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Original Scientific Article

Photochemical and Thermal Transformations of Thiophene *o*-Distyrylbenzene Analogues in Acidic Media†

Dragana Vuk,[a] Željko Marinić,[b] Krešimir Molčanov,[c] Biserka Kojić-Prodić,[c] and Marija Šindler-Kulyk,[a,*]

[a]*Department of Organic Chemistry, Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19, HR-10000 Zagreb, Croatia*
[b]*Center for NMR, Ruđer Bošković Institute, Bijenička cesta 54, HR-10000 Zagreb, Croatia*
[c]*Department of Physical Chemistry, Ruđer Bošković Institute, Bijenička cesta 54, HR-10000 Zagreb, Croatia*

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Abstract. Intramolecular photochemical reactions of thiophene analogues of *o*-distyrylbenzene, 2,2'-(*o*-phenylenedivinylene)dithiophenes (**1a**,**b**), 3,3'-(*o*-phenylenedivinylene)dithiophene (**2a**) and 3,3'-(*o*-phenylenedivinylene)dibenzothiophene (**2b**), were studied in acidic media at low concentrations. A 1,6- and 1,5-ring closure of hexatriene system leading to dihydronaphthalene or indene derivatives, respectively, was observed. (doi: 10.5562/cca2120)

Keywords: electrocyclization, photochemistry, protonation, thiophenes, *o*-divinylbenzenes

INTRODUCTION

Our recent research on the intramolecular photochemical reactions of conjugated thiophene derivatives[1,2] continues the work on furan[3–10] and pyrrole[11–16] derivatives of *o*-divinylbenzenes. Dithiophene derivatives **1**, **2** react differently[2] in comparison to previously studied difuran **3**[8] and dipyrrole **4**[12] derivatives (Figure 1). While difuran substituted *o*-divinylbenzenes **3**, upon irradiation in anaerobic condition at low concentrations give, *via* initial intramolecular 1,5-ring closure benzobicyclo[3.2.1]octadiene derivatives **5**,[8] dipyrrole derivatives **4** afford the dimeric product **6** as the result of initial intramolecular 1,5-ring closure followed by intermolecular addition[12] (Figure 1).

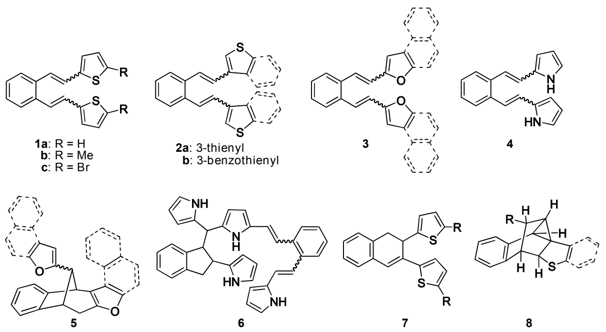

Figure 1. Chemical diagrams of the compounds studied.

In contrast, the hexatriene systems with terminal thiophene rings (**1** and **2**)[2] undergo photochemical 6π electrocyclization reactions affording 2,3-dihydronaphthalene intermediates. In the case of 2-thienyl derivatives **1**, the 1,2-dihydronaphthalenes 7 are formed by 1,5-H shift whereas the 3-thienyl derivatives **2** undergo [4+2] intramolecular reaction with thiophene or di-π-methane rearrangement giving polycyclic compound **8**. This type of ring closure, and the existence of the 2.3-dihydronaphthalene intermediates, has not been detected before in o-distyryl benzenes[17–23] or their diheteroaryl substituted *o*-divinylbenzenes.[8,12]

Stimulated by the Tong-Ing Ho's work[24–29] on photochemical behavior of styryl-furans and -thiophenes, who found that their photoreactivity could be entirely changed in acidic media. We report herein the photochemical and thermal behavior of dithiophene substituted *o*-divinylbenzenes **1** and **2** in acidic media.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-600 Spectrometer at 300 and 600 MHz. All NMR spectra were measured in $CDCl_3$ using tetramethylsilane as reference. The assignment of the signals is based on 2D-CH correlation and 2D-HH-COSY and NOESY experiments. UV spectra were measured on a Varian

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[*] Author to whom correspondence should be addressed. (E-mail: marija.sindler@fkit.hr)

Cary 50 UV/VIS Spectrophotometer. IR spectra were recorded on FTIR-ATR Vertex 70 Bruker. Mass spectra were obtained on a Varian Saturn 2200 equipped with FactorFour Capillary Column VF-5ms. Irradiations were performed in a quartz or Pyrex vessel in acetonitrile/hydrochloric acid solutions in a Rayonet reactor equipped with RPR 3000 Å and 3500 Å lamps. All irradiation experiments were carried out in deaerated solutions by bubbling a stream of argon prior to irradiation. Melting points were obtained using an Original Kofler Mikroheitztisch apparatus (Reichert, Wien) and are uncorrected. HRMS analysis were carried out on a mass spectrometer (MALDI TOF/TOF analyzer), equipped with Nd:YAG laser operating at 355 nm with firing rate 200 Hz in the positive (H+) or negative (–H) ion reflector mode. Elemental analyses were carried out on CHNS analyzer. Silica gel (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.

All procedures which required work with benzene were carried in a good ventilated hood.

Starting compounds **1a**,**b** and **2a**,**b** were prepared by Wittig reaction from *o*-xylylenebis(triphenylphosphonium bromide) and the corresponding thiophene aldehydes as described previously in the literature.[2]

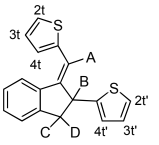
Irradiation Experiments of 1a,b and 2a,b in the Presence of Hydrochloric acid

General Procedure. A mixture of *cis,cis*-, *cis,trans*– and *trans,trans*-isomers of **1a**, **1b**, **2a** and **2b** in acetonitrile ($c = 4 \times 10^{-3}$ mol dm^{-3}), with addition of hydrochloric acid (w = 36 %, 1 ml, 35 eq), was purged with argon for 30 min and irradiated at $\lambda = 300$ nm in a Rayonet reactor (16 lamps) in a quartz vessel. After irradiation (**1a**: 2.5 h; **1b**: 4 h; **2a**: 8 h; **2b**: 2 h) the reaction mixture was neutralized with solution of sodium hydroxide (w = 10 %) and extracted with ethylacetate (4 × 5 ml). After drying over magnezium sulphate the solvents were removed in vacuo and the oily residue chromatographed on a silica gel column using petroleum ether as the eluent. The obtained mixtures of the products were rechromatographed and after the repeated column and thyn layer chromatography the photoproducts were isolated and characterized. High-molecular-weight products remained on the column.

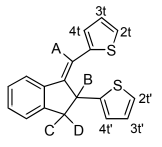
All analytical data for **7a,b, 12a** and **14** were identical to those described in our previous paper.[2] The data of the new compounds are given below.

