**). Compared to diheteroaryl systems (**1**, R=furyl), in which the intramolecular cycloaddition and *cis-trans* isomerization were the competitive processes [12], in the distyryl systems (**2** (R=phenyl) no cycloaddition photoproducts were observed [7]. The only detectable products were phototransposition products (the same M<sup>+</sup> as starting compounds) and stilbenes, presumably obtained by thermal decomposition of cyclobutane-polymeric structures. We concluded that because of dienic character of the furan ring and prevailing conformation of the furan double bonds, the excitation of the hexatriene **2** causes the [2 + 2] cycloaddition within the furan ring, rather than [2 + 2] cycloaddition of ethylenic bonds and formation of the bicyclic structures condensed with furan ring.

Here we report about the photochemistry of 2,3-distyryl benzofurans (**3**) in which the central double bond of a hexatriene system is a part of benzofuran ring. The idea was to prevent the possibility of intramolecular cycloaddition within the furan ring

and consequently force the hexatriene in the system **3** to react intramolecularly at the ethylenic bonds to obtain new heteropolycyclic structures.

## 2. Materials (Experimental)

### 2.1. General

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AV-600 Spectrometer at 300 or 600 MHz and 75 or 150 MHz, respectively. All NMR spectra were measured in  $\text{CDCl}_3$  using tetramethylsilane as reference. UV spectra were measured on a Varian Cary 50 UV-vis Spectrophotometer. The fluorescence measurements were performed by a Spex Fluorolog-2 F112AI spectrofluorimeter and by an Edinburgh Instrument 199S spectrofluorimeter. The triplet state was investigated by nanosecond laser flash photolysis using a Continuum Surelite II Nd:YAG laser. The mass spectra were obtained on a GC-MS (Varian CP-3800 GC-Saturn 2200) equipped with FFC column VF-5ms,  $30\text{ m} \times 0.25\text{ mm ID}$ .

All preparative irradiation experiments were carried out in deoxygenated benzene solutions (by bubbling a stream of argon prior to irradiation) in a pyrex vessel and in a Rayonet reactor equipped with RPR 3500 Å lamps. Melting points are uncorrected. Elemental analyses were carried out on Perkin-Elmer, Series II, CHNS Analyzer 2400. Silica gel (Merck 0.063–0.2 mm) was used for chromatographic purifications. Solvents were purified by distillation. Boiling range of petroleum ether, used for chromatographic separation, was 40–70 °C. Spectroscopic grade solvents from Fluka, spectrophotometric grade, were used in the fluorimetric determinations.

Furan-2-carbaldehyde and benzo[*b*]furancarbaldehyde was obtained from a commercial source. Aryltriphenylphosphonium salts were synthesized from the corresponding bromides and triphenylphosphine in benzene solutions according to the described procedure [6].

### 2.2. Preparation of **3a–e**

The starting compounds **3a–e** were prepared by a sequence of reactions (**I–III**) according to known methods. In the Wittig reaction (**I**), from 2-formylbenzofuran and *p*-tolyltriphenylphosphonium bromide, the 2-styryl derivative **4** was synthesized, formylated (**II**) using *N,N*-dimethylformamide and  $\text{POCl}_3$  producing formyl derivative **5** which was used for the second Wittig reaction (**III**) with various triphenylphosphonium salts resulting in 2,3-distyryl derivatives **3a–e** (Scheme 1).

#### 2.2.1. Preparation of 2-[2-(4-methylphenyl)ethenyl]benzo[*b*]furan (**4**)

A solution of sodium ethoxide (0.11 g, 4.8 mmol in 10 mL ethanol) was added dropwise to a stirred solution of 4-methylbenzyltriphenylphosphonium bromide (1.72 g, 3.5 mmol) and 2-benzo[*b*]furancarbaldehyde (0.5 g, 3.4 mmol) in absolute ethanol (50 mL). Stirring was continued under a stream of nitrogen for one day at RT. After removal of the solvent, the residue was worked up with water and benzene ( $3 \times 20\text{ mL}$ ) and dried with

$\text{MgSO}_4$ . The crude reaction mixture was chromatographed on silica gel column using petroleum ether as eluent: yield 77% (0.14 g); according to  $^1\text{H}$  NMR spectroscopy, a mixture of 37% *cis* and 63% *trans* isomers (separated by repeated column chromatography).

*cis*-**4**:  $R_f$  0.74 (petroleum ether/diethyl ether 10:1); colorless oil; UV (EtOH)  $\lambda_{\text{max}}$  ( $\epsilon$ ) 320 (16480), 234 (12520) nm;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  7.35–7.47 (m, H-ar, 4H), 7.21–7.23 (m, 1H) 7.15–7.19 (m, H-ar, 4H), 6.65 (d,  $J = 12.6\text{ Hz}$ , H-et, 1H), 6.62 (s, H-f, 1H), 6.43 (d,  $J = 12.6\text{ Hz}$ , H-et, 1H), 2.39 ppm (s,  $\text{CH}_3$ , 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  153.78 (s), 153.61 (s), 137.20 (s), 133.58 (s), 131.7 (d), 128.41 (2d), 128.35 (2d), 128.23 (s), 123.92 (d), 122.28 (d), 120.26 (d), 116.96 (d), 110.55 (d), 105.40 (d), 20.84 ppm (q); MS (EI)  $m/z$  (%) 234 ( $\text{M}^+$ , 100%).

