Electronic Supplemental Information (ESI) for Manuscript Chemical Communications

Remote Substituent Effects on the Photooxygenation of 9,10-Diarylanthracenes: Strong Evidence for Polar Intermediates

Werner Fudickar and Torsten Linker*

Experimental Details:

Diphenylanthracene **1a** and tetraphenylcyclopentadienone (tetracyclone) were purchased from Aldrich in the highest available qualities. All other reagents were purchased from Aldrich and used without further purifications. Solvents were dried according to standard procedures. Column chromatography was performed using Merck silica gel 60. TLC was performed on silica gel coated aluminium foils (0.25 mm thick, 60 F_{254} , Merck, Germany). ¹H and ¹³C NMR spectra were recorded on a Bruker AC 300 spectrometer at 300 MHz and 75 MHz, respectively. Deuterochloroform was used as internal standard ($\delta = 7.26$ and 77.0 ppm, respectively). IR spectra were recorded on a Perkin Elmer 16 PC FT-IR. UV-vis spectra were measured on a Unicam UV3 instrument. Cyclic voltammetry was carried out using an Amel 7050 potentiostat connected to a three electrode electrochemical cell. All measurements were performed in dichloromethane with tetrabutylammonium hexafluorophosphate as conducting salt. The reference electrode was a calomel electrode, a platinum wire was used a counter electrode and a platinum disc electrode (1 mm diameter) served as working electrode. Potentials were corrected against ferrocene oxidation ($E_a = 0.51$ V vs SCE). X-ray structures were obtained from a STOE Imaging Plate Diffraction System (IPDS II) at 210 K using graphite-monochromated Mo-K α radiation (λ =0.71073 Å).

Synthesis

The synthesis of anthracenes **1b-d**, with substituents in *para* position, has been previously reported by a similar procedure.¹

General procedure for the synthesis of the diarylanthracenes 1b-h by Suzuki coupling.

In a 100 mL three necked round bottom flask, the boronic acid (2.5 eq, 7.35 mmol), 9,10-dibromoanthracene (990 mg, 1 eq, 2.94 mmol) and K_2CO_3 (3.28 g, 23 mmol) were dissolved in toluene (40 mL), ethanol (8 mL) and water (16 mL). Argon was bubbled vigorously through the solution for 5 min followed by the addition of tetrakis-(triphenylphosphine)-palladium (254 mg, 0.2 mmol), after which argon was bubbled again through the solution for another 5 min. The solution was then refluxed for 24 hours. The work-up procedures varied and are described for each compound separately.

9,10-Bis-(4-methoxyphenyl)-anthracene 1b. A precipitate formed after the coupling reaction which was filtered off affording **1b** after crystallization from dichloromethane/cyclohexane (870 mg, 76 % yield) as white needles. Mp 288 °C (Lit. 280-281 °C).¹



¹H NMR (300 MHz, CDCl₃): δ = 3.97 (s, 6H, Me), 7.16 (d, *J*=8.6 Hz, 4H, 17-H, 19-H), 7.31-7.36 (m, 4 H, 1-H, 4-H, 5-H, 8-H), 7.41 (d, *J*=8.6 Hz, 4H, 16-H, 20-H), 7.72-7.78 (m, 4 H, 2-H, 3-H, 6-H, 7-H). ¹³C NMR (75 MHz, CDCl₃): δ = 55.7 (q, Me), 114.2 (d, C-17, C-19), 125.2 (d, C-2, C-3, C-6, C-7), 127.4 (d, C-1, C-4, C-5, C-8), 130.6 (s, C-11, C-12, C-13, C-14), 131.4 (s, C-9, C-10), 131.5 (s, C-15), 132.7 (d, C-16, C-20), 159.4 (s, C-18). UV/vis (CHCl₃, 0.98*10⁻⁴ M): λ_{max} (nm, ε)= 398 (9217), 377 (9867), 359 (6051), 242 (2734).

