Synthesis of Alkyl-Substituted Helianthrones and Mesonaphthobianthrone by Highly Regioselective Photocyclization of Bianthronylidenes

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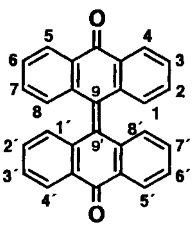
The synthesis of the novel alkyl-substituted helianthrones **8a**, **c** and mesonaphthobianthrone **9** by photocyclization of the corresponding bianthronylidenes **7a**, **b** is described. Regioselectivity and scope of the photocyclizations of **7a** and **7b** depend on the substitution pattern. The structures of **7a** and **8a** have been established by X-ray crystallography and indicate an isomerization about the central double bond of **7a** in the photoreaction. The structures of the protonated species of **8a** and **9** are elucidated, and their optical absorption and emission behavior is examined.

The photochemical reactivity of bianthronylidene **1**[1] and its derivatives has been the subject of numerous investigations[2−6]. While derivatives carrying substituents in the 1(1′)- and 8(8′)-positions show remarkable photochemical stability, the corresponding unsubstituted species can be converted into mesonaphthobianthrone **2** photochemically[7]. Since many natural pigments contain the framework of **2**[9,10], a detailed knowledge of the influence of different substituents on the photocyclization efficiency and the resulting regioselectivity is significant, both from a preparative and biochemical viewpoint.

Helianthrone[8] **3** was identified as an intermediate in the oxidative cyclization of bianthrone in organic solvents[3−6] and in strongly acidic media[5]. Due to the photochemical instability of **3** in solution, however, its isolation during the photoreaction was difficult and possible only in small quantities and low yields. Furthermore, investigations on a preparative scale failed due to the low solubility of the cyclized oxidation products **2** and **3**.



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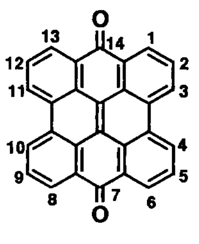

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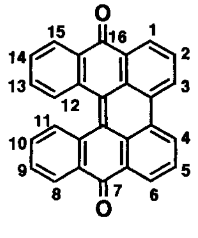

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In this paper we describe irreversible photochemical cyclization of **7a** and **7b**, which leads to **8a** resp. **8c** and **9**. The introduction of two different alkyl substituents in the 2- and 2′-positions, while causing sufficient solubility of the cyclized products in common organic solvents, has a strong influence on the photoreactivity. Protonation of **8a** and **9** leads to deeply colored compounds **10**, **11a**, which are promising candidates for novel dyes.

Results and Discussion

Synthesis of Bianthronylidenes 7a and 7b

The syntheses of **7a**, **b** are largely based on known procedures. Extension to the novel alkylated derivatives of **1**, however, requires several modifications (see Experimental). The anthraquinones **4a**, **4b** (substituted in the 2- and 3- or 2- and 6-positions) serve as starting materials[11]. Reduction with zinc dust/HCl in acetic acid[12] leads to the anthrones **5a**, **5b**, which, in turn, are treated with nitrobenzene in xylene[13] to yield the bianthronyls[14] **6a**, **b**. The commonly used oxidative coupling methods with iron(III) chloride[15] or nitric acid[16] are not efficient in this case. The resulting 2,2′-substituted bianthronyls exist as a mixture of *meso* and D/L modifications, due to the formation of two chiral centers in the coupling reaction[17,18]. This is reflected in the ^{1}H-NMR spectrum of **6b**, which shows a doubling of signals in the aromatic region, due to a superposition of proton signals of both diastereomers. This result is further supported by the observation of two product spots in the TLC. In contrast, ^{1}H- and ^{13}C-NMR spectra of **6a** do not show the presence of diastereomers.

The bianthronyls **6a**, **b** are enolized with KOH in ethanol and dehydrogenated with 1,4-benzoquinone to yield the (*E*)/(*Z*) mixtures **7a** and **7b**[19]. The presence of these (*E*)/(*Z*) isomers[19] of **7a**, **b** manifests itself by the appearance of two sets of signals with the same coupling pattern in the ^{1}H-NMR spectrum. In the case of **7b**, a 1:1 isomeric mixture

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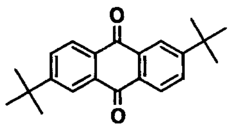
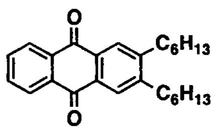
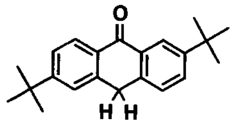


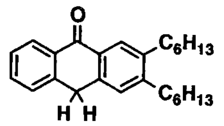
4a



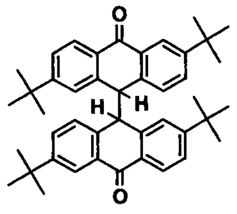
4b



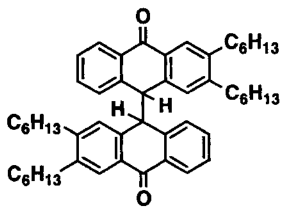
5a



5b

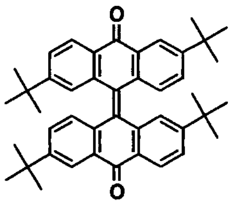


6a

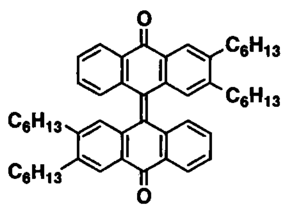


6b

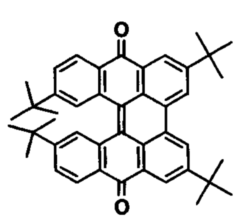
is found by integration of the relative signal intensities, while one isomer of **7a** is preferably formed, which can be isolated in 83% yield by fractional crystallization in the dark. The isomeric purity is confirmed by the simple splitting pattern and the number of resonances in the NMR spectra (^{1}H, ^{13}C). An X-ray crystal structure analysis of **7a** (see Figure 1) indicates the preferred formation of the (*E*) isomer under the present experimental conditions. This result is reminiscent of the behavior of bianthrones which are replaced in the 1(1′)- and 8(8′)-positions by sterically demanding groups[19]. These also adopt an (*E*) configuration for steric reasons. Furthermore, the steric influence of the *tert*-butyl groups in the 2,2′-positions on the isomeric ratio in **7a** is demonstrated.



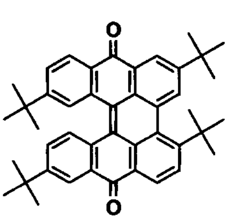
7a (E)



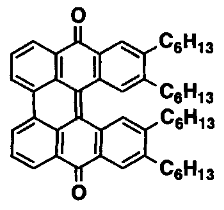
7b (E)/(Z)



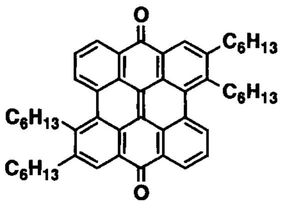
8a



8b (not formed)



8c



9

X-Ray Structure Analysis of 7a

The asymmetric unit was found to have two different conformers **7a1** and **7a2** (Figures 1a and 1b), both located at a center of inversion. Each conformer shows the typical "butterfly" molecular geometry of bianthrone[2,20]. The central double bonds connecting the anthrone moieties are in both cases untwisted and possess a length of 1.34(1) Å. The lengths of the lateral bonds 9–9a and 9–8a of **7a1** are

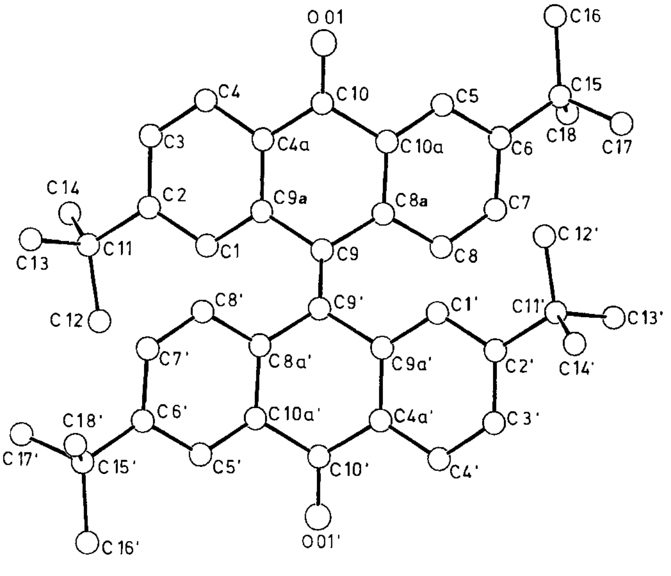


Fig. 1a. Crystal structure and numbering of *E*-**7a1** (ORTEP plot)