*trans*-**4**:  $R_f$  0.78 (petroleum ether/diethyl ether 10:1); colorless crystals; mp 129–130 °C; UV (EtOH)  $\lambda_{\text{max}}$  ( $\epsilon$ ) 354 (21760, sh), 337 (32510), 326 (27870, sh) 235 (6690) nm;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  7.53 (dt,  $J = 7.5$ ; 1.5 Hz, H-ar, 2H), 7.45 (m, H-ar, 3H), 7.29 (d,  $J = 16.2\text{ Hz}$ , H-et, 1H), 7.16–7.27 (m, 3H), 6.96 (d,  $J = 16.2\text{ Hz}$ , H-et, 1H), 6.65 (s, H-f, 1H), 2.37 ppm (s,  $\text{CH}_3$ , 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  152.28 (s), 154.84 (s), 138.22 (s), 133.81 (s), 130.26 (d), 129.59 (2d), 126.64 (2d), 124.50 (d), 122.84 (d), 120.76 (d), 115.94 (d), 110.87 (d), 104.76 (d), 21.34 ppm (q); MS (EI)  $m/z$  (%) 234 ( $\text{M}^+$ , 100%); Anal. Calcd for  $\text{C}_{17}\text{H}_{14}\text{O}$ : C, 87.15; H, 6.02. Found: C, 86.98; H, 5.87.

#### 2.2.2. Preparation of

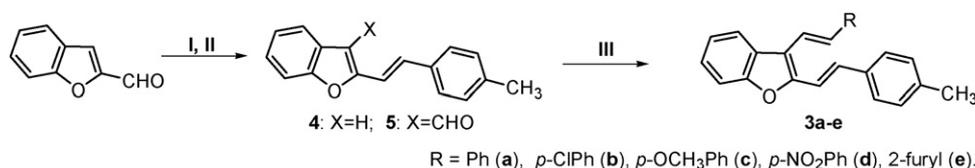
##### 2-[2-(4-methylphenyl)ethenyl]-3-benzo[*b*]furancarbaldehyde (**5**)

To the *trans*-**4** (0.30 g, 1.3 mmol) in dry dimethylformamide (2.5 mL) at  $\sim 10^\circ\text{C}$  phosphorus oxychloride (0.20 g, 1.3 mmol) was added and stirred for 15 min. The reaction mixture was allowed gradually to warm up to room temperature, stirred for six days, worked up with 10% NaOH solution and the product extracted with diethyl ether. The ether extracts were washed with water and then dried with  $\text{MgSO}_4$ . After column chromatography on silica gel using petroleum ether/diethyl ether (0–5%) as eluent the *trans*-**5** was isolated in 45% yield.

*trans*-**5**:  $R_f$  0.36 (petroleum ether/diethyl ether 10:1); yellow crystals; mp 131–132 °C; IR (evaporated film from  $\text{CHCl}_3$ ) 1659 ( $\text{C}=\text{O}$ ), 1626 ( $\text{C}=\text{C}$ )  $\text{cm}^{-1}$ ; UV (EtOH)  $\lambda_{\text{max}}$  ( $\epsilon$ ) 367 (33660), 281 (13020), 268 (11860, sh) 243 (13380) nm;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  10.44 (s, CHO, 1H), 8.14 (d,  $J = 7.4\text{ Hz}$ , H-ar, 1H), 7.67 (d,  $J = 16.0\text{ Hz}$ , H-et, 1H), 7.48–7.56 (m, 3H,  $\text{H}_{\text{ar}}$ ), 7.46 (d,  $J = 16.0\text{ Hz}$ , H-et, 1H), 7.36 (t,  $J = 7.7\text{ Hz}$ , H-ar, 1H), 7.35 (t,  $J = 7.70\text{ Hz}$ , H-ar, 1H), 7.24 (d,  $J = 7.7\text{ Hz}$ , H-ar, 2H), 2.40 ppm (s,  $\text{CH}_3$ , 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  183.83 (d, CHO), 164.50 (s), 162.18 (s), 154.08 (s), 140.26 (s), 137.27 (d), 132.66 (s), 129.80 (2d), 127.60 (2d), 126.15 (d), 124.67 (d), 116.66 (s), 111.59 (d), 110.86 (d), 21.51 ppm (q); MS (EI)  $m/z$  (%) 262 ( $\text{M}^+$ , 100%); Anal. Calcd for  $\text{C}_{18}\text{H}_{14}\text{O}_2$ : C, 82.42; H, 5.38. Found: C, 82.77; H, 5.44.

#### 2.2.3. Preparation of distyrylbenzofurans **3a–e**

To the stirred solutions of the corresponding aryltriphenylphosphonium salts (0.5 mmol) in absolute ethanol (50 mL) a solution of sodium ethoxide (0.5 mmol in 5 mL absolute ethanol) was added dropwise. After stirring the reaction mixture for 30 min the solution of *trans*-**5** (0.5 mmol) was added. Stirring was continued



**Scheme 1.** **I** ( $p\text{-MeC}_6\text{H}_4\text{CH}_2\text{P}^+\text{Ph}_3\text{Br}^-$ , NaOEt/EtOH); **II** ( $\text{HCONMe}_2$ ,  $\text{POCl}_3/\text{DMF}$ ); **III** ( $p\text{-RC}_6\text{H}_4\text{CH}_2\text{P}^+\text{Ph}_3\text{Br}^-$ , NaOEt/EtOH).

under a stream of nitrogen for one day at RT. After removal of the solvent, water was added to the residue, extracted with benzene and the benzene extracts dried with MgSO<sub>4</sub>. The products (**3a–c**, **e**) were purified by column chromatography on silica gel using petroleum ether and petroleum ether/diethyl ether (0–3%) mixtures as eluent. The 2,3-distyrylbenzofuran **3d** was prepared by some modified procedure: to the prepared ylide from *p*-nitrophenyltriphenylphosphonium bromide and sodium ethoxide in benzene the *trans*-**5** was added, stirred overnight and worked out as described for **3a–c**, **e**.