9,10-Bis-(4-methylphenyl)-anthracene 1c. A precipitate formed after the coupling reaction which was filtered off affording **1c** after crystallization from dichloromethane/cyclohexane (860 mg, 81 % yield) as white powder. Mp 282 °C (Lit. 280-281 °C).¹



¹H NMR (300 MHz, CDCl₃): δ = 2.56 (s, 6H, Me), 7.31-7.35 (m, 4H, 1-H, 4-H, 5-H, 8-H), 7.37-.744 (m, 8H, H-16, H-17, H-18, H-19), 7.72-7.76 (m, 4H, 2-H, 3-H, 6-H, 7-H). ¹³C NMR (75 MHz, CDCl₃): δ = 21.7 (q, Me), 125.2 (d, C-2, C-3, C-6, C-7), 127.4 (d, C-1, C-4, C-5, C-8), 129.4 (d, C-17, C-19), 130.4 (s, C-11, C-12, C-13, C-14), 131.6 (d, C-16, C-20), 136.4 (s, C-9, C-10), 137.4 (s, C-15). UV/vis (CHCl₃, 1.5*10⁻⁴ M): λ_{max} (nm, ϵ)= 397 (10003), 376 (10760), 357 (6646).

9,10-Bis-(4-cyanophenyl)-anthracene 1d. A precipitate formed after the coupling reaction which was filtered off affording **1d** as white powder (820 mg, 74 % yield). Mp 230 °C (lit 226 °C).¹



¹H NMR (300 MHz, CDCl₃): δ = 7.39-7.43 (m, 4H, 1-H, 4-H, 5-H, 8-H), 7.55-7.60 (m, 4H, 2-H, 3-H, 6-H, 7-H), 7.62 (d, *J*=8,2 Hz, 4H, H-16, H-20), 7.94 (d, *J*=8,2 Hz, 4H, H-17, H-19). ¹³C NMR (75 MHz, CDCl₃): δ = 112.3 (s, C-18), 119.1 (s, CN), 126.3 (d, C-2, C-3, C-6, C-7), 126.7 (d, , C-1, C-4, C-5, C-8), 129.7 (s, C-11, C-12, C-13, C-14), 132.5 (d, C-16, C-20), 132.7 (d, C-17, C-19). UV/vis (CHCl₃, 1.47*10⁻⁴ M): λ_{max} (nm, ϵ)= 395 (13292), 375 (14204), 356 (9231), 338 (4340).

cis-9,10-Bis-(2-methoxyphenyl)-anthracene 1e. A solid was formed after cooling, which was separated by filtration and assigned to the *trans* isomer (460 mg, 40 % yield). It was not further used within this work. The filtrate (a mixture of the *cis* isomer and the mono coupling product) was washed with brine, dried over sodium sulfate and the solvent was removed under reduced pressure. After chromatography (hexanes/ethyl acetate 10:1) a white powder was obtained, which was assigned to the *cis* isomer (415 mg, 36% yield). Mp 308 °C. The overall yield of both isomers was 880 mg, (76 %).



¹H NMR (300 MHz, CDCl₃): δ = 3.67 (s, 6 H, Me), 7.18-7.24 (m, 4 H, 17-H, 18-H), 7.32-7.36 (m, 6 H, 2-H, 3-H, 6-H, 7-H, 20-H), 7.57 (dt, *J* = 7.4, 1.8 Hz, 2 H, 19-H), 7.67-7.70 (m, 4 H, 1-H, 4-H, 5-H, 8-H). ¹³C NMR (75 MHz, CDCl₃): δ = 55.6 (q, Me), 111.3 (d, C-17), 120.6 (d, C-18), 124.7 (d, C-2, C-3, C-6, C-7), 126.9 (d, C-1, C-4, C-5, C-8), 127.7 (s, C-11, C-12, C-13, C-14), 129.2, 130.1 (2 d, C-19, C-20), 133.0, 133.7 (2 s, C-9, C-10, C-15), 158.1 (s, C-16). IR (cm⁻¹, KBr): $\tilde{\nu}$ = 3059, 2933, 2833, 1597, 1577, 1494, 1459, 1432, 1274, 1243, 1106, 1046, 1022, 942, 752, 665. Elemental analysis calcd (%) for C₂₈H₂₂O₂ (390.2): C 86.13, H 5.68; found: C 85.73, H 5.51. UV/vis (CHCl₃, 0.94*10⁻⁴ M): λ_{max} (nm, ε)= 396 (10190), 376 (10500), 357 (6363), 340 (2875).

