Formation and Reactivity of 2-Styryl-1,4-benzoquinones

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The 2-styryl-1,4-benzoquinones **7a,b**, generated by the oxidation of the corresponding hydroquinones **6a,b**, dimerize at room temperature in a Diels–Alder reaction. The strictly chemo-, regio- and stereoselective process can be rationalized by means of frontier orbital interactions. The polycyclic adducts **8a,b** undergo a further intramolecular cycloaddition (**8a,b** → **10a,b**) after oxidation on silica gel.

Introduction

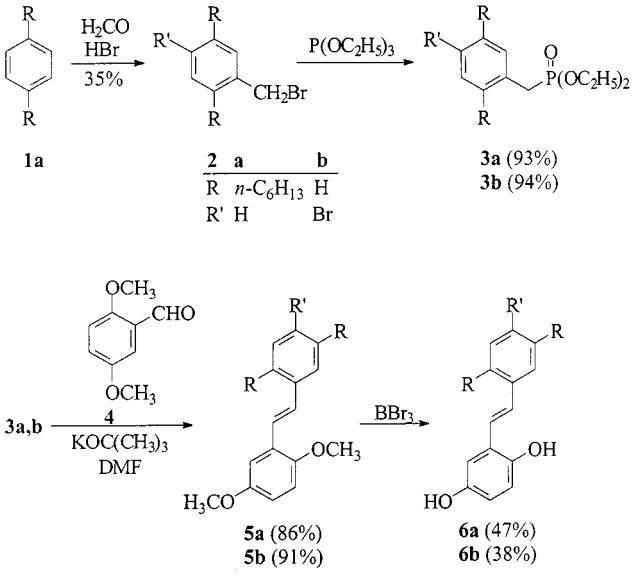
Oligo- and poly(1,4-phenylenevinylene)s (OPV, PPV) represent a class of compounds, which are of high current interest in materials science, since many different applications such as semiconductors, photoconductors, electroluminescent systems, materials for nonlinear optics, and negative photoresists have been found.[1−6] One problem of these materials is an often-observed aging in the presence of oxygen or other oxidants.[7] This sensitivity towards oxygen increases with the increasing energy of the HOMO; thus, electron-rich compounds like, for example, alkoxy-substituted OPVs or PPVs are particularly prone to oxidation reactions. The cleavage of the olefinic double bonds leading to terminal formyl or carboxy groups (via 1,2-dioxetanes) is a plausible process. In addition to this degradation, we observed a crosslinking of the chains. Therefore we present here a study of the parent system, discussing two differently substituted (*E*)-stilbenes in both of which one hydroquinone ring is oxidized to 1,4-benzoquinone.

Results and Discussion

The 2-styrylhydroquinones **6** seemed to be appropriate precursors for the generation of the corresponding quinones. We started the preparation of **6a** (Scheme 1) with 1,4-dihexylbenzene (**1a**), whose bromomethylation gave the derivative **2a**, which was subsequently transformed in an almost quantitative Arbusov reaction to the phosphonate **3a**. An analogous process yielded the phosphonate **3b** from **2b**, which is commercially available. The Wittig−Horner reaction with 2,5-dimethoxybenzaldehyde (**4**) furnished the *trans*-stilbenes **5a,b** in high yields. The cleavage of the two methyl ether functions (**5a,b** → **6a,b**) was achieved by reaction with boron tribromide. The Wittig−Horner reactions of **3a,b** with unprotected 2,5-dihydroxybenzaldehyde proved not to be useful on a preparative scale. The two hexyl groups in **5a** guarantee an improved solubility, whereas the bromo substituent in **5b** confers different electronic properties.

Oxidation of the hydroquinone **6a** with silver(I) oxide led to the desired quinone **7a**,[8] which spontaneously dimerized in solution (Scheme 2) to give the tricyclic tetraketone *rac*-**8a**. Obviously the 2-styryl-1,4-benzoquinone **7a** had reacted in a neutral Diels−Alder reaction with the olefinic double bond and the conjugated double bond in the quinone ring serving as the 4π component and the latter double bond in another molecule as the 2π component. The oxidation of **6b** under the same conditions delivered the expected quinone **7b**, which could be isolated. Its dimerization to *rac*-**8b** in a Diels−Alder reaction took place in solution in chloroform after two days. Obviously, small electronic effects cause different reaction rates for the dimerization.