The physical data of the separated *trans,trans* isomers of distyrylbenzofurans **3a–e**: *trans,trans*-2-[2-(4-methylphenyl)ethenyl]-3-(2-phenylethenyl)benzo[*b*]furan (*trans,trans*-**3a**): Yield 75%; R<sub>f</sub> 0.66 (petroleum ether/diethyl ether 10:1); yellow-green crystals; mp 150–151 °C; UV (EtOH) λ<sub>max</sub> (ε) 392 (29450, sh), 373 (37750), 358 (32440, sh), 312 (22960, sh), 304 (25540), 286 (25510), 278 (23360, sh), 242 (10890) nm; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.91 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.49 (dd, *J* = 7.9; 1.5 Hz, 3H), 7.40 (m, 2H), 7.32–7.37 (m, 3H), 7.29–7.31 (m, 2H), 7.28 (d, *J* = 16.2 Hz, H-et, 1H), 7.22 (d, *J* = 16.2 Hz, H-et, 1H), 7.20 (d, *J* = 7.9 Hz, H-et, 2H), 2.38 (s, CH<sub>3</sub>, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 154.14 (s), 152.34 (s), 137.94 (s), 137.32 (s), 133.45 (s), 130.36 (d), 129.63 (d), 129.06 (2d), 128.27 (2d), 127.12 (d), 126.87 (s), 126.32 (2d), 125.76 (2d), 124.68 (d), 122.62 (d), 120.41 (d), 118.10 (d), 112.47 (d), 110.55 (d), 20.86 ppm (q, CH<sub>3</sub>); MS (ESI) *m/z* (%) 337 (MH<sup>+</sup>, 100%); Anal. Calcd for C<sub>25</sub>H<sub>20</sub>O: C, 89.25; H, 5.99. Found: C, 89.46; H, 5.98.

*trans,trans*-2-[2-(4-methylphenyl)ethenyl]-3-[2-(4-chlorophenyl)ethenyl]benzo[*b*]furan (*trans,trans*-**3b**): Yield 43%; R<sub>f</sub> 0.77 (petroleum ether/diethyl ether 10:0.2); yellow-green crystals; mp 168 °C; UV (EtOH) λ<sub>max</sub> (ε) 376 (35940), 306 (26350), 287 (24250) nm; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.89 (dd, *J* = 7.2; 2.0 Hz, 1H), 7.50 (m, 5H), 7.38 (d, *J* = 16.0 Hz, 1H), 7.29–7.37 (m, 5H), 7.22–7.25 (m, 3H), 7.21 (d, *J* = 16.0 Hz, 1H), 2.39 ppm (s, CH<sub>3</sub>, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 154.62 (s), 153.10 (s), 138.58 (s), 136.32 (s), 133.84 (s), 133.14 (s), 131.17 (d), 129.59 (2d), 128.92 (2d), 128.59 (d), 127.39 (2d), 127.17 (s), 126.85 (2d), 125.27 (d), 123.19 (d), 120.85 (d), 119.21 (d), 115.60 (s), 112.75 (d), 111.11 (d), 21.38 ppm (q); MS (ESI) *m/z* (%) 370 (M<sup>+</sup>, 100%), 141 (12), 188 (10); Anal. Calcd for C<sub>25</sub>H<sub>19</sub>ClO: C, 80.96; H, 5.16. Found: C, 80.83; H, 5.27.

*trans,trans*-2-[2-(4-methylphenyl)ethenyl]-3-[2-(4-methoxyphenyl)ethenyl]benzo[*b*]furan (*trans,trans*-**3c**): Yield 76%; R<sub>f</sub> 0.69 (petroleum ether/diethyl ether 10:0.2); yellow-green crystals; mp 145–146 °C; UV (EtOH) λ<sub>max</sub> (ε) 378 (36770), 306 (32200), 290 (29730, sh) nm; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.90 (d, 1H, = 7.8 Hz), 7.55–7.45 (m, 5H), 7.38–7.27 (m, 4H), 7.25–7.17 (m, 4H), 6.95 (d, 2H, *J* = 8.1 Hz), 3.86 (s, 3H, OCH<sub>3</sub>), 2.38 ppm (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 159.36 (s), 154.61 (s), 152.34 (s), 138.32 (s), 134.03 (s), 130.63 (s), 130.42 (d), 129.76 (d), 129.55 (2d), 127.47 (2d), 127.45 (s), 126.77 (2d), 125.11 (d), 123.01 (d), 120.92 (d), 116.50 (d), 116.15 (s), 114.23 (2d), 113.08 (d), 111.01 (d), 55.38 (q), 21.36 ppm (q); MS (ESI) *m/z* (%) 366 (M<sup>+</sup>, 100%), 141 (12), 188 (10); Anal. Calcd for C<sub>26</sub>H<sub>22</sub>O<sub>2</sub>: C, 85.22; H, 6.05. Found: C, 85.21; H, 6.12.

