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Photochemical transformation of β,β′-dithienyl substituted *o*-divinylbenzenes leading to 1,2-dihydronaphthalenes or fused pentacyclic compounds: first evidence of electrocyclization process via 2,3-dihydronaphthalene intermediates

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ABSTRACT

The photochemical behaviour of 2,2′-(*o*-phenylenedivinylene)dithiophenes (**7a**–**c**), 3,3′-(*o*-phenylenedivinylene)dithiophene (**8a**) and 3,3′-(*o*-phenylenedivinylene)dibenzothiophene (**8b**) was studied under the low concentrations. An intramolecular reaction via the 2,3-dihydronaphthalene intermediate has been observed in all studied examples accompanied by dimerization and polymerization. The 1,2-dihydro-2,3-dithienylnaphthalenes (**9a**–**c**) were isolated (7–9%) from the 2-thiophene derivatives while the 3-thiophene derivatives gave polycyclic structures (13–44% yield).

1. Introduction

Intramolecular photochemical cycloadditions of heteroaryl substituted *o*-divinylbenzenes (**1**, **2**) to polycyclic compounds have been the subject of intense investigations by us.[1–3] In one of our previous papers[2a] on the photochemistry of styryl substituted furan derivatives[1,2] we described for the first time the photochemical approach to the furano-fused bicyclo[3.2.1]octadiene structure **3** by simple irradiation of 2-(*o*-vinylstyryl)furan derivative **1a** (Fig. 1).

Further investigation of the 3-(*o*-vinylstyryl)furan derivative[1] **1b** gave the similar furano-fused bicyclo[3.2.1]octadiene structure **4** along with the benzobicyclo[2.1.1]hexene structure **5**. Benzofuran derivative **1c** gave also upon irradiation the bicyclo[3.2.1]octadiene structure[2d] **3** while its naphthofuran analogue, due to the fast complex formation in the excited state, gave intermolecular [2+2] cycloadducts even at the 10^{-4} M concentrations.[2e] This prompted us to study the difuran-substituted *o*-divinylbenzenes **2a**–**c** and to determine the influence of annelation on the course of the photoreaction. Introduction of a second annelated furan moiety to *o*-divinylbenzene resulted in an intra- and intermolecular complexation and formation of two different classes of heteropolycyclic compounds.[2f] Of the compounds examined the most selective was

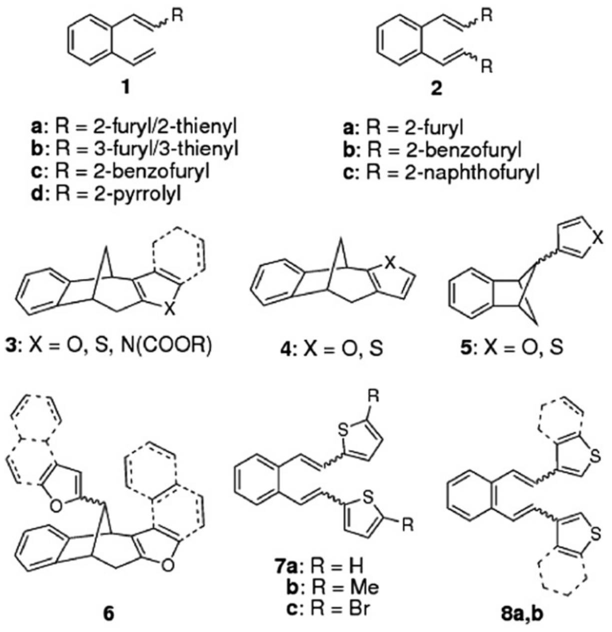

Fig. 1. Chemical diagrams of the compounds studied.

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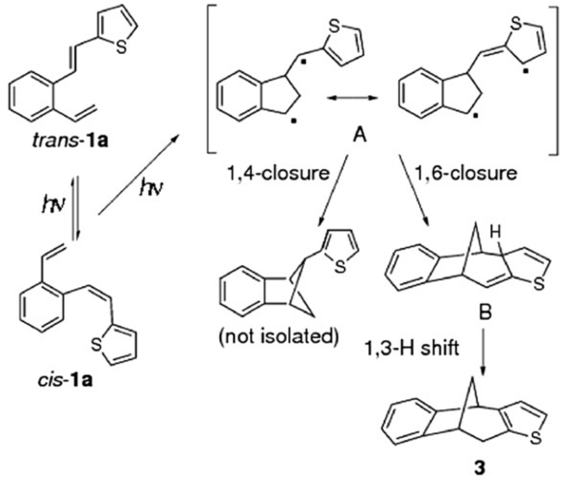
dinaphthofuran derivative **2c**, which gave only the *exo*-bicyclo[3.2.1]octadiene derivative **6** at low concentrations or only the cyclophane derivative at high concentration. The same methodology applied to styryl substituted pyrrole derivatives[3] gave completely different photoproducts. It was found that only alkoxycarbonyl substituted pyrrole derivatives[3e] cyclise to the pyrrolo-fused bicyclo[3.2.1]octadiene structure **3**. The (*o*-vinylstyryl)thiophene derivatives[1] **1a**,**b** underwent the same intramolecular cycloaddition as the furan derivative and furnished polycyclic structures **3**, **4**, and **5**. The common photochemical property of the examined furan (**1a**–**c** and **2a**–**c**) and thiophene (**1a**,**b**) derivatives of *o*-divinylbenzenes was the initial intramolecular ring closure to five-membered ring intermediate **A** followed by preferable 1,6-closure to **B** and aromatization via 1,3-hydrogen shift to the bicyclo[3.2.1]octadiene skeleton **3**. For simplicity the mechanism of these intramolecular cycloadditions is presented with thiophene derivative **1a** in Scheme 1.



Scheme 1.

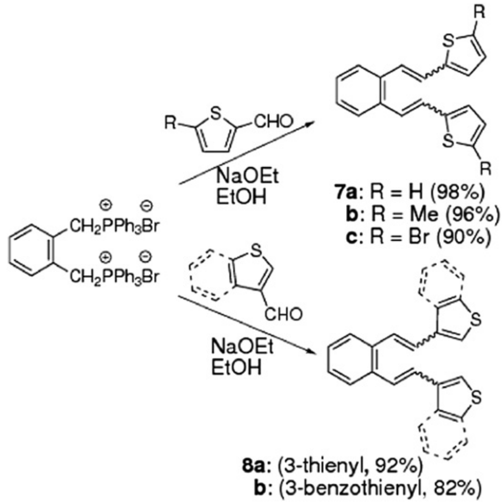
Since the photochemistry of monosubstituted thiophene derivatives **1a**,**b** was comparable to the photochemistry of furan derivatives[1] we anticipated that the introduction of the second thiophene moiety, like in the case of introduction of second furan moiety, might not have the dramatic influence on the excited state properties of this new hexatriene system.

In a continuation of our interest in heteropolycyclic compounds with incorporated bicyclo[3.2.1]octadiene structures, derivatives of a bicyclo[3.2.1]octane skeleton found in numerous important biologically active natural products,[4] we present here for the first time the photochemical transformations of dithiophene derivatives **7** and **8**.

