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Photobehaviour of 2- and 3-heteroaryl substituted *o*-divinylbenzenes; formation of fused 2,3- and 3,2-heteroareno-benzobicyclo[3.2.1]octadienes and 3-heteroaryl benzobicyclo[2.1.1]hexenes

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

Abstract

New β-3-thienyl (**8**) and β-3-furyl derivatives of *o*-divinylbenzene (**9**) have been synthesised and their photochemical behaviour compared with 2-thienyl (**7**) and 2-furyl derivatives (**2**). Whereas the β-(2-heteroaryl) substituted *o*-divinylbenzenes (**7** or **2**) give only bicyclo[3.2.1]octadiene structure (**14** or **1**) by 1,6-ring closure of the biradical intermediate, β-(3-heteroaryl) substituted *o*-divinylbenzenes (**8** or **9**) give bicyclo[3.2.1]octadiene structure (**23** or **24**) and bicyclo[2.1.1]hexene structure (**25** or **26**) by 1,6- and 1,4-ring closure, respectively. This photochemical approach provides a simple method to 2,3- and 3,2-fused thiophene and furan polycyclic compounds.

Keywords: Oxygen heterocycles; Sulfur heterocycles; Furan; Thiophene; Photochemistry; Photocycloaddition; Synthesis

1. Introduction

There is an increasing interest in the bicyclo[3.2.1]octane structures since they represent the basic framework of numerous important biologically active natural compounds or their metabolites. Their skeleton has also proved to be useful reactive intermediate in various stereoselective transformations making these derivatives powerful building blocks in organic synthesis.[1] In one of our previous papers[2] on the photochemistry of styryl substituted furan derivatives[2–12] we demonstrated for the first time the photochemical approach to furano-fused bicyclo[3.2.1]octadiene structure (**1**) by simple irradiation of 2-(*o*-vinylstyryl)furan (**2**) (Fig. 1). On the other hand, their nitrogen analogues, pyrrole derivatives (**3**),[13–20] gave completely different photoproducts. It was found that only alkoxycarbonyl substituted pyrrole derivatives[21] gave pyrrolo-fused benzobicyclo[3.2.1]octadiene structure (**4**). In the case of 2-(*o*-vinylstyryl)furans with the substituent in position 3 of the furan ring (**5**) formation of the bicyclo[2.1.1]hexene structure (**6**) was observed,[9] presumably due to the steric reasons.

In continuation of our interest for the effect of heteroatoms, as well as their position in the heteroaromatic ring on the

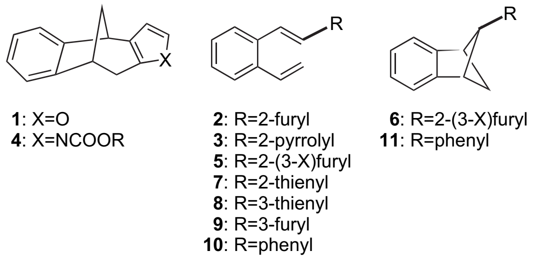

Figure 1.

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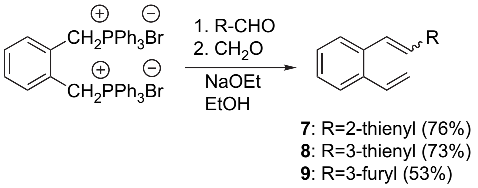
formation of heteropolycyclic compounds, we present here for the first time the photochemical behaviour of thiophene derivatives (**7**, **8**) and furan derivative (**9**). We anticipated that introduction of sulfur as heteroatom, by replacing the furan moiety with the thiophenes, may have influence on the excited state properties of this new hexatriene system and as a consequence the formation of diverse photoproducts. Based solely on the aromaticity of heterocycles,[22,23] the thiophene being more aromatic than furan, it might be expected that thiophene derivative **7** resembles the photochemical behaviour of its parent benzene derivative **10**, which upon irradiation closes to bicyclo[2.1.1]hexene **11**.[24–28]

2. Results and discussion

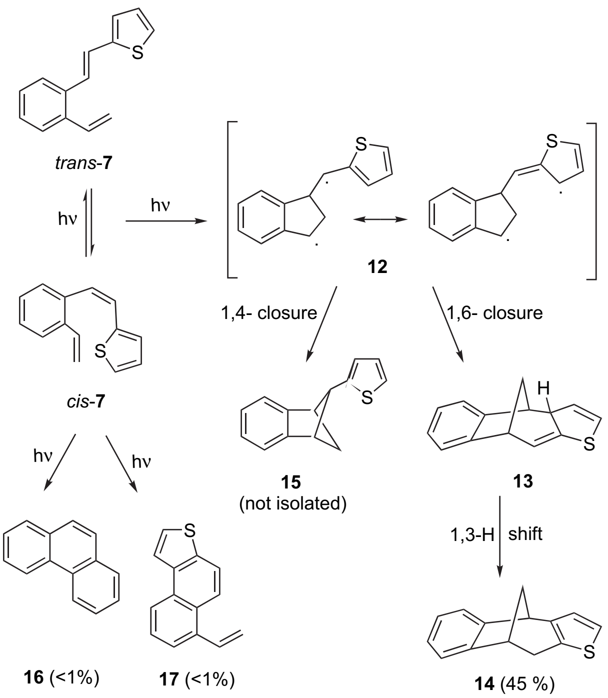
Starting compounds, 2-[2-(2-ethenylphenyl)ethenyl]thiophene (**7**),[3] 3-[2-(2-ethenylphenyl)ethenyl]thiophene (**8**) and 3-[2-(2-ethenylphenyl)ethenyl]furan (**9**) were synthesised in a good to very good yields (50–85%) by the Wittig reaction of β,β-*o*-xylyl(ditriphenylphosphonium) dibromide and the corresponding aldehydes (Scheme 1) according to the general procedure described for the β-heteroaryl-*o*-divinylbenzenes.[3] They were obtained as mixtures of trans- (60–70%) and cis-isomer (30–40%) that were separated by column chromatography and characterised spectroscopically.