The four protons on the central ring of the two phenanthrene derivatives **8a,b** give simple ABCX spin patterns in the ^{1}H NMR spectra. The olefinic proton 10-H gives rise to a triplet (δ = 7.07 for **8a** and δ = 7.00 for **8b**); the coupling constants ^3J(10-H, 9-H) and ^4J(10-H, 4a-H) are both 3.3 Hz. The homoallylic coupling ^5J(9-H, 4a-H) has virtually the same size, and 9-H also gives a triplet signal (δ =



Scheme 1. Preparation of the 2-styrylhydroquinones **6a,b**

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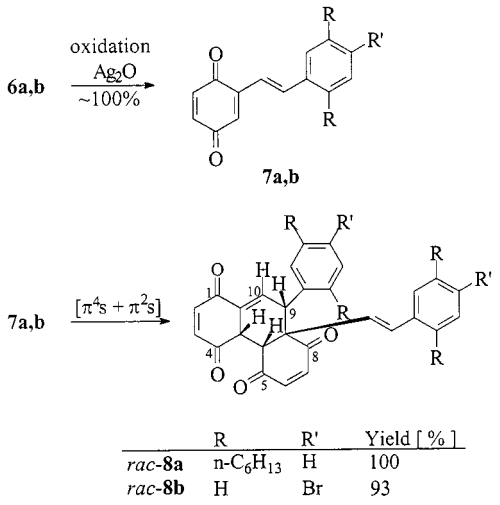


	R	R'	Yield [%]
rac-**8a**	n-C_6H_{13}	H	100
rac-**8b**	H	Br	93

Scheme 2. Oxidation of **6a,b** to the 2-styryl-1,4-benzoquinones **7a,b** and subsequent Diels–Alder dimerization to the phenanthrene derivatives **8a,b**

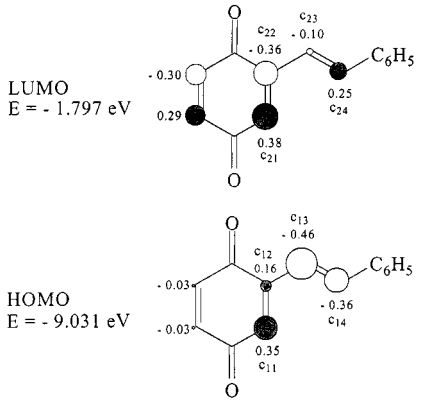
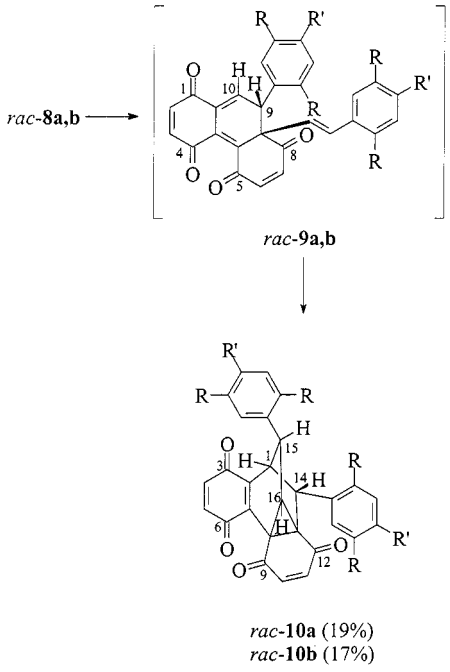


Figure 1. Frontier orbitals of 2-styryl-1,4-benzoquinone calculated by AM1



Scheme 3. Dehydrogenation of **8a,b** and intramolecular Diels–Alder cycloaddition to **10a,b**

4.55 for **8a** and δ = 4.19 for **8b**). The protons 4a-H (δ = 3.46 for **8a** and δ = 3.40 for **8b**) and 4b-H (δ = 4.06 for **8a** and δ = 4.12 for **8b**) show a typical *cis* coupling with ^3J = 4.2 Hz and 4.3 Hz, respectively. The transannular couplings ^4J(4b-H, 9-H) and ^5J(4b-H, 10-H) are below 1.0 Hz, and therefore 4b-H appears as a doublet. The assignment of the signals is based on ^{1}H,^{1}H and ^{1}H,^{13}C shift correlation measurements as well as on decoupling and NOE experiments. The resulting structures **8a,b** are similar to the dimers of other 2-styryl-1,4-benzoquinones obtained in electrochemical oxidation processes.[9,10]

The quantitative dimerization **7a,b** → **8a,b** is a chemo-, regio- and *endo*-stereoselective process. Semiempirical quantum mechanics provide an explanation. Figure 1 shows the frontier orbitals calculated by AM1.[11] In contrast to the 4π component, there are, in principal, three possibilities for the 2π component, namely both of the C=C double bonds in the quinone ring and the olefinic double bond of the styryl group in **7a,b**. The size of the coefficients c_{ij} evidently favors the substituted side in the quinone ring. The four remaining chemo- and regioselective variants can be judged by the HOMO–LUMO interactions in this neutral Diels–Alder reaction:

$$S_1 = (c_{11}\cdot c_{21} + c_{14}\cdot c_{22}) + (c_{21}\cdot c_{11} + c_{24}\cdot c_{12}) >$$
$$S_2 = (c_{11}\cdot|c_{22}| + |c_{14}|\cdot c_{21}) + (c_{21}\cdot c_{12} + c_{24}\cdot c_{11}) >$$
$$S_3 = (c_{11}\cdot|c_{23}| + |c_{14}|\cdot c_{24}) + (c_{21}\cdot|c_{13}| + |c_{24}|\cdot c_{14}) >$$
$$S_4 = (c_{11}\cdot c_{24} + c_{14}\cdot c_{23}) + (c_{21}\cdot|c_{14}| + |c_{24}|\cdot c_{13})$$

The chemoselectivity refers to S_1, $S_2 > S_3$, S_4 and the regioselectivity to $S_1 > S_2$; this means that the sterically more hindered C=C double bond of the quinone ring acts as the 2π component, and it adds so that the aryl and styryl groups in **8a,b** are fixed on neighboring carbon atoms.

When the compounds **8a,b** were stored in the refrigerator, they could be kept for several months; however, consecutive reactions were observed on silica gel at room temperature. From **8a,b** we obtained the dehydrogenated products **10a,b** (Scheme 3).[12] We assume that an oxidation **8a,b** → **9a,b** and another, now intramolecular, [2π + 4π] cycloaddition takes place.

The resulting polycyclic system *rac*-**10a,b** contains a three-membered ring with a characteristic coupling ^1J(^{13}C, ^{1}H) of 180 Hz. This HC-16 group belongs to a sequence of four adjacent methine groups in the central tricyclo[3.2.1.0^{8,13}]octene moiety. The assignment of the ^{1}H and ^{13}C NMR signals given in Figure 2 is based on one- and two-dimensional NMR techniques.

Steric reasons do not permit an opposite orientation of the 2π component in the cycloaddition, therefore the stereo-

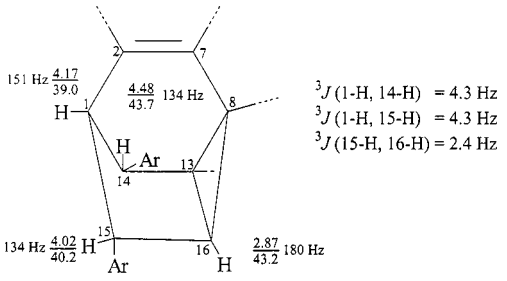


Figure 2. ^{1}H and ^{13}C NMR spectroscopic data [chemical shifts and ^1J(C,H) coupling constants] of the central tricyclo[3.2.1.0^{8,13}]octene scaffold of **10a**

chemistry of *rac*-**10a,b** is a consequence of the stereochemistry of *rac*-**8a,b**. Both compounds contain four carbonyl groups. The corresponding δ_C values are between 181 and 199 as one would expect for 1,4-benzoquinone and cyclohex-2-ene-1,4-dione substructures.

Conclusion

The substituted 2-styrylhydroquinones **6a,b** yield the corresponding 2-styrylquinones **7a,b** in quantitative oxidation reactions. Compound **7a** dimerizes spontaneously in solution, and **7b** upon standing dissolved in chloroform within two days. The dimerization represents a chemo-, regio- and stereoselective Diels−Alder reaction, a process which can be understood in terms of frontier orbital theory. The obtained cycloadducts **8a,b** undergo oxidation on silica gel and subsequent intramolecular cycloadditions to form **10a,b**.

Experimental Section

General Remarks: Melting points (uncorrected): Büchi apparatus. − NMR: Bruker AM 400 and WT 200, $CDCl_3$ as solvent if not otherwise stated, TMS as internal standard. − MS: Varian MAT CH7A and Finnigan MAT 95.