cis-9,10-Bis(2-methylphenyl)-anthracene 1f. The purification and isolation was carried out as described for compound 1e. The yield of the *trans* isomer was 340 mg (33 %). Column chromatography (hexanes/ethyl acetate 50:1) of the filtrate afforded the *cis* isomer in the last fraction (yield 310 mg, 30 %) as white needles after crystallization from dichloromethane/cyclohexane. Mp 330 °C.

The overall yield of both isomers was 650 mg (63%).



¹H NMR (300 MHz, CDCl₃): $\delta = 1.95$ (s, 6 H, Me), 7.4-7.5 (m, 6 H, 2-H, 3-H, 6-H, 7-H, 17-H), 7.32-7.3 (m, 6 H, 18-H, 19-H, 20-H), 7.56-7.61 (m, 4 H, 1-H, 4-H, 5-H, 8-H). ¹³C NMR (75 MHz, CDCl₃): $\delta = 19.7$ (q, Me), 125.1 (d, C-2, C-3, C-6, C-7), 125.8 (s, C-18), 126.7 (d, C-1, C-4, C-5, C-8), 127.8 (s, C-11, C-12, C-13, C-14), 129.7, 130.0, 131.3 (3 d, C-17, C-19, C-20), 136.2, 137.8, 138.4 (3 s, C-9, C-10, C-15, C-16). mp=330 °C. IR (cm⁻¹, KBr): $\tilde{V} = 3056$, 3012, 2918, 1489, 1438, 1382, 941, 771, 753. Elemental analysis calcd (%) for C₂₈H₂₂ (358.3): C 93.81, H 6.19; found: C 93.61, H 6.27. UV/vis (CHCl₃, 0.8*10⁻⁴ M): λ_{max} (nm, ε)= 396 (12028), 375 (13225), 357 (7950), 339 (3500). Aggregation at higher concentration observed.

cis-9,10-Bis(2-cyanophenyl)-anthracene 1g. Application of the common conditions for Suzuki coupling from 9,10-dibromoanthracene and 2-cyanophenylboronic acid failed. A modified procedure starting from the neopentylborate was carried out by heating 2-cyanophenylneopentylborate (3.16 g, 10 eq, 14.7 mmol), 9,10-dibromoanthracene (500 mg, 1 eq, 1,47 mmol) and K₂CO₃ (1.6 g, 11 mmol) in toluene (40 mL), ethanol (8 mL) and water (16 mL) under argon atmosphere at reflux for 24 hrs. After cooling a solid has formed which was separated by filtration. This solid was assigned to the insoluble *trans* isomer (150 mg, 30 % yield). The filtrate (a mixture of the *cis* isomer and the mono coupling product) was washed with brine, dried over sodium sulfate and the solvent was removed under reduced pressure. The residue was subjected to column chromatography (hexanes/ethyl acetate 3:1) affording the *cis* isomer in the last fraction (140 mg, 26% yield). Recyrstallization from dichloromethane/cyclohexane afforded white needles, which were analyzed by X-ray crystal structure analysis. The overall yield was 290 mg (56 %). Mp 315 °C.



¹H NMR (300 MHz, CDCl₃): δ = 7.40-7.46 (m, 4 H, 2-H, 3-H, 6-H, 7-H), 7.50-7.56 (m, 4 H, 4 H, 1-H, 4-H, 5-H, 8-H), 7,59 (d, *J* = 7.7 Hz, 2 H, 20-H), 7,70 (dd, *J* = 7.6 Hz, 7.7 Hz, 2 H, 18-H), 7.85 (dd, *J* = 7.6 Hz, 7.7 Hz, 2H, 19-H), 7,99 (d, *J* = 7.6 Hz, 2H, 17-H). ¹³C NMR (75 MHz, CDCl₃): δ = 115.8 (s, C-16), 117.5 (s, CN), 126.4 (d, C-2, C-3, C-6, C-7), 126.6 (d, C-1, C-4, C-5, C-8), 128.9 (d, C-20), 130.2 (s, C-11, C-12, C-13, C-14), 132.8 (d, d) = 7.6 Hz, 7.7 Hz, 2H, 12.8 (d) = 7.6 Hz, 7.7 Hz, 12.8 (d) = 7.6 Hz, 12.8 Hz, 12.8

C-18), 132.9 (d, C-19), 133.7 (d, C-17), 134.2 (s, C-10), 143.1 (s, C-15). Elemental analysis calcd (%) for $C_{28}H_{16}N_2$ (380.3): C 88.42, H 4.21, N 7.36; found: C 88.01, H 4.22, N 7.32. UV/vis (CHCl₃, 1.21*10⁻⁴ M): λ_{max} (nm, ϵ)= 394 (11962), 373 (12191), 355 (7380), 338 (3348).

cis-9,10-Bis-(2,4-dimethoxyphenyl)-anthracene 1h. The work-up was carried out as described for compound 1e. The yield of the *trans* isomer was 385 mg (32 %). After chromatography of the filtrate (hexanes/ethyl acetate 10:1) a white powder was obtained, which was recrystallized from dichloromethane/cyclohexane affording white needles (375 mg, 29 % yield). Mp 309 °C.

The overall yield was 760 mg (61 %).



¹H NMR (300 MHz, CDCl₃): δ = 3.64 (s, 6H, *ortho*MeO), 3.97 (s, 6H, *para*MeO), 6.73-6.78 (m, 4H, 17-H, 20-H), 7.22 (d, *J*=8.1 Hz, 2H, 19-H), 7.31-7.36 (m, 4H, 1-H, 4-H, 5-H, 8-H), 7.69-7.74 (m, 4H, 2-H, 3-H, 6-H, 7-H). ¹³C NMR (75 MHz, CDCl₃): δ = 55.8 (q, *para*MeO), 56.0 (q, *ortho*MeO), 99.4 (d, C-17), 105.0 (d, C-19), 120.6 (s, C-15), 125.0 (d, C-2, C-3, C-6, C-7), 127.4 (C-1, C-4, C-5, C-8), 131.0 (s, C-11, C-12, C-13, C-14), 133.7 (d, C-20), 133.9 (s, C-9, C-10), 159.5 (s, C-16), 161.2 (C-18). Elemental analysis calcd (%) for C₃₀H₂₆O₄ (450.4): C 79.92, H 5.77; found: C 79.83, H 5.82. UV/vis (CHCl₃, 1.06*10⁻⁴ M): λ_{max} (nm, ε)= 396 (11943), 375 (12452), 357 (7481).

Sensitized photooxidation of the anthracenes. The photooxidations were carried out in 20 mL glass tubes sealed with a rubber stopper, where the anthracene (0.5 mmol) and a catalytic amount of methylene blue were dissolved in CH_2Cl_2 (10 mL). The tube was irradiated with two sodium lamps (200 W) at 0 °C while a slow steady stream of oxygen was maintained throughout the irradiation. The course of the photooxidation was monitored by TLC and stopped after complete conversion. The solvent was removed under vacuum at room temperature and the crude product was purified by column chromatography.

9,10-Bis-(4-methoxyphenyl)-9,10-dihydro-9,10-epidioxidoanthracene 2b. Yield 192 mg (93 %) after chromatography (cyclohexane/ethyl acetate 3:1).



¹H NMR (300 MHz, CDCl₃): δ = 3.59 (s, 6H, Me), 7.16 (d, *J*=8.9 Hz, 4H, 16-H, 20-H), 7.18-7.22 (m, 8H, 1-H, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H), 7.63 (d, *J*=8.9 Hz, 4H, 17-H, 19-H). ¹³C NMR (75 MHz, CDCl₃): δ = 55.7 (q, Me), 99.7 (s, C-9, C-10), 114.1 (d, C-17, C-19), 123.7 (d, C-16, C-20), 125.4 (s, C-15), 127.7 (d, C-1, C-4, C-5, C-8), 129.0 (d, C-2, C-3, C-6, C-7), 140.9 (s, C-11, C-12, C-13, C-14), 159.7 (s, C-18). HRMS (ESI+) calcd for C₂₈H₂₂O₄: 423.1596; found: 423.1616.

9,10-Bis-(4-methyphenyl)-9,10-dihydro-9,10-epidioxidoanthracene 2c. Yield 192 mg (93 %) after chromatography (cyclohexane/ethyl acetate 5:1).



¹H NMR (300 MHz, CDCl₃): $\delta = 2.52$ (s, 6H, Me), 7.21 (br, m, 8H, 1-H, 2-H, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H), 7.45 (d, *J*=8.0 Hz, 4H, H-17, H-19), 7.59 (d, *J*=8.0 Hz, 4H, H-16, H-20). ¹³C NMR (75 MHz, CDCl₃): $\delta = 21.7$ (q, Me), 84.4 (s, C-9, C-10), 123.8 (d, C-16, C-20), 127.5 (d, C-1, C-4, C-5, C-8), 127.9 (d, C-17, C-19), 128.8 (s, C-15), 129.3 (d, C-2, C-3, C-6, C-7), 138.3 (C-18), 140.8 (s, C-11, C-12, C-13, C-14). HRMS (ESI+) calcd for C₂₈H₂₂O₂: 391.1674; found: 391.1681.

9,10-Bis-(4-cyanoyphenyl)-9,10-dihydro-9,10-epidioxidoanthracene 2d. Yield 185 mg (89 %) after chromatography (cyclohexane/ethyl acetate 3:1).



¹H NMR (300 MHz, CDCl₃): δ = 7.06-7.11 (m, 4H, 2-H, 3-H, 6-H, 7-H), 7.26-7.31 (m, 4H, 1-H, 4-H, 5-H, 8-H), 7.84 (d, *J*=8.4 Hz, 4H, 16-H, 20-H), 7.97 (d, *J*=8.4 Hz, 4H, 17-H, 19-H).). ¹³C NMR (75 MHz, CDCl₃): δ = 90.8 (s, C-9, C-10), 101.4 (s, C-18), 103.2 (s, CN), 123.6 (d, C-2, C-3, C-7, C-8), 125.4 (s, C-15), 128.7 (d, C-1, C-4, C-5, C-8), 128.8 (d, C-16, C-20), 132.6 (d, C-17, C-19), 139.4 (s, C-11, C-12, C-13, C-14).

9,10-Bis-(2-methoxyphenyl)-9,10-dihydro-9,10-epidioxidoanthracene 2e. Yield 190 mg (91 %) after chromatography (cyclohexane/ethyl acetate 3:1).



¹H NMR (300 MHz, CDCl₃): δ = 3.75 (s, 6 H, 21-H), 6.96-6.99 (m, 4 H, 2-H, 3-H, 6-H, 7-H), 7.15-7.18 (m, 4 H, 1-H, 4-H, 5-H, 8-H), 7.21 (d, *J* = 7.6 Hz, 4 H), 7.55 (dt, *J* = 7.5, 1.7 Hz, 2 H), 7.73 (dd, *J* = 7.4, 1.1 Hz, 2 H, 20-H). ¹³C NMR (75 MHz, CDCl₃): δ = 55.0 (q, Me), 83.4 (s, C-9, C-10), 111.0 (d, C-17), 121.5 (d), 122.9 (s, C-15), 123.6 (d, C-2, C-3, C-6, C-7), 126.8 (d, C-1, C-4, C-5, C-8), 127.4 (d), 129.7 (d), 137.7 (s, C-11, C-12, C-13, C-14), 156.2 (s, C-16). IR (cm⁻¹, KBr): $\tilde{\nu}$ = 3071, 2936, 2835, 1602, 1583, 1493, 1461, 1435, 1266, 1245, 1025, 910, 754, 662, 639. Elemental analysis calcd (%) for C₂₈H₂₂O₄ (422.3): C 79.62, H 5.21; found: C 79.61, H 5.34.

9,10-Bis-(2-methylphenyl)-9,10-dihydro-9,10-epidioxidoanthracene 2f. Yield 175 mg (91 %) after chromatography (cyclohexane/ethyl acetate 3:1).



¹H NMR (300 MHz, CDCl₃): δ = 2.28 (s, 6 H, 21-H), 7.08-7.05 (m, 4 H, 2-H, 3-H, 6-H, 7-H), 7.22-7.25 (m, 4 H, 1-H, 4-H, 5-H, 8-H), 7.38-7.52 (m, 6 H, 17-H, 18-H, 19-H), 7.73 (d, *J* = 7.2 Hz, 2 H, 20-H). ¹³C NMR (75)

MHz, CDCl₃): $\delta = 22.9$ (q, C-21), 84.0 (s, C-9, C-10), 124.2 (d, C-2, C-3, C-6, C-7), 126.3, 126.7 (2 d, C-17, C-18), 127.8 (d, C-1, C-4, C-5, C-8), 128.3, 131.3 (2 d, C-19, C-20), 133.0, 135.6, 137.7 (3 s, C-11, C-12, C-13, C-14, C-15, C-16). IR (cm⁻¹, KBr): $\tilde{\nu} = 3059$, 2920, 1491, 1458, 1437, 1383, 1246, 1024, 942, 767, 751, 666. Elemental analysis calcd (%) for C₂₈H₂₂O₂ (390.2): C 86.13, H 5.68; found: C 85.81, H 5.82.

9,10-Bis-(2-cyanophenyl)-9,10-dihydro-9,10-epidioxidoanthracene 2g. Yield 185 mg (90 %) after chromatography (cyclohexane/ethyl acetate 3:1).



¹H NMR (300 MHz, CDCl₃): δ = 7.12-7.16 (m, 4H, 2-H, 3-H, 6-H, 7-H), 7.32-7.38 (m, 4H, 1-H, 4-H, 5-H, 8-H), 7.67-7.73 (m, 2H, 18-H), 7.84-7.89 (m, 2H, 19-H), 7.95 (d, *J*=7.7 Hz, 2H, 20-H), 8.05 (d, *J*=7.7 Hz, 2H, 17-H). ¹³C NMR (75 MHz, CDCl₃): δ = 84.5 (s, C-9, C-10), 113.2 (s, C-16), 118.1 (s, CN), 124.0 (d, C-2, C-3, C-7, C-8), 126.4 (s, C-18), 127.8 (d, C-17), 128.8 (d, C-1, C-4, C-5, C-8), 129.4 (d, C-20), 134.1 (d, C-19), 134.5 (d, C-15), 137.2 (s, C-11, C-12, C-13, C-14). HRMS (ESI+) calcd for C₂₈H₁₆N₂O₂: 414.1344; found: 414.1353.

9,10-Bis-(2,4-dimethoxyphenyl)-9,10-dihydro-9,10-epidioxidoanthracene 2h. Yield 215 mg (91 %) after chromatography (cyclohexane/ethyl acetate 3:1).



¹H NMR (300 MHz, CDCl₃): δ = 3.75 (s, 6H, *ortho*Me), 3.96 (s, 6H, *para*Me), 6.71 (dd, *J*=2.3 Hz, 8.5 Hz, 2H, 19-H), 6.78 (d, *J*=2.3 Hz, 2H, 17-H), 6.97-7.0 (m, 4H, , 2-H, 3-H, 6-H, 7-H), 7.14-7.17 (m, 4H, 1-H, 4-H, 5-H, 8-H), 7.62 (d, *J*=8.5 Hz, 2H, 20-H). ¹³C NMR (75 MHz, CDCl₃): δ = 55.4 (q, *para*Me), 55.8 (q, *ortho*Me), 88,7 (s, C-9, C-10), 99.5 (d, C-17), 105.2 (d, C-19), 115.9 (s, C-20), 123.9 (d, C-1, C-4, C-5, C-8), 127.12 (d, C-2, C-3, C-6, C-7), 128.4 (s, C-11, C-12, C-13, C-14), 138.7 (s, C-15), 157.8 (s, C-16), 161.4 (s, C-18).

Determination of the kinetic rate constants of the photooxidation in solution:

At low concentration of the substrate (~10⁻⁴ M), the consumption of the substrate can be expressed by the following equation:² $-d[M]/dt = \varphi_{ISC} * k_r/k_d * [M]$

Thus, from plotting ln[M] against $\varphi_{ISC} * k_r/k_d$ and by neglecting physical quenching by the substrate $(k_r[M] \leq k_d)$ the chemical rate constant, k_r , of the anthracenes **1a-h** can be calculated. Values for the rate of singlet oxygen quenching by solvent, k_d , were taken from literature data for CHCl₃ ($k_d=0.8*10^5 \text{ s}^{-1}$),³ and the quantum efficiency of singlet oxygen formation, φ_{ISC} , was determined by the slope of the logarithmic plot of the disappearance of diphenylanthracene **1a** as reference (k_r in CHCl₃ = $3*10^6 \text{ M}^{-1}\text{s}^{-1}$).⁴

The decrease of the anthracene chromophore was followed by UV/vis spectroscopy. In order assure absolute reproducibility, all measurements were carried out by using a stock solution of the sensitizer methylene blue (10 mg) in dichloromethane (100 mL). The dye does not absorb in the region between 350-400 nm, where the extinction of the anthracene was recorded. The anthracene concentration was adjusted to 10⁻⁴ M. Pure oxygen was bubbled into the dichloromethane solution in quartz tube, which was sealed finally. Under a pressure of 1 atm the concentration of oxygen in the solution should be about 1*10⁻² M. The tube was irradiated by a sodium lamp in a fixed distance and the temperature was kept at 20 °C. Rate constants were determined from the slopes of the semi logarithmic plots of the concentration, derived from the extinction at 374 nm, versus time.



Figure 1. Disappearance of the anthracenes 1a-h under steady state irradiation in the presence of a sensitizer.

Cyclic Voltammetry:

The anthracenes were dissolved in dichloromethane (1 mM) and voltammogramms were recorded in the presence of tetrabutyammonium hexafluorophosphate (TBAPF₆) (0.1 M) at a scan rate of 100 mV/s versus SCE. After the measurement, ferrocene (50 mg) was added and the voltammogramm was measured again. The potential of the anthracenes remained unchanged. For the determination of the potentials, the anodic peak of the ferrocene/ ferrocenium redox couple was adjusted to 0.51 V.



Figure 2. Comparison of the voltammogramms of *ortho* and *para* substituted anthracenes. Left: methoxy 1b and 1e; right: cyano 1d and 1g.

Thermolyses and determination of kinetic parameters.

The endoperoxides were dissolved in 1,2-xylene $(1*10^{-4} \text{ M})$ and heated in quartz cuvettes in the dark at 60, 70, 80, 90 and 100 °C. The appearance of the parent anthracene was followed by UV/vis spectroscopy. The increase of absorption intensity followed first order kinetics and finally, when intensity changes subsided, the sample was heated for another hour at 120 °C for termination. The rate constants k were determined from semi logarithmic plots of the calculated concentrations of parent anthracenes (A_{final}-A_t)/ ϵ against time as shown in Figure 3.



Figure 3. Thermolyses of the endoperoxides 2a-h at 100 °C.

Straight lines were obtained from plotting the logarithm of the rate constant against the reciprocal temperature. The activation energy and the Arrhenius coefficient was calculated directly from the slope and the intercept, respectively (Figure 4).



Figure 4. Arrhenius diagrams of the thermolysis of the endoperoxides 2a-h.

Values of ΔH_A and ΔS_A were derived analogously from plotting lnk-lnT versus 1/T according to the Eyring equation: $\ln (k/T) = -\Delta H_A/RT + \ln k_B/h + \Delta S_A/R$

Determination of the yields of singlet oxygen production:

The endoperoxides were provided from stock solutions of ~ 20 mg endoperoxide in dichloromethane (25 mL) by a sample of 2 mL, corresponding to ~0.005 mmol. Tetracyclone (TC) (10 mL) was added from a stock solution of TC (55 mg) in dichloromethane (50 mL), corresponding to 0.0289 mmol (6-7 fold excess of TC over the endoperoxide). The solvent was removed at low pressure at rt and the mixture was dissolved in toluene (1 mL). The tube was degassed with nitrogen, sealed and heated at 90 °C for 14 hrs in the dark. TC reacts with the released singlet oxygen to a stable and colourless peroxide. UV spectra were taken and the absorption of TC at 510 nm after thermolysis was compared with the spectrum of an analogous sample (identical concentrations) before heating. Neither the endoperoxide nor the parent anthracene absorb at this wavelength. The decrease, therefore, corresponds to the amount of TC consumed by ${}^{1}O_{2}$. The singlet oxygen yield is calculated from the equation: $\Phi_{102} = ([TC]_{before} - [TC]_{after})*100/[parent anthracene]$

For the determination of [parent anthracene], a sample of the endoperoxide without TC from the same stock (identical concentration) was heated under identical conditions and the amount of [parent anthracene] was obtained from the extinction coefficient. All experiments were carried out three times and the average value is listed in Table 2. The average error is <10 %.

Crystal structures:

Crystallographic data are presented in Table 1. Details of the structures as well as further details of the X-ray measurements and the structure solution an refinement well be described in a separate paper.⁵



Figure 5. Crystal structure of *cis*-9,10-bis-(2-methoxyphenyl)-anthracene 1e.



Figure 6. Crystal structure of *cis*-9,10-bis(2-cyanophenyl)-anthracene 1g.

 Table 1. Crystal data of cis-9,10-bis-(2-methoxyphenyl)-anthracene 1e and cis-9,10-bis(2-cyanophenyl)-anthracene 1g.

	1e	1g
Chemical formula	$C_{28}H_{22}O_2$	$C_{28}H_{16}N_2$
Formula weight	390.46	380.43
Crystal system	orthorhombic	monoclinic
Unit-cell dimensions:		
a [Å]	17.4125(9)	10.9801(10)
b [Å]	11.1909(5)	14.1658(15)
c [Å]	21.1510(12)	12.9428(13)
α, β, γ [°]	90, 90, 90	90, 92.150(8), 90
Volume [Å ³]	4121.5(4)	2011.7(3)
Temperature [K]	210	210
Space group	P bca	$P 2_1/c$
No. of formula units in unit cell	8	4
Number of reflections		
measured	25136	12604
independent / R _{int}	3630 / 0.034	3504 / 0.049
Final R values		
$R_1 / wR_2 [I > 2s(I)]$	0.0388 / 0.1005	0.0357 / 0.0841
R_1 / wR_2 (all data)	0.0499 / 0.1060	0.0550 / 0.0899



Figure 6. Crystal structure of 9,10-diphenylanthracene 1a.⁶

References:

- (1) S. Kotha, A. K. Ghosh and K. D. Deodhar, Synthesis, 2004, 4, 549.
- (2) F. Wilkinson, W. P. Helman and A. B. Ross, J. Phys. Chem. Ref. Data, 1995, 24, 663.
- (3) J.-M. Aubry, B. