1,4-Benzoquinones with Styryl Substituents

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2-Styryl-1,4-benzoquinone (1) and compounds 2 and 3 containing 1 as a substructure all proved to be highly reactive towards thermal or photochemical \( [4\pi + 2\pi] \) cyclodimerization reactions. Chemo-, regio- and stereoselective processes lead to dimers (compounds 1-10), which can undergo secondary reactions consisting of the addition of nucleophiles combined with a twofold keto-enol tautomerism (10/11). An alternative process is dehydrogenation/oxidation followed by an intramolecular \( [4\pi + 2\pi] \) cycloaddition (10/11).

Introduction

Oligo- and poly(1,4-phenylenevinylene)s (OPV and PPV, respectively) and related compounds are attracting a great deal of attention in materials science for their electroluminescent, semiconductive, photoconductive, NLO material, photoelectric, photoresistive, and other, properties.[11] Alkoxy substituents on the benzene rings — especially in the 2- and 5-positions — not only enhance solubility and facilitate processability, but also improve the electronic and optoelectronic properties of the substance. However, these systems are particularly prone to oxidation reactions because of their high-lying HOMOs.[12] Recently we published[13] a paper on the oxidation of 2-styrylhydroquinones as model compounds which showed that the generated 2-styryl-1,4-benzoquinones 1 are extremely susceptible to dimerization reactions. The corresponding C-C bond formations in OPVs and PPVs may thus contribute towards the observed crosslinking that occurs as these materials age. Therefore we extended our studies to the series of quinones 1 and generated the related quinones 2 and 3 (Scheme 1) which are derivatives of 1,4-distyrylbenezene. Overall, the present knowledge on quinones with conjugated side chains is very limited.[12–16]

Results and Discussion

The preparation of the target compounds 1a–d was based on benzaldehydes with protected hydroxy functions in the 2- and 5-positions. Allyl, methyl and tert-butyldimethylsilyl groups were used as protecting groups. The Horner reaction between 2,5-dialklyoxybenzaldehyde and diethyl 2,5-dimethylbenzylphosphonate provided the stilbene derivative 4a in 74% yield. Analogous procedures led to the compounds 4b and 4c in 86% and 91% yield, respectively.[13] The stilbene 4d was obtained in a yield of 86% by a Wittig reaction between 2,5-bis(tert-butyldimethylsilyloxy)benzaldehyde and 4-bromo-2,5-dipropoxybenzyltriphenylphosphonium bromide. The E configuration predominated strongly in compounds 4a–c, whereas 4d contained an appreciable amount of the Z isomer. After subsequent deprotection, only the E isomer was present for all stilbenes 5a–d by NMR spectroscopic analysis. Three different deprotection treatments were applied according to the group to be
removed: NaBH₄ in the presence of Pd⁰ for the cleavage of allyl, BBr₃ for the cleavage of methyl and tetrabutylammonium fluoride for the cleavage of silyl. The first method was the most successful and gave the highest yields. The oxidation of 5a–d was performed with Ag₂O and led, in quantitative yields, to the quinones 1a–d. However, quinones 1b and 1d dimerized in situ and only 1a and 1c[13] could be isolated as monomers (Scheme 2).

The attempt to synthesize 2,5-distyrylbenzoquinones 2 started with 1,4-dihexylbenzene, which was obtained in a yield of 60% by the reaction of 1,4-dibromobenzene and n-hexylmagnesium bromide in the presence of Ni²⁺[14]. A subsequent Rieche–Gross formylation furnished 2,5-dihexylbenzaldehyde in 74% yield, which was then used for a Horner reaction. The other component of the Horner reaction was tetraethyl [2,5-dimethoxy-1,4-phenylenebis(methylene)]diphosphonate, which was obtained in a yield of 58% by the Arbusow reaction between 1,4-bis(bromomethyl)-2,5-dimethoxybenzene and triethyl phosphite. The bis(bromomethyl) compound (87% yield), together with the mono(bromomethyl) product (yield 12%), account for an almost quantitative bromomethylation of 1,4-dimethoxybenzene. The Horner reaction led to the E,E distyrylbenzene 6 (57% yield), whose methoxy groups were cleaved with lithium diphenylphosphide. The resulting hydroquinone 7 (24%) was treated with NaOCl which led by quantitative oxidation to the quinone 2a, which is, according to MS, a mixture of monomeric, dimeric and trimeric species (Scheme 2).

The synthetic approach to the twofold quinones 3 started with the E,E configured distyrylbenzene derivatives 8a and 8b, which were obtained from Horner reactions. The bromomethylation of 1,4-dihexylbenzene yielded 62% of 1,4-bis(bromomethyl)-2,5-dihexylbenzene and 35% of 1-bromomethyl-2,5-dihexylbenzene. The Arbusow reaction of the dibromo product with triethyl phosphite gave 85% of tetraethyl [2,5-dihexyl-1,4-phenylenebis(methylene)]diphospho-

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**Scheme 2.** Preparation of 1,4-benzoquinones with styryl groups; reagents: (a) NaBH₄, Pd[PC₆H₅]₄, THF; (b) BBr₃, CH₂Cl₂; (c) (n-C₃H₇)₄N⁺F⁻, THF; (d) Ag₂O, MgSO₄, (C₂H₅)_₂O; (e) LiP(C₆H₅)₂, THF; (f) NaOCl, aliquat 336, HCl, H₂O/CHCl₃.
nate which furnished 75% of 8a by Horner reaction with 2,5-diallyloxybenzaldehyde, and 63% of 8b by Horner reaction with 2,5-dimethoxybenzaldehyde. The cleavage of four methyl ether functions turned out to be very difficult, therefore we undertook the cleavage of fourfold allyl ether 8a by reduction with NaBH₄ in the presence of Pd₄, which resulted in a yield of 44%. The deprotected bishydroquinone 9a was oxidized in the final reaction step with Ag₂O. The quantitative process yielded the bisbenzoquinone 3a, which precipitated from diethyl ether and thus did not oligomerize. However, if 3a was dissolved in chloroform, oligomerization occurred at room temperature as evidenced by FD-MS analysis which indicated peaks for dimeric, trimeric and tetrameric species.

The aforementioned dimerization of 1a–d is a highly chemo-, regio- and stereoselective Diels–Alder reaction which yielded the 4aR*,4bS*,8aR*,9S* configuration of the phenanthrene derivatives 10a–d. Similar dimers have been obtained by electrochemical oxidation. An explanation for the selectivities based on frontier orbital theory was given in the previous paper. Apart from 10d, the dimeric systems 10a–c are fairly stable in the pure state and in solution, although they undergo a complicated series of reactions in the presence of silica gel. The predominant route furnished the polycyclic compounds 11a–d (Scheme 3); MS analysis of 11a–d indicated that a dehydrogenation/oxidation process had occurred. An intramolecular cycloaddition of the olefinic 2π component of the styryl group and the newly generated 4π component then ensued. The regioselective [4π + 2π] process is a consequence of the steric arrangement. Thus, the 4aR,4bS,8aR,9S configuration of 10a–d led to the 1R,8S,13S,14S,15S,16S configuration of 11a–d [and accordingly (4aS,4bR,8aS,9R)-10a–d led to (1S,8R,13R,14R,15R,16R)-11a–d].

In the presence of nucleophiles such as water or ethanol, the dimers 10 undergo an acid-catalyzed addition reaction in the 1- and 10-positions, accompanied by aromatization of one of the six-membered rings. Since a second tautomeric keto-enol transformation is involved, three of the four carbonyl groups disappear in the transformations 10a,b → 12a–c.

Inspired by a related reaction, we also studied the photochemistry of 1a (Scheme 4). Irradiation in C₆D₆ at wavelengths greater than 410 nm yielded the dimer 10a. Interestingly, the photochemical [4π + 2π] cycloaddition, which is forbidden as a concerted reaction, showed the same high chemo-, regio- and stereoselectivity as the thermal Diels–Alder reaction. However, in contrast to the quantitative thermal process, analysis by ¹H NMR spectroscopy of the photoreaction revealed small amounts of a further product. Thus, the photochemical reaction is much faster.
than the thermal process (e.g., at 60 °C), but on the whole is somewhat less selective.

Upon exposure to sunlight, crystals of 1a are transformed into the dimer 13.[17] The topochemical process represents a head-to-tail [2π + 2π] cycloaddition whereby the trans configurations of the original double bonds are preserved in the generated four-membered ring. E1Z photo-induced isomerization was not observed either in solution or in the solid state.

Conclusion

1,4-Benzquinones with styryl groups are extremely reactive species and readily undergo [4π + 2π] cycloaddition reactions. They are highly chemo-, regio- and stereoselective both in thermal and in photochemical dimerizations (1 → 10). If more than one styryl-substituted 1,4-benzoquinone unit is present in the starting material the oligomeric cycloadducts 2a (n = 2, 3) and 3a (n = 2–4), are formed. Moreover, the dimers can add nucleophiles like water or ethanol (10 → 12), a reaction which is catalyzed by acid and can readily occur on the surface of silica gel.[18] Another secondary reaction of the dimers is dehydrogenation/oxidation, which is followed by an intramolecular [4π + 2π] cycloaddition (10 → 11).

Experimental Section

General Remarks: Melting points were measured using a Büchi apparatus and are uncorrected. NMR spectra were measured on Bruker AM 400 and WT 200 instruments using CDCl3 as the solvent, unless otherwise stated, with TMS as an internal standard. MS spectra were measured on Finnigan MAT 95 and Varian MAT CH7A instruments.

Preparation of (E)-2-(2,5-Diallyloxyphenyl)-1-(2,5-dimethylphenyl)ethene (4a): 2,5-Diallyloxybenzaldehyde (4.78 g, 39.5 mmol), ethene (4a) K2CO3 (6.33 g, 45.8 mmol) and a trace of KI were added to a solution of 2,5-dihydroxybenzaldehyde (2.0 g, 14.5 mmol) in acetone (30 mL). After stirring at room temperature overnight the solid particles were removed and the solvent evaporated under reduced pressure (10−2 Pa). The product was purified by vacuum distillation (bp 164 °C/930 Pa) to afford a colorless liquid (yield 2.17 g, 69%). 1H NMR (CDCl3); δ = 1.22 (t, 6 H, CH3), 2.27 (s, 3 H, CH3), 2.31 (s, 3 H, CH3), 3.11 (d, [J1H,1H] = 22.0 Hz, 2 H, CH2P), 3.97 (m, 4 H, OCH2), 6.92 (d, 1 H, arom. H), 7.03 (m, 2 H, arom. H) ppm. 13C NMR (CDCl3); δ = 16.2, 16.4 (CH3), 19.4, 20.9 (Ar-CH3), 31.0 (d, [J1C,1H] = 138.1 Hz, CH2P), 62.0, 62.1 (OCH2), 127.8 (d, [J1C,1H] = 4.0 Hz, arom. CH), 129.7 (d, [J1C,1H] = 96.5 Hz, arom. C6), 130.6 (d, [J1C,1H] = 3.2 Hz, arom. CH), 131.3 (d, [J1C,1H] = 5.6 Hz, arom. CH), 133.8 (d, [J1C,1H] = 6.4 Hz, arom. C6), 135.3 (d, [J1C,1H] = 4.0 Hz, arom. C6) ppm. MS (EI, 70 eV); m/z (%) = 256 (83) [M+]; 199 (60), 119 (100). C13H21O3P (256.3): calculated C 60.93, H 8.26; found C 60.90, H 8.56.

(E)-2-(2,5-Diallyloxyphenyl)-1-(2,5-dimethylphenyl)ethene (4a): A solution of 2,5-diallyloxybenzaldehyde (5.89 g, 0.03 mol) and diethyl 2,5-dimethylbenzylphosphonate (7.0 g, 0.03 mol) in dry DME (150 mL) was added dropwise to a suspension of NaH (60% dispersion in mineral oil; 10.8 g, 0.27 mol), in dry DME (90 mL). After stirring at room temperature overnight, water (20 mL) was cautiously added dropwise and the solution extracted with chloroform (200 mL) which was then washed with brine and dried with Na2SO4. The solvent was evaporated under vacuum (10° Pa) and the product purified by column chromatography over silica gel (70−230 mesh, 4 × 30 cm) using petroleum ether (b.p. 40−70 °C)/diethyl ether (30:1) as eluent. The product 4a was obtained as a viscous oil (yield 6.39 g, 74%).[19] 1H NMR (CDCl3); δ = 2.34 (s, 3 H, CH3), 2.36 (s, 3 H, CH3), 4.53 (m, 4 H, OCH2), 5.28 (m, 2 H, allyl CH3), 5.42 (m, 2 H, allyl CH2), 6.07 (dd, 2 H, allyl CH), 6.76 (dd, 1 H, arom. H), 6.82 (d, 1 H, arom. H), 6.97 (dd, 1 H, arom. H), 7.05 (d, 1 H, arom. H), 7.16 (m, 2 H, arom. H), 7.30 (“s”, 2 H, olefin H), 7.42 (br, s, 1 H, arom. H) ppm. 13C NMR (CDCl3); δ = 19.5, 21.1 (CH3), 69.5, 70.3 (OCH2), 113.3, 114.1, 114.2, 124.4, 126.1, 127.6, 128.2, 130.3 (arom. and olefin CH), 117.3, 117.6 (allyl CH2), 128.4, 132.8, 135.5, 136.5, 150.7, 153.0 (arom. C6), 133.6, 133.7 (allyl CH) ppm. FD-MS: m/z (%) = 320 (100) [M+]; C13H21O3P (256.3): calculated C 82.46, H 7.55; found C 81.92, H 7.25.

The stilbene derivatives 4b and 4c and their precursors were prepared according to literature methods.[13,20−22]

(E)-1-{2,5-Bis[(E)-2,5-bis(dimethylsilyloxy)phenyl]-2,5-dipropoxyphenyl}ethene (4d): 4-Bromo-2,5-dipropoxybenzyltriphenylphosphonium Bromide: A solution of 1-bromo-4-bromomethyl-2,5-dipropoxybenzene[23] (10.0 g, 0.03 mol) in dry acetonitrile (20 mL) was added dropwise under argon to a solution of triphenylphosphane (7.07 g, 0.03 mol) in dry acetonitrile (20 mL). The mixture was heated to reflux for two days and the precipitated product collected by filtration. The filtrate was concentrated under vacuum (10° Pa) and acetone added (50 mL), leading to the precipitation of additional product. The total yield was 12.97 g (77%) of a colorless solid, m.p. 218 °C. 1H NMR (CDCl3); δ = 0.70 (t, 3 H, CH3), 0.88 (t, 3 H, CH3), 1.26 (m, 2 H, CH2), 1.58 (m, 2 H, CH2), 3.22 (t, 2 H, OCH2), 3.60 (t, 2 H, OCH2), 5.24 (d, [J1H,1H] = 14.0 Hz, 2 H, CH2P), 6.74 (s, 1 H, arom. H), 7.30 (d, [J1H,1H] = 2.8 Hz, 1 H, arom. H), 7.64 (m, 15 H, C6H15) ppm. 13C NMR (CDCl3); δ = 10.2, 10.5 (CH3), 22.2, 22.4 (CH2), 25.0 (d, [J1H,1H] = 48 Hz, CH2P), 69.9, 71.4 (OCH2), 112.6, 115.3, 149.6, 151.0 (arom. C6), 116.2, 118.0 (arom. CH), 130.0, 130.1, 134.2, 134.6 (C6H15) ppm. FD-MS: m/z (%) = 550/548 (100) [C31H33Br2O2P], Br isotope pattern. C31H33Br2O2P (628.4): calculated C 59.25, H 5.29; found C 59.52, H 5.19.