*trans,trans*-2-[2-(4-methylphenyl)ethenyl]-3-[2-(4-nitrophenyl)ethenyl]benzo[*b*]furan (*trans,trans*-**3d**): Yield 37%; R<sub>f</sub> 0.47 (petroleum ether/diethyl ether 10:0.5); orange crystals; mp 179 °C; UV (EtOH) λ<sub>max</sub> (ε) 398 (29360), 328 (38860) nm; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.26 (d, *J* = 8.4 Hz, 2H), 7.91 (dd, *J* = 7.2; 1.8 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 16.1 Hz, 1H), 7.54–7.48 (m, 4H), 7.44 (d, *J* = 15.9 Hz, 1H), 7.42–7.30 (m, 2H), 7.29 (d, *J* = 15.9 Hz, 1H), 7.22 (d, *J* = 16.1 Hz, 1H), 7.21 (m, 1H), 2.40 ppm (s, CH<sub>3</sub>, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 154.76 (s), 154.46 (s), 144.33 (s), 139.00 (s), 133.55 (s), 133.53 (s), 132.39 (d), 129.65 (2d), 128.00 (s), 127.12 (2d), 126.49 (2d), 125.60 (d), 124.25 (2d), 123.54 (d), 123.28 (d), 120.84 (d), 115.14 (s), 112.24 (d), 111.26 (d), 21.41 ppm (q); MS (ESI)

*m/z* (%) 382 (MH<sup>+</sup>, 100%); Anal. Calcd for C<sub>25</sub>H<sub>19</sub>NO<sub>3</sub>: C, 78.72; H, 5.02. Found: C, 78.81; H, 5.04.

*trans,trans*-2-[2-(4-methylphenyl)ethenyl]-3-[2-(2-furyl)ethenyl]benzo[*b*]furan (*trans,trans*-**3e**): Yield 67%; R<sub>f</sub> 0.78 (petroleum ether/diethyl ether 10:0.5); yellow-orange crystals; mp 141–142 °C; UV (EtOH) λ<sub>max</sub> (ε) 405 (19010, sh), 385 (30940), 368 (32480), 35 (26150, sh), 310 (34780), 293 (29670, sh), 247 (11490) nm; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.86 (dd, *J* = 7.5; 1.5 Hz, H-ar, 1H), 7.49 (m, 4H), 7.36 (d, *J* = 16.2, H-et, 1H), 7.18–7.37 (m, 6H), 7.04 (d, *J* = 16.2 Hz, H-et, 1H), 6.47 (dd, *J* = 3.3; 1.8 Hz, 1H), 6.40 (d, *J* = 1.8 Hz, 1H), 2.38 ppm (s, CH<sub>3</sub>, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 154.15 (s), 153.04 (s), 152.46 (s), 141.61 (d), 137.92 (s), 137.62 (s), 133.47 (s), 130.32 (d), 129.06 (2d), 126.65 (s), 126.36 (2d), 124.68 (d), 122.61 (d), 120.32 (d), 117.03 (d), 116.48 (d), 112.39 (d), 111.31 (d), 110.57 (d), 107.88 (d), 20.87 ppm (q); MS (EI) *m/z* (%) 326 (M<sup>+</sup>, 100%), 285 (15), 257 (30), 115 (15); Anal. Calcd for C<sub>23</sub>H<sub>18</sub>O<sub>2</sub>: C, 84.64; H, 5.56. Found: C, 84.19; H, 5.62.

### 2.3. Irradiation experiments

#### 2.3.1. Photochemical experiments

A solution of *trans,trans*-**3a–e** in benzene (e.g. 7 × 10<sup>-2</sup> M) was purged with argon for 30 min and irradiated in a Rayonet reactor at 350 nm. The reaction course was followed combining NMR and GC-MS. GC operating conditions for all experiments: column temperature programmed from 110 to 300 °C (3 min isothermal) at a rate of 33 °C min<sup>-1</sup>; carrier gas: helium; flow rate: 1 mL min<sup>-1</sup>; injector temperature: 300 °C; volume injected: 5 μL.

After complete conversion (16 h) of starting compounds **3a–e** the following chromatograms (*t*<sub>ret.</sub> (min), M<sup>+</sup>, %comp.) were obtained: **3a**: 5.06', M<sup>+</sup> 180 (5% **8a**); 5.42', M<sup>+</sup> 208 (5% **6**); 5.80', M<sup>+</sup> 194 (7% **7a**); 6.07', M<sup>+</sup> 208 (83% **6**). **3b**: 5.42', M<sup>+</sup> 208 (14% **6**); 5.77', M<sup>+</sup> 228 (11% **7b**); 6.10', M<sup>+</sup> 208 (32% **6**); 6.52', M<sup>+</sup> 228 (42% **7b**); 7.01', M<sup>+</sup> 248 (1% **8b**). **3c**: 5.42', M<sup>+</sup> 208 (4% **6**); 6.01', M<sup>+</sup> 224 (9% **7c**); 6.08', M<sup>+</sup> 208 (63% **6**); 6.75', M<sup>+</sup> 224 (24% **7c**). **3d**: 5.42', M<sup>+</sup> 208 (13% **6**); 6.10', M<sup>+</sup> 208 (56% **6**); 6.55', M<sup>+</sup> 239 (31% **7d**). **3e**: 5.33', M<sup>+</sup> 160 (3% **8e**); 5.41', M<sup>+</sup> 208 (3% **6**); 5.71', M<sup>+</sup> 184 (21% **7e**); 6.09', M<sup>+</sup> 208 (73% **6**). (Two same mass signals at different retention times represent *cis* and *trans* isomers.)