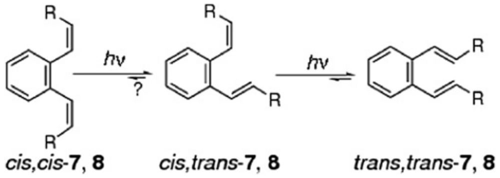
2. Results and discussion

Starting compounds **7a**–**c** and **8a**,**b** were synthesized by the Wittig reaction from *o*-xylylenebis(triphenylphosphonium bromide) and the corresponding thiophene aldehydes (Scheme 2).

They were obtained in very good yields as mixtures of cis,cis-, cis,trans- and trans,trans-isomers with the cis,trans- and trans,-trans-isomers being dominant. All isomers of dithiophene derivative **7a** and **8** were separated and completely characterized by spectroscopic methods.[5] Preliminary photochemical experiments were performed by irradiation of ethanolic solution of *cis*,*cis*-**7a**, *cis*,*trans*-**7a** and *trans*,*trans*-**7a** as well as isomers **8a** separately in quartz tubes and the process followed by UV spectral changes (details given in Fig. 1, Supplementary data). From these experiments cis→trans isomerization (Scheme 3) is presumed to be the primary process although the reverse process is not ruled out.[6]

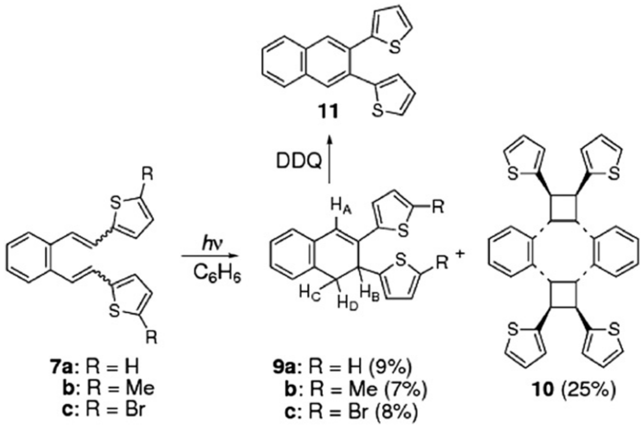


Scheme 2.



Scheme 3.

Preparative experiments with 2-thiophene derivatives, **7a**–**c**, were performed by irradiation of the mixtures of three isomers as 10^{-3} M benzene solutions purged with argon at 300 nm for 17–28 h leading to complete consumption of the starting material. Besides some traces of unidentified compounds and a lot of high-molecular-weight materials, which remained on the column during the separation, the dihydronaphthalenes **9** were isolated in very low yields (7–9%) as the only intramolecular photochemical products (Scheme 4). No product has been found with a bicyclo



Scheme 4.

[3.2.1]octadiene structure **6**, like in difuran derivatives photochemistry.[2f] It is interesting to note that only the unsubstituted thiophene derivative **7a** afforded under the same reaction conditions the dimeric cycloadduct **10** in 25% yield.

The isolated photoproducts **9a**–**c** were completely characterized by spectroscopic methods. Their ^{1}H NMR spectra all show a similar characteristic ABX pattern between 3 and 4.5 ppm. Proof that this three-proton system is a part of a six-membered ring was found upon aromatization to the naphthalene derivative[7] **11** following treatment with DDQ. Moreover, the dihydronaphthalene structure was confirmed by X-ray analysis of the product **9a** (Fig. 2). In the crystal **9a** reveals orientational disorder, the molecule of the asymmetric unit is rotated approximately 180° about C4–C5 bond with the population 0.57:0.43. This disorder enables rather compact packing with a density of 1.375 g cm^{-3} supported by C–H π interactions between disordered molecules. C–H of the thiophene rings of both orientations interact with the π-systems of thiophene rings and the dihydronaphthalene moiety (rings C7A–C12A) (details given in Supplementary data).

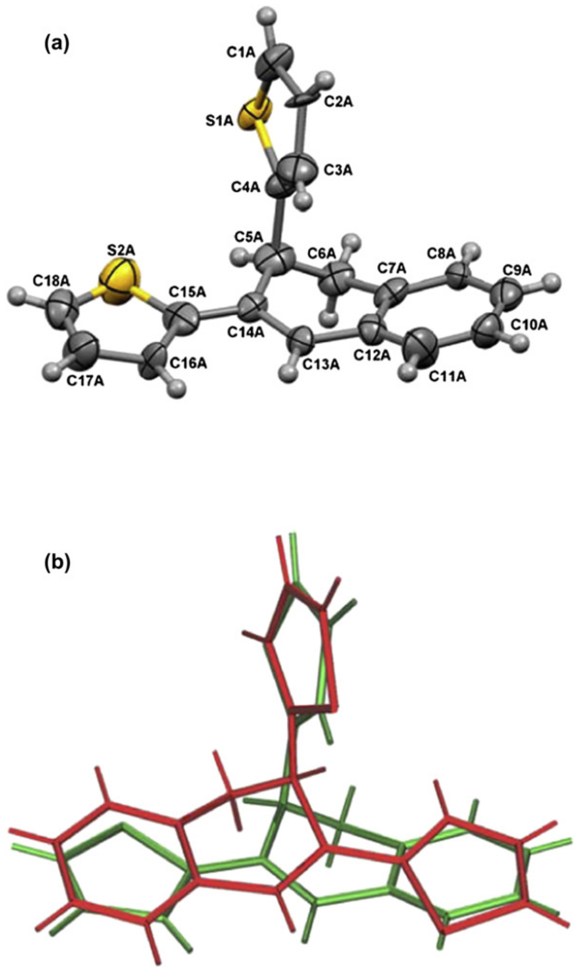
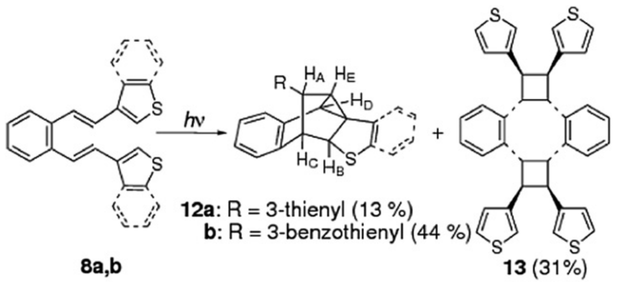


Fig. 2. (a) ORTEP drawing of the more populated orientation of **9a** and (b) the overlap of the molecules in the two orientations observed in the crystal.

The experiments with 3-thiophene derivatives, **8a**,**b**, were performed in a similar way as those of 2-thiophene derivatives (**7a**–**c**). The mixtures of three isomers, as 10^{-3} M benzene solutions purged with argon, were irradiated at 300 nm (**8a**) and 350 nm (**8b**) for 16–17 h. To our surprise no traces of dihydronaphthalene products were found, as by irradiation of 2-thiophene analogues. The polycyclic structures **12a** or **12b**, isolated in 13% and 44% yields, respectively, were the only intramolecular products (Scheme 5). The 3-thiophene derivative **8a**, as in the case of unsubstituted thiophene derivative **7a**, afforded under the same reaction conditions the dimeric cycloadduct **13** in 31% yield.



Scheme 5.

The isolated photoproducts **12a** and **12b** show in the aliphatic region of the ^{1}H NMR spectrum very similar 5-proton pattern (details given in Fig. 2, Supplementary data), being shifted for benzothiophene derivative to the lower field, indicating on the same structure. Based on additional NMR techniques (COSY, NOESY) the signals are completely assigned to protons A–E. The polycyclic structure was confirmed by X-ray analysis of the product **12b** (Fig. 3). Displacement ellipsoids are drawn at 50% probability and hydrogen atoms are shown as spheres of arbitrary radii. Geometric parameters for analogous chemical bonds in both molecules are comparable at the level of three standard deviations for each measured parameter. Even the same type of distortions of

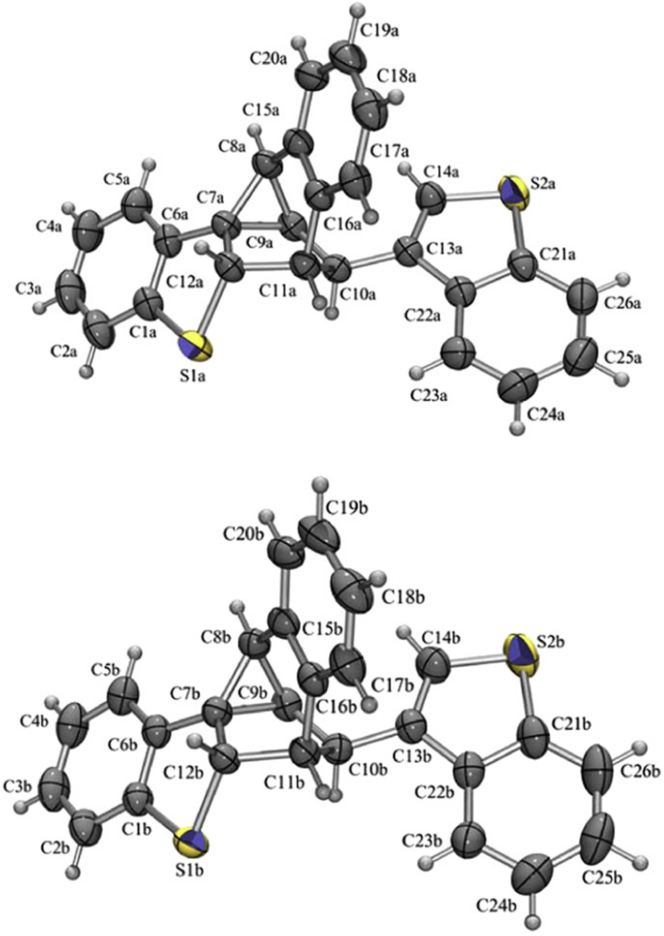
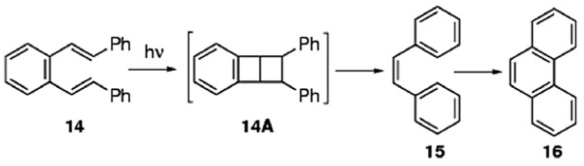


Fig. 3. ORTEP drawing of two symmetry-independent molecules of **12b**.

thiophene rings (S1A and S1B) fused to tricyclo moiety reveal twisted conformations whereas thiophene rings S2A and S2B are planar.

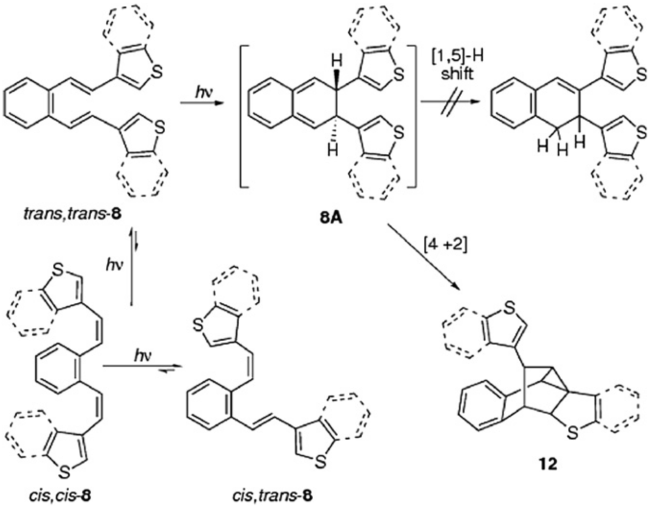
The photochemistry of dithiophene derivatives **7**, **8** could be compared partly with the photochemistry of 1,2-distyrylbenzene (**14**),[8,9] whose photoprocesses accompanying photoisomerization[6] are still not completely understood. It has been found that 1,2-distyrylbenzene does not photocyclize,[8c] even at very low concentrations, the main photoreaction is dimerization.[8] In the crystal[9] or adsorbed on silica gel[8a,b] it undergoes an intramolecular cycloaddition reaction to give a bicyclo[2.1.1]hexene derivative (structural type **5**). Stilbene (**15**) is formed[8c,d] as a side product, accompanied by phenanthrene (**16**) on irradiation of 1,2-distyrylbenzene in dilute solutions. The formation of stilbene is explained[8c] by an unimolecular process (Scheme 6) via cycloadduct **14A**, which has never been detected.



Scheme 6.

The photophysical properties of 1,2-distyrylbenzene[6,10] have been investigated. The disappearance of the trans,trans-isomer was found to be accompanied by the formation of a compound absorbing in the range of 420 nm.[6a] This product was assigned to 2,3-diphenyl-2,3-dihydronaphthalene formed by cyclization of a compressed rotamer of the trans,trans-isomer, as hypothesized previously.[8d] Under these experimental conditions the presence of such a species was not found for the compound where the phenyl group was replaced by a 2-thienyl group.[6a]

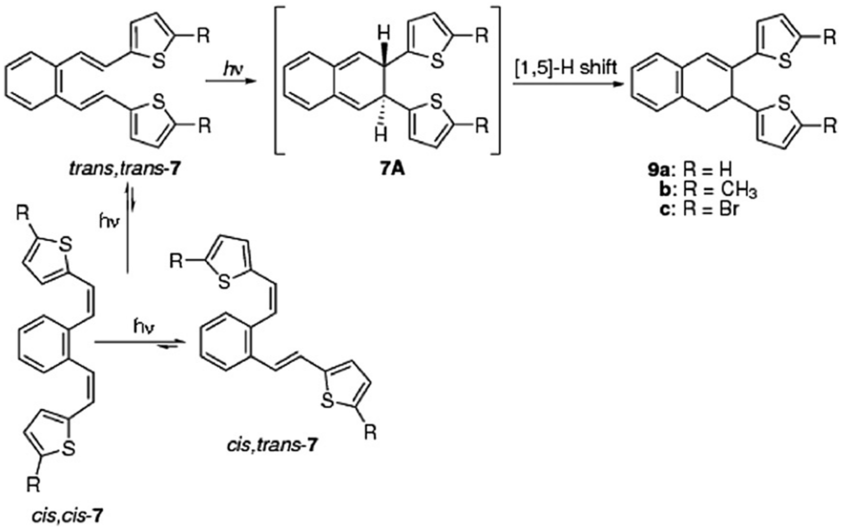
Based on our experimental results the dithiophene derivatives **7** and **8** do not undergo intramolecular cycloaddition but an electrocyclization process with formation of 2,3-dihydronaphthalene intermediates **7A** or **8A**, respectively (Schemes 7 and 8). The unstable 2-thiophene dihydronaphthalene intermediates **7A** undergo 1,5-H shift and give stable 1,2-dihydronaphthalene derivatives **8a**–**c** (Scheme 7). The 3-thiophene dihydronaphthalene intermediates **8A** are trapped intramolecularly by the double bond of thiophene ring giving the polycyclic compounds **12** (Scheme 8). This is the first example of a 6π electrocyclization process in diheteroaryl substituted *o*-divinylbenzenes that includes both vinyl groups. Due to the introduction of a sulfur heteroatom relevant photophysical properties[11] can be induced and the alternative reaction pathways are possible.