Scheme 1.

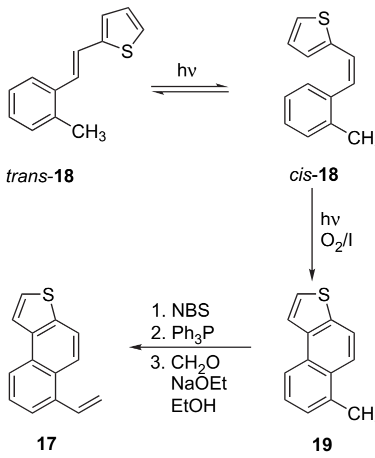
The irradiation experiments were performed under anaerobic conditions and in petroleum ether as a solvent. On irradiation of 2-thienyl substituted *o*-divinylbenzene **7** (Scheme 2) the thieno-fused benzobicyclo[3.2.1]octadiene **14** was isolated as the main product in 45% yield. In addition, minor quantities of phenanthrene (**16**) and vinylnaphthothiophene (**17**) were found in the first fractions during the column chromatography and the high-molecular-weight products remained on the column.

The photoproducts are easily identified by their NMR spectra, using one- and two-dimensional NMR techniques, and their comparison with the spectra of photoproducts, previously obtained on irradiation of 2-[2-(2-ethenylphenyl)ethenyl]furan (**2**).[2] The proposed mechanism for the formation of the main product, bicyclo[3.2.1]octadiene derivative **14**, as in the case of furan derivative **2**,[2] involves intramolecular cycloaddition via biradical intermediate **12** followed by preferred 1,6-ring closure to **13** and subsequent 1,3-H shift. The 2-thienyl-bicyclo[2.1.1]hexene derivative **15**, which could be formed by 1,4-ring closure of **12**, was not detected. The 1,4-ring closure was also not observed on irradiation of 2-[2-(2-ethenylphenyl)-ethenyl]furan (**2**)[2,4,8,9] contrary to the photochemical properties of the corresponding phenyl analogous **10**, *o*-vinylstilbene,[24,25] where the main product was the phenyl-benzobicyclo[2.1.1]hexene **11**.



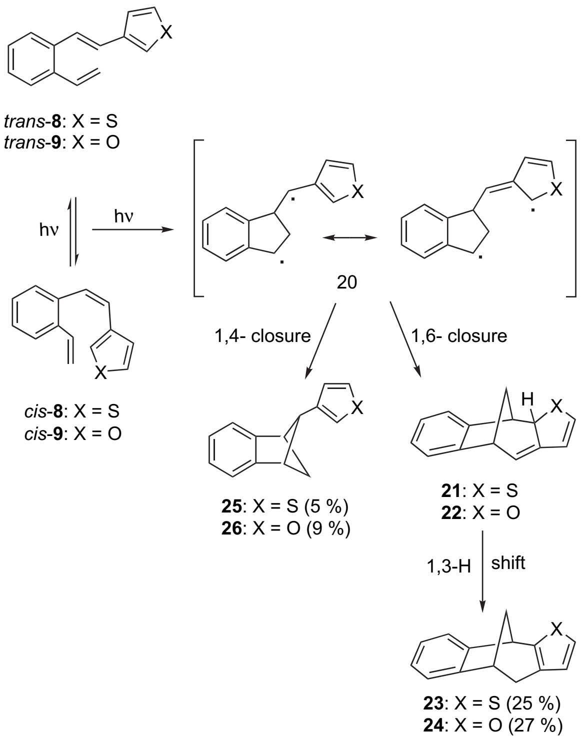
Scheme 2.

Formation of byproducts **16** and **17** can occur from the cis-configuration of **7** by two different mechanisms: the intramolecular photoinduced [4+2] cycloaddition followed by elimination of H_2S produces phenanthrene (**16**)[29] while photochemical electrocyclization process leads to vinylnaphthothiophene **17**. The presence of phenanthrene (**16**) was confirmed by comparison of its ^1H NMR spectrum with the ^1H NMR spectrum of authentic sample. The structure of new 6-vinylnaphtho[2,1-*b*]thiophene (**17**), formed in too small quantities to be analysed completely, was confirmed by its independent synthesis. The vinylnaphthothiophene derivative **17** was prepared by photochemical ring closure of **18** to **19** followed by a sequence of reactions according to Scheme 3.



Scheme 3.

Irradiation of 3-[2-(2-ethenylphenyl)ethenyl]thiophene (**8**) until the full conversion and under the same conditions as 2-thienyl derivative **7**, gave, after chromatographic separation on silica gel, not only the expected bicyclo[3.2.1]octadiene derivative **23**, as in case of 2-furyl **1** and 2-thienyl derivative **7**, but also the bicyclo[2.1.1]hexene derivative **25**. Formation of both bicyclic systems is explained via the same intermediate, biradical **20**, followed by possible 1,6- and 1,4-ring closure, respectively (Scheme 4). Further investigation of the hitherto unknown 3-furyl analogue, 3-[2-(2-ethenylphenyl)ethenyl]furan (**9**), afforded very similar results: bicyclo[3.2.1]octadiene derivative **24** and bicyclo[2.1.1]hexene derivative **26** were isolated, besides oxidation and high-molecular-weight products.