2-{(Z)-[2-(2-thienyl)-2,3-dihydro-1H-inden-1-ylidene]-methyl}thiophene (cis-***9a***)

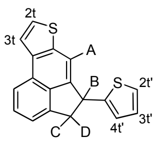
Yield 5 %; colourless oil; UV (EtOH) $\lambda_{\max}$/nm: 325 and 238 (log ε/dm^{3}mol^{-1}cm^{-1}: 3.85 and 4.22); IR $\nu_{\max}$/cm^{-1}: 2922, 1589, 1223, 1078, 748, 694; ^{1}H NMR ($CDCl_3$) δ/ppm: 7.61 (d, 1H, J = 7.9 Hz, H-ar), 7.28 (d, 1H, J = 7.5 Hz, H-ar), 7.24–7.26 (m, 1H, H-2t), 7.23 (dt, 1H, J = 7.5; 0.8 Hz, H-ar), 7.16–7.19 (m, 1H, H-2t'), 7.07–7.11 (m, 2H, H-4t, H-ar), 7.01 (dd, 1H, $J_{2t,3t}$ = 5.0; $J_{3t,4t}$ = 3.5 Hz, H-3t), 6.94–6.97 (m, 2H, H-3t', H-4t'), 6.37 (s, 1H, H-A), 4.47–4.52 (m, 1H, H-B), 3.50 (dd, 1H, $J_{B,C}$ = 8.3; $J_{C,D}$ = 15.8 Hz, H-C), 3.10 (dd, 1H, $J_{B,D}$ = 6.0; $J_{C,D}$ = 15.8 Hz, H-D); ^{13}C NMR ($CDCl_3$) δ/ppm: 148 (s), 148 (s), 145 (s), 140 (s), 138 (s), 129 (d), 127 (d), 127 (d), 126 (d), 126 (d), 125 (d), 125 (d), 125 (d), 125 (d), 124 (d), 116 (d, C_A), 48 (d, C_B), 41 (t, $C_{C/D}$); *Anal. Calcd.* mass fraction of elements, w/% for $C_{18}H_{14}S_2$ (M_r = 294.43) are: C 73.43, H 4.79, S 21.78; found C 73.32, H 4.96.



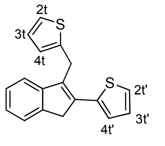
cis-**9a**: R = H
cis-**9b**: R = CH_3



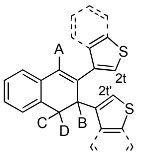
trans-**9a:** R = H
trans-**9b:** R = CH_3



10a: R = H
10b: R = CH_3



11a: R = H
11b: R = CH_3



13a: (3-thienyl)
13b: (3-benzothienyl)

2-{(E)-[2-(2-thienyl)-2,3-dihydro-1H-inden-1-ylidene]-methyl}thiophene (trans-***9a***)

Yield 2 %; colourless crystals; m.p. 78 °C; UV (EtOH) $\lambda_{\max}$/nm: 346, 331, 317 and 237 (log ε/dm^{3}mol^{-1}cm^{-1}: 4.28, 4.37, 4.22, sh and 4.09); IR $\nu_{\max}$/cm^{-1}: 2922, 1421, 1223, 903, 748, 694; ^{1}H NMR ($CDCl_3$) δ/ppm: 7.64 (d, 1H, J = 6.9 Hz, H-ar), 7.17–7.40 (m, 5H), 7.01–7.09 (m, 2H), 6.97 (dd, 1H, J = 4.8; 3.7 Hz), 6.78–6.86 (m, 2H), 4.88 (d, 1H, $J_{B,C}$ = 8.0 Hz; H-B), 3.63 (dd, 1H, $J_{B,C}$ = 8.0; $J_{C,D}$ = 16.4 Hz, H-C), 3.10 (d, 1H, $J_{C,D}$ = 16.4 Hz, H-D); ^{13}C NMR ($CDCl_3$) δ/ppm: 148 (s), 144 (s), 143 (s), 141 (s), 141 (s), 129 (d), 127 (d), 127 (2d), 126 (d), 126 (d), 126 (d), 124 (d), 123 (d), 120 (d), 115 (d), 43 (d, C_B), 43 (t, $C_{C/D}$); *Anal. Calcd.* mass fraction of elements, w/% for $C_{18}H_{14}S_2$ (M_r = 294.43) are: C 73.43, H 4.79, S 21.78; found C 73.32, H 4.96.

5-(2-thienyl)-4,5-dihydroacenaphtho[4,5-b]thiophene (***10a***)

Yield 5 %; colourless oil; UV (EtOH) $\lambda_{\max}$/nm: 335, 314, 303, 292, 260, 246 and 218 (log ε/dm^{3}mol^{-1}cm^{-1}: 3.10, 3.87, 3.95, 3.80, 4.30, 4.50 and 4.17); IR $\nu_{\max}$/cm^{-1}: 2918, 1599, 1396, 1085, 692; ^{1}H NMR ($CDCl_3$) δ/ppm: 8.05 (d, 1H, J = 8.1 Hz, H-ar), 7.93 (d, 1H, J = 4.8 Hz), 7.66 (s, 1H, H-A), 7.62 (dd, 1H, J = 7.2; $J_{2,3}$ = 8.1 Hz, H-ar), 7.54 (d, 1H, J = 4.8 Hz), 7.38 (d, 1H, J = 7.2 Hz, H-ar), 7.19 (dd, 1H, J = 4.8; 2.0 Hz), 6.95–6.99 (m, 2H), 5.22 (ddd, 1H, $J_{\mathrm{B,C}}$ = 9.0; $J_{\mathrm{B,D}}$ = 5.0; J = 1.1 Hz, H-B), 4.06 (dd, 1H, $J_{\mathrm{B,C}}$ = 9.0; $J_{\mathrm{C,D}}$ = 17.3 Hz, H-C), 3.57 (dd, 1H, $J_{\mathrm{C,D}}$ = 17.3; $J_{\mathrm{B,D}}$ = 5.0 Hz, H-D); HRMS (+1H): $\mathrm{M}^+_{\mathrm{calc.}}$ 293.0459; $\mathrm{M}^+_{\mathrm{exp.}}$ 293.0466.

2-{[2-(2-thienyl)-1H-inden-3-yl]methyl}thiophene (***11a***)
Yield 4 %; yellow crystals; m.p. 95 °C; UV (EtOH) $\lambda_{\max}$/nm: 321 and 236 (log ε/dm^{3}mol^{-1}cm^{-1}: 4.30 and 4.20); IR $\nu_{\max}$/cm^{-1}: 3067, 1433, 1225, 1030, 687; ^{1}H NMR ($\mathrm{CDCl_3}$) δ/ppm: 7.43 (d, 1H, J = 7.5 Hz, H-ar), 7.31 (d, 1H, J = 7.5 Hz, H-ar), 7.28 (dd, 1H, $J_{\mathrm{2t,3t}}$ = 5.0; $J_{\mathrm{2t,4t}}$ = 0.8 Hz, H-2t), 7.25 (t, 1H, J = 7.5 Hz, H-ar), 7.20 (dd, 1H, $J_{\mathrm{3t,4t}}$ = 3.6; $J_{\mathrm{2t,4t}}$ = 0.8 Hz, H-4t), 7.18 (dt, 1H, J = 7.5; 0.8 Hz, H-ar), 7.09 (dd, 1H, $J_{\mathrm{2t',3t'}}$ = 4.9; $J_{\mathrm{2t',4t'}}$ = 1.0 Hz, H-2t'), 7.05 (dd, 1H, $J_{\mathrm{2t,3t}}$ = 5.0; $J_{\mathrm{3t,4t}}$ = 3.6 Hz, H-3t), 6.84-6.88 (m, 2H), 4.39 (s, 2H, -$\mathrm{CH_2}$'), 3.87 (s, 2H, -$\mathrm{CH_2}$); ^{13}C NMR ($\mathrm{CDCl_3}$) δ/ppm: 146 (s), 141 (s), 141 (s), 139 (s), 135 (s), 135 (s), 127 (d), 126 (d), 126 (d), 125 (d), 125 (d), 124 (d), 123 (d), 123 (d), 119 (d), 41 (t, $\mathrm{CH_2}$), 27 (t, $\mathrm{CH_2}$'); MS m/z: 294 (M^+, 100 %); *Anal. Calcd.* mass fraction of elements, w/% for $\mathrm{C_{18}H_{14}S_2}$ (M_r = 294.43) are: C 73.43, H 4.79, S 21.78; found C 73.32, H 4.96.