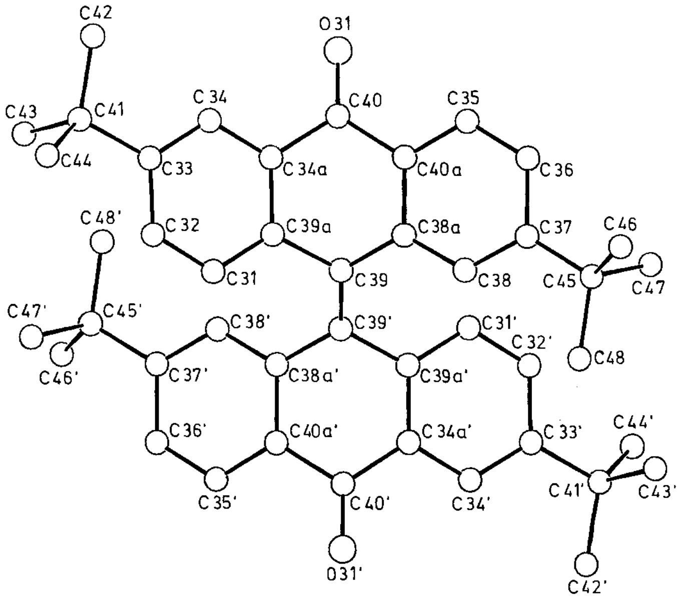


Fig. 1b. Crystal structure and numbering of *E*-**7a2** (ORTEP plot)

1.508(8) and 1.456(9) Å, respectively. The corresponding bonds of conformer **7a2** (39 – 39a, 39 – 38a) exhibit the same lengths [1.500(8), 1.450(8) Å] within the experimental error. These bond lengths are in accordance with those observed for the molecular structure of unsubstituted bianthronylidene **1**. They indicated that, similar to **1**[20], the bianthrone framework of **7a1,2** possesses a nearly isolated ethylenic group (1.31 Å) connected to essential single bonds (1.53 Å). Remarkably, the two conformers differ from the molecular geometry of **1** in the dihedral angle α between the two planar benzene rings (planar within the error limit) of each anthrone half and the plane of the central double bond (see Figure 1c). For **7a1** α is 45.2(0.3)° and for **7a2** it is 37.2(0.2)°. For comparison, the benzene rings of **1** are twisted by 40° out of the plane of the ethylenic group, which is most probably due to packing effects.

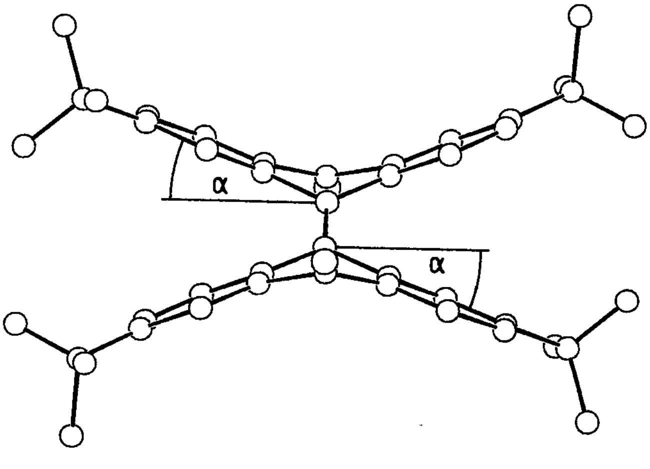


Fig. 1c. Side view of *E*-**7a1** (ORTEP plot)

Photocyclization of 7a and 7b

The oxidative cyclizations were performed in concentrated ($2.5 - 5.0 \cdot 10^{-3}$ mol/l) solutions of acetic acid in a quartz vessel. The solutions were vigorously stirred and irradiated with a 125-W high-pressure mercury lamp, until quantitative conversion of the bianthrones **7a, b** was confirmed by TLC (4 – 7 days). The photodehydrogenation of unsubstituted bianthronylidene **1** and helianthrone **3** in acetic acid is fast and leads to the sparingly soluble mesonaphthobianthrone **2** in nearly quantitative yield[4]. In contrast, photolysis of **7a** affords the strongly fluorescent helianthrone **8a** in 83% yield along with anthraquinone **4a** (10%). The ^{1}H-NMR spectrum confirms the substitution pattern. A complete assignment of the signals in the aromatic region was possible with the aid of the coupling constants, decoupling experiments, and comparison with chemical shifts of proton signals of model compounds[6]. Next to the simple appearance of the aromatic region, the existence of merely two signals in the aliphatic region (due to protons of the alkyl substituents) indicates the formation of an isomerically pure modification of **8a**. This is supported by the 18 signals (for 44 C atoms) in the ^{13}C-NMR spectrum of **8a**. Finally, the postulated structure of the helianthrone is unambiguously verified by a X-ray analysis of a single crystal (see Figure 2).

There were no indications of the photochemical formation of the positional isomer **8b** (2,4,9,13-tetra-*tert*-butylhelianthrone) and the corresponding two mesonaphthobianthrone compounds.

Photolysis of **7b** affords a tetrahexyl-substituted mesonaphthobianthrone in 76% yield along with 10% of helianthrone **8c** (whose substitution pattern was established by ^{1}H-NMR spectroscopy) and 6% of anthraquinone **4b**. Asthonishingly, the photocyclization leads to only one isomerically pure mesonaphthobianthrone compound, as is also confirmed by NMR-spectroscopic investigations. Furthermore, prolonged irradiation of the isolated tetrahexylhelianthrone **8c** for 72 h did not lead to the corresponding 2,3,4,5-tetrahexylmesonaphthobianthrone; only starting material was recovered. The photochemical stability of **8c** is due to the extreme steric hindrance of the alkyl chains in the 9-, 10-, 13-, 14-positions. Consequently, the isolated tetrahexylmesonaphthobianthrone is assigned to **9** (2,3,9,10-tetrahexylmesonaphthobianthrone). The regioselective photocyclization of **7a** to **8a** occurs regardless of the stereochemistry of the starting material. Both the reaction of an (*E*)/(*Z*) isomeric mixture and an isomerically pure (*E*) modification leads to the same cyclic product. Accordingly, the photocyclization of **7b** was performed with a 1:1 mixture of the (*E*)/(*Z*) isomers of **7b** and yielded 76% of the isomerically pure mesonaphthobianthrone **9**. This result points to an isomerization of the central double bond during the first cyclization. The helianthrones **8a, c** formed in the first cyclization step are obtained as end products in the photocyclization of **7a** and **7b**. A second cyclization is prevented by the steric repulsion of the alkyl groups in the 10- and 13-positions, resulting in photostable, partially cyclized products in solution.

X-Ray Structure Analysis of 8a

ORTEP drawings of an orange single crystal of **8a** with a referenced atomic labeling scheme are presented in Figures 2a, b. The bond lengths and angles of the perylene quinone moiety are in agreement with values reported for cercosporin[21] and ensinochrome A[22]. Due to the nonplanar configuration of the molecule **8a** (X shape), the π-bond delocalization in the five perylene quinone rings 1, 2, 4, 5, and 6 is disturbed and an alternation of short and long bond lengths is observed. Thus, the C3a–C4a bond reflects the length of resonance-shortened single bonds [1.44(1) Å], for bond C11b–C12b a typical value for a resonance-extended double bond is indicated [1.39(1) Å].

As a measure of the degree of nonplanarity in the molecule we have taken the dihedral angles between rings 2 and 6, 1 and 5, and rings 3 and 7, which are 32.7(0.4), 16.6(0.6), and 56.9(0.3)°, respectively (see also Tab. 1). It should be mentioned that the distortion of planarity of **8a** is not symmetric. Rings 1 and 3 form a dihedral angle of 28.0° (0.4), whereas the angle between rings 5 and 7 has a value of 13.3(1)°. Consequently, the two anthrone moieties of the molecule

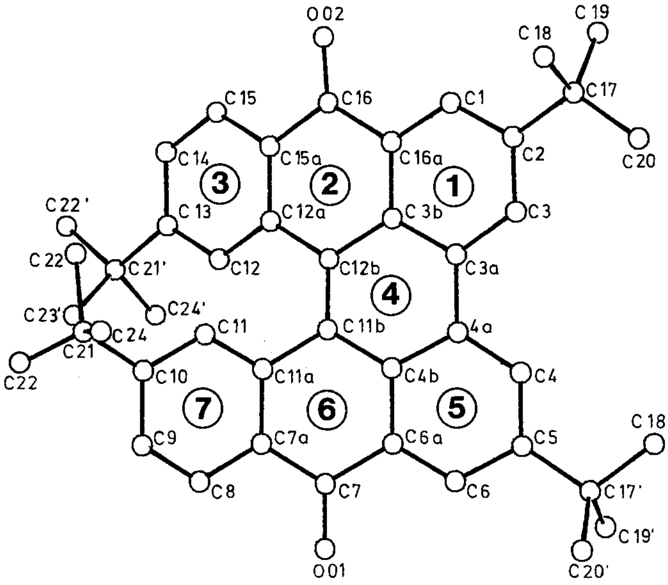


Fig. 2a. Crystal structure and numbering of **8a** (ORTEP plot)

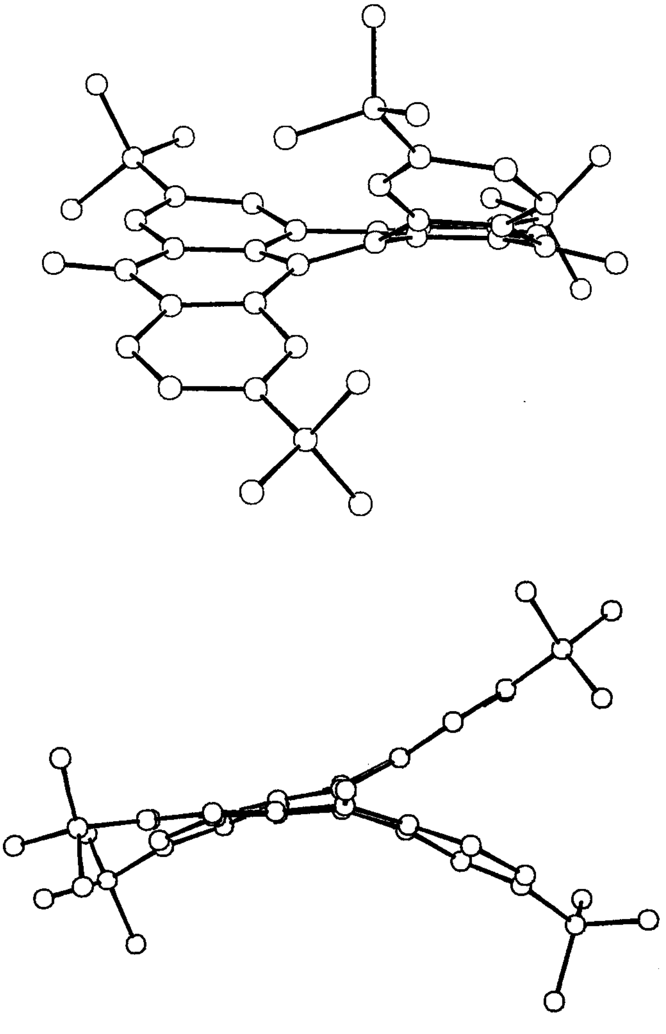


Fig. 2b. Side views of **8a** along two perpendicular axis (ORTEP plots)

are not bent in the same way. The nonplanar configuration of **8a** (X shape) is due to the strong steric hindrance between the two *peri*-hydrogen atoms (H11, H12) and the *tert*-butyl groups in the 10- and 13-positions.

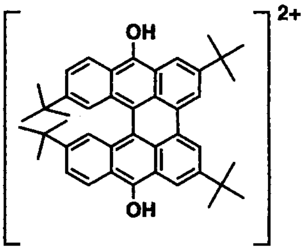
Table 1. Angles [°] between ring planes of the moleculare structure of **8a**

Plane No.	Plane No.	Dihedral Angle
1	2	10 (1)
1	3	28.0 (5)
1	4	8 (1)
1	5	16.6 (6)
1	6	17.0 (7)
1	7	29.2 (5)
2	3	18.2 (7)
2	4	16.3 (7)
2	5	26.3 (4)
2	6	26.9 (4)
2	7	39.1 (4)
3	4	34.2 (4)
3	5	43.8 (3)
3	6	45.0 (3)
3	7	56.9 (3)
4	5	15.5 (7)
4	6	13.4 (9)
4	7	25.5 (69
5	6	5 (2)
5	7	13 (1)
6	7	12 (1)

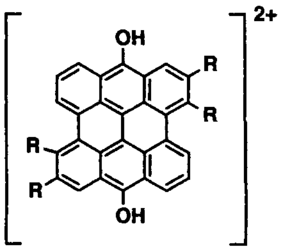
Protonation of 8a and 9

It is well established that mesonaphthobianthrone **2** and its methyl derivatives give dark red solutions in concentrated sulfuric acid, while helianthrone **3** yields dark blue-green solutions[23]. The intensive color is attributed to cationic species, formed by protonation of the quinone oxygen atoms. Apart from some contradictory suggestions in the literature, no structural determination of these colored species of **2** and **3** in sulfuric acid has been carried out to date[5,24]. For this reason, the deeply colored derivatives of **8a** and **9** were generated under argon in a degassed mixture of [D$_5$]nitrobenzene/D$_2$SO$_4$, and analyzed by ^{1}H-NMR spectroscopy. The spectra are shown in Figure 3.

The pronounced downfield shift of the aromatic proton signals (compared with **8a**, **9**) is a result of the deshielding caused by the charged electrophore. Furthermore, the typical splitting pattern of **8a** and **9** is retained in the aromatic as well as in the aliphatic regions of the ^{1}H-NMR spectra. The number of resonance signals in the ^{13}C-NMR spectra of the deeply colored compounds also demonstrates the intact molecular framework. Symmetry arguments suggest the



10



11a: R = C$_6$H$_{13}$
11b: R = H

structures **10** and **11a**, in which both quinone oxygen atoms are protonated. Surely, the NMR-spectroscopic results also agree with a monoprotonated structure[5,24], if fast alternating protonation of both quinone oxygens takes place. However, we consider the doubly protonated species **10**, **11a** and **11b** to be more likely under the strong acidic conditions used in the experiments.

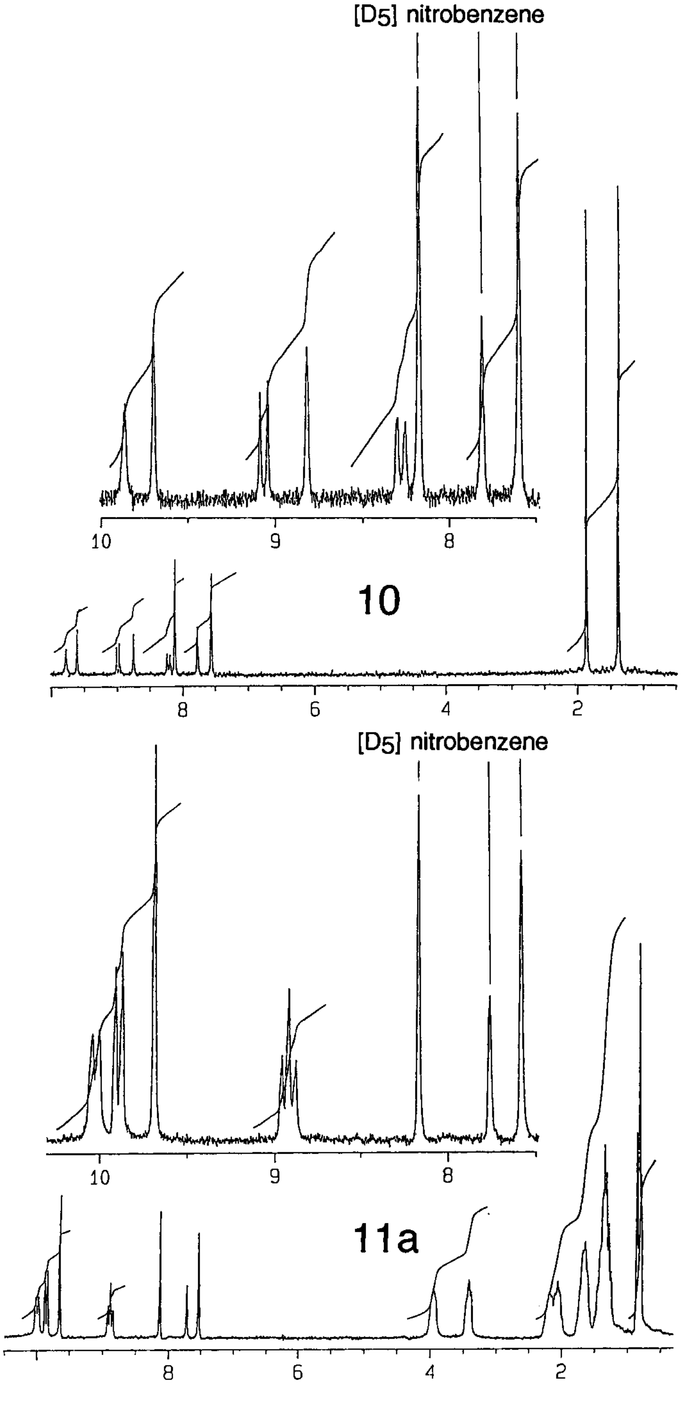


Fig. 3. ^{1}H-NMR spectra δ scale, ([D$_5$]nitrobenzene/D$_2$SO$_4$) of the species **10** and **11a** generated by protonation of **8a** and **9**

To gain insight into the absorption and emission behavior of **8a**, **9**, **10**, **11a**, and **11b**[24], comparative UV/Vis measurements were performed in appropriate solvents. Of special interest is the reversible color change during the transition of **8a**, **9** to **10**, **11a** (and the reverse reaction)[25]. The experiment was carried out by adding concentrated sulfuric acid to a solution of **8a** (**9**) in nitrobenzene. Subsequent addition of H_2O leads to quantitative recovery of the cyclic quinones **8a** and **9**. A comparison of the absorption spectra of **8a** and **10** as well as of **9** and **11a** demonstrates the color change of the reaction. These results are summarized in Figure 4 and Table 2.

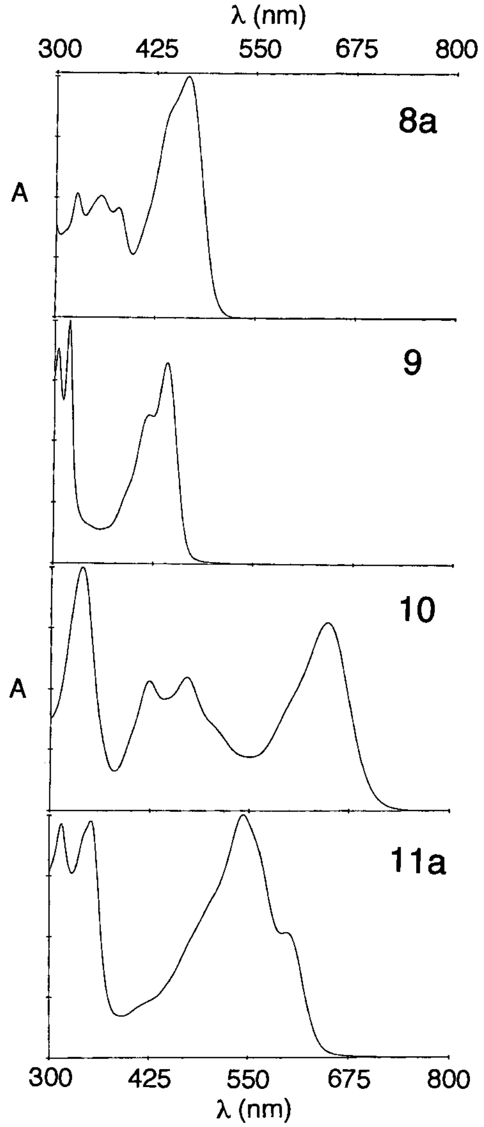


Fig. 4. Absorption spectra of **8a**, **9**, **10**, and **11a** (**8a** and **9** measured in CH_2Cl_2 as solvent, **10** and **11a** in conc. H_2SO_4)

The orange helianthrone **8a** dissolves in concentrated sulfuric acid and yields deep green **10**. The longest wavelength absorption of **10** is shifted bathochromically by 19 nm (λ_{max} = 647 nm) as compared to the unsubstituted, photolabile compound **3**[5,24]. The violet sulfuric acid solution of **11a** shows a red shift of 33 nm of both the main absorption and the longest wavelength band, as compared to the parent compound **11b**. The fluorescence bands of **11a** suffer a significant bathochromic shift of 52 nm in comparison with the unsubstituted compound **11b**.

Table 2. Selected spectroscopic data for the compounds **8a**, **9**, **10**, **11a**, and **11b**[5]

Compound	Absorption [nm] [a]		Fluorescence [nm] [a]	
	λ	ε [l/mol cm]	λ_{max}	(λ_{exc})
8a	466	32500	513	(440)
9	442	35700	469	(400)
10	647	23400	698	(610)
11a	544	42700	632	(550)
	605	21400		
11b	511	41000	580	(500)
	572	16600		

[a] Absorption and fluorescence spectra at room temperature: **8a**, **9** (in CH_2Cl_2); **10**, **11a**, and **11b** (in conc. H_2SO_4).

The large Stokes shift between the longest wavelength absorption bands and the corresponding emission bands in the partially cyclized derivatives **8a** and **10** is remarkable. While **11b** displays a Stokes shift of only 8 nm, **8a** and **10** show values of 51 and 47 nm, respectively. Such a behavior indicates a significant change in geometry when going from the S_0 to the S_1 state. In the doubly cyclized compounds **9**, **11a**, and **11b**, on the other hand, a small Stokes shift and mirror image symmetry of the fluorescence band to the corresponding longest wavelength absorption band indicate a negligible change in geometry during the transition from the ground to the first excited state. This lack of conformational mobility can be expected for rigid molecules.

Experimental

^1H and ^{13}C-NMR: Varian Gemini 200, chemical shifts relative to TMS as internal standard. – MS: Varian CH7A or VG Trio 2000. – IR: Nicolet 320 FT-IR. – UV/Vis: Perkin-Elmer Lambda 9. – Fluorescence spectra: Perkin-Elmer MPF 44a. – Column chromatography: glass columns packed with silica gel (Merck Geduran 60, 70–230 mesh) with eluants specified below. – Elemental analyses: Department of Chemistry and Pharmacy at the University Mainz. – Photolyses: 125-W high-pressure Hg lamp (Heraeus) equipped with pyrex filters (λ > 300 nm).

9,9'-Bianthronylidene (**1**) was purchased from Aldrich and used without further purification. *Mesonaphthobianthrone* (**2**)[4a], *2,3-dihexyl-1,3-butadiene*[26], and *2,6-di-tert-butylanthracene*[27] were prepared according to literature procedures. All new compounds were fully characterized.

2,6-Di-tert-butylanthraquinone (**4a**): To a stirred suspension of cerium(IV) ammonium nitrate (112 g, 0.21 mol) in 75 ml of THF and 25 ml of water 2,6-di-*tert*-butylanthracene (15 g, 0.052 mol) was added in small portions. The mixture was stirred at room temp. for 2 h, whereby the color changed from orange to red and then back to orange. After removal of the solvent, CH_2Cl_2 was added to the residue. The organic phase was washed repeatedly with water, dried ($MgSO_4$), and the solvent removed. Recrystallization from ethanol gave pure **4a**, m.p. 158°C; yield 15 g (90%). – IR (KBr): $\tilde{\nu}$ = 2950–2864 cm^{-1}, 1671, 1593, 1466, 1364, 1299, 1271, 1207, 1182, 975, 935, 869, 751. – ^1H NMR ($CDCl_3$): δ = 8.31 (d, J = 2.2 Hz, 2H; 1-, 5-H), 8.23 (d, J = 8.4 Hz, 2H; 4-, 8-H), 7.80 (dd, J = 8.4/2.2 Hz, 2H; 3-, 7-H), 1.44 [s, 18H; $C(CH_3)_3$]. – ^{13}C NMR ($CDCl_3$): δ = 183.9 (CO), 158.6, 133.9, 132.0, 131.6, 127.8, 124.4, 36.1 [$C(CH_3)_3$], 31.5 [$C(CH_3)_3$]. – MS (70 eV), m/z (%): 321 (22) [M^+ + 1], 320 (100) [M^+], 305 (86) [$M^+ - CH_3$], 57 (18) [$C(CH_3)_3^+$].

$C_{22}H_{24}O_2$ (320.4) Calcd. C 82.47 H 7.55
Found C 82.25 H 7.64

2,3-Dihexylanthraquinone (**4b**): A stirred solution of 2,3-dihexyl-1,3-butadiene (27 g, 0.12 mol) and 1,4-naphthoquinone (23.5 g, 0.14 mol) in 300 ml of ethanol was refluxed for 24 h. After cooling to room temp., the brown solid was filtered and washed with cold ethanol. The crude solid was then dissolved in ethanol (1 l) and treated with solid KOH. Oxygen was then bubbled through the rapidly stirred solution for 3 h. After removal of the solvent, the residue was recrystallized from ethanol to give the product **4b** as colorless needles, m.p. 87°C; yield 38.8 g (85%). – IR (KBr): $\tilde{\nu}$ = 2952–2856 cm^{-1}, 1673, 1592, 1471, 1463, 1538, 1326, 1284, 961. – ^1H NMR ($CDCl_3$): δ = 8.32–8.24 (m, 2H; 5-, 8-H), 8.06 (s, 2H; 1-, 4-H), 7.78–7.73 (m, 2H; 6-, 7-H), 2.76 (t, J = 6.7 Hz, 4H; benzylic CH_2), 1.75–1.55 (m, 4H; CH_2), 1.53–1.20 (m, 16H; CH_2), 0.91 (t, J = 6.7 Hz, 6H; CH_3). – ^{13}C NMR ($CDCl_3$): δ = 183.8 (CO), 148.6, 134.3, 131.9, 128.4, 127.6, 33.5, 32.2, 31.2, 30.0, 23.1, 14.6. – MS (70 eV), m/z (%): 377 (15) [M^+ + 1], 376 (50) [M^+], 291 (100) [M^+ – hexyl].