Scheme 4.

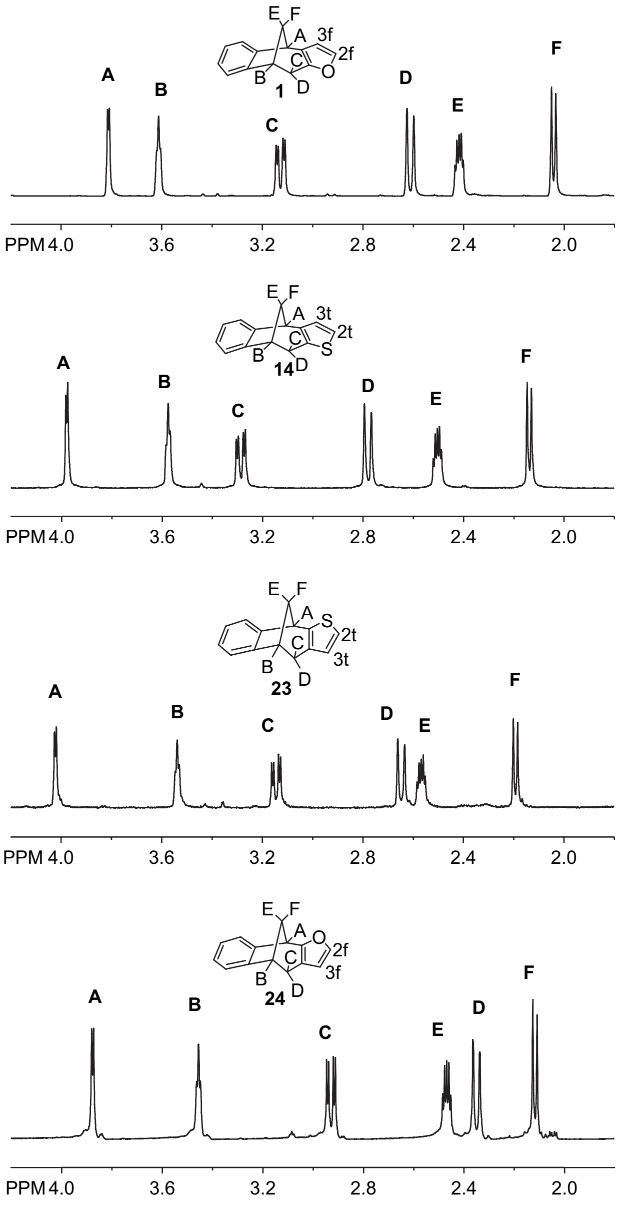


Figure 2. ^{1}H NMR spectra (600 MHz, in $CDCl_3$) of the aliphatic region of three new bicyclo[3.2.1]octadiene structures (**14**, **23**, **24**) compared with the known structure **1**.[2]

The structures of new photoproducts have been elucidated from their spectral data, ^{1}H NMR being the most informative. The aliphatic region of polycyclic compounds **1**, **14**, **23** and **24** is presented in Figure 2. The well recognisable pattern of ^{1}H NMR spectra of all photoproducts in the region between 2 and 4 ppm, undoubtedly indicates the same bicyclo[3.2.1]octadiene structure. Regardless of heteroatom, sulfur or oxygen, or its position in the ring the pattern of six aliphatic protons does not change substantially. They resonate in a narrow region: protons A appear at δ 3.81–4.03, protons B at δ 3.50–3.61 ppm, protons E at δ 2.42–2.50 ppm and protons F at δ 2.04–2.19 ppm. In somewhat wider region resonate the protons C (2.97–3.29 ppm) and protons D (2.40–2.78 ppm), which are because of vicinity of heteroatom, in structures **1** and **14**, shifted to the lower field in relation to the same protons in structures **24** and **23**. The polycyclic compounds **25** and **26** have also well recognisable ^{1}H NMR spectra showing the symmetric benzobicyclo[2.1.1]hexene structure (Fig. 3).

The isolated yields on bicyclic structures in case of irradiation of 3-styryl substituted thiophenes or 3-styryl substituted furans were in the same range. The difference in photochemical behaviour between thiophene and furan derivatives is in the rate of conversion. Thus, for the same conversion the irradiation time of thiophene derivatives is considerably longer than irradiation time of furan derivatives. To get more insight into this process the reaction course of all four compounds, the 2-thienyl derivative **7** and 3-thienyl derivative **8** as well as the 2-furyl **2** and 3-furyl **9**, was followed by examination of NMR spectra of the reaction mixtures obtained in the time intervals on parallel irradiation of the sample solutions. After 30 min of irradiation the ^{1}H NMR spectrum of 2-thienyl derivative **7**,

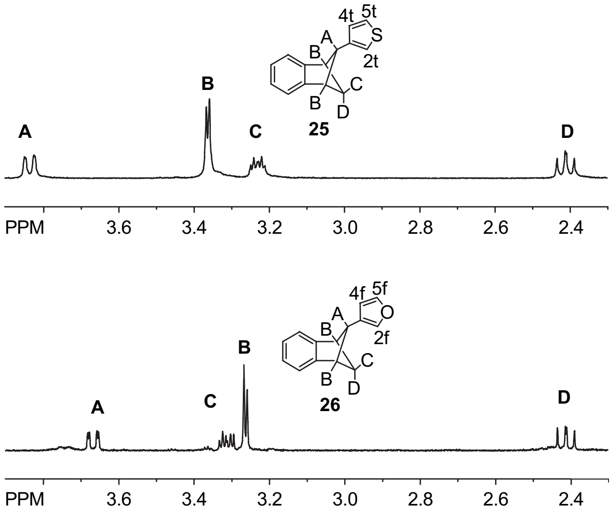


Figure 3. ^1H NMR spectra (in $CDCl_3$) of the aliphatic region of two bicyclo[2.1.1]hexenes (**25**, **26**).

using internal standard, showed only the presence of starting material, *cis*-**7** (72%) and *trans*-**7** (14%), while the photomixture of 2-furyl derivative **2** contained *cis*-**2** (22%), *trans*-**2** (10%) and already 23% of bicyclic [3.2.1] structure **1**. The 3-styryl thiophene **8** and 3-styryl furan derivative **9** mixtures did not differ significantly. After 30 min of irradiation the photomixture of 3-thienyl derivative **8** contained *cis*-**8** (63%), *trans*-**8** (8%), bicyclic [3.2.1] structure **23** (3%) and bicyclic [2.1.1] structure **25** (3%) while the 3-furyl derivative **9** contained *cis*-**9** (35%), *trans*-**9** (10%), bicyclic [3.2.1] structure **24** (3%) and bicyclic [2.1.1] structure **26** (1%). After 1 h of irradiation the 2-furyl derivative **2** was fully consumed while 2-thienyl **7** (74%), 3-thienyl **8** (46%) and 3-furyl **9** (37%) were still present in the reaction mixture, respectively. It should be mentioned that in all experiments besides trans–cis isomerisation, intramolecular cycloaddition reactions and formation of bicyclic structures, decomposition and formation of high-molecular-weight products are competitive processes.

3. Conclusion

o-Vinyl furo- and thienostilbenes (**2**, **7**–**9**) show comparable photochemical behaviour. Based on the experimental data we propose the formation of bicyclo[3.2.1]octadiene structures (**1**, **14**, **23**, **24**) as well as bicyclo[2.1.1]hexene structures (**25**, **26**) via the same type of resonance stabilised biradicals, **2A**–**2C** or **3A**–**3B** (Figs. 4 and 5).

Irradiation of 2-furyl and 2-thienyl derivatives afforded only bicyclo[3.2.1]octadiene structures **1** and **14**, respectively, due to the sterically and electronically most favourable 1,6-ring closure, via **2B**. This is in accord with the results obtained on irradiation of 5- and 3-substituted 2-styrylfurans.[4,9] In the case of 5-furan substitution (R=Ph)[4] with electronically most favourable **2C** (Fig. 4), which could undergo sterically unfavourable 1,8-ring closure, only traces of intramolecular bicyclic [3.2.1] structure have been found, besides high-molecular-weight products as a result of competitive processes.

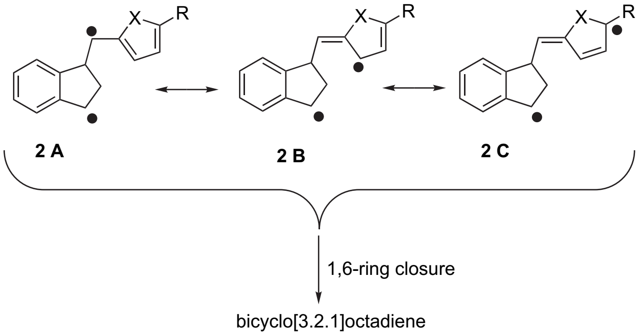


Figure 4.

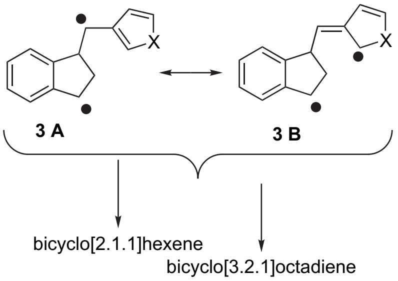


Figure 5.

In the case of 3-furan substitution[9] (Fig. 6) only the 1,4-ring closure took place due to the streric hinderance of the methyl group. We assume that even if the 1,6-ring closure is operating, via the more stable biradical **2(3x)B** in comparison to **2(3x)A**, the formed bicyclic structure opens back to the starting compound. Moreover, the 1,3-H shift, which normally follows and stabilises the whole system by irreversible aromatisation, is not in this case possible. Contrary to 2-heteroaryl unsubstituted derivatives (**2**, **7**) the 3-heteroaryl unsubstituted derivatives (**8**, **9**) give upon irradiation the biradical **3A**–**3B**, which closes to both bicyclic systems via 1,4- and 1,6-ring closure (Fig. 5). The probability for 1,4- and 1,6-ring closure is in this case roughly equal, as the **3B** is less stable due to the vicinity of heteroatom. According to ^1H NMR data, from experiments after short time of irradiation, the yield of both types of bicyclic structures is in the same range (2–3%). The isolated yields on bicyclic [2.1.1] structures (**25**, **26**) are relatively low, compared to major bicyclic [3.2.1] structures (**23**, **24**). The reason could be due to thermal instability of bicyclic [2.1.1] structures, which after prolonged irradiation

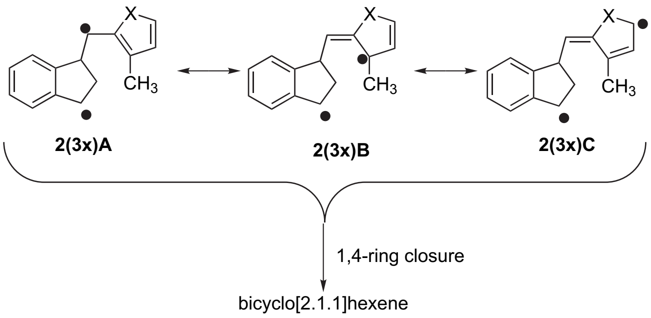


Figure 6.

time undergo cycloreversion into the starting compounds. The starting compound can be excited again giving cycloadduct products.