2-methyl-5-{(Z)-[2-(5-methyl-2-thienyl)-2,3-dihydro-1H-inden-1-ylidene]methyl}thiophene (cis-***9b***)
Yield 5 %; colourless oil; UV (EtOH) $\lambda_{\max}$/nm: 334 and 244 (log ε/dm^{3}mol^{-1}cm^{-1}: 3.94 and 4.28); IR $\nu_{\max}$/cm^{-1}: 2922, 1599, 1412, 1231, 689; ^{1}H NMR ($\mathrm{CDCl_3}$) δ/ppm: 7.78 (d, 1H, J = 7.4 Hz, H-ar), 7.27 (d, 1H, J = 7.4 Hz, H-ar), 7.22 (dt, 1H, J = 7.4; 0.6 Hz, H-ar), 7.11 (dt, 1H, J = 7.4; = 0.6 Hz, H-ar), 6.88 (d, 1H, $J_{\mathrm{3t,4t}}$ = 3.4 Hz, H-4t), 6.72 (d, 1H, $J_{\mathrm{3t',4t'}}$ = 3.4 Hz, H-4t'), 6.64 (dd, 1H, $J_{\mathrm{3t,4t}}$ = 3.4; $J_{\mathrm{3t,CH3}}$ = 1.0 Hz, H-3t), 6.57 (dd, 1H, $J_{\mathrm{3t',4t'}}$ = 3.4; $J_{\mathrm{3t',CH3'}}$ = 1.1 Hz, H-3t'), 6.32 (s, 1H, H-A), 4.35–4.39 (m, 1H, H-B), 3.43 (dd, 1H, $J_{\mathrm{C,D}}$ = 15.8; $J_{\mathrm{B,C}}$ = 8.3 Hz, H-C), 3.12 (dd, 1H, $J_{\mathrm{C,D}}$ = 15.8; $J_{\mathrm{B,D}}$ = 6.1 Hz, H-D), 2.47 (d, 3H, $J_{\mathrm{3t,CH3}}$ = 1.0 Hz, -$\mathrm{CH_3}$), 2.42 (d, 3H, $J_{\mathrm{3t',CH3'}}$ = 1.1 Hz, -$\mathrm{CH_3}$'); ^{13}C NMR ($\mathrm{CDCl_3}$) δ/ppm: 146 (s), 146 (s), 145 (s), 139 (s), 139 (s), 138 (s), 138 (s), 129 (d), 126 (d), 126 (d), 125 (d), 125 (d), 125 (d), 124 (2d), 117 (d, $\mathrm{C_A}$), 48 (d, $\mathrm{C_B}$), 41 (t, $\mathrm{C_{C,D}}$), 15 (q), 15 (q); *Anal. Calcd.* mass fraction of elements, w/% for $\mathrm{C_{20}H_{18}S_2}$ (M_r = 322.49) are: C 74.49, H 5.63, S 19.89; found C 74.88, H 5.88.

8-methyl-5-(5-methyl-2-thienyl)-4,5-dihydroacenaphto[4,5-b]thiophene (***10b***)
Yield 7 %; colourless oil; UV (EtOH) $\lambda_{\max}$/nm: 338, 322, 309, 297, 260, 250 and 217 (log ε/dm^{3}mol^{-1}cm^{-1}: 3.21, 3.86, 3.99, 3.86, 4.39, 4.49 and 4.13); IR $\nu_{\max}$/cm^{-1}: 2918, 1460, 1225, 689; ^{1}H NMR ($\mathrm{CDCl_3}$) δ/ppm: 7.94 (dd, 1H, J = 8.2; 0.6 Hz, H-ar), 7.52–7.62 (m, 3H), 7.33 (dd, 1H, J = 7.1; 0.6 Hz, H-ar), 6.72 (d, 1H, $J_{\mathrm{3t',4t'}}$ = 3.3 Hz, H-4t'), 6.59 (dd, 1H, $J_{\mathrm{3t',4t'}}$ = 3.3; $J_{\mathrm{3t',-CH3}}$ = 1.0 Hz, H-3t'), 5.10 (ddd, 1H, $J_{\mathrm{B,C}}$ = 8.6; $J_{\mathrm{B,D}}$ = 4.3; J = 1.0 Hz, H-B), 3.99 (ddd, 1H, $J_{\mathrm{C,D}}$ = 17.1; $J_{\mathrm{B,C}}$ = 8.6; J = 1.0 Hz, H-C), 3.51 (ddd, 1H, $J_{\mathrm{C,D}}$ = 17.1; $J_{\mathrm{B,D}}$ = 4.3; J = 1.0 Hz, H-D), 2.67 (d, 1H, J = 1.0 Hz, -$\mathrm{CH_3}$), 2.43 (d, 1H, J = 1.0 Hz, -$\mathrm{CH_3}$); HRMS: $\mathrm{M}^+_{\mathrm{calc.}}$ 320.0693; $\mathrm{M}^+_{\mathrm{exp.}}$ 320.0695.

2-methyl-5-{[2-(5-methyl-2-thienyl)-1H-inden-3-yl]methyl}tiophene (***11b***)
Yield 26 %; yellow crystals; m.p. 101–102 ºC; UV (EtOH) $\lambda_{\max}$/nm: 333 and 240 (log ε/dm^{3}mol^{-1}cm^{-1}: 4.29 and 4.19); IR $\nu_{\max}$/cm^{-1}: 2960, 1429, 795, 719; ^{1}H NMR ($\mathrm{CDCl_3}$) δ/ppm: 7.42 (d, 1H, J = 7.3 Hz, H-ar), 7.30 (d, 1H, J = 7.3 Hz, H-ar), 7.24 (dt, 1H, J = 7.3; 0.4 Hz, H-ar), 7.16 (dt, 1H, J = 7.3; 1.0 Hz, H-ar), 7.02 (d, 1H, $J_{\mathrm{3t,4t}}$ = 3.5 Hz, H-4t), 6.71 (dd, 1H, $J_{\mathrm{3t,4t}}$ = 3.5; $J_{\mathrm{3t,CH3}}$ = 1.0 Hz, H-3t), 6.64 (d, 1H, $J_{\mathrm{3t',4t'}}$ = 3.4 Hz, H-4t'), 6.51 (dd, 1H, $J_{\mathrm{3t',4t'}}$ = 3.4; $J_{\mathrm{3t',CH3}}$ = 1.0 Hz, H-3t'), 4.29 (s, 2H, -$\mathrm{CH_2}$'), 3.82 (s, 2H, -$\mathrm{CH_2}$), 2.49 (d, 3H, $J_{\mathrm{3t,CH3}}$ = 1.0 Hz, -$\mathrm{CH_3}$), 2.38 (d, 3H, $J_{\mathrm{3t',CH3}}$ = 1.0 Hz, $\mathrm{CH_3}$'); ^{13}C NMR ($\mathrm{CDCl_3}$) δ/ppm: 146 (s), 141 (s), 139 (s), 139 (s), 137 (s), 137 (s), 135 (s), 134 (s), 126 (d), 125 (d), 125 (d), 124 (d), 124 (d), 124 (d), 123 (d), 119 (d), 41 (t), 27 (t), 15 (q), 15 (q); *Anal. Calcd.* mass fraction of elements, w/% for $\mathrm{C_{20}H_{18}S_2}$ (M_r = 322.49) are: C 74.49, H 5.63, S 19.89; found C 74.88, H 5.88.