2-Bromomethyl-1,4-dihexylbenzene (2a): A 33% solution of HBr in glacial acetic acid (7.1 mL, 0.04 mol) was added dropwise at room temperature to 1,4-dihexylbenzene (**1a**) (9.0 g, 0.04 mol) and paraformaldehyde (1.2 g, 0.04 mol), dissolved in glacial acetic acid (25 mL). The mixture was heated to 95 °C and kept at this temperature for 3 days. After cooling to room temp., the mixture was diluted with water (100 mL) and extracted with diethyl ether (150 mL). The organic phase was neutralized with a saturated solution of $NaHCO_3$, dried with Na_2SO_4 and the solvents evaporated. Column chromatography of the residue on silica gel (70−230 mesh, 8 × 30 cm) using petroleum ether (b.p. 40−70 °C) as eluent yielded 4.33 g (35%) of **2a** as a colorless liquid. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88 (m, 6 H, CH_3), 1.33 (m, 12 H, CH_2), 1.58 (m, 4 H, CH_2), 2.54 (t, 2 H, CH_2), 2.67 (t, 2 H, CH_2), 4.52 (s, 2 H, CH_2Br), 7.07 (m, 3 H, aromat. H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.1, 14.1 (CH_3), 22.6, 22.6, 29.0, 29.4, 31.0, 31.3, 31.7, 31.8, 32.0, 32.1, 35.4 (CH_2), 129.0, 129.6, 130.5 (C-3, C-5, C-6), 135.0 (C-2), 139.0, 140.9 (C-1, C-4). − MS (EI, 70 eV): *m*/*z* (%) = 340/338 (5) [M$^{+\cdot}$] Br isotope pattern, 189 (100). − $C_{19}H_{31}Br$ (339.4): calcd. C 67.25, H 9.21; found C 67.13, H 9.36.

Diethyl 2,5-Dihexylbenzylphosphonate (3a): Compound **2a** (3.0 g, 8.9 mmol) and triethylphosphite (2.91 g, 17.5 mmol) were heated for 4 h at 170 °C. The excess triethylphosphite was then removed under vacuum (10^2 Pa). The product was purified by column chromatography on silica gel (70−230 mesh, 4 × 40 cm) using petroleum ether (b.p. 40−70 °C)/ethyl acetate (5:4) as eluent; 3.22 g (92%) of **3a** was obtained as an almost colorless liquid. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.86 (m, 6 H, CH_3), 1.27 (m, 18 H, CH_2 and CH_3 of OC_2H_5), 1.54 (m, 4 H, CH_2), 2.52 (t, 2 H, CH_2), 2.62 (t, 2 H, CH_2), 3.14 (d, $|^2J(PH)|$ = 22.0 Hz, 2 H, CH_2P), 3.96 (m, 4 H, OCH_2), 6.96 (dd, 1 H, 4-H), 7.06 (m, 2 H, 3-H, 6-H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.1, 14.1 (CH_3), 16.3 (CH_3 of OC_2H_5), 22.6, 29.4, 30.8, 31.5, 32.6, 35.4 (CH_2, partly superimposed), 30.4 (d, $|^1J(CP)|$ = 138 Hz, CH_2P), 62.1 (OCH_2), 127.1, 128.9, 129.2 (C-3, C-4, C-6), 130.8, 138.7, 140.2 (C-1, C-2, C-5). − MS (EI, 70 eV): *m*/*z* (%) = 396 (100) [M$^+$], 339 (43). − $C_{23}H_{41}O_3P$ (396.6): calcd. C 69.66, H 10.42; found C 69.82, H 10.25.

Diethyl 4-Bromobenzylphosphonate (3b): This compound was prepared according to a procedure described in the literature.[13]

(*E*)-1-(2,5-Dihexylphenyl)-2-(2,5-dimethoxyphenyl)ethene (5a): A solution of **3a** (4.0 g, 10.1 mmol) and 2,5-dimethoxybenzaldehyde (**4**) (1.68 g, 10.1 mmol) in dry DMF (100 mL) was added dropwise to a solution of potassium *tert*-butoxide (4.0 g, 50.5 mmol) in dry DMF (80 mL) under argon at 0 °C. The mixture was stirred at room temperature overnight and then poured into ice/water (200 mL) and 2 M HCl (10 mL). After extraction with dichloromethane (100 mL) the organic phase was washed with water (50 mL) and a saturated solution of $NaHCO_3$ (50 mL) and dried with Na_2SO_4. The solvent was evaporated under vacuum (1 kPa) and the product purified by column chromatography on silica gel (70−230 mesh, 4 × 40 cm) with chloroform as eluent; yield: 3.55 g (86%) of **5a** as an almost colorless oil. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (m, 6 H, CH_3), 1.33 (m, 12 H, CH_2), 1.60 (m, 4 H, CH_2), 2.61 (t, 2 H, CH_2), 2.70 (t, 2 H, CH_2), 3.82 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 6.79 (dd, 1 H, aromat. H), 6.84 (d, 1 H, aromat. H), 7.02 (dd, 1 H, aromat. H), 7.08 (d, 1 H, aromat. H), 7.15 (d, 1 H, aromat. H), 7.31/7.38 (AB, $^3J_{trans}$ = 16.4 Hz, 2 H, olefin. H), 7.46 (d, 1 H, aromat. H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.1, 14.1 (CH_3), 22.6, 29.1, 29.3, 31.3, 31.6, 31.7, 33.2, 35.7 (CH_2, partly superimposed), 55.7, 56.3 (OCH_3), 112.2, 113.1, 114.2, 124.1, 125.7, 127.5, 127.6, 129.5 (aromat. and olefin. CH), 127.9, 135.9, 138.0, 140.6, 151.5, 153.6 (aromat. C_q). − FD-MS: *m*/*z* (%) = 408 (100) [M$^{+\cdot}$]. − $C_{28}H_{40}O_2$ (408.6): calcd. C 82.30, H 9.87; found C 82.15, H 10.03.