The irradiation of deaerated (by bubbling pure nitrogen) solutions of **3a–e** in *n*-hexane and acetonitrile was also performed in mild conditions (~10<sup>-4</sup> M, low dose of the monochromatic excitation light). The excitation wavelength, corresponding to the maximum of the first band of the absorption spectrum of the studied compounds, was isolated from a 150 W high pressure Xenon lamp by a monochromator. The photoreaction was monitored by HPLC using a Waters apparatus equipped with analytical ProntoSIL 200-3-C30 (3 μm, 250 × 4 mm) column and UV diode-array detector, acetonitrile (sometimes containing small percentages of water) being used as eluent. The photoconversion percentages were determined on the basis of the isosbestic points between the absorption spectra of the different isomers.

#### 2.3.2. Fluorescence measurements

The fluorescence spectra of **3a–e** were measured by a Spex Fluorolog-2 F112AI spectrofluorimeter. Dilute solutions (absorbance <0.1 at the excitation wavelength, λ<sub>exc</sub>) were used. The emission quantum yields were determined at λ<sub>exc</sub> corresponding to the maximum of the first absorption band (λ<sub>max</sub>). 9,10-diphenylanthracene in cyclohexane was used as fluorimetric standard (φ<sub>F</sub> = 0.90 in de-aerated solvent [22]).

Fluorescence lifetimes were measured by an Edinburgh Instrument 199S spectrofluorimeter, using the single photon counting method (resolution time ≈ 0.3 ns). For the very short-living **3d** a Spex Fluorolog-τ2 apparatus, based on the phase modulation technique, was used (resolution time up to tens of ps).

### 2.3.3. Transient experiments

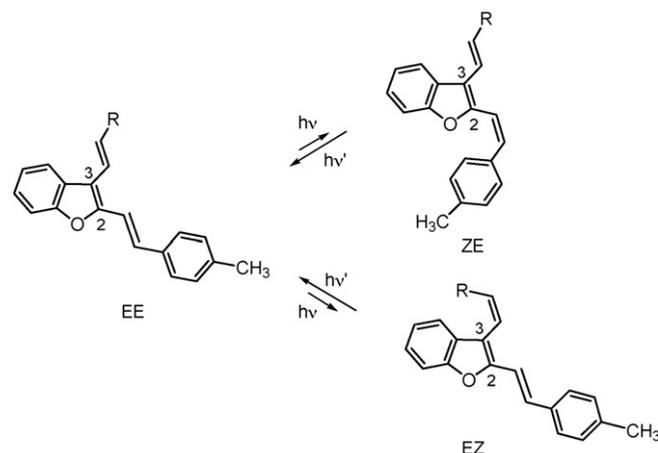
The triplet state was investigated by nanosecond laser flash photolysis ( $\lambda_{exc} = 355 \text{ nm}$ ) using a Continuum Surelite II Nd:YAG laser. The quantum yield of singlet oxygen production ( $\phi_{\Delta}$ ) in the presence of air was obtained by measuring its phosphorescence in *n*-hexane with a germanium diode using phenalene as standard ( $\phi_{\Delta} = 0.95$  [23]).

Further details on spectrophotometric, fluorimetric and laser flash photolysis measurements are reported elsewhere [24].

## 3. Results and discussion

### 3.1. Photochemical experiments

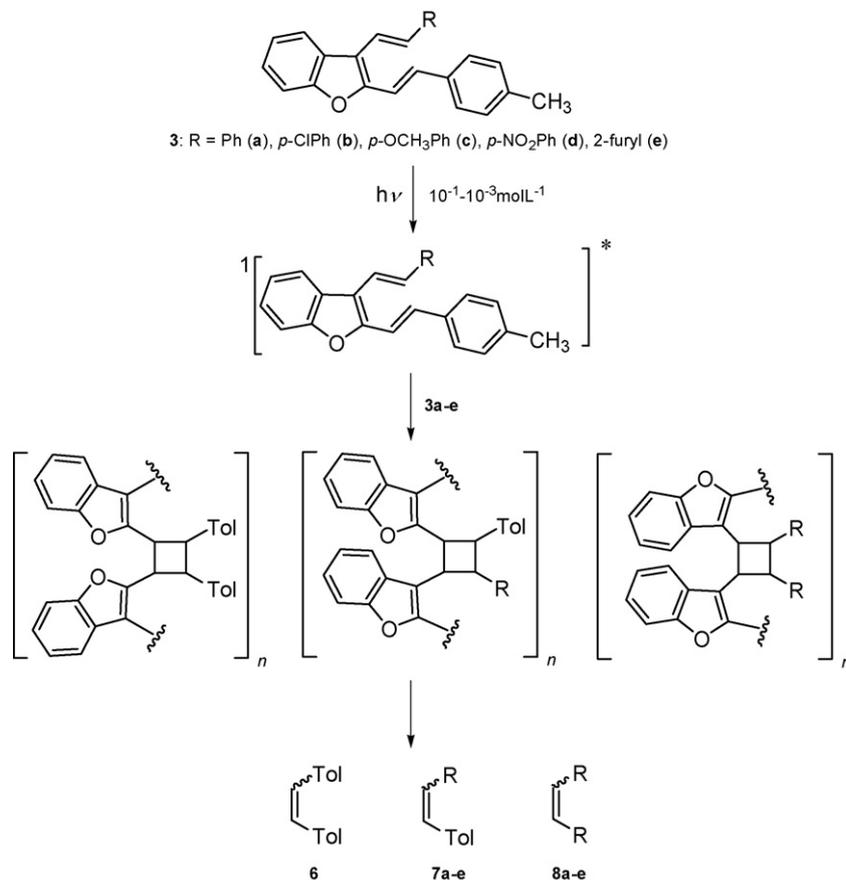
The irradiation experiments were performed in benzene solutions of lower ( $10^{-3} \text{ M}$ ) and higher ( $10^{-1} \text{ M}$ ) concentrations. After shorter time of irradiation only the starting compounds, *trans,trans*-distyryl derivatives **3a–e**, were detected in their NMR spectra. Neither *trans–cis* isomerization nor an intramolecular cycloaddition reaction was seen besides the formation of high-molecular-weight tarry material which on purification by column chromatography remained on silica gel. After prolonged irradiation time (over night) only small quantities of stilbenes (**6–8**) (Scheme 2) were detected in photo mixtures by GC–MS, presumably obtained from thermal decomposition of polymeric cyclobutane structures. In the photomixtures of higher concentrations ( $10^{-1} \text{ M}$ ) the stilbenes were detected after shorter irradiation time. It is interesting to emphasize that in all irradiation experiments of these asymmetrically disubstituted benzofurans **3a–e** the stilbene **6** was one of the most prominent signal in the chromatogram. This 4,4'-dimethylstilbene (**6**) could not be formed by thermal



**Scheme 3.** Geometrical isomers involved in the photoreactions of **3a** and **3b**.

decomposition of the intramolecular adducts but only from the intermolecular processes. A similar mechanism has been reported for analogous compounds [5,19]. These results imply that the 2,3-distyrylbenzofurans are photostable and do not give the intramolecular products.

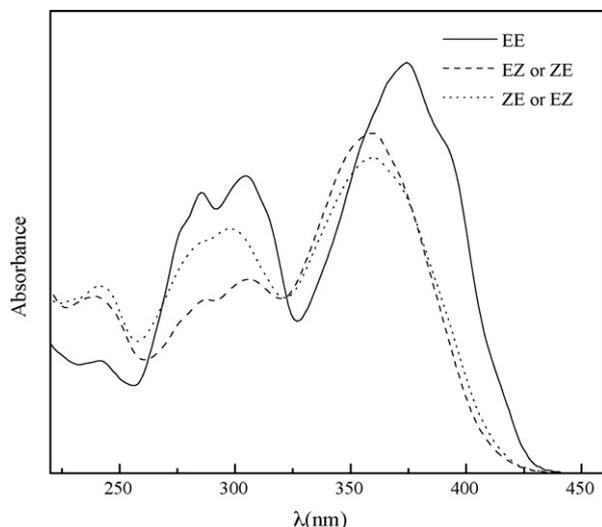
As a matter of fact, the irradiation of the *trans,trans* (E,E) isomers of these asymmetric compounds, in mild conditions (see Section 2.3.1) and in a polar solvent (acetonitrile), produced only isomerization towards the *trans,cis* (E,Z) and *cis,trans* (Z,E) geometrical isomers (see Scheme 3) with very low yield (in the case of **3a** and **3b** only, Table 1). An even lower (practically undetectable) reactivity was observed for the same compounds in *n*-hexane.



**Scheme 2.** Photochemistry of **3a–e** in benzene at high concentrations ( $\geq 10^{-3} \text{ M}$ ).

**Table 1**  
Photoreaction quantum yields for **3a** and **3b** in acetonitrile at room temperature ( $\lambda_{\text{exc}} = 370$  nm).

Compound	$\phi_{\text{EE} \rightarrow \text{ZE}}$	$\phi_{\text{EE} \rightarrow \text{EZ}}$
<b>3a</b>	0.01	0.06
<b>3b</b>	0.03	0.03



**Fig. 1.** Absorption spectra of EE, EZ and ZE isomers of **3b** in acetonitrile at room temperature, normalized at the isosbestic points, as obtained by the HPLC analyses.

The two photoproducts, separated by HPLC, reconverted to EE by irradiation in acetonitrile giving the possibility to determine the isosbestic points between the photoproducts and EE absorption spectra. The UV–vis spectra of the EE, EZ and ZE isomers of **3b**, recorded in the same solvent, are reported in Fig. 1 as an example (an assignment of the dashed and dotted spectra to EZ and ZE is not possible at this stage). As usually observed in analogous compounds [20,25], the presence of a double bond in *cis* configuration leads to a hypochromic absorption spectrum, blue shifted with respect to that of EE.

In the case of the unsubstituted compound (**3a**), the two photoproducts assigned to the geometrical isomers (EZ and ZE), where one or the other double bond isomerizes, were produced with different quantum yields. In analogy with the findings reported for a related compound (2,3-distyrylfuran) where the presence of oxygen in the *ortho* position with respect to the double bond was found to inhibit the rotation [26], the larger value of the photoisomerization quantum yield could be assigned to the rotation of the double bond attached at the 3 position of the benzofuran ring (isomer EZ).