3,3'-(1,2-dihydronaphthalene-2,3-diyl)dithiophene (***13a***)
Yield 16 %; colourless crystals; m.p. 95–97 ºC; UV (EtOH) $\lambda_{\max}$/nm: 327, 311, 301 and 234 (log ε/dm^{3}mol^{-1}cm^{-1}: 3.94, sh, 4.12, 4.09, sh and 4.17); IR $\nu_{\max}$/cm^{-1}: 2918, 1460, 1225, 689; ^{1}H NMR ($\mathrm{CDCl_3}$) δ/ppm: 7.37 (dd, 1H, J = 5.1; 1.3 Hz), 7.27–7.30 (m, 2H), 7.23 (dd, 1H, J = 2.9; 1.3 Hz), 7.17–7.18 (m, 2H), 7.11 (dd, 1H, J = 4.9; 2.9 Hz), 7.03 (d, 1H, J = 7.4 Hz), 7.01 (s, 1H, H-A), 6.87–6.88 (m, 1H), 6.84 (dd, 1H, J = 5.0; 1.3 Hz), 4.18 (dd, 1H, $J_{\mathrm{B,C}}$ = 7.3; $J_{\mathrm{B,D}}$ =1.6 Hz, H-B), 3.44 (ddd, 1H, $J_{\mathrm{C,D}}$ = 15.6; $J_{\mathrm{B,C}}$ =7.3; $J_{\mathrm{C,ar}}$ =1.1 Hz, H-C), 3.02 (dd, 1H, $J_{\mathrm{C,D}}$ = 15.6; $J_{\mathrm{B,D}}$ =1.6 Hz, H-D); ^{13}C NMR ($\mathrm{CDCl_3}$) δ/ppm: 142 (s), 135 (s), 134 (2s), 132 (s), 128 (d), 127 (d), 127 (d), 126 (d), 126 (d), 125 (d), 125 (d), 125 (d), 123 (d), 120 (d), 120 (d, $\mathrm{C_A}$), 38 (d, $\mathrm{C_B}$), 36 (t, $\mathrm{C_{C,D}}$); HRMS: $\mathrm{M}^+_{\mathrm{calc.}}$ 294.0531; $\mathrm{M}^+_{\mathrm{exp.}}$ 394.0537.

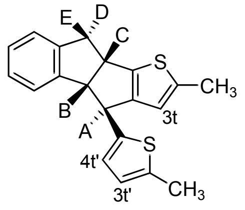
3,3'-(1,2-dihydronaphthalene-2,3-diyl)dibenzo[b]thiophene (***13b***)
Yield 21 %; colourless crystals; m.p. 90–93 ºC; UV (EtOH) $\lambda_{\max}$/nm: 315, 300, 292 and 231 (log ε/dm^{3}mol^{-1}cm^{-1}: 3.94, 3.99, 3.94 and 4.50); IR $\nu_{\max}$/cm^{-1}: 2957, 1443, 731; ^{1}H NMR ($\mathrm{CDCl_3}$) δ/ppm: 8.19 (d, 1H, J = 8.0 Hz, H-ar), 7.87 (d, 1H, J = 8.0 Hz, H-ar), 7.84 (dt, 1H, J = 8.0; 1.0 Hz, H-ar), 7.44 (dt, 1H, J = 7.6; 1.0 Hz, H-ar), 7.42 (dt, 1H, J = 7.6; 1.0 Hz, H-ar), 7.37 (dd, 1H, J = 7.6; 1.0 Hz, H-ar), 7.34 (dd, 1H, J = 7.6; 1.0 Hz, H-ar), 7.19–7.26 (m, 3H), 7.10 (dd, 1H, J = 8.0; 1.0 Hz, H-ar), 7.09 (dd, 1H, J = 8.0; 1.0 Hz, H-ar), 7.06 (s, 1H), 6.94 (d, 1H, J = 7.4 Hz, H-ar), 4.52 (dd, 1H, $J_{\mathrm{B,C}}$ = 7.3; $J_{\mathrm{B,D}}$ = 1.6 Hz, H-B), 3.62 (dd, 1H, $J_{\mathrm{C,D}}$ = 15.6; $J_{\mathrm{B,C}}$ =7.3 Hz, H-C), 3.16 (dd, 1H, $J_{\mathrm{C,D}}$ = 15.6; $J_{\mathrm{B,D}}$ = 1.6 Hz, H-D); ^{13}C NMR ($\mathrm{CDCl_3}$) δ/ppm: 141 (s), 140 (s), 138 (s), 138

(s), 137 (s), 135 (s), 135 (s), 134 (s), 133 (s), 129 (d), 128 (d), 128 (d), 127 (d), 127 (d), 124 (2d), 124 (d), 124 (d), 123 (d), 123 (d), 123 (d), 123 (d), 123 (d), 1210 (d), 38 (d), 35 (t); HRMS: $M^{+}_{\text{calc.}}$ 394.0855; $M^{+}_{\text{exp.}}$ 394.0844.

Irradiation Experiments of 1a,b in the Presence of Sulphuric Acid

A mixture of *cis,cis*-, *cis,trans*- and *trans,trans*-isomers of **1a** and **1b** in acetonitrile ($c = 4 \times 10^{-3}$ mol dm^{-3}), with addition of sulphuric acid (w = 36 %, V = 1 ml, 50 eq), was purged with argon for 30 min and irradiated at 300 nm in a Rayonet reactor (16 lamps) in a quartz vessel for 4 h. After irradiation the reaction mixture was neutralized with solution of sodium hydroxide (w = 10 %) and extracted with ethylacetate (4 × 5 ml). After drying over magnezium sulphate the solvents were removed in vacuo and the oily residue chromatographed on a silica gel column using petroleum ether as the eluent. The photoproducts **7a** (20 %)**, 7b** (10 %), **10b** (3 %) and **15** (15 %) were isolated followed by a mixture of several unidentified products (< 2 %). High-molecular-weight products remained on the column.

2-methyl-4-(5-methyl-2-thienyl)-4,4a,9,9a-tetrahydro-benzo[4,5]pentaleno[1,2-b]thiophene (***15***)
Yield 15 %; colourless crystals; m.p. 74–75 ºC; UV (EtOH) λ_{max}/nm: 274 and 242 (log ε/dm^{3}mol^{-1}cm^{-1}: 2296 and 14571); IR ν_{max}/cm^{-1}: 2908, 1479, 1117, 744; ^{1}H NMR (CDCl$_3$) δ/ppm: 7.42 (d, 1H, J = 7.4 Hz, H-ar), 7.15–7.23 (m, 3H, H-ar), 6.63 (d, 1H, J = 3.3 Hz, H-4t'), 6.58 (dd, 1H, J = 1.1; 3.3 Hz, H-3t'), 6.37 (d, 1H, J = 0.8 Hz, H-3t), 4.49 (s, 1H, H-A), 4.33 (d, 1H, J = 6.9 Hz, H-B), 4.21 (dd, 1H, J = 8.5; 6.9 Hz, H-C), 3.35 (dd, 1H, J = 16.2; 8.5 Hz, H-D), 3.08 (dd, 1H, J = 16.2; 1.3 Hz, H-E), 2.44 (d, 3H, J = 0.8 Hz, -CH$_3$'), 2.39 (s, 3H, -CH$_3$); ^{13}C NMR (CDCl$_3$) δ/ppm: 148 (s), 146 (s), 145 (s), 144 (s), 144 (s), 142 (s), 138 (s), 127 (d), 127 (d), 125 (d), 125 (d), 124 (d), 123 (d), 120 (d), 66 (d), 50 (d), 45 (d), 39 (t); HRMS: $M^{+}_{\text{calc.}}$ 322.0855; $M^{+}_{\text{exp.}}$ 322.0858.



15

Heating of 1a and 1b in Acetonitrile / Hydrochloric Acid Solutions

A mixture of *cis,cis*-, *cis,trans*- and *trans,trans*-isomers of **1a** or **1b** ($c = 4 \times 10^{-3}$ mol dm^{-3}) was dissolved in acetonitrile with addition of hydrochloric acid (w = 36 %, V = 1 ml, 35 eq) and refluxed for 16 hours. After cooling to room temperature the reaction mixture was neutralized with solution of sodium hydroxide (w = 10 %) and extracted with ethylacetate (4 × 5 ml). After drying over magnezium sulphate the solvents were removed in vacuo and the oily residue chromatographed on a silica gel column using petroleum ether as the eluent. The following compounds were isolated from **1a** or **1b**, respectively: *trans,trans*-**1a** (24 %), *trans*-**9a** (46 %), **11a** (21 %) and *trans*-**9b** (42 %)**, 11b** (14 %).

Heating of 2a and 2b in Acetonitrile / Hydrochloric Acid Solutions

A mixture of *cis,cis*-, *cis,trans*- and *trans,trans*-isomers of **2a** or **2b** (**2a**: $c = 4 \times 10^{-3}$ mol dm^{-3}; **2b**: $c = 3 \times 10^{-3}$ mol dm^{-3}) was dissolved in acetonitrile with addition of hydrochloric acid (w = 36 %, V = 1 ml, 35 eq) and refluxed for 17 hours. After cooling to room temperature the reaction mixture was neutralized with solution of sodium hydroxide (w = 10 %) and extracted with ethylacetate (4 × 5 ml). After drying over magnezium sulphate the solvents were removed in vacuo and the oily residue chromatographed on a silica gel column using petroleum ether as the eluent. Only the mixture of **2a** and **2b** isomers, respectively was recovered.

Irradiation of *cis*-9a,b and 10a,b Mixtures in the Presence of Iodine

An acetonitrile solution ($c = 4 \times 10^{-3}$ mol dm^{-3}) of compounds *cis*-**9** and **10** is irradiated in the presence of iodine at 350 nm for 4 hours. After irradiation the solvent was removed in vacuo and the oily residue chromatographed on a silica gel column using petroleum ether as the eluent. The compounds **10a** and **10b**, respectively, were isolated.

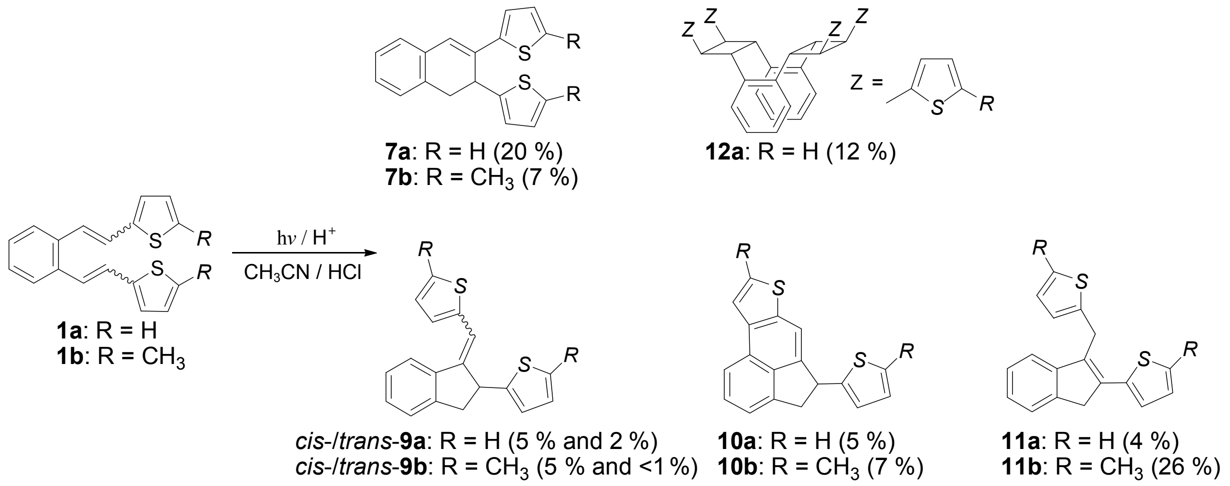
Heating of *cis*-9a,b or *trans*-9a,b in the Presence of Iodine

A toluene solution ($c = 8 \times 10^{-3}$ mol dm^{-3}) of compounds *cis*-**9** or *trans*-**9** or a mixture was refluxed in the presence of iodine for 1.5 hours. After cooling to the room temperature the solvent was removed in vacuo and the oily residue chromatographed on a silica gel column using petroleum ether as the eluent. The compounds **11a** (60 %) and **11b** (80 %), respectively, were isolated.

RESULTS AND DISCUSSION

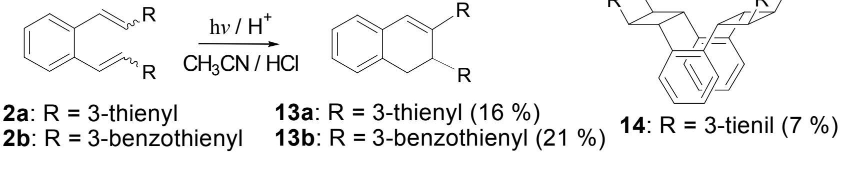
Compounds **1** and **2**, prepared by Wittig reaction from *o*-xylylenebis(triphenylphosphonium bromide) and the corresponding thiophene aldehydes as described,[2] were irradiated in argon purged acetonitrile solutions

($c \sim 4 \times 10^{-3}$ mol dm^{-3}) with the addition of hydrochloric acid. After irradiation, the reaction mixture was neutralized with sodium hydroxide solution, extracted with ethyl acetate and after the evaporation of the solvents the residue chromatographed on silica gel column using petroleum ether as eluent. The ^{1}H NMR spectra of **1a** and **1b** photomixtures showed signals of the dihydronaphthalene products **7a** and **7b**, respectively, also obtained on irradiation of the starting compounds in neutral media,[2] along with several additional signals of the products in different ratio, depending on the starting compounds (Scheme 1).



Scheme 1.

In contrast, photomixtures obtained on irradiation of 3-thienyl derivatives **2a** and **2b** (Scheme 2) contained no polycyclic structures **8** (Figure 1), like those found on irradiation in neutral media, but instead the dihydronaphthalene derivatives **13a** and **13b**, respectively, were produced. Dimeric cyclophane products **12a** (Scheme 1) and **14** (Scheme 2) have been also isolated. In all irradiation experiments, material remained on the column as unidentified high-molecular-weight products.



Scheme 2.

The isolated photoproducts were characterized by spectroscopic methods. The aliphatic region of the ^{1}H NMR spectra of intramolecular photoproducts found on irradiation of unsubstituted 2-thienyl derivative **1a** is presented in Figure 2. Each shows similar characteristic three-proton pattern of ABX systems, except **11a**. Signals shift to lower or higher magnetic field depending on the structure. The different photoproducts behave similarly during column chromatography which greatly complicates their separation and characterization.