We find that this photochemical approach provides a simple method to 2,3- and 3,2-fused thiophene and furan polycyclic compounds, which can be the scaffolds for diverse transformations.

4. Experimental

4.1. General

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 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 petroleum ether solutions in a Rayonet reactor equipped with RPR 3000 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. 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. Thin layer chromatography (TLC) was performed on Merck precoated silica gel 60 F$_{254}$ plates. Solvents were purified by distillation.

Thiophene-2-carbaldehyde, thiophene-3-carbaldehyde and furan-3-carbaldehyde were obtained from a commercial source; β,β-*o*-xylyl(ditriphenylphosphonium) dibromide was prepared from *o*-xylyldibromide and triphenylphosphine in dimethylformamide.[3]

4.2. Preparation of **7–9**

Starting compounds **7–9** were prepared by Wittig reaction from *o*-xylylenebis(triphenylphosphonium bromide) and the corresponding aldehydes, thiophene-2-carbaldehyde, thiophene-3-carbaldehyde and furan-3-carbaldehyde, respectively, as described in the literature[3] for 2-[2-(2-ethenylphenyl)ethenyl]thiophene. To a stirred solution of the triphenylphosphonium salt (0.001 mol) and the corresponding aldehyde (0.011 mol) in absolute ethanol (200 mL), a solution of sodium ethoxide (0.253 g, 0.011 mol in 15 mL of absolute ethanol) was added dropwise. Stirring was continued under a stream of nitrogen for 1 h at rt. Under the stream of dry nitrogen, gaseous formaldehyde (obtained by decomposition of paraformaldehyde taken in excess, 1.5 g) was introduced and the next quantity of sodium ethoxide (0.253 g, 0.011 mol in 15 mL of absolute ethanol) was added dropwise. The reaction was completed 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 **7–9** were separated by repeated column chromatography on silica gel using petroleum ether as the eluent. The first fractions yielded cis-isomer and the last fractions trans-isomer. The 2-[2-(2-ethenylphenyl)ethenyl]thiophene (**7**) is described.[3] The data of the new compounds **8** and **9** are given below.

4.2.1. 3-[2-(2-Ethenylphenyl)ethenyl]thiophene (**8**)

Yield 73.0%; according to ^{1}H NMR spectra a mixture of 39% *cis*-**8** and 61% *trans*-**8**.

cis-**8**: R_f 0.44 (petroleum ether); colourless oil; UV (EtOH) λ_{max} (log ε) 250 (3.96); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.56 (d, J=7.9 Hz, 1H, H-ar), 7.14–7.30 (m, 3H, H-ar), 7.00 (dd, J=5.0, 3.0 Hz, 1H), 6.95 (d, J=3.0 Hz, 1H), 6.90 (dd, J=17.5, 11.0 Hz, 1H, −C*H*=CH$_2$), 6.66 (d, J=5.0, 1H), 6.65 (d, J=12.0 Hz, 1H, −CH=C*H*−), 6.59 (d, J=12.0 Hz, 1H, −C*H*=CH−), 5.67 (dd, J=17.5, 1.0 Hz, 1H, −CH=C*H$_2$*), 5.21 (dd, J=11.0, 1.0 Hz, 1H, −CH=C*H$_2$*); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 137.8 (s), 136.4 (s), 135.6 (s), 134.5 (d), 129.1 (d), 127.5 (d), 127.4 (d), 127.3 (d), 127.1 (d), 125.0 (d), 125.0 (d), 124.3 (d), 124.0 (d), 114.8 (t); IR 3009, 1691, 1414, 991, 771 cm^{-1}; MS *m*/*z* (%) 212 (M$^+$, 100).

trans-**8**: R_f 0.42 (petroleum ether); colourless oil; UV (EtOH) λ_{max} (log ε) 299 (4.41), 250 (4.26); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.20–7.56 (m, 8H), 7.08 (dd, J=17.4; 11.0 Hz, 1H, −C*H*=CH$_2$), 6.98 (d, J=16.1 Hz, 1H, −CH=C*H*−), 5.64 (dd, J=17.4, 1.3 Hz, 1H, −CH=C*H$_2$*), 5.36 (dd, J=11.0, 1.3 Hz, 1H, −CH=C*H$_2$*); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 140.3 (s), 136.3 (s), 135.6 (s), 135.0 (d), 127.9 (d), 127.5 (d), 126.6 (d), 126.4 (d), 126.2 (d), 126.0 (d), 125.2 (d), 125.0 (d), 122.5 (d), 116.5 (t); IR 3055, 1626, 1474, 959, 768 cm^{-1}; MS *m*/*z* (%) 212 (M$^+$, 100). Anal. Calcd for C$_{14}$H$_{12}$S: C, 79.20; H, 5.70. Found: C, 79.49; H, 5.60.

4.2.2. 3-[2-(2-Ethenylphenyl)ethenyl]furan (**9**)

Yield 53.0%; according to ^{1}H NMR spectra a mixture of 28% *cis*-**9** and 72% *trans*-**9**.

cis-**9**: R_f 0.44 (petroleum ether); colourless oil; UV (EtOH) λ_{max} (log ε) 243 (4.15); ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.58 (d, J=7.8 Hz, 1H, H-ar), 7.28 (m, 1H, H-ar), 7.20–7.26 (m, 3H, 2H-ar, H-2f), 7.15 (d, J=1.4 Hz, 1H, H-5f), 6.90 (dd, J=17.6, 11.0 Hz, 1H, −C*H*=CH$_2$), 6.58 (d, J=11.8 Hz, 1H, −C*H*=CH−), 6.48 (d, J=11.8 Hz, 1H, −CH=C*H*−), 5.87 (d, J=1.4 Hz, 1H, H-4f), 5.68 (dd, J=17.6, 1.1 Hz, 1H, −CH=C*H$_2$*), 5.22 (dd, J=3.2; 1.1 Hz, 1H, −CH=C*H$_2$*); ^{13}C NMR (CDCl$_3$, 150 MHz) δ 142.0 (d, C$_{2f}$/C$_{5f}$), 141.6 (d, C$_{2f}$/C$_{5f}$), 136.3 (s), 135.5 (s), 134.4 (d), 129.0 (d), 127.4 (d), 127.1 (d), 127.1 (d), 124.7 (d), 122.0 (s), 121.0 (d), 114.6 (t), 109.6 (d, C$_{4f}$); IR 2914, 2839, 1634, 1470, 1277, 1016, 752 cm^{-1}; MS *m*/*z* (EI) 196 (M$^+$, 100%), 167 (15), 117 (5).

trans-**9**: R_f 0.42 (petroleum ether); colourless oil; UV (EtOH) λ_{max} (log ε) 289 (4.30), 247 (4.25), 226 (4.18, sh); ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.52 (d, J=0.6 Hz, 1H, H-2f), 7.49 (dd, J=7.5; 1.4 Hz, 1H, H-ar), 7.46 (dd, J=7.5; 1.4 Hz, 1H, H-ar), 7.41 (m, 1H, H-5f), 7.22–7.28 (m, 2H, H-ar), 7.09 (d, *J*=16.0 Hz, 1H, −C*H*=CH−), 7.07 (dd, *J*=17.4; 10.9 Hz, 1H, −C*H*=CH$_2$), 6.83 (d, *J*=16.0 Hz, 1H, −CH=C*H*−), 6.66 (dd, *J*=16.0; 0.6 Hz, 1H, H-4f), 5.64 (dd, *J*=17.4; 1.3 Hz, 1H, −CH=C*H*$_2$), 5.35 (dd, *J*=10.9; 1.3 Hz, 1H, −CH=C*H*$_2$); ^{13}C NMR (CDCl$_3$, 150 MHz) δ 143.2 (d, C_{2f}/C_{5f}), 140.5 (d, C_{2f}/C_{5f}), 135.7 (s), 135.1 (s), 134.5 (d), 127.4 (d), 126.9 (d), 126.1 (d), 125.6 (d), 125.6 (d), 124.3 (s), 120.3 (d), 115.9 (t), 106.9 (d, C_{4f}); IR 2945, 2837, 1680, 1470, 964, 748 cm^{-1}; MS *m*/*z* (EI) 196 (M$^+$, 100%), 167 (10); HRMS: $M^{+}_{calcd.}$ 196.088266; $M^{+}_{exp.}$ 196.090431.

4.3. Irradiation experiments of 7–9

A mixture of cis- and trans-isomers of **7**–**9** in petroleum ether (**7**: 7.1×10^{-3} M; **8**: 2.4×10^{-3} M; **9**: 5.1×10^{-3} M) was purged with argon for 30 min and irradiated at 350 nm (**7**) and 300 nm (**8**, **9**) in a Rayonet reactor (16 lamps) in a quartz vessel. The reaction course was followed by GC–MS and ^{1}H NMR measurements. After irradiation of **7**–**9** (**7**: 92 h; **8**: 64 h; **9**: 17 h) the solvent was removed in vacuo and the oily residue chromatographed on a silica gel column using petroleum ether as the eluent.

4.3.1. Irradiation of 2-[2-(2-ethenylphenyl)ethenyl]-thiophene (7)

Traces of phenanthrene (**16**, <1%) and 6-vinylnaphtho-[2,1-*b*]thiophene (**17**, <1%) were found in the enriched first chromatographic fractions followed by 2,3-[3,2-*b*-thieno]-6,7-benzobicyclo[3.2.1]octa-2,6-diene (**14**, 661 mg, 45%). High-molecular-weight products (56%) remained on the column.

*4.3.1.1. 6-Vinylnaphtho[2,1-b]thiophene (**17**).* The compound is identical with the authentic sample **17**, independently prepared by a sequence of reactions: a benzene solution of 2-(*o*-methylstyryl)thiophene (**18**)[30] was irradiated in the presence of iodine and obtained 6-methylnaphtho[2,1-*b*]thiophene (**19**)[31] subjected to bromination with NBS, treatment with triphenylphosphine, followed by Wittig reaction with formaldehyde (Scheme 3) in overall yield of 11%.

