Synthesis and Photochemistry of β,β′-Di(2-furyl)-Substituted *o*-Divinylbenzenes: Intra- and/or Intermolecular Cycloaddition as an Effect of Annelation

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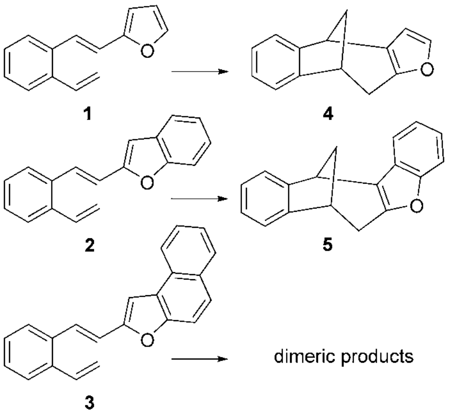
Dedicated to Professor Wim Laarhoven on the occasion of his 80th birthday

Abstract: New heteroaryl-substituted *o*-divinylbenzenes, 2,2′-(1,2-phenylenedivinylene)difuran (**9**), 2,2′-(1,2-phenylenedivinylene)bisbenzo[*b*]furan (**10**), and 2,2′-(1,2-phenylenedivinylene)bisnaphtho[2,1-*b*]furan (**11**), were prepared and irradiated at various concentrations; intramolecular photocycloaddition and intermolecular [2+2] twofold photoaddition reactions took place to give bicyclo[3.2.1]octadiene derivatives **12**–**14** and cyclophane derivatives **15**–**17**, respectively. Compound **11** was the most selective of these *o*-divinylbenzenes, which, owing to π–π intra- or intermolecular complexation, gave only the *exo*-bicyclo[3.2.1]octadiene derivative **14** at low concentrations, and only the cyclophane derivative **17** at high concentrations.

Keywords: cycloaddition · cyclophanes · dimerization · heteroaromatics · photochemistry

Introduction

The photochemistry of styryl-substituted furan derivatives has been thoroughly investigated.[1–8] Furan (**1**) and benzo[*b*]furan (**2**) derivatives of *o*-divinylbenzenes give, upon irradiation in dilute petroleum ether or benzene solutions, benzobicyclo[3.2.1]octadiene derivatives **4**[1] and **5**,[4] respectively, as the main photoproducts (Scheme 1). No intramolecular cycloaddition product was found upon irradiation of the naphthofuran derivative **3**[4] in dilute solution under the same conditions. The only observed products were traces of dimeric cyclobutane derivatives. The formation of these dimeric products was confirmed by the irradiation of high concentrations of **3**.[5] The intermolecular cycloaddition reaction can be explained[5] by of the probable complexation of **3** by π–π interactions. Similar results were obtained on irradiation of high concentrations of **2**, whereas the furan derivative **1** gave only high-molecular-weight and decomposition products. It was concluded that in monosubstituted *o*-divinylbenzenes **1**–**3**, annelation increases the intermolecular complexation and results in the formation of dimeric products.



Scheme 1.

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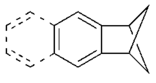
We have found many examples in the literature of mono- and diaryl-substituted *o*-divinylbenzene derivatives[9–31] that undergo intra- and/or intermolecular photocycloaddition reactions. The nature of the substituent, as well as its position, has an important influence on the course of the reaction in which various polycyclic structures, such as **6**, **7** and **8**, are produced. Thus, β,β′-diphenyl-*o*-divinylbenzene, even at very low concentrations ($<10^{-5}$ M), undergoes photodimerization to give products of structural type **8**,[23–25] whereas in the crystal form [21] or adsorbed onto silica gel[25] it undergoes an intramolecular cycloaddition reaction to give a bicyclo[2.1.1]hexene derivative (structural type **6**). Only a few examples of reactions that involve diheteroaryl-substituted *o*-divinylbenzene derivatives have been found: the photochemistry of *o*-phenylenedivinylenedipyrroles,[32–34] nitrogen analogues of **9**, and the photochemistry of the diquinoxalinyl *o*-divinylbenzene derivative.[35] Whereas the dipyrrole derivative, after photoexcitation followed by electron and hydrogen transfer, undergoes ring closure to the indane derivative, which then reacts further with the starting compound to give dimeric products, the diquinoxaline derivative showed photostability in the crystalline state.



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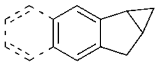

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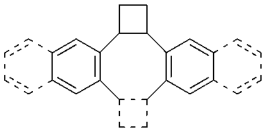

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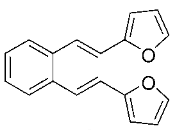
Herein, we describe for the first time the synthesis and photochemistry of the difuran-substituted *o*-divinylbenzenes **9**–**11**, a study that was undertaken to determine the influence of annelation on the course of the reaction. In contrast to the monofuran derivatives **1**–**3**, introduction of the second annelated furan moiety to *o*-divinylbenzene could result in intramolecular complexation to give upon irradiation interesting annelated bicyclo[3.2.1]octadiene structures, derivatives of a bicyclo[3.2.1]octane skeleton found in numerous important biologically active natural products.[36–38]



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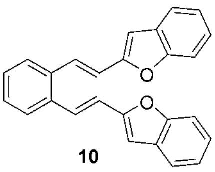

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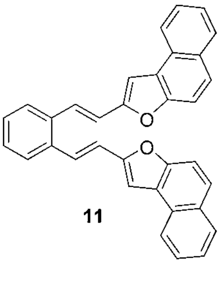

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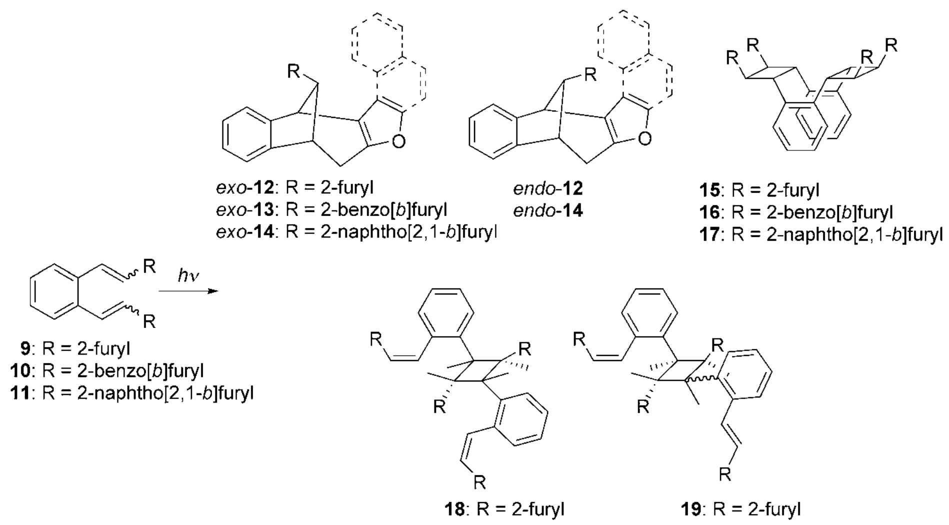
Results

The starting materials, diheteroaryl-substituted *o*-divinylbenzenes **9**–**11**, were prepared by the Wittig reaction of β,β′-*o*-xylyl(ditriphenylphosphonium) dibromide and the corresponding aldehydes according to the general procedure described for the heteroarylstilbene analogues.[39] They were obtained in moderate-to-good yields (49–85%) as mixtures of *cis,cis*, *cis,trans* and *trans,trans* isomers with the *cis,trans* isomers being dominant. The isomers of **9**–**11** were separated by a combination of column chromatography and thin-layer chromatography on silica gel and identified spectroscopically. In the series of compounds **9**–**11**, because of increased annelation, all three geometric isomers show a bathochromic shift in the UV spectrum and an increase in the molar absorption coefficients, as expected. The geometric isomers can be easily identified in their ^{1}H NMR spectra by the characteristic vicinal coupling constants of the *cis*- and *trans*-ethylenic protons. The ratios of the isomers were determined from the NMR spectra and by GC-MS measurements.