(E)-1,2,5-Bis[(E)-2,5-bis(dimethylsilyloxy)phenyl]-2,5-dipropoxyphenylethane (4d): A 2.7 M solution of n-butyllithium in heptane...
(6.3 mL, 17 mmol) was added by syringe to a suspension of 4-bromo-2,5-dipropoxybenzyltriphenylphosphonium bromide (9.43 g, 15 mmol) in dry THF (150 mL) at −10 °C under argon. After stirring for 3 h at room temperature, a solution of 2,5-bis(tert-butylidimethylsilyloxy)benzaldehyde (5.0 g, 15 mmol) in dry THF (25 mL) was added to the reaction mixture. The mixture was stirred at room temperature for 30 min and then poured onto ice/water (200 mL). After extraction with diethyl ether (200 mL), the organic phase was washed with water and dried with Na2SO4. The solvent was evaporated under vacuum (102 Pa) and the product purified by column chromatography over silica gel (70–230 mesh, 4 × 30 cm) using petroleum ether (b.p. 40–70 °C)/diethyl ether (20:1) as eluent. An E/Z mixture of 4d was obtained as a yellow liquid (yield 6.51 g, 86%). Transformation to the E isomer, a colorless oil, was performed by refining the mixture in toluene (100 mL) with iodine (40 mg) for 2 h. 1H NMR (CDCl3): δ = 0.18 (s, 6 H, SiCH3), 0.19 (s, 6 H, SiCH3), 0.97 [s, 9 H, C(CH3)3], 1.04 [s, 9 H, C(CH3)3], 1.06 (t, 3 H, CH3), 1.07 (t, 3 H, CH3), 1.80 (m, 4 H, CH2), 3.88 (t, 2 H, OCH2), 3.91 (t, 2 H, OCH2), 6.62 (dd, 1 H, arom. H), 6.67 (dd, 1 H, arom. H), 7.00 (m, 2 H, arom. H), 7.21 (d, 1 H, hydroquinone ring), 6.67 (d, 1 H, hydroquinone ring), 7.06 (br. s, 2 H, arom. H), 7.44 (br. s, 1 H, arom. H) ppm. FD-MS: [M + H]+ = 239 (100), 193 (27), 157 (16), 139 (14). 13C NMR (CDCl3): δ = 19.0, 20.6 (CH3), 69.3, 70.1 (OCH2), 111.5, 114.0, 114.0, 115.7, 116.6 (arom. CH), 121.8, 127.2, 147.8, 149.9, 150.1, 152.7 (arom. Cq), 124.3, 124.4 (olefin CH) ppm. MS (EI, 70 eV): m/z (%): 328 (100) [M+], 176 (56), 135 (12).

(E)-2-[2-(2,5-Dimethylphenyl)ethenyl]benzoquinone (1a): MgSO4 (1.53 g, 12.7 mmol) and freshly-prepared Ag2O (1.16 g, 5.0 mmol) were added to a solution of 7a (0.60 g, 2.5 mmol) in dry diethyl ether (140 mL). After stirring for 30 min at room temperature the solid particles were removed and washed several times with diethyl ether (40 mL). The solvent of the combined organic phases was removed under vacuum (102 Pa) to provide 1a as a red solid (yield 0.60 g, 100%), m.p. > 200 °C. 1H NMR (CDCl3): δ = 2.33 (s, 3 H, CH3), 2.37 (s, 3 H, CH3), 6.77 (m, 2 H, benzoquinone ring), 6.87 (br. s, 1 H, benzoquinone ring). 7.00/7.09 (AB, Jtrans = 16.1 Hz, 2 H, o-H), 7.06 (br. s, 2 H, arom. H), 7.44 (br. s, 1 H, arom. H) ppm. 13C NMR (CDCl3): δ = 19.3, 21.0 (CH3), 119.9, 126.5, 127.6, 130.4, 130.7 (arom. and olefin CH), 134.1, 134.7, 135.9 (arom. Cq), 135.7, 136.5, 136.7 (CH, benzoquinone ring), 142.2 (Cq, benzoquinone ring), 187.1, 187.7 (CO) ppm. FD-MS: m/z (%): 239 (100) [M + H]+. C16H14O2 (238.3): calcld. C 80.65, H 5.92; found C 80.81, H 5.89.

Preparation of (E,E)-2,5-Bis(2,5-dihexylstyrlyl)-1,4-dimethoxybenzene (6)

2,5-Dihexylbenzaldehyde: Titanium tetrachloride (11.27 mL, 19.49 g, 103 mmol) was added dropwise to a solution of 1,4-dihexylbenzene (15.0 g, 61 mmol) in dry dichloromethane (150 mL) at 0 °C. After stirring for 30 min at 0 °C, dichloromethyl methyl ether (8.13 mL, 10.48 g, 92 mmol) was added. The mixture was stirred for 2 h at room temperature and then poured onto ice/water (200 mL). The separated water layer was extracted with dichloromethane (200 mL). The combined organic phases were washed with water followed by a saturated solution of NaHCO3 and then dried with Na2SO4. After removal of the solvent under reduced pressure (1 kPa), the product was purified by column chromatography over silica gel (70–230 mesh, 10 × 15 cm) using petroleum ether (b.p. 40–70 °C)/diethyl ether (20:1) as eluent. The product was obtained as a colorless liquid (yield 12.4 g, 74%). 1H NMR (CDCl3): δ = 0.86 (t, 3 H, CH3), 1.29 (m, 12 H, CH2), 1.57 (m, 4 H, CH2), 2.61 (t, 2 H, CH2), 2.96 (t, 2 H, CH2), 7.15 (d, 1 H, 3-H), 7.29 (dd, 1 H, 4-H), 7.62 (d, 1 H, 6-H), 10.26 (s, 1 H, CHO) ppm. 13C NMR (CDCl3): δ = 14.1, 14.1 (CH2), 22.6, 22.6, 28.9, 29.2, 31.2, 31.7, 32.0, 32.5, 35.3 (CH2, partly superimposed), 130.8, 130.9 (C-3, C-6), 134.0, 143.2 (C-2, C-5), 192.4 (CHO) ppm. FD-MS: m/z (%): 324 (100) [M+], C18H18O2 (274.3): calcld. C 83.15, H 7.02; found C 83.17, H 7.17.
chloroform (80 mL) and the solution dried with Na2SO4. After filtration, partial evaporation of the solvent under vacuum (102 Pa) enabled precipitation of colorless crystals (yield 10.14 g, 87%), m.p. 73 °C. The remaining reaction mixture was added to water (100 mL) and the precipitate isolated by filtration and purified by column chromatography over silica gel (70–230 mesh, 3 × 10 cm) using toluene as eluent. The monobromomethyl compound thus obtained formed almost colorless crystals (yield 1.1 g, 12%), m.p. 73 °C.