$C_{26}H_{32}O_2$ (376.5) Calcd. C 82.94 H 8.57
Found C 82.83 H 8.46

2,6-Di-tert-butylanthrone (**5a**): To a heated suspension of **4a** (5 g, 15.6 mmol) and tin dust (3.65 g, 32 mmol) in 200 ml of acetic acid was added dropwise with stirring 13 ml of conc. HCl. After the addition was complete, the solution was refluxed for 3 h. The warm reaction mixture was then filtered and the solvent removed. The crude product was recrystallized from acetic acid, then from ethanol to give **5a** (3.4 g, 71%), m.p. 139°C. – IR (KBr): $\tilde{\nu}$ = 2952–2862 cm^{-1}, 1665, 1607, 1363, 1336, 1318, 1279, 1179, 972, 917, 845, 670. – ^1H NMR ($CDCl_3$): δ = 8.40 (d, J = 2.1 Hz, 1H; 1-H), 8.31 (d, J = 8.3 Hz, 1H; 8-H), 7.65 (dd, J = 8.3/2.1 Hz, 1H; 7-H), 7.51 (dd, J = 8.3/2.1 Hz, 1H; 3-H), 7.45 (d, J = 2.1 Hz, 1H; 5-H), 7.42 (d, J = 8.3 Hz, 1H; 4-H), 4.32 (s, 2H; 9-H), 1.41 [s, 9H; $C(CH_3)_3$], 1.38 [s, 9H; $C(CH_3)_3$]. – ^{13}C NMR ($CDCl_3$): δ = 184.0 (CO), 155.9, 149.7, 140.2, 137.6, 131.6, 129.8, 129.7, 128.1, 127.2, 124.7, 124.2, 123.5, 34.9 [$C(CH_3)_3$], 34.6 [$C(CH_3)_3$], 32.0 (bisbenzylic CH_2), 31.1 [$C(CH_3)_3$], 30.4 [$C(CH_3)_3$]. – MS (70 eV), m/z (%): 307 (53) [M^+ + 1], 306 (100) [M^+], 291 (78) [$M^+ - CH_3$], 250 (93) [$M^+ - C(CH_3)_3$], 235 (38) [$M^+ - CH_3 - C(CH_3)_3$], 57 (13) [$C(CH_3)_3^+$].

$C_{22}H_{26}O$ (306.5) Calcd. C 86.22 H 8.55
Found C 86.18 H 8.53

2,3-Dihexylanthrone (**5b**): Anthraquinone **4b** (5.0 g, 13.3 mmol), tin dust (2.8 g, 24 mmol), and 10 ml conc. of HCl were allowed to react in 200 ml of glacial acetic acid as described for **5a**. The crude product was recrystallized, first from ethanol, then from ethyl acetate to yield **5b** (3.17 g, 66%). – IR (KBr): $\tilde{\nu}$ = 2976–2833 cm^{-1}, 1662, 1596, 1483, 1385, 1326, 1309, 1268, 1178, 1058, 953, 833. – ^1H NMR ($CDCl_3$): δ = 8.70–8.60 (m, 1H; 1H, 8-H), 8.13 (s, 1H; 1-H), 7.61–7.40 (m, 3H; 5-, 6-, 7-H), 7.23 (s, 1H; 4-H), 4.28 (s, 2H; 9-H), 2.68 (t, J = 7.8 Hz, 4H; benzylic CH_2), 1.62–1.34 (m, 16H; CH_2), 0.88 (m, 6H; CH_3). – MS (70 eV), m/z (%): 363 (30) [M^+ + 1], 362 (100) [M^+], 291 (21) [$M^+ - C_2H_5 - C_3H_7$], 277 (81) [$M^+ - 2\ C_3H_7$], 221 (52) [$M^+ - 2\ C_5H_{11}$], 207 (15) [$M^+ - C_5H_{11} - C_6H_{13}$].

$C_{26}H_{34}O$ (362.6) Calcd. C 86.14 H 9.45
Found C 86.01 H 9.28

2,2',6,6'-Tetra-tert-butyl-9,9'-bianthronyl (**6a**): Anthrone **5a** (4.0 g, 13 mmol) was dissolved in 200 ml of *o*-xylene under Ar. To this solution were added nitrobenzene (1.7 ml, 20 mmol) and then 1 ml of conc. HCl. The resulting solution was refluxed for 3 h. After concentration of the reaction mixture, the crude product was filtered. The product was then further purified by recrystallization from ethyl acetate to afford **6a** (2.6 g, 62%), m.p. 295°C. – IR (KBr): $\tilde{\nu} = 2970-2867$ cm^{-1}, 1662, 1602, 1364, 1340, 1318, 1299, 1288, 1255, 1178, 843, 732, 609. – ^{1}H NMR ($CDCl_3$): $\delta = 8.12$ (d, $J = 1.9$ Hz, 2H; 5-, 5′-H), 7.84 – 7.79 (m, 4H; 3-, 3′-, 4-, 4′-H), 7.72 (d, $J = 8.3$ Hz, 2H; 8-, 8′-H), 7.27 (dd, $J = 8.3/1.9$ Hz, 2H; 7-, 7′-H), 5.98 (d, $J = 1.9$ Hz, 2H; 1-, 1′-H), 4.74 (s, 2H; 9-, 9′-H), 1.42 [s, 16H; $C(CH_3)_3$], 1.07 [s, 18H; $C(CH_3)_3$]. – ^{13}C NMR ($CDCl_3$): $\delta = 183.2$ (CO), 154.3, 150.7, 140.4, 137.5, 134.0, 132.6, 131.0, 128.3, 126.7, 125.5, 125.3, 123.7, 54.0 (C-9, -9′), 35.0 [$C(CH_3)_3$], 34.8 [$C(CH_3)_3$], 31.4 [$C(CH_3)_3$], 30.7 [$C(CH_3)_3$]. – MS (70 eV), m/z (%): 610 (30) [M^+], 305 (100) [M^+ – anthronyl], 290 (23) [M^+ – anthronyl – CH_3], 275 (15) [M^+ – anthronyl – 2 CH_3], 57 (11) [$C(CH_3)_3{}^+$].

$C_{44}H_{50}O_2$ (610.9) Calcd. C 86.51 H 8.25
Found C 86.23 H 8.12

2,2′,3,3′-Tetrahexyl-9,9′-bianthronyl (**6b**): Anthrone derivative **5b** (4.0 g, 13 mmol) was dissolved in 150 ml of *o*-xylene under Ar. To the solution were added nitrobenzene (1.7 ml, 20 mmol) and 1 ml of conc. HCl. The reaction mixture was then refluxed for 2 h. After removal of the solvent, the residue was chromatographed (CH_2Cl_2/petroleum ether, 1:1). The crude product was purified by recrystallization from acetic acid to yield **6b** (2.77 g, 55%). – IR (KBr): $\tilde{\nu} = 3012-2823$ cm^{-1}, 1632, 1574, 1409, 1317, 1288, 1203, 1120, 938, 806, 760. – ^{1}H NMR ($CDCl_3$): $\delta = 8.05-7.93$ (m, 2H; 5-, 5′-H), 7.75, 7.68 (2s, 2H; 4-, 4′-H), 7.53 – 7.33 (m, 4H; 6-, 6′-, 7-, 7′-H), 7.14 – 7.06, 6.88 – 6.70 (2m, 2H; 8-, 8′-H), 6.61, 6.32 (2s, 2H; 1-, 1′-H), 4.67, 4.62 (2s, 2H; 9-, 9′-H), 2.76 – 2.36 (m, 8H; benzylic CH_2), 1.75 – 1.25 (m, 32H; CH_2), 1.05 – 0.90 (m, 12H; CH_3). – MS (70 eV), m/z (%): 723 (15) [M^+ + 1], 722 (22) [M^+], 362 (82) [M^+ + 1 – anthronyl], 361 (100) [M^+ – anthronyl].