Scheme 8.

3. Conclusion

On irradiation of 2,2′-(*o*-phenylenedivinylene)dithiophenes (**7a**–**c**), 3,3′-(*o*-phenylenedivinylene)dithiophene (**8a**) and 3,3′-(*o*-phenylenedivinylene)dibenzothiophene (**8b**) in dilute solution, besides unidentified degradation and high-molecular-weight products, the only intramolecular process observed was electrocyclization and 1,6-ring closure of the divinyl moiety. The formed 2,3-dihydronaphthalene intermediates, **7A** or **8A**, undergo 1,5-H shift or [4+2] intramolecular cycloaddition, respectively, giving the products. The formation of the products **9a**–**c** by the double



Scheme 7.

photochemical 1,3-H shift or products **12a**,**b** through di-π-methano rearrangement might not be excluded. The cyclophane derivatives **10** and **12** are formed as the result of intermolecular double [2+2] photocycloaddition.

4. Experimental section

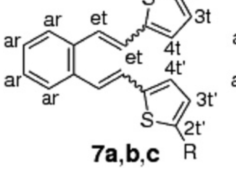
4.1. General experimental information

The ^{1}H spectra were recorded on a spectrometer at 300 and 600 MHz. The ^{13}C NMR spectra were registered at 75 and 150 MHz, respectively. 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 experiments. UV spectra were measured on an UV/VIS Cary 50 spectrophotometer. IR spectra were recorded on an FTIR-ATR (film). Mass spectra were obtained on a GC–MS system. Irradiation experiments were preformed in a quartz vessel in benzene solution in a photochemical reactor equipped with 3000 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 microscope equipped apparatus and are uncorrected. HRMS analysis were carried out on a mass spectrometer (MALDI TOF/TOF analyser), 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 analyser. Silica gel (0.063–0.2 mm) was used for chromatographic purifications. Thin-layer chromatography (TLC) was performed silica gel 60 F_{254} plates. Solvents were purified by distillation.

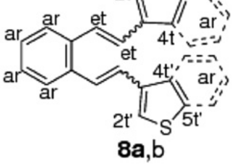
All procedures, which required work with benzene were carried in a good ventilated hood. Thiophene-2/3-carbaldehyde, 5-methyl- and 5-bromothiophene-2-carbaldehyde and benzo[*b*]thiophene-3-carbaldehyde were obtained from a commercial source, β,β-*o*-xylyl(ditriphenylphosphonium) dibromide was prepared from *o*-xylyldibromide and triphenylphosphine in dimethylformamide.[12]

4.2. General method for the synthesis of 7a–c and 8a,b

To a stirred solution of the triphenylphosphonium salt (0.005 mol) and the corresponding aldehyde (0.011 mol) in absolute ethanol (100 mL) the solution of sodium ethoxide (0.253 g, 0.011 mol in 15 mL of absolute ethanol) was added dropwise. The reaction was complete within 3–4 h (usually was left to stand overnight). After removal of the solvent, the residue was worked up with water and benzene. The benzene extracts were dried (anhydrous $MgSO_4$) and concentrated. The crude reaction mixture was purified and the isomers of products **7** and **8** were separated by repeated column chromatography on silica gel using petroleum ether as the eluent. The first fractions yielded cis,cis-, cis,trans- and the last fractions trans,trans-isomers. The data of the new compounds **7a**–**c** and **8a**,**b** are given below. All isomers of 2,2′-(1,2-phenylenedivinylene) dithiophene (**7a**), 3,3′-(1,2-phenylenedivinylene)dithiophene (**8a**) and 3,3′-(1,2-phenylenedivinylene)dibenzo[*b*]thiophene (**8b**) are separated and described by spectroscopic methods whereas in the case of **7b** and **7c** only trans,trans-isomers are isolated.



7a,**b**,**c**



8a,b

*4.2.1. 2,2′-(1,2-Phenylenedivinylene)dithiophene (**7a**).* Yield 1.44 g (98%); according to ^{1}H NMR spectra a mixture of 10% *cis,cis*-**7a**, 40% *cis,trans*-**7a** and 50% *trans,trans*-**7a**. *Compound cis,cis-**7a***: R_f 0.72 (petroleum ether/dichloromethane=7:3); colourless crystals; mp 80 °C; UV (EtOH) λ_{max} (log ε) 296 (4.24), 259 (4.12, sh); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.45 (d, J=9.0 Hz, 2H, H-ar), 7.32 (d, J=9.0 Hz, 2H, H-ar), 7.06 (d, $J_{2t,3t}$=5.0 Hz, 2H, H-2t), 6.92 (d, $J_{3t,4t}$=3.6 Hz, 2H, H-4t), 6.86 (dd, $J_{2t,3t}$=5.0 Hz, $J_{3t,4t}$=3.6 Hz, 2H, H-3t), 6.71 (d, J=11.8 Hz, 2H, H-et), 6.47 (d, J=11.8 Hz, 2H, H-et); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 139.9 (s), 136.6 (s), 129.8 (d), 128.2 (d), 127.9 (d), 127.4 (d), 126.3 (d), 125.8 (d), 123.7 (d); IR 2918, 1437, 1051, 964, 764 cm^{-1}.

*Compound cis,trans-**7a***: R_f 0.72 (petroleum ether/dichloromethane=7:3); colourless crystals; mp 88–89 °C; UV (EtOH) λ_{max} (log ε) 334 (4.66); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.68 (d, J=7.5 Hz, 1H, H-ar′), 7.35 (t, J=7.5 Hz, 1H, H-ar′), 7.32 (d, J=7.5 Hz, 1H, H-ar), 7.23–7.30 (m, 1H, H-ar), 7.18 (d, J=16.1 Hz, 1H, H-et′), 7.16 (d, $J_{2t',3t'}$=4.9 Hz, 1H, H-2t′), 7.09 (d, J=16.1 Hz, 1H, H-et′), 7.05 (d, $J_{2t,3t}$=4.9 Hz, 1H, H-2t), 7.03 (d, $J_{3t',4t'}$=3.6 Hz, 1H, H-4t′), 6.97 (dd, $J_{2t',3t'}$=4.9 Hz, $J_{3t',4t'}$=3.6 Hz, 1H, H-3t′), 6.94 (d, $J_{3t,4t}$=3.7 Hz, 1H, H-4t), 6.89 (d, J=11.8 Hz, 1H, H-et), 6.86 (dd, $J_{2t,3t}$=4.9 Hz, $J_{3t,4t}$=3.7 Hz, 1H, H-3t), 6,63 (d, J=11.8 Hz, 1H, H-et); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.1 (s), 139.9 (s), 135.2 (s), 135.6 (s), 130.1 (d), 128.5 (d), 128.1 (d), 127.8 (d), 127.5 (d), 126.9 (d), 126.2 (d,d), 126.2 (d), 126.1 (d), 125.3 (d), 124.9 (d), 124.4 (d), 123.0 (d); IR 2918, 1437, 1051, 964, 764 cm^{-1}.

*Compound trans,trans-**7a***: R_f 0.72 (petroleum ether/dichloro methane=7:3); colourless crystals; mp 91–92 °C; UV (EtOH) λ_{max} (log ε) 344 (4.34), 307 (4.50); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.52 (d, J=5.7 Hz, 2H, H-ar), 7.22–7.28 (m, 4H, H-ar, H-et), 7.20 (d, $J_{2t,3t}$=5.0 Hz, 2H, H-2t), 7.11 (d, J=16.0 Hz, 2H, H-et), 7.08 (d, $J_{3t,4t}$=3.5 Hz, 2H, H-4t), 7.01 (dd, $J_{2t,3t}$=5.0 Hz, $J_{3t,4t}$=3.5 Hz, 2H, H-3t); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 142.6 (s), 135.0 (s), 127.2 (d), 127.2 (d), 126.1 (d), 125.7 (d), 125.6 (d), 124.1 (d), 123.8 (d); IR 3059, 1691, 1394, 1202, 951, 692 cm^{-1}. Anal. Calcd for $C_{18}H_{14}S_2$: C, 73.43; H, 4.79. Found: C, 73.74; H, 4.83.

*4.2.2. 5,5′-Dimethyl-2,2′-(1,2-phenylenedivinylene)dithiophene (**7b**).* Yield 1.55 g (96%); according to ^{1}H NMR spectra a mixture of 10% *cis,cis*-**7b**, 50% *cis,trans*-**7b** and 40% *trans,trans*-**7b**..

*Compound trans,trans-**7b***: R_f 0.65 (petroleum ether/dichloro methane=7:3); yellow crystals; mp 97 °C; UV (EtOH) λ_{max} (log ε) 358 (4.31), 312 (4.49); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.50 (d, J=9.1 Hz, 2H, H-ar), 7.23 (d, J=9.2 Hz, 2H, H-ar), 7.13 (d, J=15.9 Hz, 2H, H-et), 7.02 (d, J=15.9 Hz, 2H, H-et), 6.87 (d, $J_{3t,4t}$=3.2 Hz, 2H, H-4t), 6.66 (d, $J_{3t,4t}$=3.2 Hz, 2H, H-3t), 2.50 (s, 6H, $-CH_3$); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 140.6 (s), 139.0 (s), 135.0 (s), 127.0 (d), 126.0 (d), 125.9 (d), 125.3 (d), 124.3 (d), 124.0 (d), 15.2 (q); IR 2910, 1682, 1447, 1038, 785 cm^{-1}; HRMS: M^+_{calcd} 322.0855; M^+_{found} 322.0858. Anal. Calcd for $C_{20}H_{18}S_2$: C, 74.49; H, 5.63. Found: C, 74.53; H, 5.55.

*4.2.3. 5,5′-Dibromo-2,2′-(1,2-phenylenedivinylene)dithiophene (**7c**).* Yield 2.03 g (90%); according to ^{1}H NMR spectra a mixture of 10% *cis,cis*-**7c**, 40% *cis,trans*-**7c** and 50% *trans,trans*-**7c**. *Compound trans,trans-**7c***: R_f 0.82 (petroleum ether/dichloromethane=7:3); yellow crystals; mp 108–109 °C; UV (EtOH) λ_{max} (log ε) 351 (4.44), 316 (4.63); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.49 (d, J=9.2 Hz, 1H, H-ar), 7.26 (d, J=9.2 Hz, 1H, H-ar), 7.11 (d, J=15.6 Hz, 1H, H-et), 6.98 (d, J=15.6 Hz, 1H, H-et), 6.97 (d, $J_{3t,4t}$=3.8 Hz, 1H, H-4t), 6.82 (d, $J_{3t,4t}$=3.8 Hz, 1H, H-3t); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 144.5 (s), 135.1 (s), 130.6 (d), 128.0 (d), 126.6 (d), 126.5 (d), 126.3 (d), 123.9 (d), 111.5 (s); IR 2905, 2052, 1516, 939, 766 cm^{-1}; HRMS: M^+_{calcd} 448.8674; M^+_{found} 448.8670. Anal. Calcd for $C_{18}H_{12}Br_2S_2$: C, 47.81; H, 2.67. Found: C, 47.62; H, 2.64.

*4.2.4. 3,3′-(1,2-Phenylenedivinylene)dithiophene (**8a**).* Yield 1.35 g (92%); according to ^{1}H NMR spectra a mixture of 20% *cis,cis*-**8a**, 50% *cis,trans*-**8a** and 30% *trans,trans*-**8a**. *Compound cis,cis-**8a***: R_f 0.38 (petroleum ether/dichloromethane=9:1); colourless crystals; mp 32 °C; UV (EtOH) λ_{max} (log ε) 272 (4.27); ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.33 (d, J=9.1 Hz, 2H, H-ar), 7.19 (d, J=9.1 Hz, 2H, H-ar), 7.08 (dd, $J_{4t,5t}$=5.0 Hz, $J_{2t,5t}$=2.9 Hz, 2H, H-5t), 7.02 (dd, $J_{2t,5t}$=2.9 Hz, $J_{2t,4t}$=1.1 Hz, 2H, H-2t), 6.76 (dd, $J_{4t,5t}$=5.0 Hz, $J_{2t,4t}$=1.1 Hz, 2H, H-4t), 6.56 (d, J=12.0 Hz, 2H, H-et), 6.51 (d, J=12.0 Hz, 2H, H-et); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 137.9 (s), 136.5 (s), 128.9 (d), 127.6 (d), 127.4 (d), 126.8 (d), 124.3 (d), 124.2 (d), 123.7 (d); IR 3007, 1418, 959, 791 cm^{-1}.

*Compound cis,trans-**8a***: R_f 0.32 (petroleum ether/dichloromethane=9:1); colourless crystals; mp 60 °C; UV (EtOH) λ_{max} (log ε) 304 (4.36); ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.64 (dd, J=7.8, 1.0 Hz, 1H, H-ar), 7.28 (td, J=7.8, 1.1 Hz, 1H, H-ar), 7.22–7.26 (m, 3H), 7.18–7.20 (m, 1H), 7.17 (td, J=7.8, 1.0 Hz, 1H, H-ar), 7.14 (d, J=16.2 Hz, 1H, H-et), 7.04 (d, J=16.2 Hz, 1H, H-et), 7.04 (dd, J=5.0, 3.0 Hz, 1H), 7.01 (dd, J=3.0, 1.0 Hz, 1H), 6.71 (dd, J=5.0, 1.0 Hz, 1H), 6.69 (d, J=12.0 Hz, 1H, H-et), 6.64 (d, J=12.0 Hz, 1H, H-et); ^{13}C NMR (CDCl$_3$, 150 MHz) δ 139.9 (s), 137.8 (s), 136.4 (s), 135.2 (s), 129.3 (d), 127.5 (d), 127.4 (d), 127.2 (d), 126.9 (d), 126.3 (d), 125.6 (d), 125.0 (d), 124.8 (d), 124.6 (d), 124.4 (d), 124.1 (d), 123.7 (d), 122.0 (d); IR 3089, 1416, 1080, 775 cm^{-1}.

*Compound trans,trans-**8a***: R_f 0.25 (petroleum ether/dichloromethane=9:1); colourless crystals; mp 120 °C; UV (EtOH) λ_{max} (log ε) 316 (4.42), 281 (4.54); ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.54 (d, J=9.1 Hz, 2H, H-ar), 7.37 (dd, $J_{4t,5t}$=5.0 Hz, $J_{2t,4t}$=0.8 Hz, 2H, H-4t), 7.33 (d, $J_{4t,5t}$=5.0 Hz, $J_{2t,5t}$=2.9 Hz, 2H, H-5t), 7.28 (d, J=16.1 Hz, 2H, H-et), 7.26–7.30 (m, 4H, H-ar, H-2t), 7.00 (dd, J=16.1 Hz, 2H, H-et); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 139.9 (s), 135.4 (s), 127.1 (d), 126.1 (d), 126.0 (d), 125.8 (d), 124.9 (d), 124.5 (d), 122.1 (d); IR 3097, 1470, 960, 775 cm^{-1}; HRMS: M$^+_{calcd}$ 294.0531; M$^+_{found}$ 294.0540. Anal. Calcd for $C_{18}H_{14}S_2$: C, 73.43; H, 4.79. Found: C, 73.38; H, 4.69.

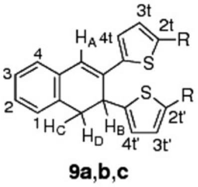
*4.2.5. 3,3′-(1,2-Phenylenedivinylene)dibenzo[b]thiophene (**8b**).* Yield 1.62 g (82%); according to ^{1}H NMR spectra a mixture of 20% *cis,cis*-**8b**, 50% *cis,trans*-**8b** and 30% *trans,trans*-**8b**. *Compound cis,cis-**8b***: R_f 0.64 (petroleum ether/dichloromethane=7:3); colourless oil; UV (EtOH) λ_{max} (log ε) 307 (4.11), 234 (4.64); ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.77 (dd, J=7.4, 1.0 Hz, 2H, H-ar), 7.74 (dd, J=7.4, 1.0 Hz, 2H, H-ar), 7.35 (dt, J=7.4, 1.0 Hz, 2H, H-ar), 7.32 (dt, J=7.4, 1.0 Hz, 2H, H-ar), 7.24 (d, J=9.1 Hz, 2H, H-ar), 7.05 (d, J=9.1 Hz, 2H, H-ar), 6.95 (s, 2H), 6.82 (d, J=12.0 Hz, 2H, H-et), 6.75 (d, J=12.0 Hz, 2H, H-et); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 139.6 (s), 138.5 (s), 136.6 (s), 132.1 (s), 130.5 (d), 129.2 (d), 127.3 (d), 124.3 (d), 124.3 (d), 124.1 (d), 122.7 (d), 122.6 (d), 121.9 (d); IR 3057, 1425, 1074, 733 cm^{-1}.

*Compound cis,trans-**8b***: R_f 0.59 (petroleum ether/dichloromethane=7:3); colourless crystals; mp 102–103 °C; UV (EtOH) λ_{max} (log ε) 318 (4.29), 237 (4.60); ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.78–7.85 (m, 3H), 7.68–7.72 (m, 2H), 7.20–7.36 (m, 10H), 7.17 (dt, J=7.6, 1.1 Hz, 1H, H-ar), 6.95 (2d, J=10.6 Hz, 2H, H-et), 6.94 (s, 1H); ^{13}C NMR (CDCl$_3$, 150 MHz) δ 140.0 (s), 139.1 (s), 138.2 (s), 137.2 (s), 136.2 (s), 135.1 (s), 133.8 (s), 131.1 (s), 129.9 (d), 129.1 (d), 127.9 (d), 127.3 (d), 127.2 (d), 125.2 (d), 124.3 (d), 124.0 (d), 123.9 (d), 123.8 (d), 123.7 (d), 122.9 (d), 122.4 (d), 122.1 (d), 121.6 (d), 121.6 (d), 121.4 (d), 121.1 (d); IR 3057, 1423, 906, 731 cm^{-1}.

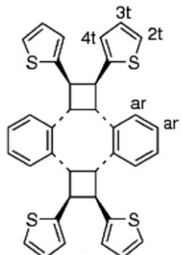
*Compound trans,trans-**8b***: R_f 0.57 (petroleum ether/dichloromethane=7:3); colourless crystals; mp 128–129 °C; UV (EtOH) λ_{max} (log ε) 340 (4.35, sh), 315 (4.47), 260 (4.37, sh), 241 (4.58); ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.98 (dd, J=7.4, 1.3 Hz, 1H, H-ar), 7.88 (dd, J=7.4, 1.3 Hz, 1H, H-ar), 7.67 (d, J=9.1 Hz, 1H, H-ar), 7.57 (s, 1H), 7.55 (d, J=16.1 Hz, 1H, H-et), 7.40 (dd, J=7.4, 1.3 Hz, 1H, H-ar), 7.39 (dd, J=7.4, 1.3 Hz, 1H, H-ar), 7.36 (d, J=9.1 Hz, 1H, H-ar), 7.24 (d, J=16.1 Hz, 1H, H-et); ^{13}C NMR (CDCl$_3$, 150 MHz) δ 140.0 (s), 137.3 (s), 135.6 (s), 133.8 (s), 127.7 (d), 127.5 (d), 126.3 (d), 124.1 (d), 123.9 (d), 123.0 (d), 122.5 (d), 121.7 (d), 121.4 (d); IR 3024, 1423, 955, 748 cm^{-1}; HRMS: M$^+$, found 394.0832. $C_{26}H_{18}S_2$ requires 394.0844.

4.3. Irradiation experiments of 7a–c and 8a,b

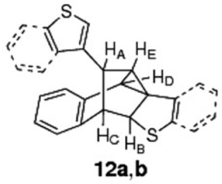
A mixture of cis,cis-, cis,trans- and trans,trans-isomers of **7a**, **7b**, **7c**, **8a** or **8b** in benzene (**7a** 9.4×10^{-4} M; **7b**,**c** 1.0×10^{-3} M; **8a** 1.0×10^{-3} M; **8b** 1.3×10^{-3} M) was purged with argon for 30 min and irradiated at 300 and 350 nm (**8b**) in a Rayonet reactor (16 lamps) in a quartz vessel. After irradiation (**7a**: 23 h; **7b**: 28 h, **7c**: 17 h; **8a**: 6 h; **8b**: 17 h) the solvent was removed in vacuo and the oily residue chromatographed on a silica gel column using petroleum ether as the eluent. The photoproducts **9a–c** and **12a**,**b** were isolated from the enriched first chromatographic fractions followed by a mixture of several unidentified products (<2%) and dimers **10** and **13**. High-molecular-weight products remained on the column.