1,4-Bis(bromomethyl)-2,5-dimethoxybenzene: 1H NMR (CDCl3): δ = 3.85 (s, 6 H, OCH3), 4.51 (s, 4 H, CH2Br), 6.85 (s, 2 H, 3-H, 6-H) ppm. 13C NMR (CDCl3): δ = 28.6 (C-H), 56.3 (OCH3), 113.9 (C-3, C-6), 127.4 (C-1, C-4), 151.3 (C-2, C-5) ppm. MS (EI, 70 eV): m/z (%) = 326.4/324.5/322.5 (23) [M+]. Br2 isotope pattern, 245/243.1 (100). C6H12Br2O2 (230.5): calcd. C 33.2, 35.7 (CH2), 56.4 (OCH3), 110.1, 125.7, 127.6, 129.5 (arom. CH), 124.3, 127.4 (olefin CH2), 137.3, 136.0, 138.0, 140.6, 151.7 (arom. Cg) ppm. FD-MS: m/z (%) = 679 (100) [M]+. CgH18O2 (678.5): calcd. C 84.87, H 10.22; found C 84.45, H 10.37.

1,4-Bromomethyl-2,5-dimethoxybenzene: 1H NMR (CDCl3): δ = 3.75 (s, 3 H, OCH3), 3.84 (s, 3 H, OCH3), 4.52 (s, 2 H, CH2Br), 6.80 (m, 2 H, arom. H), 6.88 (m, 1 H, arom. H) ppm. 13C NMR (CDCl3): δ = 28.9 (CH2), 55.6, 56.2 (OCH3), 112.2, 115.0, 116.4 (arom. CH), 127.0 (C-1, C-4), 151.7, 153.4 (C-2, C-5) ppm. MS (EI, 70 eV): m/z (%) = 232/230 (16) [M]+. Br2 isotope pattern, 151 (100). C6H12BrO2 (231.9): calcd. C 46.78, H 4.80; found C 47.01, H 4.89.

Tetraethyl [2,5-Dimethoxy-1,4-phenylenebis(methylene)]diphosphonate: 1,4-Bis(bromomethyl)-2,5-dimethoxybenzene (10.9 g, 34 mmol) and triethylphosphite (13.3 g, 80 mmol) were kept for 5 h at 170 °C. After stirring for 15 min at room temperature, the mixture was diluted with water (200 mL) and extracted with diethyl ether (80 mL) and the solution dried with Na2SO4 and concentrated under vacuum. Purification required repeated column chromatography over silica gel (70–230 mesh, 3 cm) with chloroform (80 mL) followed by removal of the solvent under reduced pressure (1 kPa). Purification of the crude product was achieved by recrystallization from ethyl acetate (80 mL) at −5 °C and evaporating the solvent under reduced pressure (1 kPa). The mixture was then dried with Na2SO4 and cooled to room temperature before being dried with Na2SO4 and concentrated under vacuum at 102 °C. The mixture was then stirred at room temperature for 5 h and then poured onto a mixture of ice/water (100 mL) and 2 M HCl, was added slowly to a suspension of 1,4-dihexylbenzene (5.23 g, 21.3 mmol) and paraformaldehyde (250 mL) to give a yellow oil (yield 24 mg, 100%) consisting of a mixture of monomeric, dimeric and trimeric species. Attempted separation of the mixture was unsuccessful and therefore only characterization by IR and MS is reported. IR (neat): ν = 2940 cm−1, 2850, 1760, 1450, 1450, 1365, 1270, 1230, 1180, 960, 880, 820, 720. FD-MS: m/z (%): 649.2 (100) [M + H]+, 1298.2 (29) [M2 + H]+, 1946.7 (7) [M3 + H]+.