(*E*)-1-(4-Bromophenyl)-2-(2,5-dimethoxyphenyl)ethene (5b): A solution of **3b** (2.89 g, 9.41 mmol) and 2,5-dimethoxybenzaldehyde (**4**) (1.56 g, 9.41 mmol) in dry DMF (80 mL) was added dropwise to a solution of potassium *tert*-butoxide (5.27 g, 47.1 mmol) in dry DMF (90 mL) under argon at 0 °C. The mixture was stirred at room temperature overnight and then poured into ice/water (200 mL) and 2 M HCl (10 mL). After extraction with dichloromethane (200 mL) the organic phase was washed with water (50 mL) and a saturated solution of $NaHCO_3$ (50 mL) and dried with Na_2SO_4. The solvent was evaporated under vacuum (1 kPa) and the product purified by column chromatography on silica gel (70−230 mesh, 4 × 50 cm) using a mixture of petroleum ether (b.p. 40−70 °C) and diethyl ether (5:1) as eluent; yield: 2.73 g (91%) of **5b** as colorless crystals, m.p. 75 °C. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.80 (s, 3 H, OCH_3), 3.83 (s, 3 H, OCH_3), 6.79 (dd, 1 H, aromat. H), 6.82 (d, 1 H, aromat. H), 7.00/7.42 (AB, $^3J_{trans}$ = 16.4 Hz, 2 H, olefin. H), 7.11 (d, 1 H, aromat. H), 7.37/7.45

(AA′BB′, 4 H, aromat. H). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.8, 56.2 (OCH_3), 111.7, 112.3, 114.0, 124.1, 128.0, 128.1, 131.7 (aromat. and olefin. CH), 121.1, 126.9, 136.8, 151.5, 153.8 (aromat. C_q). − MS (EI, 70 eV): *m*/*z* (%) = 320/318 (100) [$M^{+\cdot}$] Br isotope pattern, 305 (10), 224 (17). − $C_{16}H_{15}BrO_2$ (319.2): calcd. C 60.21, H 4.74; found C 60.26, H 4.81.

(*E*)-2-[2-(2,5-Dihexylphenyl)ethenyl]hydroquinone (6a): A 1.0 M solution of boron tribromide (42.65 mL, 42.65 mmol) in *n*-hexane was added with a syringe to a cold solution of **5a** (3.59 g, 8.8 mmol) in dichloromethane (350 mL) at 0 °C. The reaction was followed by TLC (SiO_2, CH_2Cl_2). After 4 h of stirring at room temperature, the reaction mixture was poured into ice/water (300 mL) and the water layer was extracted with the same volume of ethyl acetate. The combined organic phases were washed with brine, dried with Na_2SO_4 and the solvents evaporated. The residue was purified by column chromatography on silica gel (70−230 mesh, 4 × 40 cm) using a mixture of petroleum ether (b.p. 40−70 °C) and ethyl acetate (3:2) as eluent; yield: 1.57 g (47%) **6a** as a liquid, which solidified at 5 °C in the refrigerator. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85 (m, 6 H, CH_3), 1.28 (m, 12 H, CH_2), 1.58 (m, 4 H, CH_2), 2.58 (t, 2 H, CH_2), 2.67 (t, 2 H, CH_2), 6.63 (dd, 1 H, hydroquinone ring), 6.70 (d, 1 H, hydroquinone ring), 6.98 (d, 1 H, hydroquinone ring), 7.01 (dd, 1 H, aromat. H), 7.06 (d, 1 H, aromat. H), 7.15/ 7.31 (AB, $^3J_{trans}$ = 16.1 Hz, 2 H, olefin. H), 7.41 (d, 1 H, aromat. H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 14.0 (CH_3), 22.6, 22.6, 29.1, 29.2, 31.2, 31.5, 31.7, 31.7, 33.1, 35.7 (CH_2), 113.3, 115.4, 117.0 (CH, hydroquinone ring), 123.4, 125.7, 127.9, 128.8, 129.5 (aromat. and olefin. CH), 126.2, 135.6, 138.0, 140.7, 147.2, 149.6 (aromat. C_q). − MS (EI, 70 eV): *m*/*z* (%) = 380 (100) [$M^{+\cdot}$], 309 (15). − $C_{26}H_{36}O_2$ (380.6): calcd. C 82.06, H 9.53; found C 81.79, H 9.66.

(*E*)-2-[2-(4-Bromophenyl)ethenyl]hydroquinone (6b): A 1.0 M solution of boron tribromide (31.3 mL, 31.3 mmol) in *n*-hexane was added with a syringe to a cold solution of **5b** (2.0 g, 6.3 mmol) in dichloromethane (240 mL) at 0 °C. After stirring for 16 h at room temperature, the reaction mixture was poured into ice/water (350 mL) and the water layer was extracted with 200 mL of ethyl acetate. The combined organic phases were washed with brine, dried with Na_2SO_4 and the solvents evaporated. The residue was purified by column chromatography on silica gel (70−230 mesh, 4 × 50 cm) using a mixture of petroleum ether (b.p. 40−70 °C) and ethyl acetate (5:3) as eluent; yield: 693 mg (38%) of a colorless solid with m.p. 195 °C. − ^{1}H NMR (200 MHz, [D_6]DMSO): δ = 6.54 (dd, 1 H, hydroquinone ring), 6.67 (d, 1 H, hydroquinone ring), 6.93 (d, 1 H, hydroquinone ring), 7.05/ 7.36 (AB, $^3J_{trans}$ = 16.6 Hz, 2 H, olefin. H), 7.48/7.54 (AA′BB′, 4 H, aromat. H), 8.80 (s, 1 H, OH), 9.13 (s, 1 H, OH). − ^{13}C NMR (50 MHz, [D_6]DMSO): δ = 111.9, 116.1, 116.6 (CH, hydroquinone ring), 119.1, 123.7, 136.9, 147.9, 149.9 (aromat. C_q), 124.7, 126.1, 128.1, 131.5 (aromat. and olefin. CH). − MS (EI, 70 eV): *m*/*z* (%) = 292/290 (100) [$M^{+\cdot}$] Br isotope pattern, 165 (24). − $C_{14}H_{11}BrO_2$ (291.2): calcd. C 57.76, H 3.81; found C 57.41, H 3.98.

(*E*)-2-[2-(4-Bromophenyl)ethenyl]benzoquinone (7b): $MgSO_4$ (800 mg, 6.64 mmol) and freshly prepared Ag_2O (727 mg, 3.14 mmol) were added to a solution of **6b** (500 mg, 1.72 mmol) in dry diethyl ether (40 mL). After stirring for 2 h at room temperature the solid parts were removed and the solvent evaporated under vacuum (10^2 Pa). Compound **7b** (498 mg) was obtained in quantitative yield as a dark red solid, m.p. 190 °C. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.77 (m, 2 H, benzoquinone ring), 6.85 (d, 1 H, benzoquinone ring), 7.06/ 7.37 (AB, $^3J_{trans}$ = 16.4 Hz, 2 H, olefin. H), 7.39/ 7.49 (AA′BB′, 4 H, aromat. H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 120.1, 135.0, 141.7 (aromat. and benzoquinone ring C_q), 123.8, 128.3, 129.0, 132.1 (aromat. and olefin. CH), 136.6, 136.7, 136.8 (CH, benzoquinone ring), 186.8, 187.5 (CO). − MS (EI, 70 eV): *m*/*z* (%) = 290/288 (100) [$M^{+\cdot}$] Br isotope pattern, 164 (31). − $C_{14}H_9BrO_2$ (289.1): calcd. C 58.16, H 3.14; found C 58.03, H 3.42.