It was thus necessary to perform the additional photochemical and thermal experiments (Scheme 3) that, in combination with column and thin layer chromatography, allow us easier separation and identification of the products. Photoproducts **10a** and *cis*-**9a** are inseparable as are *trans*-**9a** and **11a**. So a mixture of **10a** and *cis*-**9a** was irradiated in acetonitrile solution in the presence of iodine whereupon *cis*-**9a** underwent electrocyclization reaction to **10a**. So pure **10a** was isolated and completely characterized. When a mixture of *trans*-**9a** and **11a** was irradiated, but without iodine, *trans*-**9a** isomerizes to *cis*-**9a** which was separated more easily from **11a**. Compound **11a** is formed by thermal reaction in refluxing toluene with catalytic quantity of iodine, either from *cis*- or *trans*-**9a**.

Analogous experiments were performed with the products of methyl derivative **1b** which shows similar photoreactivity to the unsubstituted **10a** providing further proof of the product structures.

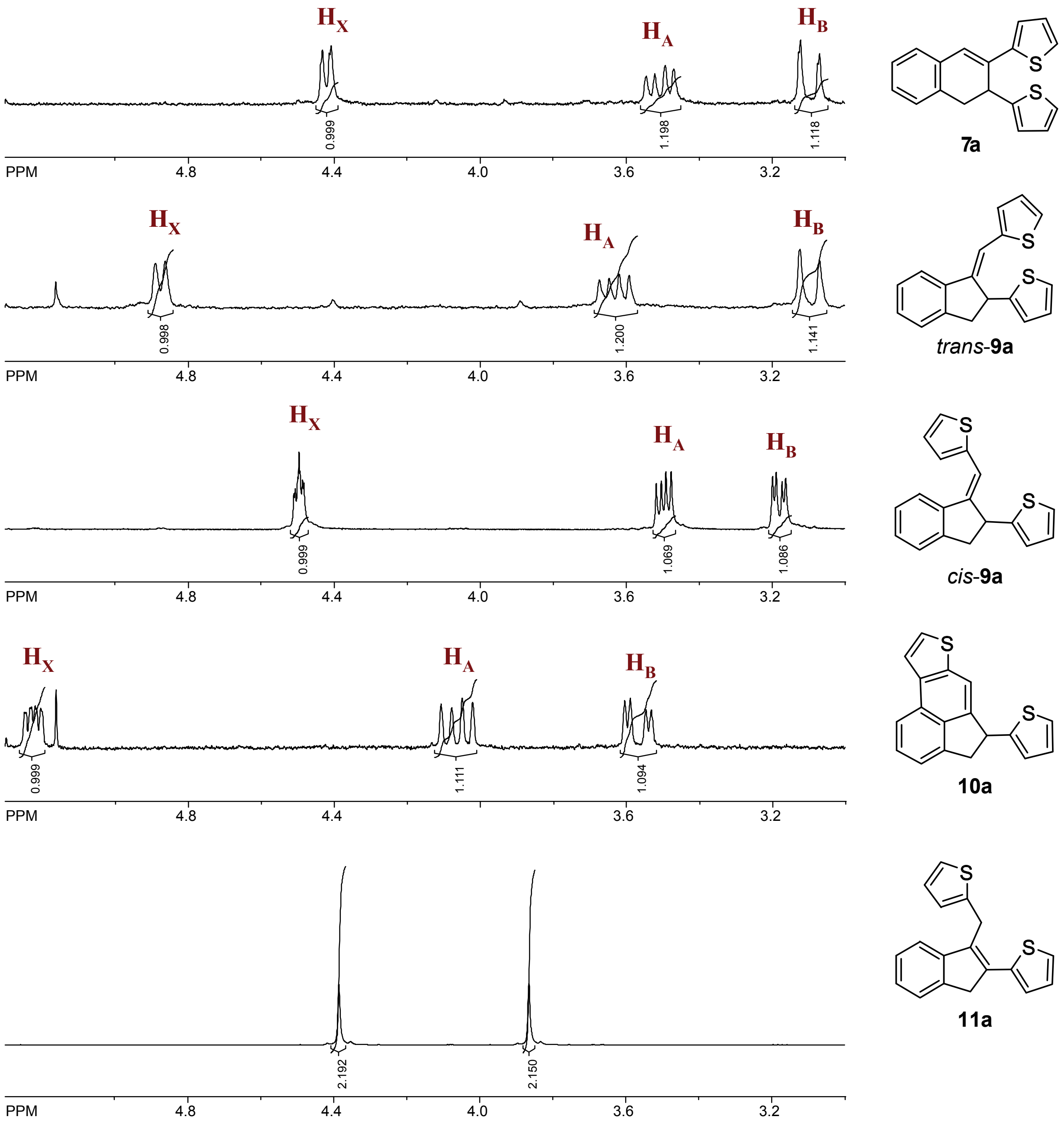
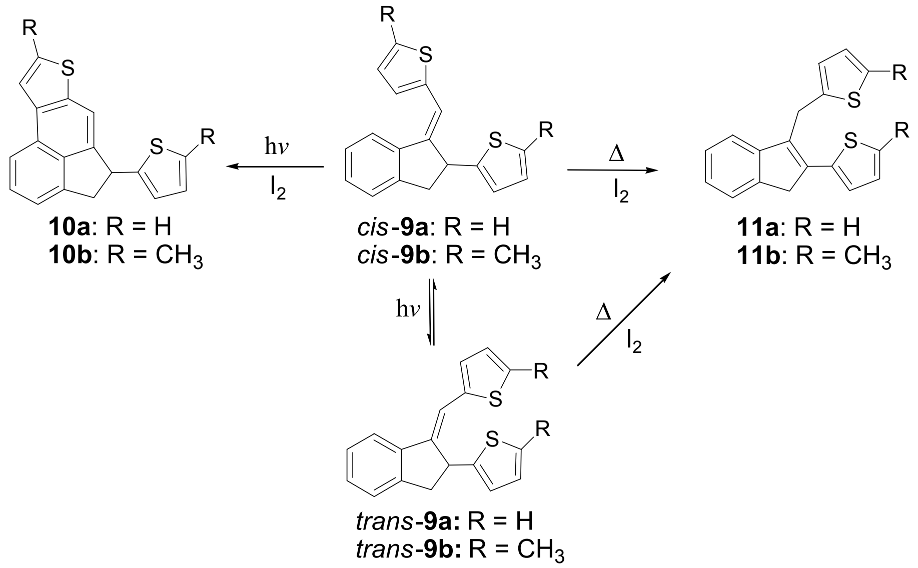


Figure 2. ^1H NMR spectra (aliphatic region) in $CDCl_3$ at 300 MHz (**7a**, **10a** and *trans*-**9a**) and at 600 MHz (*cis*-**9a** and **11a**).

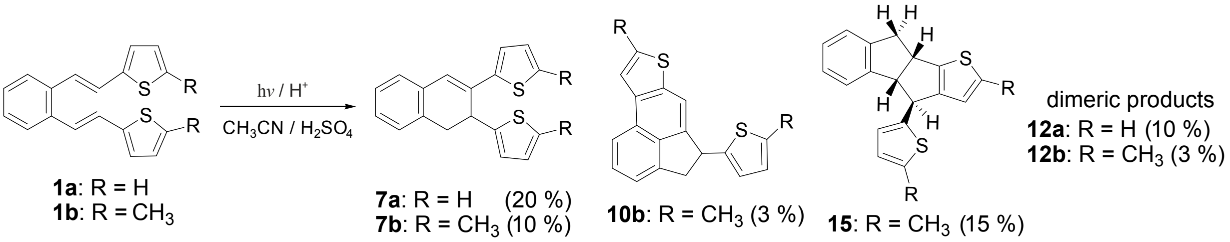
All of the experiments described were conducted in the presence of hydrochloric acid (*w* ~ 36 %). Compounds **1a** and **1b** were also irradiated under the same conditions but in the presence of sulfuric acid (diluted, *w* ~ 36 %).