Compounds **9**–**11** were irradiated in benzene solution under anaerobic conditions at 300 (compound **9**) and 350 nm (compounds **10** and **11**). Depending on the starting material, its concentration and the irradiation time, different ratios of the photoproducts **12**–**19** (Scheme 2) were formed as a result of intra- and/or intermolecular cycloaddition processes. After a very short irradiation time *cis*–*trans* isomerization to give the preferred *trans,trans* isomer was observed for all three derivatives **9**–**11**. The bicyclo[3.2.1]octadiene derivatives **12**–**14** were isolated as the major photoproducts of the irradiations performed at low concentrations, whereas at high concentrations the cyclophane derivatives **15**–**17** were isolated. The products were separated by column chromatography on silica gel and the structures deduced unequivocally from spectral studies. All of the protons were completely assigned from the ^{1}H and ^{13}C NMR spectra by using different techniques (COSY, NOESY and HSQC). As can be seen in Figure 1, the very well-resolved five-proton pattern between $\delta = 2.7$ and 5.2 ppm in the ^{1}H NMR spectra of the major photoproducts **12**–**14** unmistakably points to the formation of the same bicyclo[3.2.1]octadiene structure. The singlet assigned to proton **A** is the more affected and is shifted strongly toward a low field owing to the anisotropic effect of the benzene and naphthalene rings, respectively. In the previously obtained bicyclo[3.2.1]octadiene derivatives[1,2,4,6] with no substituent on the methano bridge carbon, proton **A** couples only with the *exo*-oriented proton and appears as a narrow doublet. As the *endo*-oriented proton does not couple with proton **A** the *exo* structure was assigned. The *exo* orientation of the



Scheme 2.

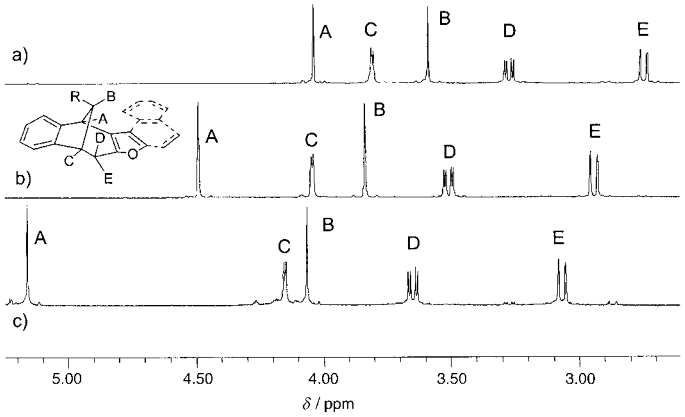


Figure 1. ^{1}H NMR spectra (in $CDCl_3$) of the aliphatic region of three *exo*-bicyclo[3.2.1]octadiene derivatives: a) *exo*-**12**; b) *exo*-**13**; c) *exo*-**14**.

heteroaryl group at the methano bridge carbon was also confirmed by X-ray crystallographic analysis of *exo*-**13** (Figure 2).

Minor quantities of *endo*-**12** and *endo*-**14** were seen only in enriched chromatographic fractions and were identified by the characteristic couplings of proton **A** and the *exo*-oriented proton **B** as well as by other characteristic chemical shifts and couplings in the aliphatic region. The major photoproducts formed on irradiation of higher concentrations of **9**–**11** were cyclophane derivatives which were obtained by a twofold cyclodimerization reaction. Of the many possible cyclophane structures one stereoisomer (**15**, **16**, or **17**, respectively) was exclusively formed for all the derivatives (Scheme 2). The formation of a cyclophane structure of high symmetry was obvious from the ^{1}H NMR spectra in which the absence of ethylenic protons and the presence of only two signals corresponding to two cyclobutane rings was observed. The number of carbon signals in the ^{13}C NMR spectra was halved but the molecular ion in the MS spectrum pointed to the dimer structure. The cyclophane structure **15** was also confirmed by X-ray analysis (Figure 3).

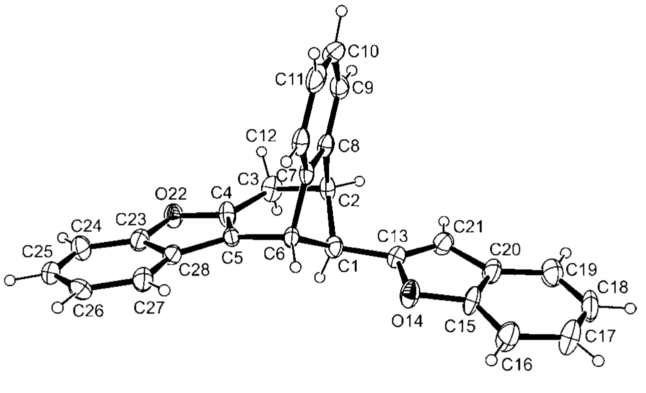


Figure 2. Molecular structure of *exo*-**13** (ORTEP diagram).

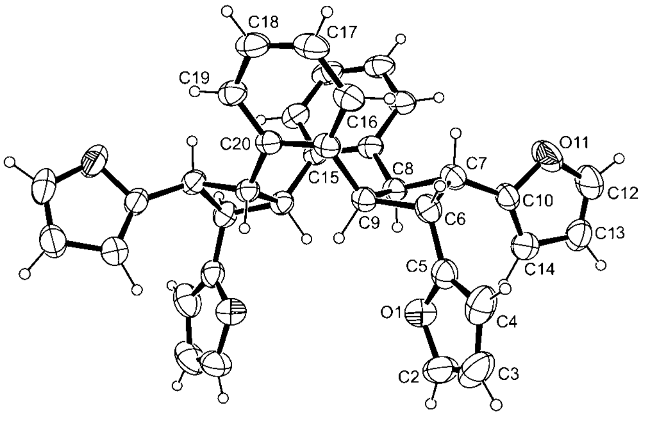


Figure 3. Molecular structure of **15** (ORTEP diagram).

The formation of photoadducts with only one cyclobutane ring was not observed on irradiation of **11**, while traces of cyclobutane photoproducts were seen on irradiation of **10**, according to the ^{1}H NMR spectra. However, upon irradiation of the difuran derivative **9**, two head-to-tail cyclobutane derivatives, **18** and **19**, were isolated in 8 and 5% yields, respectively (Scheme 2). The existence of the same basic $M^+/2$ peak in the mass spectra of both derivatives, a peak which is identical to the M^+ peak of the starting molecule **9**, and the nonexistence of fragments characteristic of an unsymmetrical reversion pointed to the formation of the head-to-tail adducts. The ^{1}H NMR spectrum of the cyclobutane derivative **18** exhibits two doublet-of-doublets at $\delta = 4.51$ and

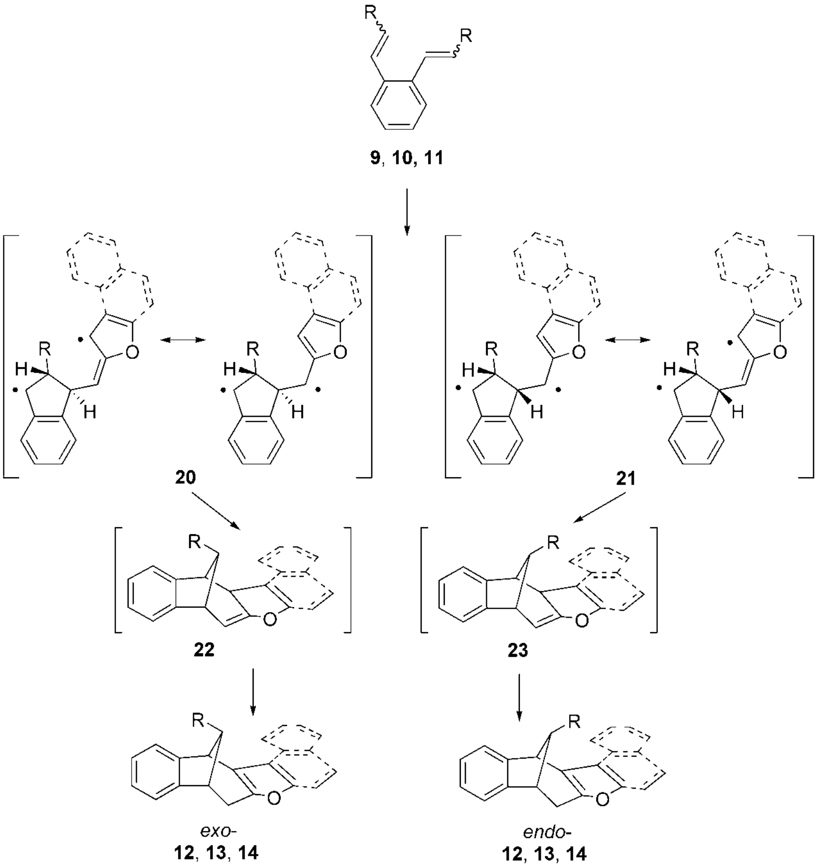
4.36 ppm, which correspond to the four protons of the cyclobutane and the ^{13}C NMR spectrum reveals two signals at $\delta = 44.17$ and 39.84 ppm which correspond to the four carbon atoms. Product **19** has four different protons which appear as three signals at $\delta = 4.70$, 4.56, and 4.24 ppm (dd, m, dd) in its ^{1}H NMR spectrum in a ratio of 1:2:1, respectively. The ^{13}C NMR spectrum of **19** shows four signals at $\delta = 44.27$, 44.04, 40.30, and 39.36 ppm. The configuration of the furo-styryl substituents was deduced from the ethylenic coupling constants, product **19** having two values, J_{cis} and J_{trans}, whereas **18** only one, J_{cis}. The stereochemistry of the cyclobutane protons and substituents was determined from the ^{1}H NMR spectra based on the differences between their chemical shifts and patterns, and by comparison with previously obtained results from similar systems.[5] Whereas for structure **18** the stereochemistry is completely defined, for structure **19** the configuration at one of the carbon atoms could not be assigned because of complicated overlapping of the signals of aromatic protons.

Experiments were performed to examine and compare the influence of annelation on the product distribution at various concentrations of the diheteroaryl *o*-divinylbenzenes. A 1×10^{-1} M solution of the bisnaphthofuran derivative **11** gave the cyclophane **17** as the sole product. The furan and benzofuran derivatives **9** and **10**, under the same conditions, gave mainly cyclophanes as well as the bicyclo[3.2.1]octadiene derivatives **12** (5–10%) and **13** (5–10%), respectively, based on ^{1}H NMR spectra. At a concentration of 1×10^{-3} M usually used for intramolecular reactions, the ratio of isolated products was: 1.2 (**12**):1.0 (**15**) from **9**; 4.0 (**13**):1.0 (**16**) from **10** and only **14** from **11**.

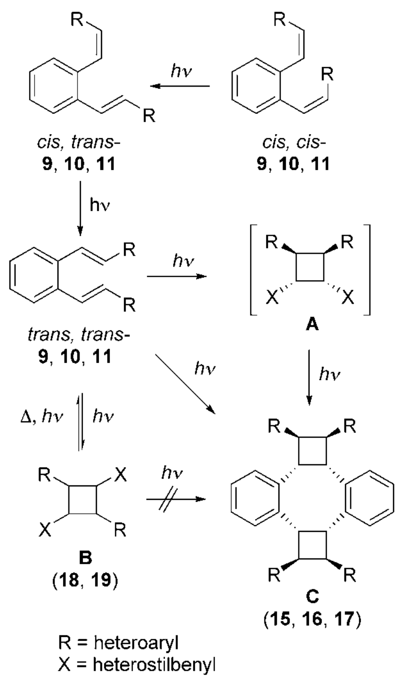
Discussion

The main photoproduct obtained from the irradiation of the derivatives **9**–**11** under the conditions for intramolecular reactions was the bicyclo[3.2.1]octadiene derivative, the *exo* isomer being the sole (*exo*-**13**) or predominant (*exo*-**12**, *exo*-**14**) product. The stereoselective formation of the *exo* isomer can be explained (Scheme 3) by the preferred *trans* ring closure to the indane intermediate **20**, presumably for steric reasons. Then, **20** ring-closes via **22** by the same mechanism as seen in the reactions of the mono-furan and mono-benzofuran derivatives of *o*-divinylbenzene[1,4,6] to yield *exo*-**12**, -**13**, and -**14**, respectively. The formation of the *endo* isomer, found only in traces (**12**, **14**), can be explained by *cis* ring closure to give the indane intermediate **21**, which, via **23**, gave *endo*-**12** and *endo*-**14**.

The main photoproduct obtained upon irradiation of high concentrations of the diheteroaryl derivatives **9**–**11** was the cyclophane **C** (Scheme 4), which was formed by a twofold intermolecular *syn* head-to-head $[2\pi+2\pi]$ cycloaddition reaction. The other cyclophane isomers, which have cyclobutane rings with different geometries, were not isolated, as was found for the irradiation of the diaryl derivative *trans*,-*trans*-*o*-distyrylbenzene.[24] Such a high regio- and stereospecific process can be ascribed to steric factors and strong attractive interactions between π systems.[40–42] Presumably, as with 2,3-distyrylnaphthalene,[27] the population of the rotamers of **9**–**11** and the electronic and steric effects in the excimers are decisive factors. It is known[24,27,30,31] that excimers with a parallel arrangement of as many π centers as possible are preferred. A possible cycloaddition path to the cyclophanes is as follows: all three derivatives **9**–**11** rapidly isomerize to the *trans,trans* isomer which can then react stepwise, either via the head-to-head cycloadduct **A**, to cyclophane **C** or directly to give **C** in one step. If the cyclodimerization involves the head-to-tail addition process, the cycloadduct **B** is formed but cannot react to give cyclophane **C**



Scheme 3. Mechanism for the formation of the bicyclo[3.2.1]octadiene structures **12**–**14**.



Scheme 4. Possible cycloaddition path to the cyclophanes **15**–**17**.

because of its geometry. Since, upon a shorter irradiation time of the difuran derivative **9**, small quantities of structure **B** (**18**, **19**) were found in the reaction mixture, it is presumed that the adduct **B** undergoes thermal cycloreversion[43] to the starting compound **9** which then reacts to give the preferred adduct **A**. The failure to isolate adduct **B** upon irradiation of the annelated derivatives **10** and **11** points to the extreme influence of increasing π–π interactions in the series of furan, benzofuran and naphthofuran aromatics, and therefore the preferred formation of **C** directly or via **A**.

From these results it is obvious that the steric and electronic factors overlap. In the case of **9** the steric hindrance to an intramolecular ring closure to **20** or **21** is more important than π–π interactions. Therefore, to obtain the bicyclo[3.2.1]octadiene derivative **12** as the sole product, a concentration below 10^{-4} M is necessary. For the bisnaphthofuran derivative **11** the increased intramolecular π–π interactions due to the naphthalene moiety outweigh the steric effects of these large groups and cause intramolecular ring closure and the formation of the bicyclo[3.2.1]octadiene derivative **14**. For the benzofuran derivative **10** the π–π interactions and steric effects compete. Relative to the furan derivative **9**, the steric and electronic effects in **10** are stronger, but relative to **11** they are weaker.

Conclusions

Herein we have demonstrated an interesting photochemical pathway to two different classes of heteropolycyclic compounds. In concentrated solutions β,β′-diheteroaryl-substituted *o*-divinylbenzenes **9**–**11** regio- and stereospecifically produce cyclophane structures **15**–**17** that have a hydrophobic cavity and an electron-rich recognition site of four furan oxygen atoms, and thus might be used as molecular tweezers. On the other hand, irradiation of dilute solutions of **9**–**11** furnishes molecules with the pharmaceutically interesting bicyclo[3.2.1]octane skeleton. Of the β,β′-diheteroaryl-substituted *o*-divinylbenzenes **9**–**11** examined, the most selective is **11**, which, owing to π–π intra- or intermolecular complexation, gives only the *exo*-bicyclo[3.2.1]octadiene derivative **14** at low concentrations or only the cyclophane derivative at high concentrations **17**.