Compound **17**: R_f 0.46 (petroleum ether); colourless crystals; mp 100 °C; UV (EtOH) λ_{max} (log ε) 308 (4.07), 246 (4.48), 235 (4.44); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 8.31 (d, *J*=8.1 Hz, 1H, H-ar), 8.05 (d, *J*=9.1 Hz, 1H), 8.00 (dd, *J*=5.4, 0.5 Hz, 1H), 7.93 (dd, *J*=9.1, 0.5 Hz, 1H), 7.67 (d, *J*=8.1 Hz, 1H, H-ar), 7.60 (d, *J*=5.4 Hz, 1H), 7.59 (t, *J*=8.1 Hz, 1H, H-ar), 7.54 (dd, *J*=17.3, 10.9 Hz, 1H, −C*H*=CH$_2$), 5.82 (dd, *J*=17.3, 1.5 Hz, 1H, −CH=C*H*$_2$), 5.52 (dd, *J*=10.9, 1.5 Hz, 1H, −CH=C*H*$_2$); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 136.7 (s), 135.9 (s), 135.8 (s), 134.5 (d), 129.0 (s), 128.0 (s), 125.7 (d), 125.4 (d), 123.0 (d), 122.8 (d), 121.8 (d), 120.3 (d), 120.2 (d), 116.9 (t); MS *m*/*z* 210 (100%). Anal. Calcd for $C_{14}H_{10}S$: C, 79.96; H, 4.79. Found: C, 79.84; H, 4.94.

*4.3.1.2. 2,3-[3,2-b-Thieno]-6,7-benzobicyclo[3.2.1]octa-2,6-diene (**14**).* R_f 0.33 (petroleum ether); colourless crystals; mp 90 °C; UV (EtOH) λ_{max} (log ε) 270 (3.00), 267 (3.07), 255 (3.40), 228 (3.90); ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.30 (d, *J*=7.1 Hz, 1H, H-ar), 7.11 (d, 1H, *J*=7.1 Hz, H-ar), 7.08 (t, 1H, *J*=7.1 Hz, H-ar), 7.04 (t, *J*=7.1 Hz, 1H, H-ar), 6.97 (d, $J_{2t,3t}$=5.0 Hz, 1H, H-2 t), 6.82 (d, $J_{2t,3t}$=5.0 Hz, 1H, H-3 t), 3.98 (d, $J_{A,E}$=4.3 Hz, 1H, H-A), 3.58 (t, *J*=4.5 Hz, 1H, H-B), 3.29 (dd, $J_{B,C}$=4.5 Hz, $J_{C,D}$=16.5 Hz, 1H, H-C), 2.78 (d, $J_{C,D}$=16.5 Hz, 1H, H-D), 2.47–2.54 (m, 1H, H-E), 2.14 (d, $J_{E,F}$=10.3 Hz, 1H, H-F); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 151.4 (s), 144.9 (s), 141.8 (s), 131.6 (s), 126.4 (d), 126.3 (d), 125.0 (d, C_{3t}), 123.6 (d), 122.2 (d, C_{2t}), 120.8 (d), 42.4 (d, C_A), 42.2 (t, $C_{E,F}$), 40.6 (d, C_B), 31.6 (t, $C_{C,D}$); IR 2941, 1468, 1136, 748 cm^{-1}; MS *m*/*z* 212 (100%). Anal. Calcd for $C_{14}H_{12}S$: C, 79.20; H, 5.70. Found: C, 79.24; H, 5.88.

4.3.2. Irradiation of 3-[2-(2-ethenylphenyl)ethenyl]-thiophene (8)

In the first fractions *exo*-5-(3-thienyl)benzobicyclo[2.1.1]-hex-2-ene (**25**, 11 mg, 5%) was isolated followed by 2,3-[2,3-*b*-thieno]-6,7-benzobicyclo[3.2.1]octa-2,6-diene (**23**, 55 mg, 25%). High-molecular-weight products (70%) remained on the column.

*4.3.2.1. exo-5-(3-Thienyl)benzobicyclo[2.1.1]hex-2-ene (exo-**25**).* R_f 0.39 (petroleum ether); colourless crystals; mp 64 °C; UV (EtOH) λ_{max} (log ε) 275 (3.35), 268 (3.34), 263 (3.34), 240 (3.91); ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.32 (dd, $J_{2t,5t}$=2.9 Hz, $J_{4t,5t}$=4.9 Hz, 1H, H-5t), 7.22–7.27 (m, 2H, H-ar), 7.19 (ddd, $J_{2t,4t}$=1.1; $J_{2t,5t}$=2.9; $J_{2t,A}$=1.1 Hz, 1H, H-2t), 7.08 (dd, $J_{2t,4t}$=1.1 Hz, $J_{4t,5t}$=4.9 Hz, 1H, H-4t), 7.00 (d, *J*=8.0 Hz, 2H, H-ar), 3.83 (dd, $J_{2t,A}$=1.1 Hz, $J_{A,D}$=7.4 Hz, 1H, H-A), 3.36 (d, $J_{B,C}$=2.5 Hz, 2H, H-B), 3.23 (dt, $J_{B,C}$=2.5 Hz, $J_{C,D}$=6.4 Hz, 1H, H-C), 2.41 (dd, $J_{A,D}$=7.4; $J_{C,D}$=6.4 Hz, 1H, H-D); ^{13}C NMR (CDCl$_3$, 150 MHz) δ 152.7 (2s), 141.8 (s), 128.2 (d, C_{3t}), 125.3 (d, C_{2t}), 124.2 (2d), 121.3 (d, C_{5t}), 118.7 (2d), 74.2 (d, C_A), 60.5 (t, $C_{C,D}$), 49.3 (d, C_B); IR 2891, 2854, 1435, 1080, 835, 750 cm^{-1}; MS *m*/*z* (ES) 212 (100%). Anal. Calcd for $C_{14}H_{12}S$: C, 79.20; H, 5.70. Found: C, 79.55; H, 5.67.