Unsubstituted thienyl derivative **1a** (Scheme 4) gave dihydronaphthalene **7a** in the same yield as in hydrochloric acid, but no other products of 1,5-ring closure were detected. Methyl derivative **1b** reacts by 1,6- and 1,5-ring closure giving expected products **7b** and **10b**, respectively, along with a new product **15**, the structure of which is determined by spectroscopic methods. ^1H NMR spectrum (Figure 3) shows in the aliphatic region five hydrogen signals on cyclopentalenic structure. Proton H_B is coupled only with H_C (J = 6.9 Hz) which is coupled with H_D (J = 8.5 Hz). H_A appears as a singlet and the geminal protons H_D and H_E are in mutual coupling (J = 16.2 Hz). The structure is confirmed by X-Ray analysis (Figure 4).

To determine that all these isolated products are the result of photoinduced reactions we kept the acidic solutions of compounds **1** and **2** in darkened cuvettes while exposing them to the conditions of the Rayonet (t ~ 40 °C). No reaction was detected leading to



Scheme 3.



Scheme 4.

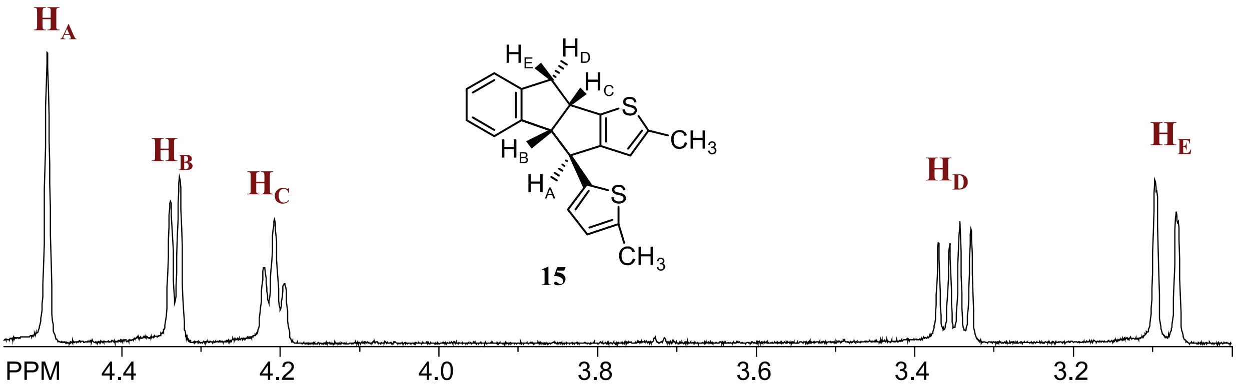


Figure 3. ^{1}H NMR spectrum (aliphatic region) of **15** (600 MHz) in $CDCl_3$.

conclusion that the products formed on irradiation were formed by photoinduced processes. Acetonitrile solutions of the starting compounds **1** and **2** were also refluxed for 16–22 hours. No reaction was observed without addition of acid. When compounds **1a,b** were refluxed in acidic acetonitrile solution two indene derivatives **9** and **11** have been formed (Scheme 5), found also in photoinduced experiments, but in much higher yield.

The formation of thermal products *trans*-**9** and **11** can be explained *via* carbocation intermediates **A** and **B** as shown in Scheme 6.

A plausible mechanism for the formation of the photoproducts is presented in Scheme 7. Assuming polarization (**A**, **A'**) in the excited state[30] this enables an

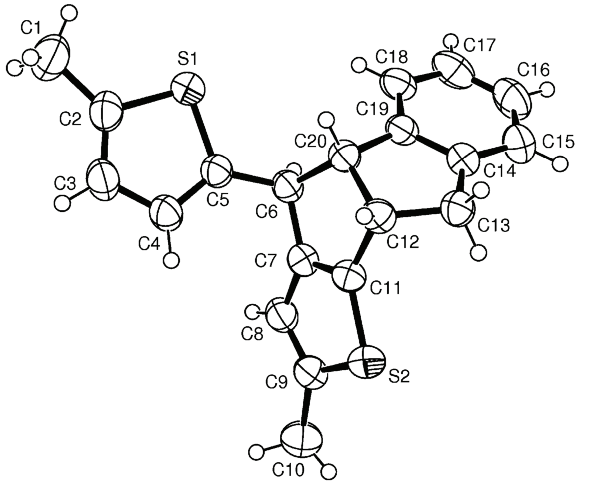
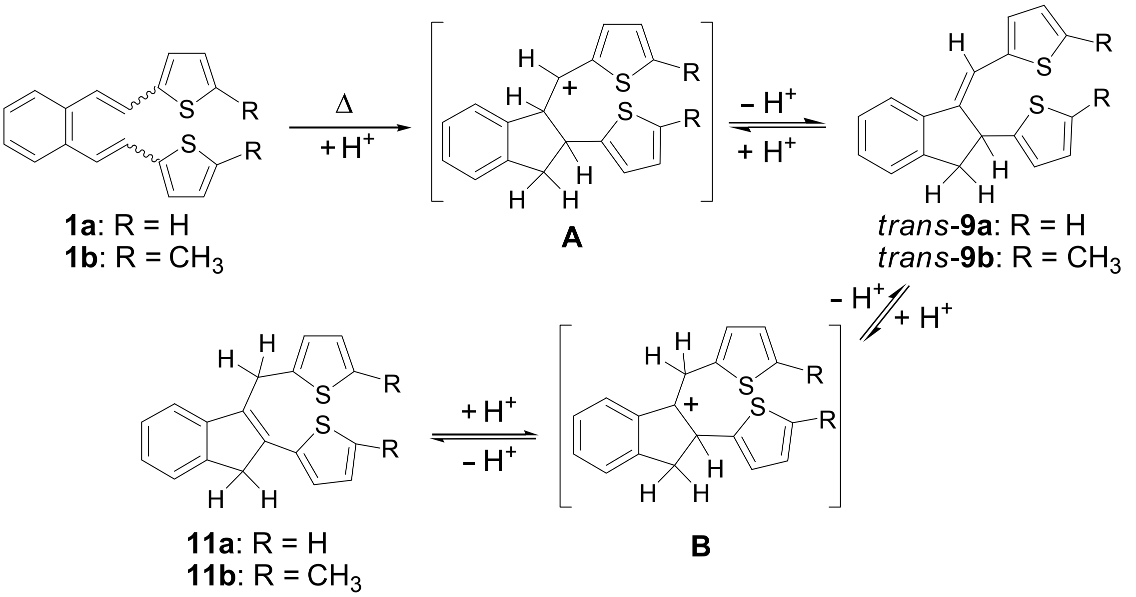


Figure 4. ORTEP drawing of **15**. Displacement ellipsoids are drawn for the probability of 50 % and hydrogen atoms are shown as spheres of arbitrary radii.



Scheme 6.