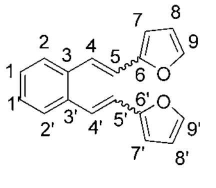
Experimental Section

General: The ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 spectrometer at 300 and 75 MHz, respectively, and on a Bruker AV-600 spectrometer at 600 MHz. All NMR spectra were measured in $CDCl_3$ using tetramethylsilane as the reference. The assignment of the signals is based on 2D-CH correlation and 2D-HH-COSY, LRCOSY and NOESY experiments. UV spectra were measured on a Varian Cary 50 UV/VIS spectrophotometer. Mass spectra were obtained on a Varian Saturn 2200 instrument equipped with a FactorFour Capillary Column VF-5 ms and on a Platform LCZ spectrometer (Micromass, UK). Melting points were obtained by using an Original Kofler Mikroheitztisch apparatus (Reichert, Wien) and are uncorrected. Elemental analyses were carried out on a Perkin-Elmer Series II CHNS Analyzer 2400. Silica gel (Merck 0.05–0.2 mm) was used for chromatographic purifications. Solvents were purified by distillation.

Furan-2-carboxaldehyde and benzo[*b*]furan-2-carboxaldehyde were obtained from a commercial source. Naphtho[2,1-*b*]furan-2-carboxaldehyde was prepared from 2-hydroxynaphthocarboxaldehyde according to a described procedure.[44]

Preparation of 9, 10, and 11: Starting compounds **9**–**11** were prepared from the β,β′-*o*-xylyl(ditriphenylphosphonium) dibromide and the corresponding aldehydes, furan-2-carboxaldehyde, benzo[*b*]furan-2-carboxaldehyde and naphtho[2,1-*b*]furan-2-carboxaldehyde, respectively. A solution of sodium ethoxide (0.51 g, 0.022 mol in 15 mL ethanol) was added dropwise to a stirred solution of β,β′-*o*-xylyl(ditriphenylphosphonium) dibromide (7.88 g, 0.01 mol) and the corresponding aldehydes (0.022 mol) in absolute ethanol (100 mL). Stirring was continued under a stream of nitrogen for one day at room temperature. After removal of the solvent, the residue was worked up with water and benzene. The benzene extracts were dried and concentrated. The crude reaction mixture was purified and the isomers of products **9**–**11** were separated by repeated column chromatography on silica gel using petroleum ether and a petroleum ether/diethyl ether (0–5%) mixture as eluent.

After the separation of mono-styryl by-products, the first fractions yielded the *cis,cis* isomer and the last fractions the *cis,trans* and *trans,trans* isomers. The characterization data for the new compounds **9**–**11** are given below.



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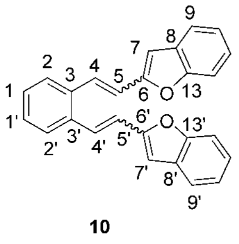

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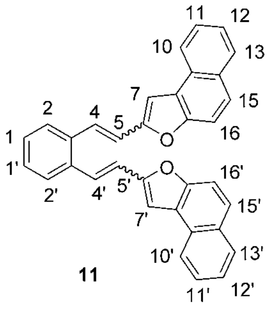

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2,2′-(1,2-Phenylenedivinylene)difuran (9): Yield 85.4 %; according to ^{1}H NMR spectroscopy, a mixture of 26 % *cis,cis*, 46 % *cis,trans* and 28 % *trans,trans* isomers. Unreacted furan-2-carboxaldehyde remained on the column.

***cis,cis*-9**: Yellow oil; $R_f = 0.61$ (petroleum ether/CH_2Cl_2 9:1); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.47$ (m, 1 H, H-1/2), 7.26 (m, 1 H, H-1/2), 7.22 (m, 1 H, H-9), 6.45 (d, $J = 12.0$ Hz, 1 H, H-5), 6.39 (d, $J = 12.0$ Hz, 1 H, H-4), 6.23 (dd, $J = 1.8$, 3.0 Hz, 1 H, H-8), 6.07 ppm (d, $J = 3.0$ Hz, 1 H, H-7); ^{13}C NMR ($CDCl_3$): $\delta = 152.14$ (s, C-6), 141.37 (d, C-9), 136.40 (s, C-3), 128.88 (d, C-1/2), 127.01 (d, C-1/2), 126.70 (d, C-4), 118.82 (d, C-5), 111.01 (d, C-8), 109.48 ppm (d, C-7); UV (EtOH): λ_{max} ($\log\varepsilon$) = 284 nm (4.22); MS (EI): *m/z* (%): 262 (10) [M^+], 233 (100), 181 (17).

***cis,trans*-9**: Yellow oil; $R_f = 0.55$ (petroleum ether/CH_2Cl_2 9:1); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.62$ (d, $J = 7.8$ Hz, 1 H, H-2/2′), 7.37 (m, 1 H, H-9/9′), 7.35 (d, $J = 7.2$ Hz, 1 H, H-2/2′), 7.30 (t, $J = 7.8$ Hz, 1 H, H-1/1′), 7.18–7.24 (m, 3 H, H-1/1′, H-9/9′, H-4′), 6.84 (d, $J = 15.6$ Hz, 1 H, H-5′), 6.62 (d, $J = 12.6$ Hz, 1 H, H-4), 6.56 (d, $J = 12.6$ Hz, 1 H, H-5), 6.39 (dd, $J = 1.8$, 3.6 Hz, 1 H, H-8′), 6.32 (d, $J = 3.0$ Hz, 1 H, H-7′), 6.23 (dd, $J = 1.8$, 3.0 Hz, 1 H, H-8), 5.95 ppm (d, $J = 3.6$ Hz, 1 H, H-7); ^{13}C NMR ($CDCl_3$): $\delta = 152.98$ (s, C-6′), 151.68 (s, C-6), 141.65 (d, C-9′), 141.05 (d, C-9), 136.15 (s, C-3), 134.72 (s, C-3′), 129.11 (d, C-1/2), 127.21 (d, C-1′/2′), 126.79 (d, C-1/2), 126.28 (d, C-1′/2′), 124.56 (d, 2 C, C-4, C-4′), 119.39 (d, C-5), 117.37 (d, C-5′), 111.09 (d, C-8/8′), 110.76 (d, C-8/8′), 109.15 (d, C-7), 108.15 ppm (d, C-7′); UV(EtOH): λ_{max} ($\log\varepsilon$) = 324 nm (4.27); MS (EI): *m/z* (%): 262 (8) [M^+], 233 (100), 181 (15).

***trans,trans*-9**: Yellow crystals, m.p. 179–180 °C; $R_f = 0.51$ (petroleum ether/CH_2Cl_2 9:1); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.54$ [m, 2 H, H(ar)], 7.43 (d, $J = 1.8$ Hz, 2 H, H-9), 7.42 (d, $J = 16.2$ Hz, 2 H, H-5), 7.25 [m, 2 H, H(ar)], 6.81 (d, $J = 16.2$ Hz, 2 H, H-4), 6.44 (dd, $J = 1.8$, 3.6 Hz, 2 H, H-8), 6.38) ppm (d, $J = 3.6$ Hz, 2 H, H-7); ^{13}C NMR ($CDCl_3$): $\delta = 153.30$ (s, C-6), 142.14 (d, C-9), 135.44 (s, C-3), 127.56 (d, C-1/2), 126.04 (d, C-1/2), 124.53 (d, C-4), 118.69 (d, C-5), 111.53 (d, C-8), 108.73 ppm (d, C-7); UV (EtOH): λ_{max} ($\log\varepsilon$) = 337 (4.23), 298 nm (4.36); MS (EI): *m/z* (%): 262 (70) [M^+], 233 (100), 181 (13); elemental analysis calcd (%) for $C_{18}H_{14}O$ (262.3): C 82.42, H 5.38; found: C 82.30, H 5.45.

2,2′-(1,2-Phenylenedivinylene)bisbenzo[*b*]furan (10): Yield 53.7 %; according to ^{1}H NMR spectroscopy, a mixture of 26 % *cis,cis*, 37 % *cis,trans* and 37 % *trans,trans* isomers. Unreacted benzo[*b*]furan-2-carboxaldehyde remained on the column.

***cis,cis*-10**: Yellow oil; $R_f = 0.40$ (petroleum ether/CH_2Cl_2 4:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.57$ (dd, $J = 3.6$, 5.4 Hz, 2 H, H-1/2), 7.39 (d, $J = 8.1$ Hz, 2 H, H-9/12), 7.38 (dd, $J = 3.6$, 5.4 Hz, 2 H, H-1/2), 7.33 (d, $J = 8.1$ Hz, 2 H, H-9/12), 7.21 (dd, $J = 7.2$, 8.1 Hz, 2 H, H-10/11), 7.15 (dd, $J = 7.2$, 8.1 Hz, 2 H, H-10/11), 6.74 (d, $J = 12.3$ Hz, 2 H, H-4/5), 6.54 (d, $J = 12.3$ Hz, 2 H, H-4/5), 6.44 ppm (s, 2 H, H-7); ^{13}C NMR ($CDCl_3$): $\delta = 154.01$ (s), 153.66 (s), 136.09 (s), 130.34 (d), 129.04 (d), 128.46 (s), 127.44 (d), 124.26 (d), 122.54 (d), 120.64 (d), 119.23 (d), 110.80 (d), 105.91 ppm (d); UV (EtOH): λ_{max} ($\log\varepsilon$) = 307 nm (4.46); MS (EI): *m/z* (%): 362 (100) [M^+], 231 (20), 131 (8).

***cis,trans*-10**: Yellow crystals, m.p. 82–85 °C; $R_f = 0.36$ (petroleum ether/CH_2Cl_2 4:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.74$ (d, $J = 7.8$ Hz, 1 H), 7.05–7.58 (m, 12 H), 7.00 (d, $J = 15.9$ Hz, 1 H, H-4/5), 6.95 (d, $J = 12.3$ Hz, 1 H, H-4′/5′), 6.76 (d, $J = 12.3$ Hz, 1 H, H-4′/5′), 6.67 (s, 1 H, H-7), 6.36 ppm (s, 1 H, H-7′); ^{13}C NMR ($CDCl_3$): $\delta = 154.92$ (s), 154.61 (s), 154.03 (s), 153.64 (s), 136.46 (s), 134.74 (s), 130.44 (d), 129.63 (d), 128.00 (d), 127.76 (d), 127.71 (d), 125.33 (d), 124.55 (d), 124.34 (d), 122.73 (d), 122.61 (d), 120.76 (d), 120.69 (d), 120.13 (d), 117.94 (d), 110.87 (d), 110.84 (d), 105.92 (d), 105.40 ppm (d); UV (EtOH): λ_{max} ($\log\varepsilon$) = 342 nm (4.52); MS (EI): *m/z* (%): 362 (100) [M^+], 231 (27), 131 (12).

***trans,trans*-10**: Yellow crystals, m.p. 164 °C; $R_f = 0.35$ (petroleum ether/CH_2Cl_2 4:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.68$ (d, $J = 15.9$ Hz, 2 H, H-4/5), 7.55 (dd, $J = 3.5$, 5.7 Hz, 2 H, H-1/2), 7.48 (d, $J = 7.2$ Hz, 2 H, H-8/12), 7.46 (d, $J = 7.1$ Hz, 2 H, H-8/12), 7.20–7.29 (m, 4 H, H-10/11 and H-1/2), 7.16 (dd, $J = 6.3$, 8.5 Hz, 2 H, H-10/11), 6.88 (d, $J = 15.9$ Hz, 2 H, H-4/5), 6.66 ppm (s, 2 H, H-7); ^{13}C NMR ($CDCl_3$): $\delta = 155.52$ (s), 155.42 (s), 135.89 (s), 129.53 (s), 128.64 (d), 128.06 (d), 126.98 (d), 125.20 (d), 123.37 (d), 121.34 (d), 119.50 (d), 11.50 (d), 106.06 ppm (d); UV (EtOH): λ_{max} ($\log\varepsilon$) = 356 (4.55), 316 nm (4.74); MS (EI): *m/z* (%): 362 (100) [M^+], 231 (30), 131 (10); elemental analysis calcd (%) for $C_{26}H_{18}O_2$ (362.4): C 86.16, H 5.01; found: C 86.00, H 5.05.

2,2′-(1,2-Phenylenedivinylene)bisnaphtho[2,1-*b*]furan (11): Yield 49.4 %; according to ^{1}H NMR spectroscopy, a mixture of 29 % *cis,cis*, 38 % *cis,trans* and 33 % *trans,trans* isomers. Unreacted naphtho[2,1-*b*]furan-2-carboxaldehyde remained on the column.

***cis,cis*-11**: Colorless crystals, m.p. 165–168 °C; $R_f = 0.61$ (petroleum ether/CH_2Cl_2 3:2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.81$–7.84 (m, 4 H, H-10), 7.34–7.70 [m, 12 H, H(ar)], 6.95 (s, 2 H, H-7), 6.76 [d, $J = 12.0$ Hz, 2 H, H(et)], 6.62 ppm [d, $J = 12.0$ Hz, 2 H, H(et)]; ^{13}C NMR ($CDCl_3$): $\delta = 153.42$ (s), 151.74 (s), 136.37 (s), 130.18 (s), 129.54 (d), 129.25 (d), 128.60 (d), 127.60 (d), 127.31 (s), 126.02 (d), 125.36 (d), 124.37 (d), 123.97 (s), 123.30 (d), 119.40 (d), 112.01 (d), 105.03 ppm (d); UV (EtOH): λ_{max} ($\log\varepsilon$) = 344 (4.54), 297 nm (4.86); MS (ESI): *m/z* (%): 462.6 (18) [M^+], 295.5 (34), 145.2 (79), 83.3 (100).

***cis,trans*-11**: Colorless crystals, m.p. 170–172 °C; $R_f = 0.59$ (petroleum ether/CH_2Cl_2 3:2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.09$ [d, $J = 8.1$ Hz, 1 H, H(ar)/*trans*], 7.14–7.94 [m, 16 H, H(ar)], 7.15 (s, 1 H, H-7/*trans*), 7.09 [d, $J = 16.2$ Hz, 1 H, H(et)/*trans*], 6.96 [d, $J = 12.6$ Hz, 1 H, H(et)/*cis*], 6.85 (s, 1 H, H-7/*cis*), 6.84 ppm [d, $J = 12.9$ Hz, 1 H, H(et)/*cis*]; ^{13}C NMR (too small a quantity for analysis); UV (EtOH): λ_{max} ($\log\varepsilon$) = 365 (4.62), 345 (4.64), 220 nm (4.88); MS (ESI): *m/z* (%): 462.6 (33) [M^+], 295.5 (21), 145.2 (69), 83.3 (100).