***rel*-(4a*S*,4b*R*,8a*S*,9*R*)-9-(2,5-Dihexylphenyl)-8a-[(*E*)-2-(2,5-dihexylphenyl)ethenyl]-4a,4b,8a,9-tetrahydrophenanthrene-1,4,5,8-tetrone (*rac*-8a):** $MgSO_4$ (250 mg, 2.08 mmol) and freshly prepared Ag_2O (244 mg, 1.06 mmol) were added to a solution of **6a** (200 mg, 0.53 mmol) in dry diethyl ether (10 mL). After stirring for 1 h at room temperature the solid parts were removed and the solvent evaporated under vacuum (10^2 Pa). Compound **8a** (199 mg) was obtained as a red oil in a quantitative yield. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.77−0.86 (m, 12 H, CH_3), 1.26−1.60 (m, 32 H, CH_2), 2.23−2.58 (m, 8 H, CH_2), 3.46 (m, 1 H, 4a-H), 4.06 (d, ^3J = 4.2 Hz, 1 H, 4b-H), 4.55 (t, ^3J = ^5J = 3.3 Hz, 1 H, 9-H), 5.97/6.20 (AB, ^3J = 10.3 Hz, 2 H) and 6.95/7.03 (AB, ^3J = 10.3 Hz, 2 H) [2-H/3-H and 6-H/7-H], 6.39 (d, 1 H), 6.92 (dd, 1 H) 6.99 (d, 1 H) 7.04 (m, 2 H) 7.32 (“s”, 1 H) [aromat. H], 6.42/6.78 (AB, ^3J = 16.1 Hz, 2 H, olefin. H), 7.07 (t, ^3J = ^4J = 3.3 Hz, 1 H, 10-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 13.9 (CH_3), 22.4, 22.5, 28.9, 29.0, 29.1, 29.2, 31.2, 31.3, 31.4, 31.5, 31.6, 31.6, 31.7, 32.6, 33.1, 35.2, 35.5 (CH_2, partly superimposed), 42.5 (C-9), 43.1 (C-4a), 53.4 (C-4b), 59.2 (C-8a), 126.1, 128.3, 128.4, 129.5, 130.5, 131.1 (aromat. CH), 129.4, 132.0 (olefin. CH), 132.0, 134.1, 135.2, 137.6, 138.2, 141.0, 141.1 (C-10a and aromat. C_q), 137.8 (C-10), 138.7, 139.8, 140.5, 142.1 (C-2, C-3, C-6, C-7), 183.8 (C-1), 194.0, 194.9, 198.2 (C-4, C-5, C-8). − FD-MS: *m*/*z* (%) = 757 (100) [$M^{+\cdot}$]. − $C_{52}H_{68}O_4$ (757.1): calcd. C 82.49, H 9.05; found C 82.11, H 8.81.

***rel*-(4a*S*,4b*R*,8a*S*,9*R*)-9-(4-Bromophenyl)-8a-[(*E*)-2-(4-bromophenyl)ethenyl]-4a,4b,8a,9-tetrahydrophenanthrene-1,4,5,8-tetrone (*rac*-8b):** Compound **7b** (200 mg, 0.7 mmol) was dissolved in $CHCl_3$ (10 mL) and the mixture allowed to stand for two days. The solution was then concentrated under vacuum (10^2 Pa) and pure **8b** precipitated after adding a mixture of petroleum ether (b.p. 40−70 °C) and ethyl acetate (5:3) to the residue; yield: 185 mg (93%) yellow solid, m.p. 169 °C. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.40 (m, 1 H, 4a-H), 4.12 (d, ^3J = 4.3 Hz, 1 H, 4b-H), 4.19 (t, 1 H, ^3J = ^5J = 3.3 Hz, 9-H), 6.07/6.25 (AB, ^3J = 10.3 Hz, 2 H) and 6.95/7.02 (AB, ^3J = 10.6 Hz, 2 H) [2-H/3-H and 6-H/7-H], 6.44 (“s”, 2 H, olefin. H), 6.64 (br. s, 2 H), 7.26 (d, 2 H), 7.31 (d, 2 H), 7.45 (d, 2 H) [aromat. H], 7.00 (t, ^3J = ^4J = 3.3 Hz, 1 H, 10-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.2 (C-4a), 46.4 (C-9), 52.4 (C-4b), 58.6 (C-8a), 122.6, 122.6, 132.7, 134.4, 136.0 (C-10a and aromat. C_q), 128.2, 131.9, 132.0, 132.1 (aromat. CH), 130.8, 131.3 (olefin. CH), 135.0 (C-10), 139.4, 139.6, 140.7, 142.1 (C-2, C-3, C-6, C-7), 184.0 (C-1), 193.6, 194.7, 198.9 (C-4, C-5, C-8). − FD-MS: *m*/*z* (%) = 580/578/576 (47) [$M^{+\cdot}$] Br_2 isotope pattern, 290 (94), 288 (100). − $C_{28}H_{18}Br_2O_4$ (578.3): calcd. C 58.16, H 3.14; found C 58.14, H 3.07.