Preparation of the (E,E)-2,5-Bis(2,5-dihexyloxystyril)-1,4-dihydroxybenzenes 8a and 8b: Bromomethylation of 1,4-Dihexylbenzene: A 23% solution of HBr in glacial acetic acid (11.3 mL, 63.8 mmol) was added dropwise to a suspension of 1,4-dihexylbenzene (5.23 g, 21.3 mmol) and paraformaldehyde (1.91 g, 63.8 mmol) in glacial acetic acid (45 mL). The mixture was stirred for 6 days at 95 °C, cooled to room temperature, diluted with water (200 mL) and extracted with diethyl ether (200 mL). The organic phase was separated, washed with water and dried with MgSO4. Evaporation of the solvent under reduced pressure (1 kPa) furnished 2a as a red oil (yield 24 mg, 100%) consisting of a mixture of monomeric, dimeric and trimeric species. Attempted separation of the mixture was unsuccessful and therefore only characterization by IR and MS characterization is reported. IR (neat): ν = 2940 cm−1, 2850, 1760, 1450, 1450, 1365, 1270, 1230, 1180, 960, 880, 820, 720. FD-MS: m/z (%): 649.2 (100) [M + H]+, 1298.2 (29) [M2 + H]+, 1946.7 (7) [M3 + H]+.
2-Bromomethyl-1,4-dihexylbenzene: \[ ^1 \text{H NMR (CDCl}_3\]: } \delta = 0.88 (m, 6 H, CH\textsubscript{3}), 1.30 (m, 12 H, CH\textsubscript{2}), 1.58 (m, 4 H, CH\textsubscript{2}), 2.54 (t, 2 H, CH\textsubscript{2}), 2.67 (t, 2 H, CH\textsubscript{2}), 4.52 (s, 2 H, CH\textsubscript{2}Br), 7.07 (m, 3 H, arom. H) ppm. \[ ^{13} \text{C NMR (CDCl}_3\]: } \delta = 14.1, 14.1 (CH\textsubscript{3}), 22.6, 22.6, 29.0, 29.4, 31.0, 31.3, 31.7, 31.8, 32.0, 32.1, 35.4 (CH\textsubscript{2}), 129.0, 129.6, 130.5 (arom. CH), 135.0, 139.0, 140.9 (arom. C\textsubscript{q}) ppm. MS (EI, 70 eV): m/z (%) = 340/338 (5) \[ ^{11} \text{B} \] isotope pattern, 259 (19), 189 (100). C\textsubscript{4}H\textsubscript{11}Br (339.4): calc. C 67.25, H 9.21; found C 67.12, H 9.36.

Tetraethyl [2,5-Dihexyl-1,4-phenylenebis(methylene)]diphosphonate: 2,5-Bis(bromo-methyl)-1,4-dihexylbenzene (9.0 g, 0.02 mol) and freshly-prepared Ag\textsubscript{2}O (183 mg, 0.8 mmol) were added to a solution of KOC(CH\textsubscript{3})\textsubscript{3} (6.57 g, 58.6 mmol) in dry THF (100 mL) and the mixture was stirred at room temperature overnight. After filtering the Ag\textsubscript{2}O precipitate, the filtrate was acidified with 2 \text{M HCl (5 mL). After extraction with dichloromethane and ethyl acetate (5:2) as eluent,} the product was purified by column chromatography over silica gel (70–230 mesh, 3 × 40 cm) using petroleum ether (b.p. 40–70 °C) as eluent. Preparative HPLC chromatography was carried out on a silica gel column (250 mm × 25 mm, 5 μm, 20 cm) using ethyl acetate as eluent. The product was obtained as a yellow solid (yield 404 mg, 75%), m.p. 122 °C.

1H NMR (CDCl\textsubscript{3}): δ = 0.84 (m, 6 H, CH\textsubscript{3}), 2.05 (t, 2 H, CH\textsubscript{2}), 2.51 (t, 2 H, CH\textsubscript{2}), 3.10 (d, J\textsubscript{CH2CH2} = 10.4 Hz, 4 H, olefin CH\textsubscript{2}), 6.08 (m, 4 H, olefin CH), 6.75 (dd, 2 H, arom. H) ppm. FD-MS: m/z (%) = 515 (100) \[ ^{11} \text{B} \] isotope pattern, 510 (25), 419 (105) ppm. FD-MS: m/z (%) = 510 (100) \[ ^{11} \text{B} \] isotope pattern, 505 (24) ppm. C\textsubscript{34}H\textsubscript{42}O\textsubscript{4} (514.3): calcd. C 79.77, H 7.61; found C 79.74, H 8.22; found C 79.79, H 8.50.

(2-E)-2,5-Diisocyano-1,4-benzene (3a): MgSO\textsubscript{4} (230 mg, 1.9 mmol) and freshly-prepared Ag\textsubscript{2}O (183 mg, 0.8 mmol) were added to a solution of 9a (100 mg, 0.19 mmol) in dry diethyl ether (15 mL). After stirring at room temperature overnight, the solid was removed by filtration and the filtrate was added to a solution of 3a as a red solid (yield 100 mg, 100%), m.p. >200 °C. 1H NMR (CD\textsubscript{3}ODMSO): δ = 0.84 (m, 6 H, CH\textsubscript{3}), 1.29 (m, 12 H, CH\textsubscript{2}), 1.52 (m, 4 H, CH\textsubscript{2}), 2.71 (m, 4 H, CH\textsubscript{2}), 6.52 (dd, 2 H, hydroquinone rings), 6.67 (d, 2 H, hydroquinone rings), 6.91 (br. s, 2 H, hydroquinone rings), 7.24 (br. “s”, 4 H, olefin H), 7.40 (s, 2 H, arom. H), 8.76 (s, 2 H, OH), 9.07 (s, 2 H, OH) ppm. 13C NMR (CD\textsubscript{3}ODMSO): δ = 13.9 (CH\textsubscript{3}), 22.0, 28.5, 30.9, 31.0, 32.4 (CH\textsubscript{2}), 111.9, 115.6, 116.5, 124.5, 125.1 (arom. and olefin CH), 124.3, 134.6, 137.8, 147.8, 149.9 (arom. C\textsubscript{q}) ppm. FD-MS: m/z (%) = 515.0 (100) \[ ^{11} \text{B} \] isotope pattern, C\textsubscript{34}H\textsubscript{42}O\textsubscript{4} (514.3): calcd. C 79.34, H 8.22; found C 79.27, H 8.50.