*4.3.2.2. 2,3-[2,3-b-Thieno]-6,7-benzobicyclo[3.2.1]octa-2,6-diene (**23**).* R_f 0.33 (petroleum ether); colourless crystals; mp 50–52 °C; UV (EtOH) λ_{max} (log ε) 269 (3.32), 262 (3.53), 254 (3.71), 243 (3.74); ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.30 (d, *J*=7.1 Hz, 1H, H-ar), 7.02–7.16 (m, 3H, H-ar), 6.90 (d, $J_{2t,3t}$=5.0 Hz, 1H), 6.63 (d, $J_{2t,3t}$=5.0 Hz, 1H), 4.03 (d, $J_{A,E}$=4.4 Hz, 1H, H-A), 3.54 (t, *J*=4.7 Hz, 1H, H-B), 3.15 (dd, $J_{B,C}$=4.7 Hz, $J_{C,D}$=16.3 Hz, 1H, H-C), 2.65 (d, $J_{C,D}$=16.3 Hz, 1H, H-D), 2.54–2.59 (m, 1H, H-E), 2.19 (d, $J_{E,F}$=10.3 Hz, 1H, H-F); ^{13}C NMR (CDCl$_3$, 150 MHz) δ 150.0 (s), 144.8 (s), 139.6 (s), 129.8 (s), 127.8 (d), 126.0 (d), 125.9 (d), 123.1 (d), 120.4 (d), 120.2 (d), 42.0 (t), 41.0 (d), 39.5 (d), 31.6 (t); IR 2926, 2827, 1468, 1294, 696 cm^{-1}; MS *m*/*z* 212 (100%). Anal. Calcd for $C_{14}H_{12}S$: C, 79.20; H, 5.70. Found: C, 79.52; H, 5.64.

*4.3.3. Irradiation of 3-[2-(2-ethenylphenyl)ethenyl]furan (**9**)*

In the first fractions *exo*-5-(3-furyl)benzobicyclo[2.1.1]hex-2-ene (**26**, 45 mg, 9%) was isolated followed by 2,3-[2,3-*b*-furo]-6,7-benzobicyclo[3.2.1]octa-2,6-diene (**24**, 135 mg, 27%). High-molecular-weight products (64%) remained on the column.

*4.3.3.1. exo-5-(3-Furyl)benzobicyclo[2.1.1]hex-2-ene (exo-**26**).* R_f 0.39 (petroleum ether); colourless oil; UV (EtOH) λ_{max} (log ε) 267 (2.99), 261 (2.92), 255 (2.87); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.42–7.45 (m, 2H, H-2f, H-5f), 7.26–7.23 (m, 2H, H-ar), 6.98–7.01 (m, 2H, H-ar), 6.40–6.41 (m, 1H, H-4f), 3.65 (dd, $J_{2f,A}$=1.3 Hz, $J_{A,D}$=7.3 Hz, 1H, H-A), 3.30 (dd, $J_{B,C}$=2.3 Hz, $J_{C,D}$=6.2 Hz, 1H, H-C), 3.24 (d, $J_{B,C}$=2.3 Hz, 2H, H-B), 2.39 (dd, $J_{A,D}$=7.3 Hz, $J_{C,D}$=6.2 Hz, 1H, H-D); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 152.2 (s), 142.2 (d), 139.4 (d), 124.1 (s), 123.6 (d), 118.2 (d), 110.6 (d), 69.3 (d, C_A), 59.7 (t, $C_{C,D}$), 48.4 (d, C_B); IR 2922, 2850, 1454, 1030, 750 cm^{-1}; MS *m/z* (EI) 196 (100%). Anal. Calcd for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 85.73; H, 6.06.

*4.3.3.2. 2,3-[2,3-b-Furo]-6,7-benzobicyclo[3.2.1]octa-2,6-diene (**24**).* R_f 0.33 (petroleum ether); colourless crystals; mp 64–65 °C; UV (EtOH) λ_{max} (log ε) 274 (3.13), 267 (3.18), 260 (3.20), 248 (3.65); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.00–7.32 (m, 5H, H-ar, H-2f), 6.03 (d, $J_{2f,3f}$=2.0 Hz, 1H, H-3f), 3.92 (d, $J_{A,E}$=4.6 Hz, 1H, H-A), 3.50 (dt, $J_{B,C}$=4.7 Hz, $J_{B,D}$=1.8 Hz, $J_{B,E}$=5.1 Hz, 1H, H-B), 2.97 (dd, $J_{B,C}$=4.7 Hz, $J_{C,D}$=15.8 Hz, 1H, H-C), 2.51 (dt, $J_{A,E}$=4.6 Hz, $J_{B,E}$=5.1 Hz, $J_{E,F}$=10.3 Hz, 1H, H-E), 2.40 (dd, $J_{C,D}$=15.8; $J_{B,D}$=1.8 Hz, 1H, H-D), 2.16 (d, $J_{E,F}$=10.3 Hz, 1H, H-F); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 154.8 (s), 149.7 (s), 145.3 (s), 139.7 (d), 126.3 (d), 126.1 (d), 123.6 (d), 120.6 (d), 111.0 (d), 110.3 (s), 42.5 (t), 40.5 (d), 40.4 (d), 28.6 (t); IR 2916, 2841, 1634, 1472, 1279, 1024, 754 cm^{-1}; MS *m/z* (EI) 196 (100%). Anal. Calcd for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 85.59; H, 6.07.

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