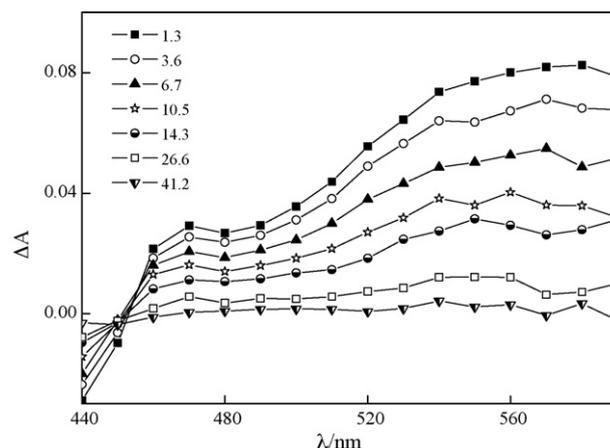
### 3.2. Photophysics of **3a–e**

The EE-distyryl derivatives **3a–e** showed in non-polar solvents an intense structured fluorescence band whose maxima are reported in Table 2 together with the emission quantum yields and lifetimes. The absorption and emission spectra showed, as

**Table 2**  
Spectral and fluorimetric parameters for **3a–e** compounds in *n*-hexane at room temperature.

Compound	$\lambda_{\text{abs}}^{\text{max}}$ (nm)	$\lambda_{\text{F}}^{\text{max}}$ (nm) <sup>b</sup>	$\phi_{\text{F}}$	$\phi_{\text{F}}^{\text{a}}$	$\phi_{\text{F}}/\phi_{\text{F}}^{\text{a}}$	$\tau_{\text{F}}$ (ns)	$\tau_{\text{F}}^{\text{a}}$ (ns)	$\tau_{\text{F}}/\tau_{\text{F}}^{\text{a}}$
<b>3a</b>	371	424, <u>452</u> , 483	0.67	0.54	1.2	3.1	2.6	1.2
<b>3b</b>	375	426, <u>454</u> , 486	0.71	0.57	1.2	3.1	2.4	1.3
<b>3c</b>	376	430, <u>459</u> , 491	0.73	0.56	1.3	3.1	2.4	1.3
<b>3d</b>	414	450, <u>480</u> , 514	0.04	0.03 <sub>6</sub>	1.1		0.2 <sup>c</sup>	
<b>3e</b>	370	445, <u>476</u> , 511	0.64	0.45	1.4	4.3	3.2	1.3

<sup>a</sup>Aerated solutions; <sup>b</sup>the main maximum is underlined; and <sup>c</sup>measured by shift-phase method.



**Fig. 2.** Transient absorption spectra of **3d** in *n*-hexane recorded at different delay times ( $\mu\text{s}$ ) after the laser excitation at room temperature.

expected, a red shift on going from the Cl- to OCH<sub>3</sub>- and to NO<sub>2</sub>-derivative if compared with the unsubstituted **3a**. An important red shift was also observed by replacing the benzene ring of **3a** with a 2-furyl group (**3e**), as previously observed for analogous compounds [20].

In principle, these flexible molecules could exist in fluid solution as a mixture of different conformations (originating by rotation around the quasi-single bonds between the double bonds and the aryl groups) in dynamic equilibrium among them, with different spectral, photophysical and photochemical properties. On the other hand, the absence of  $\lambda_{\text{exc}}$  effect on the emission spectra and the mono-exponential decays (Table 2) pointed to the presence of a prevalent conformation in solutions of non-polar solvents at room temperature [27].

The measured fluorescence quantum yields are quite high (with the exception of **3d**) and the emission quenching by oxygen is modest in agreement with relatively short singlet lifetimes (few ns). For all these compounds the emission is the main deactivation pathway and the absence of photoisomerization could be due to high torsional barriers in the singlet manifold. In the case of **3d**,  $\phi_{\text{F}}$  and  $\tau_{\text{F}}$  are reduced more than one order of magnitude. Experiments by ns laser flash photolysis on **3d** evidenced the production of a transient (not observed for the other compounds) whose absorption spectrum at different delay times with respect to the excitation pulse is shown in Fig. 2.

This transient was assigned to the lowest triplet state of **3d** on the base of its decay kinetics and the quenching by oxygen ( $k_{\text{ox}} \cong 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). The reduction of fluorescence and a parallel strong induction of intersystem crossing (ISC) by introducing NO<sub>2</sub> group is expected and well documented in similar compounds [28]. However, ISC leads to a non reactive (*trans,trans*) triplet state with a relative long lifetime (14.7  $\mu\text{s}$ , the longest lifetime recorded in different experiments) pointing to the presence of a high torsional barrier also in this state.

Since  $T_1$  is efficiently quenched by oxygen with the formation of singlet oxygen [ $\text{O}_2(^1\Delta_{\text{g}})$ ], an indirect and rough estimation of the

triplet yield for **3d** in aerated *n*-hexane was carried out by measuring the quantum yield of singlet oxygen production ( $\phi_{\Delta} = 0.55$ ), which reflects the minimum value of the  $T_1$  produced by ISC.

Preliminary results in acetonitrile showed that the photophysical parameters are little affected by the solvent polarity. The small increase of photoisomerization found in the case of **3a** and **3b**, is probably caused by a smaller activation energy in this solvent as previously reported for analogous compounds [29].

#### 4. Conclusion

These new conjugated hexatriene derivatives were found of potential interest for fluorescent probes because of their high stability and high fluorescence quantum yields.

The non-reactivity of the *trans,trans*-2,3-distyrylbenzofurans could be explained by the high efficiency of the radiative relaxation pathway which prevails on the isomerization process, which probably is strongly activated. High torsional barriers are expected also in the triplet state because considering that **3d** does not react even if a substantial population of the triplet state was observed by flash photolysis.

On the other hand, the absence of formation of intramolecular cycloaddition photoproducts could be due to conformational equilibria shifted to non suitable species.

Further experimental work (solvent and temperature effects) and MO calculations on these and related compounds are in progress [30] to better understand the role of the substituents on the nature of the excited states and to investigate the possible involvement of intramolecular charge transfer processes in their relaxation.