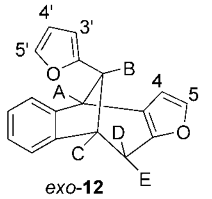
***trans,trans*-11**: Colorless crystals, m.p. 184–186 °C; $R_f = 0.57$ (petroleum ether/CH_2Cl_2 3:2); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 8.14$ (d, $J = 7.8$ Hz, 2 H, H-10), 7.95 (d, $J = 7.8$ Hz, 2 H), 7.81 (d, $J = 15.9$ Hz, 2 H, H-4/5), 7.73 (AB_q, $J = 9.0$ Hz, 4 H, H-15 and H-16), 7.67 (m, 2 H, H-1/2), 7.60 (t, $J = 7.8$ Hz, 2 H, H-11/12), 7.50 (t, $J = 7.8$ Hz, 2 H, H-11/12), 7.35 (m, 2 H, H-1/2), 7.25 (s, 2 H, H-7), 7.07 ppm (d, $J = 15.9$ Hz, 2 H, H-4/5); ^{13}C NMR ($CDCl_3$): $\delta = 154.59$ (s), 152.50 (s), 135.43 (s), 130.50 (s), 128.72 (d), 127.37 (s), 126.74 (d), 126.40 (d), 126.25 (d), 125.65 (d), 124.53 (d), 124.40 (s), 123.40 (d), 118.98 (d), 112.11 (d), 104.60 (d), 120.04 ppm (d); UV (EtOH): λ_{max} ($\log\varepsilon$) = 369 (4.76), 345 (4.94), 212 nm (5.03); MS (ESI): *m/z* (%): 462.6 (27) [M^+], 295.5 (25), 145.2 (78), 83.3 (100); elemental analysis calcd (%) for $C_{34}H_{22}O_2$ (462.5): C 88.29, H 4.79; found: C 88.60, H 4.53.

Irradiation experiments: A mixture of the *cis,cis*, *cis,trans* and *trans,trans* isomers of **9**, **10** and **11** in benzene (**9**: 1.6×10^{-3} M; **10**: 3.7×10^{-3} M; **11**: 1×10^{-3} M and 1×10^{-1} M) was purged with argon for 30 min and irradiated at 300 nm (**9**) and at 350 nm (**10** and **11**) in a Rayonet reactor in a quartz (**9**) and pyrex (**10** and **11**) tube for 6–10 h. Solvent was removed in vacuum and the oily residue subjected to chromatography on a silica gel column using petroleum ether/dichloromethane (5–50 %) as eluent.

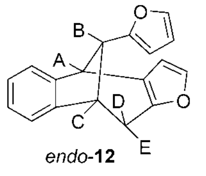
Irradiation of 2,2′-(1,2-phenylenedivinylene)difuran (9): Unreacted **9** (21 mg, 7 %) was isolated in the first fractions followed by the *exo*-bicyclo[3.2.1]octadiene derivative *exo*-**12** (110 mg, 37 %) and traces of *endo*-**12**, and the cyclobutane derivatives **18** (48 mg, 8 %) and **19** (30 mg, 5 %). In the last fractions cyclophane **15** (225 mg, 38 %) was isolated.

exo*- and *endo*-11-(2-Furyl)-9,10-dihydro-4,9-methano-4*H*-benzo[4,5]cyclohepta[1,2-*b*]furan (12)**:exo*-12**: Colorless crystals, m.p. 104–105 °C; $R_f = 0.42$ (petroleum ether/CH_2Cl_2 4:1); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 7.30$ [d, $J = 6.9$ Hz, 1 H, H(ar)], 7.24 (d, $J = 1.8$ Hz, 1 H, H-5), 7.16 (d, $J\sim1$ Hz, 1 H, H-5′), 7.11–7.03 [m, 3 H, H(ar)], 6.29 (d, $J = 1.8$ Hz, 1 H, H-4), 6.12 (dd, $J\sim1$, 3.3 Hz, 1 H, H-4′), 5.65 (d, $J = 3.3$ Hz, 1 H, H-3′), 4.04 (s, 1 H, H-A), 3.81 (d, $J = 4.8$ Hz, 1 H, H-C), 3.59 (s, 1 H, H-B), 3.26 (dd, $J = 4.8$, 16.2 Hz, 1 H, H-D), 2.74 ppm (d, $J = 16.2$ Hz, 1 H, H-E); ^{13}C NMR ($CDCl_3$): $\delta = 156.80$ (s), 150.07 (s), 146.64 (s), 142.53 (s), 140.79, 140.56 (2d), 126.71 (d), 126.35 (d), 124.36 (s), 121.17 (d), 109.88 (d), 108.08 (d), 104.89 (d), 52.63 (d, C-B), 44.97 (d, C-C), 43.85 (d, C-A), 31.36 ppm (t, C-DE), 1 signal is covered; UV (EtOH): λ_{max} ($\log\varepsilon$) = 267 (3.64), 222 nm (4.04); MS (EI): *m/z* (%): 262 (100) [M^+], 233 (5), 181 (25); elemental analysis calcd (%) for $C_{18}H_{14}O$ (262.3): C 82.42, H 5.38; found: C 82.56, H 5.29.

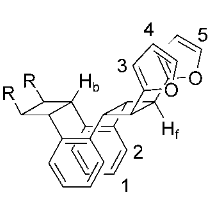
***endo*-12**: Too small a quantity to be analyzed completely; $R_f = 0.37$ (petroleum ether/CH_2Cl_2 4:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.05$ (m, 1 H, H-B), 3.78 (m, 1 H, H-C), 3.68 (d, $J = 2.4$ Hz, 1 H, H-A), 2.89 (dd, $J =$



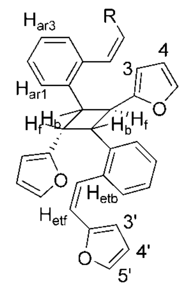
exo-**12**



endo-**12**

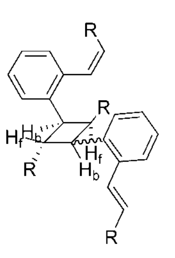


15



18

R = 2-furyl



19

16.2, 3.6 Hz, 1H, H-D), 2.57 ppm (d, $J=16.2$ Hz, 1H, H-E); MS (EI): m/z (%): 262 (100) [M^+], 233 (8), 181 (32).

***r*-1,*t*-3-Di(2-furyl)-*c*-2,*t*-4-bis{2-[2-(2-furyl)ethenyl]phenyl}cyclobutane (*r-ctt* htt dimer) (18)**: Colorless crystals, m.p. 92–94 °C; $R_f=0.21$ (petroleum ether/CH_2Cl_2 4:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.35$ [d, $J=7.8$ Hz, 2H, H(ar_1)], 7.19–7.27 [m, 6H, H(ar_2), H(ar_4), H-5′], 7.12 [dd, $J=6.9$, 7.5 Hz, 2H, H(ar_3)], 7.06 (d, $J=2.7$ Hz, 2H, H-5), 6.53 [d, $J=12.3$ Hz, 2H, H(etf)], 6.45 [d, $J=12.3$ Hz, 2H, H(etb)], 6.19 (dd, $J=2.3$, 3.0 Hz, 2H, H-4′), 6.01 (dd, $J=2.7$, 3.3 Hz, 2H, H-4), 5.81 (d, $J=3.0$ Hz, 2H, H-3′), 5.66 (d, $J=3.0$ Hz, 2H, H-3), 4.51 (dd, $J=7.5$, 7.8 Hz, 2H, H-f), 4.36 ppm (dd, $J=7.5$, 7.8 Hz, 2H, H-b); ^{13}C NMR ($CDCl_3$): $\delta=154.46$ (s), 151.99 (s), 141.23 (d), 140.95 (d), 137.33 (s), 137.21 (s), 128.68 (d), 127.18 (d), 126.98 (d), 126.01 (d), 126.01 (d), 119.18 (d), 111.04 (d), 109.71 (d), 109.37 (d), 106.54 (d), 44.17 (d), 39.84 ppm (d); UV (EtOH): λ_{max} ($\log\varepsilon$) = 282 (4.04), 227 nm (4.31); MS (EI): m/z (%): 524 (3) [M^+], 262 (36) [$M^+/2$], 233 (100), 181 (45); elemental analysis calcd (%) for $C_{36}H_{28}O_2$ (524.6): C 82.42, H 5.38; found: C 82.29, H 5.59.

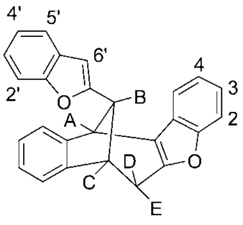
***r*-1,*t*-3-Di(2-furyl)-*c*-2,*c*-4-bis{2-[2-(2-furyl)ethenyl]phenyl}cyclobutane (*r-ctc* htt dimer) or *r*-1,*t*-3-di(2-furyl)-*c*-2,*t*-4-bis{2-[2-(2-furyl)ethenyl]phenyl}cyclobutane (*r-ctt* htt dimer) (19)**: Yellow crystals, m.p. 48–49 °C; $R_f=0.17$ (petroleum ether/CH_2Cl_2 4:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.50$–7.05 (m, 13H), 6.63 [d, $J=15.9$ Hz, 1H, H(et)], 6.54 and 6.48 [2d, $J=12.3$ Hz, 2H; H(et)], 6.48–6.43 (m, 1H), 6.35 (d, $J=3.3$ Hz, 1H), 6.22–6.17 (m, 1H), 6.10–6.05 (m, 1H), 6.04–5.98 (m, 1H), 5.82 (d, $J=3.3$ Hz, 1H), 5.79 (d, $J=3.3$ Hz, 1H), 5.65 (d, $J=3.3$ Hz, 1H), 4.70 (dd, $J=6.9$, 9.0 Hz, 2H), 4.56 (m, 4H), 4.24 ppm (dd, $J=7.2$, 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta=154.42$ (s), 154.12 (s), 153.42 (s), 151.98 (s), 142.03 (d), 141.25 (d), 141.03 (d), 140.96 (d), 137.33 (s), 137.22 (s), 136.75 (s), 136.48 (s), 128.73 (d), 127.23 (2d), 126.94 (d), 126.44 (d), 126.18 (d), 126.13 (d), 125.98 (d), 125.02 (d), 124.57 (d), 119.26 (d), 117.77 (d), 111.46 (d), 111.04 (d), 109.78 (2d), 109.39 (d), 108.35 (d), 106.71 (d), 106.67 (d), 44.27 (d), 44.04 (d), 40.30 (d), 39.36 ppm (d); UV (EtOH): λ_{max} ($\log\varepsilon$) = 273 (4.07), 221 nm (4.23); MS (EI): m/z (%): 524 (<2) [M^+], 262 (60) [$M^+/2$], 233 (100), 181 (30).

3,4,13,14-Tetra(2-furyl)pentacyclo[14.4.0.0^{2,5}.0^{6,11}.0^{12,15}]eicosa-1(20),6,8,10,16,18-hexaene (15): Colorless crystals, m.p. 242–243 °C; $R_f=0.12$ (petroleum ether/CH_2Cl_2 4:1); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=7.36$ (d, $J=2.1$ Hz, 4H, H-5), 7.18 (m, 4H, H-1/H-2), 7.08 (m, 4H, H-1/H-2), 6.32 (dd, $J=2.1$, 3.0 Hz, 4H, H-4), 6.12 (d, $J=3.0$ Hz, 4H, H-3), 4.61 (d, $J=6.0$ Hz, 4H, H-b), 4.44 ppm (d, $J=6.0$ Hz, 4H, H-f); ^{13}C NMR ($CDCl_3$): $\delta=154.58$ (s), 141.41 (d, C-5), 137.87 (s), 126.32 (d), 124.81 (d), 110.14 (d, C-4), 106.50 (d, C-3), 45.43 (d, C_b), 38.51 ppm (d, C_f); UV (EtOH): λ_{max} ($\log\varepsilon$) = 216 nm (4.40); MS (EI): m/z (%): 524 (10) [M^+], 262 (50) [$M^+/2$], 233 (100), 181 (15); elemental analysis calcd (%) for $C_{36}H_{28}O_2$ (524.6): C 82.42, H 5.38; found: C 82.47, H 5.28.

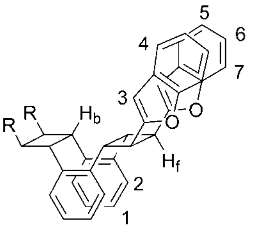
X-ray analysis: $C_{36}H_{28}O_4$, $M_r=524.6$ g mol^{-1}, monoclinic, space group: $C2/c$, $a=25.320(5)$, $b=9.249(5)$, $c=12.646(5)$ Å, $\beta=109.24(1)°$, $V=2796(2)$ Å^3, $\rho=1.246$ g cm^{-3}, $\mu=0.64$ mm^{-1}. Suitable prismatic and colorless single crystals were obtained by slow evaporation from the methanol/dichloromethane 1:1 mixture. The crystal with the dimensions $0.10\times0.12\times0.15$ mm was chosen. Three intensity control reflections measured every 120 minutes showed no significant loss of intensity during the data collection which was performed on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated CuK_α (1.54179 Å) radiation at RT [293(2)K]. Of the 2876 unique reflections collected, 1922 were observed [$I>2\sigma(I)$], $R_{int=}0.0186$. The model was refined by using the full-matrix least-squares refinement to the final $R_1=0.0544$, wR_2(all) $=0.1944$, $S=1.077$, $\Delta\rho_{max}=0.25$ and $\Delta\rho_{min}=-0.19$ eÅ^{-3}. In the final steps of refinement, the proposed weighting scheme was applied.

CCDC-250429 and CCDC-250430 contain the supplementary crystallographic data for this paper. These data 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) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Irradiation of 2,2′-(1,2-phenylenedivinylene)bisbenzo[*b*]furan (10): Unreacted **10** was isolated in the first fractions (6 mg, 4%) followed by the *exo*-bicyclo[3.2.1]octadiene derivative *exo*-**13** (73 mg, 52%) and traces of *endo*-**13**. In the last fractions cyclophane **17** (92 mg, 33%) was isolated.



exo-**13**



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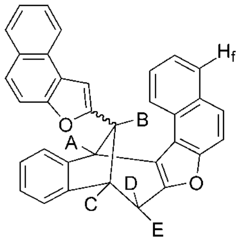
exo-13-(2-Benzo[*b*]furyl)-11,12-dihydro-6,11-methano-6*H*-benzo [4,5]cyclohepta[1,2-*b*]benzo[*d*]furan (*exo*-13): Colorless crystals, m.p. 158–159 °C; $R_f=0.31$ (petroleum ether/CH_2Cl_2 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.61$ (d, $J=7.2$ Hz, 1H), 7.32–7.43 (m, 3H, H-2, H-2′), 7.00–7.27 (m, 8H), 6.15 (s, 1H, H-6′), 4.49 (s, 1H, H-A), 4.04 (d, $J=4.8$ Hz, 1H, H-C), 3.83 (s, 1H, H-B), 3.50 (dd, $J=4.8$, 17.1 Hz, 1H, H-D), 2.94 ppm (d, $J=17.1$ Hz, 1H, H-E); ^{13}C NMR ($CDCl_3$): $\delta=159.45$ (s), 154.45 (s), 154.42 (s), 150.05 (s), 149.35 (s), 142.23 (s), 128.52 (s), 127.09 (d), 126.84 (d), 126.29 (s), 124.61 (d), 123.44 (d), 123.12 (d), 122.52 (d), 122.45 (d), 121.65 (s), 121.35 (d), 120.57 (d), 117.92 (d), 111.12 (d), 110.73 (d), 102.45 (d), 52.76 (d, C-B), 44.78 (d, C-C), 42.04 (d, C-A), 31.79 ppm (t, C-DE); UV (EtOH): λ_{max} ($\log\varepsilon$) = 304 (4.57), 254 (3.44), 217 nm (4.17); MS (ESI): m/z (%): 362.5 (30) [M^+], 145.2 (80), 83.3 (100); elemental analysis calcd (%) for $C_{26}H_{18}O_2$ (362.4): C 86.16, H 5.01; found: C 86.03, H 5.13.

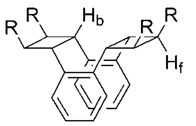
X-ray analysis: $C_{26}H_{18}O_2$, $M_r=362.4$ g mol^{-1}, monoclinic, space group: $P2_1/c$, $a=8.515(3)$, $b=11.839(4)$, $c=17.799(6)$ Å, $\beta=93.44(2)°$, $V=1791(1)$ Å^3, $\rho=1.344$ g cm^{-3}, $\mu=0.084$ mm^{-1}. The crystal, obtained by slow evaporation from a solution of methanol, was prismatic and colorless, dimensions $0.12\times0.13\times0.15$ mm. Three intensity control reflections measured every 120 min showed no significant loss of intensity during the data collection, which was performed on an Enraf-Nonius CAD4 diffractometer, using a graphite-monochromated MoK_α (0.71073 Å) radiation at RT [293(2)K]. Of the 3054 unique reflections collected, 859 were observed [$I>2\sigma(I)$], $R_{int=}0.1772$. The model was refined using the full-matrix least-squares refinement to the final $R_1=0.0675$, wR_2 (all) $=0.1863$, $S=0.908$, $\Delta\rho_{max}=0.25$ and $\Delta\rho_{min}=-0.27$ eÅ^{-3}. In the final steps of refinement, the proposed weighting scheme was applied.

3,4,13,14-Tetra(2-benzo[*b*]furyl)pentacyclo[14.4.0.0^{2,5}.0^{6,11}.0^{12,15}]eicosa-1(20),6(),8,10,16,18-hexaene (16): Colorless crystals, m.p. 193–194 °C; $R_f = 0.16$ (petroleum ether/CH_2Cl_2 7:3); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.42 (d, J = 7.2 Hz, 4H, H-4), 7.34 (d, J = 7.5 Hz, 4H, H-7), 7.08–7.25 (m, 16H), 6.56 (s, 4H, H-3), 4.83 (d, J = 6.0 Hz, 4H, H-b), 4.67 ppm (d, J = 6.0 Hz, 4H, H-f); ^{13}C NMR ($CDCl_3$): δ = 157.06 (s), 154.73 (s), 137.48 (s), 128.36 (s), 126.69 (d), 124.94 (d), 123.53 (d), 122.37 (d), 120.50 (d, C-2), 110.77 (d, C-7), 103.92 (d, C-3), 45.41 (d, C-b), 38.94 ppm (d, C-f); UV (EtOH): λ_{max} ($\log\varepsilon$) = 279 (4.04), 247 nm (4.49); MS (ESI): m/z (%): 724.5 (90) [M^+], 593.5 (55), 464.5 (100); elemental analysis calcd (%) for $C_{26}H_{18}O_2$ (724.8): C 86.16, H 5.01; found: C 86.30, H 4.91.

Irradiation of 2,2′-(1,2-phenylenedivinylene)bisnaphtho [2,1-*b*]furan (11): Because of the high selectivity of **11** in photochemical reactions, a mixture of *cis,cis*, *cis,trans* and *trans,trans* isomers of **11** was irradiated at concentrations of 1×10^{-3} and 1×10^{-1} M. In dilute solution, unreacted **11** (6 mg, 6%) was isolated in the first fractions followed by the *exo*-bicyclo[3.2.1]octadiene derivative *exo*-**14** (83 mg, 83%) and traces of *endo*-**14**. A product formed by an intermolecular reaction was not observed in the ^1H NMR spectrum. In concentrated solution, in addition to traces of unreacted **11**, only the cyclophane product **17** was isolated in 87% yield.



exo- and *endo*-**14**



17: R = 2-naphtho[2,1-*b*]furyl

exo*- and endo-15-(2-Naphtho[2,1-*b*]furyl)-13,14-dihydro-8,13-methano-8*H*-benzo[4,5]cyclohepta[1,2-*b*]naphtho[2,1-*d*]furan (14)**:exo*-14**: Colorless crystals, m.p. 238–239 °C; $R_f = 0.43$ (petroleum ether/CH_2Cl_2 3:2); ^1H NMR (600 MHz, $CDCl_3$): δ = 8.02–7.90 (m, 3H), 7.75–7.42 (m, 9H), 7.33 (d, J = 7.5 Hz, 1H), 7.13 (t, J = 7.5 Hz, 1H), 7.05 (t, J = 7.5 Hz, 1H), 6.71 (s, 1H, H_f), 5.18 (s, 1H, H-A), 4.17 (d, J = 4.5 Hz, 1H, H-C), 4.08 (s, 1H, H-B), 3.67 (dd, J = 4.5, 17.1 Hz, 1H, H-D), 3.08 ppm (d, J = 17.1 Hz, 1H, H-E); ^{13}C NMR ($CDCl_3$): δ = 158.88 (s), 151.92 (s), 151.81 (s), 149.41 (s), 149.33 (s), 142.33 (s), 130.68 (s), 130.18 (s), 129.03 (d), 128.64 (d), 128.11 (s), 127.45 (s), 127.28 (d), 127.02 (d), 126.10 (d), 125.96 (d), 124.81 (d), 124.34 (d), 124.26 (d), 124.17 (d), 124.00 (d), 123.60 (s), 123.39 (d), 123.14 (d), 122.10 (s), 121.62 (d), 120.11 (s), 112.41 (d), 112.10 (d), 101.53 (d), 53.18 (d), 44.62 (d), 44.51 (d), 32.20 ppm (t); UV (EtOH): λ_{max} ($\log\varepsilon$) = 327 (3.94), 313 (3.92), 301 (3.94), 244 (4.32), 222 nm (4.47); MS (ESI): m/z (%): 462.1 (35) [M^+], 145.2 (80), 83.3 (100); elemental analysis calcd (%) for $C_{34}H_{22}O_2$ (462.5): C 88.29, H 4.79; found: C 88.11, H 5.02.

***endo*-14**: Too small a quantity to be analyzed completely; $R_f = 0.40$ (petroleum ether/CH_2Cl_2 3:2); ^1H NMR (300 MHz, $CDCl_3$): δ = 5.23 (d, J = 3.6 Hz, 1H, H-A), 4.27 (m, 1H, H-C), 4.16 (m, 1H, H-B), 3.27 (dd, J = 17.1, 3.6 Hz, 1H, H-D), 2.89 ppm (d, J = 17.1 Hz, 1H, H-E); MS (ESI): m/z (%): 462.1 (27) [M^+], 145.2 (66), 83.3 (100).

3,4,13,14-Tetra(2-naphtho[2,1-*b*]furyl)pentacyclo[14.4.0.0^{2,5}.0^{6,11}.0^{12,15}]eicosa-1(20),6,8,10,16,18-hexaene (17): Colorless crystals, m.p. > 300 °C; $R_f = 0.27$ (petroleum ether/CH_2Cl_2 3:2); ^1H NMR (600 MHz, $CDCl_3$): δ = 7.97 (d, J = 7.8 Hz, 4H), 7.86 (d, J = 7.8 Hz, 4H), 7.59 (d, J = 8.4 Hz, 4H), 7.50 (d, J = 8.4 Hz, 4H), 7.47 (dt, J = 1.2, 7.2 Hz, 4H), 7.40 (dt, J = 1.2, 7.2 Hz, 4H), 7.33 (m, 4H), 7.16 (m, 4H), 7.13 (s, 4H), 5.06 (d, J = 6.0 Hz, 4H, H-b), 4.84 ppm (d, J = 6.0 Hz, 4H, H-a); ^{13}C NMR ($CDCl_3$): δ = 156.59 (s), 153.38 (s), 137.78 (s), 130.21 (s), 128.63 (d), 127.43 (s), 126.89 (d), 126.03 (d), 125.14 (d), 124.56 (d), 124.27 (d), 123.61 (s), 123.39 (d), 112.12 (d), 103.23 (d), 45.87 (d), 39.48 ppm (d); UV (EtOH): λ_{max} ($\log\varepsilon$) = 323 (3.85), 308 (3.97), 239 nm (4.51); MS (ESI): m/z (%): 924.2 (32) [M^+], 454.7 (77), 217.4 (100); elemental analysis calcd (%) for $C_{68}H_{44}O_4$ (924.3): C 88.29, H 4.79; found: C 88.58, H 4.41.

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