$C_{52}H_{66}O_2$ (723.1) Calcd. C 86.38 H 9.20
Found C 86.09 H 9.09

2,2′,6,6′-Tetra-tert-butyl-9,9′-bianthronylidene (**7a**): A solution of **6a** (1.5 g, 2.5 mmol) and KOH (9 g) in 300 ml of anhydrous ethanol was refluxed under Ar for 3 h. The color of the solution changed from yellow to bright red. To the cold reaction mixture was added conc. HCl dropwise until the solution turned yellow. After the addition was complete, the mixture was filtered in an inert atmosphere and the solvent removed. The residue was dissolved in 150 ml of acetone and 1,4-benzoquinone (0.80 g, 10 mmol) was added in portions, while the reaction mixture was kept in an inert atmosphere and in the dark. The crude solid was washed with cold acetone and chromatographed (CH_2Cl_2/petroleum ether, 1:1) in the dark to give 1.16 g (76%) of a mixture of (*E*)/(*Z*) isomers. The (*E*) isomer could be isolated by fractional crystallization from ethyl acetate to afford 1.16 of **7a** [83%, related to the (*E*)/(*Z*) mixture], m.p. > 310°C. – IR (KBr): $\tilde{\nu} = 2976-2865$ cm^{-1}, 1671, 1600, 1478, 1415, 1363, 1289, 1279, 1250, 1180, 854, 801, 612. – ^{1}H NMR ($CDCl_3$): $\delta = 8.13$ (d, $J = 2.1$ Hz, 2H; 2H; 5-, 5′-H), 8.04 (d, $J = 8.1$ Hz, 2H; 4-, 4′-H), 7.41 (dd, $J = 8.1/1.9$ Hz, 2H; 3-, 3′-H), 7.18 (dd, $J = 8.1/2.1$ Hz, 2H; 7-, 7′-H), 7.14 (d, $J = 1.9$ Hz, 2H, 1-, 1′-H), 7.00 (d, $J = 8.2$ Hz, 2H; 8-, 8′-H), 1.33 [s, 18H; $C(CH_3)_3$], 1.07 [s, 18H; $C(CH_3)_3$]. – ^{13}C NMR ($CDCl_3$): $\delta = 187.1$ (CO), 153.2, 151.3, 139.5, 137.0, 134.5, 132.2, 132.0, 129.3, 127.6, 127.0, 126.9, 125.4, 123.5, 35.0 [$C(CH_3)_3$], 34.9 [$C(CH_3)_3$], 31.2 [$C(CH_3)_3$], 30.8 [$C(CH_3)_3$]. – MS (70 eV), m/z (%): 609 (46) [M^+ + 1], 608 (100) [M^+], 593 (18) [M^+ – CH_3], 304 (15) [$M^+/2$].

$C_{44}H_{48}O_2$ (608.9) Calcd. C 86.80 H 7.95
Found C 86.69 H 7.88

2,2′,3,3′-Tetrahexyl-9,9′-bianthronylidene (**7b**). By analogy with **7a**, compound **6b** (1.5 g, 2.1 mmol) was treated with KOH (8 g) in 200 ml anhydrous ethanol, and then the mixture was allowed to react with 1,4-benzoquinone (0.80 g, 10 mmol) in 100 ml of acetone. After removal of the solvent, the residue was chromatographed in the dark, first with CH_2Cl_2, subsequently with CH_2Cl_2/petroleum ether (1:5) to give **7b** [(*E*)/(*Z*) mixture, 1.04 g, 69%], m.p. 102 – 103°C. The (*E*) and (*Z*) isomers could be enriched chromatographically in the dark (petroleum ether/CH_2Cl_2, 8:1). – IR (KBr): $\tilde{\nu} = 2980-2842$ cm^{-1}, 1662, 1595, 1288, 1262, 1099, 1020, 801. – ^{1}H NMR ($CDCl_3$): $\delta = 8.10-8.02$ (m, 2H; 5-, 5′-H), 7.89, 7.88 [2s, (1:1), 2H; 4-, 4′-H], 7.41 – 7.30 (m, 2H; 6-, 6′-H), 7.16 – 7.02 (m, 4H; 7-, 7′-, 8-, 8′-H), 6.86, 6.84 [2s, (1:1), 2H; 1-, 1′-], 2.72 – 2.55 (m, 4H; benzylic CH_2), 2.43 – 2.20 (m, 4H; benzylic CH_2), 1.72 – 1.57 (m, 4H; CH_2), 1.48 – 1.15 (m, 28H, CH_2), .098 – 0.82 (m, 12H, CH_3). – MS (70 eV), m/z (%): 721 (58) [M^+ + 1], 720 (100) [M^+], 361 (18) [$M^+/2$ + 1], 360 (34) [$M^+/2$].

$C_{52}H_{64}O_2$ (721.1) Calcd. C 86.62 H 8.95
Found C 86.56 H 8.76

2,5,10,13-Tetra-tert-butylhelianthrone (**8a**) {2,5,10,13-Tetra-*tert*-butyldibenzo[*a,o*]-perylene-7,16-dione}: A stirred solution of **7a** (0.50 g, 0.82 mmol) in 300 ml of acetic acid was irradiated with a 125-W high-pressure Hg lamp for 1 week. After removal of the solvent, the residue was chromatographed (CH_2Cl_2/petroleum ether, 2:1) to give 410 mg (83%) of **8a** (side product: **4a**), m.p. > 310°C. – IR (KBr): $\tilde{\nu} = 2963-2846$ cm^{-1}, 1658, 1598, 1432, 1288, 1249, 1232, 801, 668. – ^{1}H NMR ($CDCl_3$): $\delta = 8.93$ (d, $J = 2.0$ Hz, 2H; 3-, 4-H), 8.86 (d, $J = 2.0$ Hz, 2H; 1-, 6-H), 8.35 (d, $J = 8.4$ Hz, 2H; 8-, 15-H), 7.93 (d, $J = 1.9$ Hz, 2H; 11-, 12-H), 7.53 (dd, $J = 8.4/1.9$ Hz, 2H; 9-, 14-H), 1.60 [s, 18H, $C(CH_3)_3$], 1.11 [s, 18H, $C(CH_3)_3$]. – ^{13}C NMR ($CDCl_3$): $\delta = 185.1$ (q, CO), 155.0 (q), 151.2 (q), 137.8 (q), 130.9 (q), 130.5 (t), 129.8 (q), 129.2 (q), 129.1 (q), 128.9 (q), 127.9 (t), 127.1 (t), 126.9 (t), 124.6 (t), 36.0 [q, $C(CH_3)_3$], 35.5 [q, $C(CH_3)_3$], 31.9 [p, $C(CH_3)_3$], 31.2 [p, $C(CH_3)_3$]. – MS (70 eV), m/z (%): 607 (42) [M^+ + 1], 606 (100) [M^+], 592 (11) [M^+ + 1 – CH_3], 591 (35) [M^+ – CH_3], 303 (28) [$M^+/2$], 189 (36) [$M^+/2$ – 2 $C(CH_3)_3$], 57 (42) [$C(CH_3)_3{}^+$].

$C_{44}H_{46}O_2$ (606.9) Calcd. C 87.09 H 7.64
Found C 86.96 H 7.47

2,3,9,10-Tetrahexylmesonaphthobianthrone (**9**) {2,3,9,10-Tetrahexylphenanthro-[1,10,9,8-arqpo]perylene-7,14-dione} *and 9,10,13,14-Tetrahexylhelianthrone* (**8c**) {9,10,13,14-Tetrahexyldibenzo[*a,o*]-perylene-7,16-dione}: A stirred solution of **7b** (1.0 g, 1.4 mmol) in 300 ml of acetic acid was irradiated for 4 d. After removal of the solvent, the residue was chromatographed (CH_2Cl_2/petroleum ether, 1:3) to give **9** (0.76 g, 76%) and **8c** (0.10 g, 10%) (side product: **4b**).

9: IR (KBr): $\tilde{\nu} = 2957-2853$ cm^{-1}, 1650, 1581, 1408, 1334, 1274, 1262, 1099, 1082, 1044, 1019, 802, 760. – ^{1}H NMR ($CDCl_3$): $\delta = 8.20$ (d, $J = 7.7$ Hz, 2H; 4-, 11-H), 8.16 (d, $J = 7.7$ Hz, 2H; 6-, 13-H), 8.13 (s, 2H; 1-, 8-H), 7.38 (t, $J = 7.7$ Hz, 2H; 5-, 12-H), 2.95 – 2.68 (m, 8H; benzylic CH_2), 1.92 – 1.68 (m, 8H; CH_2), 1.60 – 1.35 (m, 24H; CH_2), 1.08 – 0.88 (m, 12H; CH_3). – ^{13}C NMR ($CDCl_3$): $\delta = 182.0$ (q, CO), 144.4 (q), 143.4 (q), 132.9 (t), 129.7 (q), 129.6 (t), 129.2 (q), 128.6 (q), 127.6 (q), 127.5 (t), 126.5 (t), 126.0 (q), 125.9 (t), 121.2 (q), 34.0 (s, CH_2), 33.6 (s, CH_2), 32.3 (s, CH_2), 32.2 (s, CH_2), 31.9 (s, CH_2), 30.7 (s, CH_2), 30.6 (s, CH_2), 30.4 (s, CH_2), 30.0 (s, CH_2), 23.2 (s, CH_2), 14.5 (p, CH_3), 14.3 (p, CH_3). – MS (70 eV), m/z (%): 717 (76) [M^+ + 1], 716 (100) [M^+], 659 (14) [M^+ – C_4H_9], 85 (8) [$C_6H_{13}{}^+$], 57 (12) [$C_4H_9{}^+$].

$C_{52}H_{60}O_2$ (717.0) Calcd. C 87.10 H 8.43
Found C 86.86 H 8.55

8c: IR (KBr): $\tilde{\nu}$ = 2956−2855 cm^{-1}, 1651, 1604, 1582, 1466, 1458, 1404, 1333, 1287, 768. − ^{1}H NMR (CDCl$_3$): δ = 8.89 (d, 8.1 Hz, 2H; 3-, 4-H), 8.73 (d, *J* = 7.53 Hz, 2H; 1-, 6-H), 8.17 (s, 2H; 8-, 15-H), 7.89 (t, *J* = 7.7 Hz, 2H; 2-, 5-H), 7.72 (s, 2H; 11-, 12-H), 2.68 (t, *J* = 7.6 Hz, 4H; benzylic CH$_2$), 2.36 (m, 4H; benzylic CH$_2$), 1.67−1.09 (m, 32H, CH$_2$), 0.92−0.82 (m, 12H, CH$_3$). − ^{13}C NMR (CDCl$_3$): δ = 145.2 (q), 143.2 (q), 135.3 (q), 135.2 (q), 133.7 (t), 130.6 (q), 130.1 (q), 129.2 (q), 128.9 (q), 128.8 (t), 128.5 (t), 127.7 (t), 127.5 (t), 33.2 (s, CH$_2$), 33.1 (s, CH$_2$), 32.2 (s, CH$_2$), 32.1 (s, CH$_2$), 31.3 (s, CH$_2$), 30.9 (s, CH$_2$), 30.1 (s, CH$_2$), 30.0 (s, CH$_2$), 23.1 (s, CH$_2$), 23.0 (s, CH$_2$), 14.6 (p, CH$_3$). − FD-MS, *m/z* (%): 718.4 (100) [M$^+$].

$C_{52}H_{62}O_2$ (719.1) Calcd. C 86.86 H 8.69
Found C 86.77 H 8.74

General Procedure for the Preparation of **10, 11a**, *and* **11b**: To a degassed solution (or suspension) of diketone in [D$_5$]nitrobenzene was added dropwise under Ar conc. D$_2$SO$_4$ until a color change was observed.

2,5,10,13-Tetra-tert-butyl-7,16-dihydroxyhelianthrene Dication (**10**): Green solution. − ^{1}H NMR ([D$_5$]nitrobenzene/D$_2$SO$_4$): δ = 9.76 (s, 2H; 3-, 4-H), 9.60 (s, 2H; 1-, 6-H), 8.98 (d, *J* = 8.8 Hz, 2H; 8-, 15-H), 8.74 (s, 2H; 11-, 12-H), 8.21 (dd, *J* = 8.8/1.7 Hz, 2H; 9-, 14-H), 1.87 [s, 18H; C(CH$_3$)$_3$], 1.38 [s, 18H; C(CH$_3$)$_3$]. − ^{13}C NMR ([D$_5$]nitrobenzene/D$_2$SO$_4$): δ = 185.7, 164.7, 156.6, 141.4, 136.0, 135.8, 133.9, 131.5, 131.3, 130.4, 128.4, 125.2, 124.2, 123.3, 37.3 [C-(CH$_3$)$_3$], 37.2 [C(CH$_3$)$_3$], 31.4 [C(CH$_3$)$_3$], 30.6 [C(CH$_3$)$_3$].

2,3,9,10-Tetrahexyl-7,14-dihydroxymesonaphthobisanthene Dication (**11a**): Dark violet solution. − ^{1}H NMR ([D$_5$]nitrobenzene/D$_2$SO$_4$): δ = 9.99 (d, *J* = 7.75 Hz, 2H; 4-, 11-H), 9.84 (d, *J* = 7.8 Hz, 2H; 6-, 13-H), 8.88 (t, *J* = 7.8 Hz, 2H; 5-, 12-H), 4.08−3.95 (m, 4H; benzylic CH$_2$), 3.59−3.42 (m, 4H, benzylic CH$_2$), 2.34−2.08 (m, 8H; CH$_2$), 1.88−1.65 (m, 8H; CH$_2$), 1.61−1.34 (m, 16H; CH$_2$),

Table 3. Positional parameters and isotropic temperature coefficients [Å^2] for the crystal structures of **7a1** and **7a2** (estimated standard deviations in units of the last significant digit in parentheses). The equivalent isotropic temperature coefficient was calculated as one third of the trace of the orthogonalized *U* matrix

Atom	x	y	z	U [Å2]
O1	0.5209(5)	0.2710(4)	0.3536(6)	5.8(2)
O31	0.7833(4)	0.4813(4)	0.2739(5)	5.3(2)
C10	0.5320(6)	0.1916(5)	0.3664(7)	3.6(2)
C10A	0.4419(6)	0.0840(5)	0.2783(6)	3.0(2)
C5	0.3756(6)	0.0690(5)	0.1563(7)	3.8(2)
C6	60.043(6)	-0.0318(5)	0.0645(7)	3.4(2)
C7	0.3065(6)	-0.1124(5)	0.1100(7)	3.6(2)
C8	0.3702(6)	-0.0988(5)	0.2331(7)	3.6(2)
C8A	0.4419(5)	0.0031(5)	0.3256(7)	3.0(2)
C9	0.5155(5)	0.0227(5)	0.4577(6)	2.8(2)
C9A	0.6329(6)	0.1069(5)	0.4908(6)	3.1(2)
C1	0.7347(6)	0.0984(5)	0.5547(7)	3.4(2)
C2	0.8440(6)	0.1799(5)	0.5861(7)	3.3(2)
C3	0.8444(6)	0.2651(5)	0.5488(7)	3.7(2)
C4	0.7444(6)	0.2733(5)	0.4821(7)	3.5(2)
C4A	0.6355(6)	0.1909(5)	0.4502(6)	3.1(2)
C15	0.2352(8)	-0.0473(6)	-0.0725(8)	5.5(3)
C16A	0.172(2)	-0.167(2)	-0.166(2)	5.5(5)
C16	0.245(1)	-0.167(2)	-0.166(2)	5.5(5)
C18A	0.338(2)	-0.006(2)	-0.139(2)	7.1(7)
C18	0.115(1)	-0.114(2)	-0.102(2)	11.8(7)
C17A	0.153(3)	0.019(2)	-0.053(3)	11(1)
C17	0.283(2)	-0.116(2)	-0.169(2)	14.9(9)
C11	0.9553(6)	0.1714(6)	0.6578(8)	4.3(2)
C13	1.0394(8)	0.187(1)	0.581(1)	11.4(5)
C14	1.0072(8)	0.2524(8)	0.794(1)	11.2(4)
C12	0.9372(9)	0.0678(8)	0.675(1)	11.9(5)
C40	0.8266(6)	0.4551(5)	0.1902(7)	3.3(2)
C40A	0.9377(5)	0.4396(5)	0.2235(6)	2.8(2)
C35	0.9766(6)	0.4204(5)	0.3372(7)	3.5(2)
C36	1.0729(6)	0.3954(5)	0.3637(7)	3.7(2)
C37	1.1318(5)	0.3826(5)	0.2702(7)	2.9(2)
C38	1.0912(5)	0.4034(5)	0.1585(6)	2.7(2)
C38A	1.0001(5)	0.4365(5)	0.1334(6)	2.6(2)
C39	0.9637(5)	0.4687(4)	0.0226(6)	2.4(2)
C39A	0.8339(5)	0.4289(5)	-0.0371(6)	2.6(2)
C31	0.7739(5)	0.3886(5)	-0.1715(7)	2.7(2)
C32	0.6537(5)	0.3557(5)	-0.2188(7)	3.1(2)
C33	0.5885(5)	0.3598(5)	-0.1343(7)	3.1(2)
C34	0.6477(6)	0.3959(5)	-0.0002(7)	3.7(2)
C34A	0.7683(5)	0.4283(5)	0.0479(6)	2.8(2)
C45	1.2351(6)	0.3514(5)	0.2974(7)	3.7(2)
C46	1.2064(7)	0.2528(6)	0.3338(9)	6.9(3)
C48	1.3326(7)	0.4405(7)	0.4190(9)	6.1(3)
C47	1.2830(6)	0.3367(6)	0.1834(8)	6.0(3)
C41	0.4544(6)	0.3222(6)	-0.1924(7)	3.9(2)
C43	0.398(1)	0.310(1)	-0.086(1)	4.4(4)
C43A	0.397(1)	0.343(1)	-0.091(1)	4.2(4)
C44	0.429(1)	0.4022(9)	-0.251(1)	3.2(3)
C44A	0.424(2)	0.377(1)	-0.290(2)	7.1(5)
C42	0.403(1)	0.219(1)	-0.311(1)	4.3(4)
C42A	0.406(1)	0.203(1)	-0.269(1)	3.9(3)