Tetraethyl [2,5-Diisocyano-1,4-benzene] (3b): A solution of monomeric 3a (510.7): calcd. C 79.97, H 7.50; found C 79.77, H 7.61.

(2-E)-2,5-Diisocyano-1,4-benzene (9a): A mixture of 8a (600 mg, 0.89 mmol), sodium borohydride (133 mg, 3.5 mmol) and tetrakis(triphenylphosphane)palladium (41 mg, 0.04 mmol) in dry THF (100 mL) was stirred at room temperature for 2 days. The mixture was then poured into water (100 mL) and acidified with 2 M HCl (5 mL). After extraction with dichloromethane, the organic phase was washed with brine and dried with Na\textsubscript{2}SO\textsubscript{4}. The solvent was evaporated under vacuum (10\textsubscript{2} Pa) and the resulting residue purified by column chromatography over silica gel (70–230 mesh, 3 × 40 cm) using petroleum ether (b.p. 40–70 °C) as eluent to give 9a as a greenish solid (yield: 200 mg, 44% m.p. >200 °C. 1H NMR (CD\textsubscript{3}ODMSO): δ = 0.84 (m, 6 H, CH\textsubscript{3}), 1.29 (m, 12 H, CH\textsubscript{2}), 1.52 (m, 4 H, CH\textsubscript{2}), 2.71 (m, 4 H, CH\textsubscript{2}), 6.52 (dd, 2 H, hydroquinone rings), 6.67 (d, 2 H, hydroquinone rings), 6.91 (br. s, 2 H, hydroquinone rings), 7.24 (br. “s”, 4 H, olefin H), 7.40 (s, 2 H, arom. H), 8.76 (s, 2 H, OH), 9.07 (s, 2 H, OH) ppm. 13C NMR (CD\textsubscript{3}ODMSO): δ = 13.9 (CH\textsubscript{3}), 22.0, 28.5, 30.9, 31.0, 32.4 (CH\textsubscript{2}), 111.9, 115.6, 116.5, 124.5, 125.1 (arom. and olefin CH), 124.3, 134.6, 137.8, 147.8, 149.9 (arom. C\textsubscript{q}) ppm. FD-MS: m/z (%) = 515.0 (100) \[ ^{11} \text{B} \] isotope pattern, C\textsubscript{34}H\textsubscript{42}O\textsubscript{4} (514.3): calcd. C 79.34, H 8.22; found C 79.27, H 8.50.

Oligomerization of 3a: A solution of monomeric 3a (25 mg 0.05 mmol) in chloroform (25 mL) was allowed to stand overnight. Analysis by FD-MS revealed indicative peaks (as the protonated species) for a series of oligomers of 3a (n = 1–4).
Simultaneous Transformation of rac-10a into rac-12a,b,c Compounds 12a,b were primarily obtained by column chromatography of 10a (70 mg) over silica gel (70–230 mesh, 3 × 30 cm) using chloroform (contaminated with small amounts of ethanol and water/ethyl acetate (5:1) as eluent. The ethanol adduct 12b was obtained as the first fraction (yield 32 mg, 40%) and the water adduct 12a as the second fraction (yield 26 mg, 35%).

The dimers rac-10b and rac-10c were prepared as described previously.[13] The compound rac-10d was not isolated and was directly transformed into rac-11d.

rel-(1S,8S,13R,14R,15R,16R)-14,15-Bis(2,5-dimethylphenoxy)pentacyclo[6.6.2.012.8]hexadeca-2(7),4,10-triene-3,6,9,12-tetetone (rac-11a): Column chromatography of the crude dimer 160 mg over silica gel (70–230 mesh, 3 × 70 cm) with petroleum ether (b.p. 40–70 °C) to ethyl acetate (5:1) provided 11a, a viscous oil, as the first fraction (yield 39 mg, 24%).[1] H NMR (CDCl3): δ = 1.98 (s, 3 H, CH3), 2.18 (s, 3 H, CH3), 2.23 (s, 3 H, CH3), 2.60 (s, 3 H, CH3), 2.91 (s, br. s, 1 H, 16-H), 3.59 (d, J = 2.3 Hz, 1 H, 19-H), 4.34 (d, J = 4.7 Hz, 1 H, 16-H), 6.27/6.39 (AB, J = 10.6 Hz, 2 H) and 6.74/6.83 (AB, J = 10.6 Hz, 2 H) [2-H/3-H and 6-H/7-H].

The preparation of the polycyclic compounds rac-11b and rac-11c has been described previously.[13] The compound rac-11d has been isolated previously.[13]

The preparation of the residue over silica gel (70–230 mesh, 3 × 70 cm) using petroleum ether (b.p. 40–70 °C) ethyl acetate (5:1) as eluent furnished 11d as a viscous oil (yield 31 mg, 16%).[1] H NMR (CDCl3): δ = 0.89 (t, 3 H, CH3), 0.96 (t, 3 H, CH3), 1.12 (m, 6 H, CH2), 1.59 (m, 4 H, CH2), 1.68 (q, 2 H, CH2), 1.90 (m, 2 H, CH2), 2.86 (br. s, 1 H, 16-H), 3.52 (m, 2 H, OCH2), 3.77–3.98 (m, 6 H, OCH3), 4.10 (dd, J = 4.7, J = 2.3 Hz, 1 H, 15-H), 4.55 (dd, J = 4.5 Hz, 1 H, 14-H), 4.59 (t, J = 4.5 Hz, 1 H, 1-H), 5.95 (d, 1 H, arom. H), 6.17/6.51 (AB, J = 10.3 Hz, 2 H) and 6.74/6.89 (AB, J = 10.6 Hz, 2 H) [4-H/5-H and 10-H/11-H].

Simultaneous Transformation of rac-10a into rac-12a,b,c Compounds 12a,b were primarily obtained by column chromatography of 10a (70 mg) over silica gel (70–230 mesh, 3 × 30 cm) using chloroform (contaminated with small amounts of ethanol and water/ethyl acetate (5:1) as eluent. The ethanol adduct 12b was obtained as the first fraction (yield 32 mg, 40%) and the water adduct 12a as the second fraction (yield 26 mg, 35%).

rel-(8aS,9R,10R)-9-(2,5-Dimethylphenyl)-8a-[E]-2-(2,5-dimethylphenyl)ethynyl]-8aH-9,10-dihydro-1,4,5,10-tetrahydroxyphenanthren-8-one (rac-12a): An increased yield of the water adduct 12a was accomplished by eliminating possible formation of the ethanol adduct 12b. Column chromatography of 10a (90 mg) over silica gel (70–230 mesh, 3 × 50 cm) with dichloromethane/ethyl acetate (5:1) as eluent delivered exclusively 12a as a yellow solid (yield 52 mg, 58%), m.p. 142 °C. [1] H NMR (CDCl3): δ = 1.80 (s, 3 H, CH3), 2.02 (s, 3 H, CH3), 2.18 (s, 3 H, CH3), 2.36 (s, 3 H, CH3), 2.64 (d, J = 9.2 Hz, 1 H, OH attached to C-10), 4.36 (br. s, 1 H, 9-H), 4.81 (d, J = 9.2 Hz, 1 H, 10-H), 5.62/6.70 (AB, J = 10.2 Hz, 2 H, 6-H/7-H), 6.27/6.39 (AB, J = 16.0 Hz, 2 H, OCH2), 6.65 (br. s, 1 H, arom. H), 6.76/6.86 (AB, J = 8.6 Hz, 2 H, 2-H/3-H), 6.81 (d, 1 H, arom. H), 6.84 (m, 2 H, arom. H), 6.91 (d, 1 H, arom. H), 6.99 (s, 1 H, OH attached to C-1), 7.14 (br. s, 1 H, arom. H), 8.42 (br. s, 1 H) and 8.51 (br. s, 1 H) [OH attached to C-4, C-5] ppm. [1] C NMR (CDCl3): δ = 18.9, 19.0, 20.7, 21.2 (CH3), 36.4, 40.6, 43.3, 44.3 (C-1, C-14, C-15, C-16), 38.9, 46.0 (C-8, C-13), 126.7, 127.9, 128.1, 128.2, 130.5, 130.7 (arom. CH), 132.1, 132.8, 132.9, 133.7, 135.0, 135.6, 138.1, 138.3 (C-2, C-7 and arom. Cq), 134.7, 137.0, 138.8, 139.0 (C-4, C-5, C-10, C-11), 181.8, 182.8, 189.1, 190.6 (C-3, C-6, C-9, C-12) ppm. FD-MS: m/z (%) = 477 (100) [M+ H]+. C32H32O4 (477.6): calcd. C 80.65, H 5.92; found C 80.73, H 5.49.

The preparation of the polyyclic compounds rac-11b and rac-11c has been described previously.[13] The compound rac-11d has been isolated previously.[13]
Increasing the solvent ratio to 5:3 then furnished a viscous oil which was obtained as a yellow solid (yield 32 mg, 16%; m.p. 104 °C). Column chromatography of 10b (200 mg) over silica gel (70–230 mesh, 3 × 70 cm) with petroleum ether (b.p. 40–70 °C)/diethyl ether (5:2) provided rac-11b as a viscous oil (38 mg, 19%).

**Comparision of Thermal and Photochemical Dimersizations:** A solution of quinone 1a (7.0 mg, 0.03 mmol) in 0.6 mL of C6D6 was irradiated for 30 min at 60 °C using a 300 W halogen lamp equipped with a UV filter (λ = 410 nm). For reference, a similar dimer was obtained in the thermal experiment (together with 90% of the starting material).

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[18] Irradiation at a wavelength greater than 520 nm is described in the literature.

[19] Acids, like acetic acid, with a sufficient nucleophilicity add themselves to the literature.

[20] The Wittig approach is highly known.


[30] Irradiation at a wavelength greater than 520 nm is described in the literature.

[31] Acids, like acetic acid, with a sufficient nucleophilicity add themselves to the literature.

[32] The Wittig–Horner reactions are highly trans selective in this series; cis configurations can only be detected as traces in the raw products.


[37] The assignment of the signals is based on homo- and heteronuclear shift correlation measurements.

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