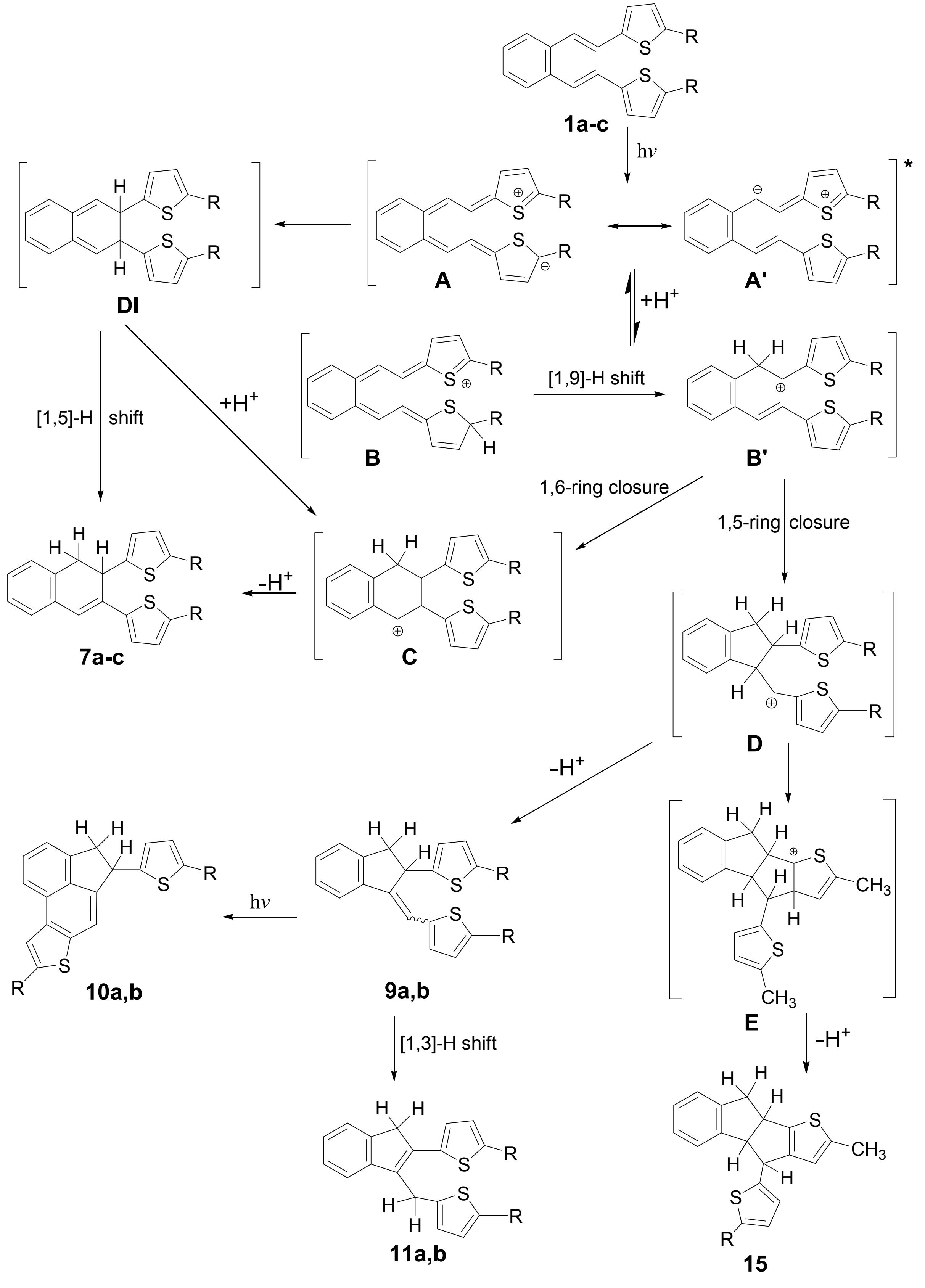
easier protonation leading to intermediate **B** which can undergo 1,9-H shift to carbocation **B'**. Carbocation **B'** undergoes 1,6-ring closure to intermediate **C** which, by deprotonation process gives the main intramolecular photoproduct **7**. The intermediate **C** is formed also by protonation of the dihydronaphthalene intermediate **DI**. 1,5-ring closure produces carbocation **D**, and by deprotonation, a mixture of *cis*- and *trans*-**9**. From the indane derivative **9** the naphthothiophene derivative **10** is formed by second photochemical electrocyclization process and the indene derivative **11** by protonation/deprotonation process, as seen in thermal reaction (Scheme 6). On irradiation of methyl derivative **1b** 1,5-ring closure is preferred and the main intramolecular product is indane derivative **11**, along with the cyclopentalene derivative **15**. This can be explained by the inductive effect of the methyl substituent and its influence on stability of the intermediates.

It is interesting that 3-thienyl derivatives **2a**,**b** afford only dihydronaphthalene derivatives **13a** or **13b**, respectively (Scheme 2), and no traces of indane derivatives or, as in neutral media, the formation of the fused tricyclo derivatives **8** is observed. This means the primary electrocyclization process (Scheme 8) to the intermediate **DI**, as in neutral media,[2] is followed by fast protonation/deprotonation process to products **13**.

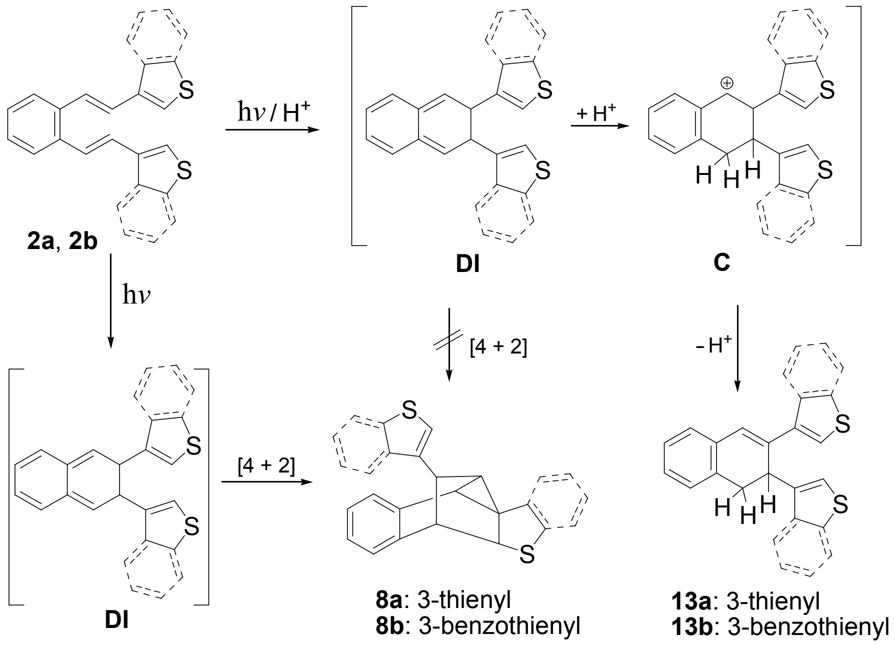
CONCLUSION

On irradiation in acidic media β,β'-2-thienyl and β,β'-3-thienyl derivatives of *o*-divinylbenzene (**1** and **2**) give 1,2-dihydronaphthalene derivatives (**7**, **13**) presumably by protonation of the starting material in the excited state followed by 1,6-ring closure or by protonation of the primarly formed 2,3-dihydronaphthalene intermadiate. The 2-thienyl **1** affords the cyclic products of 1,5-ring closure also followed by carbocation rearrangements and photochemical isomerization and electrocyclization. The total yields of the intramolecular cyclic products formed on irradiation in acidic media are much higher with regard to those in neutral media.

Only 2-thienyl derivatives (**1a,b**) reacted thermally under the described conditions giving the products of 1,5-ring closure of the hexatriene system.


1a-c
hν
A
A'
DI
+H+
B
B'
[1,9]-H shift
[1,5]-H shift
1,6-ring closure
1,5-ring closure
7a-c
-H+
C
D
E
9a,b
10a,b
11a,b
15
[1,3]-H shift
CH3

Scheme 7.



Scheme 8.

Supplementary Materials. – Crystal data and structure refinement of **15** is available free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk). CCDC 891194.

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