#### Acknowledgements

This work was supported by grants from the Ministry of Science, Education and Sports of the Republic of Croatia (grant no. 125-0982933-2926).

#### References

- [1] Th.L. Gilchrist, *Heterocyclic Chemistry*, Longman, Singapore, 1997.
- [2] A.F. Pozharskii, A.T. Soldatenkov, A.R. Katritzky, *Heterocycles in Life and Society*, Wiley, Chichester, 1997.
- [3] I. Baraldi, G. Ginocchetti, U. Mazzucato, A. Spalletti, *Chem. Phys.* 337 (2007) 168–176.
- [4] J.L. Segura, N. Martin, *J. Mater. Chem.* 10 (2000) 2403–2435.
- [5] W.H. Horspool (Ed.), *CRC Handbook of Organic Photochemistry and Photobiology*, CRC, Boca Raton, 1995.
- [6] I. Škorić, Ž. Marinić, K. Molčanov, B. Kojić-Prodić, M. Šindler-Kulyk, *Magn. Reson. Chem.* 45 (2007) 680–684.
- [7] I. Škorić, I. Flegar, Ž. Marinić, M. Šindler-Kulyk, *Tetrahedron* 62 (2006) 7396–7407.
- [8] Z.Z. Song, H.N.C. Wong, Y. Yang, *Pure Appl. Chem.* 68 (1996) 723–726.
- [9] Y. Yokoyama, M. Takashima, C. Higaki, K. Shidori, S. Moriguchi, C. Ando, Y. Murakami, *Heterocycles* 36 (1993) 1739–1742.
- [10] V. Vuligonda, M.E. Garst, A.S. Chandraratna, *Bioorg. Med. Chem. Lett.* 9 (1999) 589–594.
- [11] M. Šindler-Kulyk, L. Špoljarić, Ž. Marinić, *Heterocycles* 29 (1989) 679–682.
- [12] M. Šindler-Kulyk, G. Kragol, I. Piantanida, S. Tomšić, I. Vujković Cvijin, Ž. Marinić, B. Metelko, *Croat. Chem. Acta* 69 (1996) 1593–1602.
- [13] I. Vujković Cvijin, Ž. Marinić, M. Šindler-Kulyk, *Spectrosc. Lett.* 31 (1998) 989–1000.
- [14] M. Šindler-Kulyk, I. Škorić, S. Tomšić, Ž. Marinić, D. Mrvoš-Sermek, *Heterocycles* 51 (1999) 1355–1369.
- [15] I. Škorić, Ž. Marinić, M. Šindler-Kulyk, *Heterocycles* 53 (2000) 55–68.
- [16] I. Škorić, N. Basarić, Ž. Marinić, M. Šindler-Kulyk, *Heterocycles* 55 (2001) 1889–1896.
- [17] I. Škorić, A. Hutinec, Ž. Marinić, M. Šindler-Kulyk, *ARKIVOC* (2003) 87–97.
- [18] I. Škorić, Ž. Marinić, M. Šindler-Kulyk, *Croat. Chem. Acta* 77 (2004) 161–166.
- [19] I. Škorić, N. Basarić, Ž. Marinić, A. Višnjevac, B. Kojić-Prodić, M. Šindler-Kulyk, *Chem. Eur. J.* 11 (2005) 543–551.
- [20] S. Ciorba, G. Galiazzo, M. Šindler-Kulyk, I. Škorić, A. Spalletti, *J. Photochem. Photobiol., A* 187 (2007) 325–331.
- [21] D. Vidaković, I. Škorić, M. Horvat, Ž. Marinić, M. Šindler-Kulyk, *Tetrahedron* 64 (2008) 3928–3934.
- [22] G. Bartocci, F. Masetti, U. Mazzucato, A. Spalletti, I. Baraldi, F. Momicchioli, *J. Phys. Chem.* 91 (1987) 4733–4743.
- [23] R. Schmidt, C. Tanielian, R. Dunsbach, C. Wolff, *J. Photochem. Photobiol., A: Chem.* 79 (1994) 11–17.
- [24] P. Gajdek, R.S. Becker, F. Elisei, U. Mazzucato, A. Spalletti, *J. Photochem. Photobiol., A: Chem.* 100 (1996) 57–64.
- [25] G. Ginocchetti, G. Galiazzo, D. Pannacci, U. Mazzucato, A. Spalletti, *Chem. Phys.* 331 (2006) 164–172.
- [26] I. Baraldi, E. Benassi, S. Ciorba, M. Šindler-Kulyk, I. Škorić, A. Spalletti, *Chem. Phys.* 353 (2008) 163–169.
- [27] (a) U. Mazzucato, F. Momicchioli, *Chem. Rev.* 91 (1991) 1679; (b) G. Bartocci, A. Spalletti, U. Mazzucato, in: J. Waluk (Ed.), *Conformational Analysis of Molecules in Excited States*, Wiley-VCH, New York, 2000 (Chapter 5).
- [28] H. Görner, F. Elisei, U. Mazzucato, G. Galiazzo, *J. Photochem. Photobiol., A: Chem.* 43 (1988) 139–154.
- [29] (a) G. Bartocci, U. Mazzucato, A. Spalletti, *Recl. Trav. Chim. Pays-Bas* 114 (1995) 459–464; (b) G. Bartocci, U. Mazzucato, A. Spalletti, *Trends Phys. Chem.* 12 (2007) 1–36.
- [30] I. Baraldi et al., in preparation.