Table 4. Fractional atomic coordinates and isotropic temperature coefficients [Å^2] for the crystal structure of **8a** (see also caption of Table 3)

Atom	x/a	y/b	z/c	U(iso)
O1	0.9383(2)	0.2188(2)	1.0040(3)	0.0600
O2	1.3085(3)	0.0032(2)	1.6908(3)	0.0664
C16	0.9871(4)	0.2047(3)	1.1020(4)	0.0417
C16A	0.9438(3)	0.1850(2)	1.1887(4)	0.0374
C2	0.8081(3)	0.1785(3)	1.2455(4)	0.0428
C3A	0.9569(3)	0.1342(2)	1.3696(4)	0.0347
C3B	1.0005(3)	0.1547(2)	1.2915(4)	0.0343
C12B	1.0969(3)	0.1423(2)	1.3135(4)	0.0327
C12A	1.1416(3)	0.1844(2)	1.2483(4)	0.0346
C13	1.2777(3)	0.2462(2)	1.2388(4)	0.0411
C15A	1.0879(3)	0.2118(2)	1.1434(4)	0.0359
C11B	1.1424(3)	0.0945(2)	1.3945(4)	0.0346
C4B	1.1050(3)	0.0796(2)	1.4838(4)	0.0346
C4A	1.0153(3)	0.1027(2)	1.4739(4)	0.0370
C5	1.0463(3)	0.0742(2)	1.6747(4)	0.0388
C6A	1.1613(3)	0.0495(2)	1.5864(4)	0.0393
C7	1.2551(4)	0.0245(3)	1.6004(5)	0.0486
C7A	1.2813(3)	0.0233(3)	1.4959(4)	0.0451
C10	1.3237(3)	0.0090(3)	1.2964(4)	0.0462
C11A	1.2263(3)	0.0569(2)	1.3972(4)	0.0379
C17	0.7066(3)	0.1963(3)	1.2192(5)	0.0525
C21	1.3756(3)	0.2717(3)	1.2980(5)	0.0500
C18′	1.0220(4)	0.0804(3)	1.7831(4)	0.0447
C22	1.3422(4)	-0.0006(3)	1.1847(5)	0.0554
C1	0.8516(3)	0.1947(3)	1.1658(4)	0.0435
C3	0.8626(3)	0.1475(3)	1.3434(4)	0.0418
C12	1.2341(3)	0.2035(2)	1.2942(4)	0.0397
C14	1.2235(4)	0.2684(3)	1.1303(4)	0.0448
C15	1.1317(3)	0.2519(2)	1.0830(4)	0.0412
C4	0.9886(4)	0.0990(2)	1.5728(4)	0.0414
C6	1.1317(3)	0.0481(2)	1.6804(4)	0.0420
C8	1.3583(4)	-0.0150(3)	1.4955(5)	0.0565
C9	1.3795(4)	-0.0212(3)	1.3970(5)	0.0589
C11	1.2481(3)	0.0474(2)	1.2975(4)	0.0406
C18	0.6767(4)	0.1845(4)	1.3218(6)	0.0923
C19	0.6891(5)	0.2710(3)	1.1823(7)	0.0882
C20	0.6466(4)	0.1504(4)	1.1261(6)	0.0983
C22	1.3707(5)	0.3370(3)	1.3638(6)	0.0890
C23	1.4356(4)	0.2183(3)	1.3794(5)	0.0776
C24	1.4238(4)	0.2904(4)	1.2144(5)	0.0828
C19′	1.0286(4)	0.0095(3)	1.8400(4)	0.0642
C20′	0.9256(4)	0.1095(3)	1.7620(5)	0.0730
C21′	1.0928(4)	0.1299(3)	1.8640(5)	0.0668
C23′	1.4221(8)	-0.0490(6)	1.1951(9)	0.0686 [a]
C24′	1.2547(7)	-0.0343(7)	1.0970(9)	0.0819 [a]
C25′	1.362(1)	0.0677(6)	1.143(1)	0.0903 [a]
C23"	1.288(2)	0.048(2)	1.091(2)	0.0849 [a]
C24"	1.328(3)	-0.074(1)	1.153(3)	0.1349 [a]
C25"	1.449(2)	0.016(2)	1.208(2)	0.1435 [a]

[a] Population: C23′–C25′ 0.69(2), C23″–C25″ 0.31(2).

1.03–0.89 (m, 12H; CH$_3$). – ^{13}C NMR ([D$_5$]nitrobenzene/D$_2$SO$_4$): δ = 184.1, 162.6, 151.4, 144.2, 134.2, 134.1, 132.6, 132.5, 131.2, 128.8, 128.0, 126.2, 125.4, 122.0, 38.4 (CH$_2$), 35.4 (CH$_2$), 33.3 (CH$_2$), 33.1 (CH$_2$), 32.9 (CH$_2$), 32.6 (CH$_2$), 31.2 (CH$_2$), 31.0 (CH$_2$), 24.2 (CH$_2$), 23.9 (CH$_2$), 15.4 (CH$_3$).

7,14-Dihydroxymesonaphthobisanthene Dication (**11b**): Dark red solution. – ^{1}H NMR ([D$_5$]nitrobenzene/D$_2$SO$_4$): δ = 10.30 (d, J = 8.1 Hz, 4H; 3-, 4-, 10-, 11-H), 9.98 (d, J = 8.1 Hz, 4H; 1-, 6-, 8-, 13-H), 9.01 (t, J = 8.1 Hz, 4H; 2-, 5-, 9-, 12-H).

X-Ray Crystal Structure Analysis[28]: Enraf-Nonius CAD4 diffractometer, graphite-monochromated Cu-K_α radiation (λ [Å] = 1.5405). The structures were solved by direct methods (SIR).

7a: Yellow single crystal (0.45 × 0.25 × 0.30 mm), space group $P\bar{1}$, $a = 12.776(6)$, $b = 14.329(9)$, $c = 11.117(4)$ Å, $\alpha = 104.97(6)$, $\beta = 103.15(4)$, $\gamma = 107.48(4)°$, $V = 1769$ Å^3, $Z = 2$, ϱ(calcd.) = 1.143 g cm^{-1}, $\mu = 4.88$ cm^{-1}, 3803 reflexions were measured (observed: 2199, $I > 3\sigma(I)$, 3443 unique). The asymmetric unit cell consisted of two half molecules, each of which being positioned in an inversion center. Both molecules had one of the *tert*-butyl groups in two conformations with statistical distribution. Hydrogen atoms were placed into their computed positions by using known bonding geometries and were refined in the riding mode with isotropic temperature coefficients. During the last full-matrix least-squares refinement anisotropic temperature coefficients were calculated for all non-hydrogen atoms exept for the disordered *tert*-butyl groups. The R factors were $R = 0.075$ and $R_w = 0.0075$.

8a: Orange single crystal (0.6 × 0.25 × 0.2 mm), space group $P2_1/c$, $a = 15.335(2)$, $b = 19.408(2)$, $c = 12.543(2)$ Å, $\beta = 110.017(13)°$, $V = 3507.5$ Å^3, $Z = 4$, ϱ(calcd.) = 1.141 gcm^{-3}, $\mu = 4.92$ cm^{-1}. 4424 reflexions were measured of which 2955 with $I > 3\sigma(I)$ were considered. Hydrogen atoms were located in difference Fourier maps except for one of the *tert*-butyl groups (C21′-C24′), which was found to adopt two orientations. The hydrogen atoms of these groups were placed by using the molecular geometry. All other hydrogen atoms were refined in the riding mode with isotropic temperature factors. The population parameters of the disordered *tert*-butyl groups were included in the refinement. Carbon and oxygen atoms were refined with anisotropic temperature factors and units of weight were used throughout the refinement. An empirical absorption correction was applied. The final R factors were $R = 0.044$ and $R_w = 0.045$.

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[1] The nomenclature of compound **1** differs throughout the literature. The most common name is bianthrone, which is 10-[10-oxo-9(10*H*)-anthracenylidene]-9(10*H*)anthracenone. The name 9,9′-bianthronylidene is also used.

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