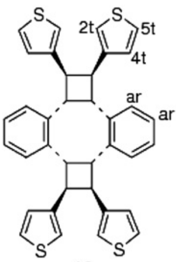
9a,b,c



10



12a,b



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*4.3.1. 2,2′-(1,2-Dihydronaphthalene-2,3-diyl)dithiophene (**9a**).* Yield 9 mg (9%); R_f 0.65 (petroleum ether/dichloromethane=7:3); colourless crystals; mp 99 °C; UV (EtOH) λ_{max} (log ε) 334 (4.14), 237 (4.16); ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.17–7.20 (m, 3H, H-2t, 2H-ar), 7.15 (d, $J_{3t,4t}$=2.9 Hz, 1H, H-4t), 7.12 (dt, J=7.3, 2.4 Hz, 1H, H-ar), 7.07 (d, J=7.3 Hz, 1H, H-ar), 7,01 (s, 1H, H-A), 6.95–6.98 (m, 2H, H-2t′, H-3t), 6.73–6.76 (m, 2H, H-3t′, H-4t′), 4.42 (dd, $J_{B,C}$=7.0 Hz, $J_{B,D}$=1.4 Hz, 1H, H-B), 3.51 (dd, $J_{C,D}$=15.7 Hz, $J_{B,C}$=7.0 Hz, 1H, H-C), 3.10 (dd, $J_{C,D}$=15.7 Hz, $J_{B,D}$=1.4 Hz, 1H, H-D); ^{13}C NMR (CDCl$_3$, 150 MHz) δ 145.2 (s), 144.3 (s), 134.6 (s), 133.6 (s), 132.4 (s), 128.2 (d), 127.6 (d), 127.5 (d), 126.8 (d), 126.4 (d), 126.3 (d), 124.4 (d), 124.3 (d), 123.7 (d), 123.4 (d), 123.1 (d, C$_A$), 38.0 (d, C$_B$), 37.1 (t, C$_{C,D}$); IR 3101, 2895, 1418, 1232, 1036, 750, 690 cm^{-1}. Anal. Calcd for $C_{18}H_{14}S_2$: C, 73.43; H, 4.79. Found: C, 73.30; H, 4.93.

*4.3.2. 2,2′-(1,2-Dihydronaphthalene-2,3-diyl)bis(5-methylthiophene) (**9b**).* Yield 7 mg (7%); R_f 0.57 (petroleum ether/dichlorometh ane=7:3); colourless crystals; mp 105 °C; UV (EtOH) λ_{max} (log ε) 341 (4.32), 241 (4.18); ^{1}H NMR (CDCl$_3$; 600 MHz) δ 7.18 (dt, J=7.3, 1.6 Hz, 1H, H-ar), 7.15 (dd, J=7.3, 1.6 Hz, 1H, H-ar), 7.11 (dt, J=7.3, 1.6 Hz, 1H, H-ar), 7.07 (d, J=7.3 Hz, 1H, H-ar), 6.96 (d, J=3.6 Hz, 1H,), 6.86 (s, 1H, H-A), 6.62 (dd, J=3.6, 1.0 Hz, 1H), 6.53 (d, J=3.4 Hz, 1H), 6.38 (dd, J=3.4, 1.0 Hz, 1H), 4.28 (dd, $J_{B,C}$=7.1 Hz, $J_{B,D}$=1.6 Hz, 1H, H-B), 3.44 (dd, $J_{B,C}$=7.1 Hz, $J_{C,D}$=15.6 Hz, 1H, H-C), 3.06 (dd, $J_{B,D}$=1.6 Hz, $J_{C,D}$=15.6 Hz, 1H, H-D), 2.45 (d, J=1.0 Hz, 3H, −CH$_3$), 2.28 (d, J=1.0 Hz, 3H, −CH$_3$); ^{13}C NMR (CDCl$_3$; 150 MHz) δ 143.1 (s), 142.2 (s), 139.3 (s), 137.7 (s), 134.9 (s), 133.9 (s), 132.6 (s), 128.3 (d), 127.3 (d), 126.8 (d), 126.3 (d), 125.9 (d), 124.4 (d), 124.1 (d), 123.9 (d), 122.0 (d, C$_A$), 37.9 (d, C$_B$), 37.1 (t, C$_{C,D}$), 15.6 (q), 15.3 (q); IR 3067, 1433, 1225, 1030, 687 cm^{-1}. Anal. Calcd for C$_{20}$H$_{18}$S$_2$: C, 74.49; H, 5.63. Found: C, 74.88; H, 5.88.

*4.3.3. 2,2′-(1,2-Dihydronaphthalene-2,3-diyl)bis(5-bromothiophene) (**9c**).* Yield 15 mg (8%); R_f 0.79 (petroleum ether/dichloromethane=7:3); colourless crystals; mp 130 °C; UV (EtOH) λ_{max} (log ε) 344 (3.96), 240 (3.85); ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.21 (d, J=7.1 Hz, 1H, H-ar), 7.16–7.19 (m, 2H, H-ar), 7.08 (d, J=7.3 Hz, 1H, H-ar), 6.93 (d, $J_{3t,4t}$=3.9 Hz, 1H, H-3t), 6.88 (s, 1H, H-A), 6.87 (d, $J_{3t,4t}$=3.9 Hz, 1H, H-4t), 6.71 (d, $J_{3t',4t'}$=3.8 Hz, 1H, H-3t′), 6.53 (d, $J_{3t',4t'}$=3.8 Hz, 1H, H-4t′), 4.24 (dd, $J_{B,C}$=7.1 Hz, $J_{B,D}$=1.6 Hz, 1H, H-B), 3.50 (dd, $J_{C,D}$=15.7 Hz, $J_{B,C}$=7.1 Hz, 1H, H-C), 3.04 (dd, $J_{C,D}$=15.7 Hz, $J_{B,D}$=1.6 Hz, 1H, H$_D$); ^{13}C NMR (CDCl$_3$, 150 MHz) δ 146.7 (s), 145.5 (s), 133.1 (s), 133.1 (s), 132.1 (s), 130.6 (d), 129.3 (d), 128.4 (d), 128.1 (d), 127.2 (d), 126.8 (d), 124.9 (d), 123.9 (d), 123.9 (d), 38.0 (d, C$_B$), 36.9 (t, C$_{C,D}$); IR 2920, 1514, 1022, 768 cm^{-1}. Anal. Calcd for C$_{18}$H$_{12}$Br$_2$S$_2$: C, 47.81; H, 2.6. Found: C, 47.55; H, 2.59.

*4.3.4. 2,2′,2″,2‴-(1,2,2a,6b,7,8,8a,12b-Octahydrodibenzo[a,e]dicyclobuta[c,g]cyclooctene-1,2,7,8-tetrayl)tetrathiophene (**10**).* Yield 30 mg (25%); R_f 0.36 (petroleum ether/dichloromethane=7:3); colourless crystals; mp 294 °C; UV (EtOH) λ_{max} (log ε): 231 (4.53); ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.19 (d, J=8.9 Hz, 4H, H-ar), 7.15 (dd, $J_{2t,3t}$=5.0 Hz, $J_{2t,4t}$=1.1 Hz, 4H, H-2t), 7.06 (d, J=8.9 Hz, 4H, H-ar), 6.92 (dd, $J_{2t,3t}$=5.0 Hz, $J_{3t,4t}$=3.5 Hz, 4H, H-3t), 6.90 (dd, $J_{3t,4t}$=3.5 Hz, $J_{2t,4t}$=1.1 Hz, 4H, H-4t), 4.66 (d, J=6.3 Hz, 4H), 4.61 (d, J=6.3 Hz, 4H); ^{13}C NMR (CDCl$_3$, 150 MHz) δ 143.1 (s), 137.5 (s), 126.2 (d), 126.0 (d), 124.7 (d), 124.6 (d), 123.7 (d), 47.7 (d), 41.4 (d); IR 2941, 1487, 1238, 1038, 685 cm^{-1}; HRMS: M$^+$, found 588.1083. C$_{36}$H$_{28}$S$_4$ requires 588.1079.

*4.3.5. 15-(3-Thienyl)-11-thiapentacyclo[7.5.1.0^{2,14}.0^{3,8}.0^{10,14}]pentadeca-3,5,7,12-tetraene (**12a**).* Yield 20 mg (13%); R_f 0.47 (petroleum ether/dichloromethane=7:3); colourless crystals; mp 69–71 °C; UV (EtOH) λ_{max} (log ε) 245 (3.88), 228 (4.35); ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.27 (d, J=7.5 Hz, 1H, H-ar), 7.13 (dt, J=7.5, 1.2 Hz, 1H, H-ar), 6.96–7.00 (m, 2H), 6.77 (d, J=7.5 Hz, 1H, H-ar), 6.50 (s and d, J=5.9 Hz, 2H), 6.33 (d, J=5.9 Hz, 1H), 5.74 (d, J=5.9 Hz, 1H), 4.40 (dd, J=4.9; 2.8 Hz, 1H, H-A), 3.90 (s, 1H, H-B), 3.55 (d, J=4.9 Hz, 1H, H-C), 3.01 (d, J=7.3 Hz, 1H, H-D), 1.89 (dd, J=7.3, 2.8 Hz, 1H, H-E); ^{13}C NMR (CDCl$_3$, 150 MHz) δ 140.2 (s), 136.2 (2s), 133.4 (s), 128.6 (d), 126.9 (d), 126.4 (d), 125.5 (d), 125.3 (d), 124.9 (d), 123.8 (d), 122.5 (d), 120.1 (d), 60.3 (d), 46.7 (d), 39.2 (d), 30.6 (d), 27.0 (d); IR 2920, 1728, 1119, 719 cm^{-1}; HRMS: M$^+$, found 294.0541. C$_{18}$H$_{14}$S$_2$ requires 294.0531.

*4.3.6. 3,3′,3″,3‴-(1,2,2a,6b,7,8,8a,12b-Octahydrodibenzo[a,e]dicyclobuta[c,g]cyclooctene-1,2,7,8-tetrayl)tetrathiophene (**13**).* Yield 46 mg (31%); R_f 0,30 (petroleum ether/dichloromethane=7:3); colourless crystals; mp 136–138 °C; UV (EtOH) λ_{max} (log ε) 231 (4.27); ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.20 (d, J=8.9 Hz, 4H, H-ar), 7.18 (dd, $J_{2t,5t}$=5.0, 2.9 Hz, 4H, H-5t), 7.06 (d, J=8.9 Hz, 4H, H-ar), 6.98 (dd, $J_{2t,5t}$=2.9 Hz, $J_{2t,4t}$=1.2 Hz, 4H, H-2t), 6.86 (dd, $J_{4t,5t}$=5.0 Hz, $J_{2t,4t}$=1.2 Hz, 4H, H-4t), 4.50 (d, 4H, J=5.5 Hz), 4.48 (d, 4H, J=5.5 Hz); ^{13}C NMR (CDCl$_3$, 150 MHz) δ 141.8 (s), 138.6 (s), 127.9 (d), 126.4 (d), 125.3 (d), 125.2 (d), 120.9 (d, C$_{2t}$), 47.0 (d), 41.0 (d); IR 2914, 1483, 1080, 746 cm^{-1}.

*4.3.7. 4.3.719-(1-Benzothien-3-yl)-9-thiahexacyclo[9.7.1.0^{2,10}.0^{2,18}.0^{3,8}.0^{12,17}]nonadeca-3,5,7,12,14,16-hexaene (**12b**).* Yield 110 mg (44%); R_f 0.40 (petroleum ether/dichloromethane=7:3); colourless crystals; mp 95–97 °C; UV (EtOH) λ_{max} (log ε) 300 (3.77), 292 (3.72), 270 (3.85), 225 (4.62); ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.86 (d, J=8.0 Hz, 1H, H-ar), 7.71 (d, J=8.0 Hz, 1H, H-ar), 7.38 (dt, J=8.0, 1.0 Hz, 1H, H-ar), 7.36 (d, J=7.5 Hz, 1H, H-ar), 7.28 (dt, J=8.0, 1.0 Hz, 1H, H-ar), 7.23 (d, J=7.5 Hz, 1H, H-ar), 7.12 (dt, J=7.5, 1.0 Hz, 1H, H-ar), 7.12 (dt, J=7.5, 1.0 Hz, 1H, H-ar), 7.05 (dt, J=7.5, 1.0 Hz, 1H, H-ar), 7.00 (dd, J=7.5, 1.0 Hz, 1H, H-ar), 6.87 (dt, J=7.5, 1.0 Hz, 1H, H-ar), 6.55 (d, J=7.5 Hz, 1H, H-ar), 6.43 (d, J=0.6 Hz, 1H, H-t), 4.72 (dd, J=4.4, 2.9 Hz, 1H, H-A), 4.10 (s, H-B), 3.80 (d, J=4.4 Hz, 1H, H-C), 3.37 (d, J=7.4 Hz, 1H, H-D), 1.98 (ddd, J=7.4, 2.9, 1.0 Hz, 1H, H-E); ^{13}C NMR (CDCl$_3$, 150 MHz) δ 145.0 (s), 140.3 (s), 138.8 (s), 138.6 (s), 136.7 (s), 134.1 (s), 133.9 (s), 127.7 (d), 127.4 (d), 126.3 (d), 126.0 (d), 125.9 (d), 125.0 (d), 124.4 (d), 124.2 (d), 123.4 (d), 122.2 (d), 121.8 (d), 121.8 (d), 120.5 (d), 60.7 (d), 46.3 (d), 38.0 (d), 34.4 (d), 26.0 (d); IR 2957, 1443, 731 cm^{-1}; HRMS: M$^+$, found 394.0828.. C$_{26}$H$_{18}$S$_2$ requires 394.0844.

4.4. Dehydrogenation of 9a with DDQ

Benzene solution (8 mg, 3.4×10^{-3} M) of 2,2′-(1,2-dihydronaphthalene-2,3-diyl)dithiophene (**9a**) was heated in the presence of 6 mg 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) for 7 h. The crude reaction mixture was purified by column chromatography on a silica gel using petroleum ether as the eluent. From the enriched first chromatographic fractions product **11** was isolated.

*4.4.1. 2,3-(2,2′-Dithienyl)naphthalene (**11**).* Yield 5 mg (63%); R_f 0.74 (petroleum ether/dichloromethane=7:3); colourless crystals with spectroscopic data identical to compound **10** obtained previously.[7]

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Supplementary data

^{1}H and ^{13}C NMR spectra of compounds **7a**–**c**, **8a**,**b**, **9a**–**c**, **10**, **12a**,**b**, **13**, UV spectra after irradiation of *cis*,*cis*-**7a**/**8a**, *cis*,*trans*-**7a**/**8a** and *trans*,*trans*-**7a**/**8a** and crystal data and structure refinement of **9a** and **12b**. Supplementary crystallographic data for **9a** and **12b** can be obtained free of charge via 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 860724 and 875101 contain the supplementary crystallographic data for this paper. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2012.06.019. These data include MOL files and InChiKeys of the most important compounds described in this article.

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