Transformation of *rac*-8a,b into *rac*-10a,b: Column chromatography of **8a,b** on silica gel (70−230 mesh, 3 × 70 cm) with petroleum ether (b.p. 40−70 °C)/diethyl ether (5:2) yielded as a first fraction viscous oils: 19% of *rac*-**10a** and 17% of *rac*-**10b**, respectively. Increasing of the solvent mixture polarity by using petroleum ether (b.p. 40−70 °C)/ethyl acetate (5:3) furnished 16% of a second component.[12]

***rel*-(1*S*,8*S*,13*R*,14*R*,15*R*,16*R*)-14,15-Bis(2,5-dihexylphenyl)pentacyclo[6.6.2.0^{2,7}.0^{8,13}.0^{13,16}]hexadeca-2(7),4,10-triene-3,6,9,12-tetrone (*rac*-10a):** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.82−0.92 (m, 12 H, CH_3), 1.06−1.71 (m, 32 H, CH_2), 2.23 (t, 2 H, CH_2), 2.45 (m, 2 H, CH_2), 2.62−2.76 (m, 4 H, CH_2), 2.87 (m, 1 H, 16-H), 4.02 (dd, ^3J = 4.3, ^3J = 2.4 Hz, 1 H, 15-H), 4.17 (t, ^3J = 4.3 Hz, 1 H, 1-H), 4.48 (d, ^3J = 4.3 Hz, 1 H, 14-H), 6.15/6.51 (AB, ^3J = 10.3 Hz, 2 H), 6.73/6.92 (AB, ^3J = 10.3 Hz, 2 H), [4-H, 5-H, 10-H, 11-H], 6.17 (d, 1 H), 6.70 (d, 1 H), 6.79 (dd, 1 H), 6.90 (dd, 1 H), 6.95 (d, 1 H), 6.99 (d, 1 H) [aromat. H]. − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.5, 22.5, 22.7, 22.7, 28.6, 28.7, 29.8, 31.0, 31.1, 31.2, 31.2, 31.6, 31.8, 31.8, 32.0, 32.0, 35.3, 35.3 (CH_2, partly superimposed), 38.7, 46.1 (C-8, C-13), 39.0 (C-1), 40.2 (C-15), 43.2 (C-16), 43.7 (C-14), 126.1, 127.3, 127.6, 127.6, 129.0, 129.2 (aromat. CH), 131.2, 132.6, 137.6, 137.9, 138.1, 138.8, 139.9, 140.3 (C-2, C-7 and aromat. C_q), 134.7, 136.9, 138.7, 138.9 (C-4, C-5, C-10, C-11), 181.7, 182.5, 189.0, 190.4 (C-3, C-6, C-9, C-12). − FD-MS: *m*/*z* (%) = 755 (100) [$M^{+\cdot}$]. − $C_{52}H_{66}O_4$ (755.1): calcd. C 82.71, H 8.81; found C 82.33, H 9.19.

***rel*-(1*S*,8*S*,13*R*,14*R*,15*R*,16*R*)-14,15-Bis(4-bromophenyl)pentacyclo[6.6.2.0^{2,7}.0^{8,13}.0^{13,16}]-hexadeca-2(7),4,10-triene-3,6,9,12-tetrone (*rac*-10b):** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.00 (br. s, 1 H, 16-H), 3.89 (dd, ^3J = 4.7, ^3J = 2.3 Hz, 1 H, 15-H), 4.14 (t, ^3J = 4.7 Hz, 1 H, 1-H), 4.34 (d, ^3J = 4.7 Hz, 1 H, 14-H), 6.23/6.54 (AB, ^3J = 10.3 Hz, 2 H), 6.77/6.90 (AB, ^3J = 10.6 Hz, 2 H) [4-H, 5-H, 10-H, 11-H], 6.69 (d, 2 H), 6.94 (d, 2 H), 7.22 (d, 2 H), 7.34 (d, 2 H) [aromat. H]. − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 38.2, 45.9 (C-8, C-13), 41.0, 41.9, 42.2, 45.5 (C-1, C-14, C-15, C-16), 121.3, 121.6, 131.0, 133.5, 134.5, 137.8 (C-2, C-7 and aromat. C_q), 128.6, 128.9, 131.7, 131.9 (aromat. CH), 134.7, 137.3, 138.9, 138.9 (C-4, C-5, C-10, C-11), 181.8, 182.3, 188.4, 190.0 (C-3, C-6, C-9, C-12). − FD-MS: *m*/*z* (%) = 578/576/574 (100) [$M^{+\cdot}$] Br_2 isotope pattern. − $C_{28}H_{16}Br_2O_4$ (576.3): calcd. C 58.36, H 2.80; found C 58.01, H 3.17.

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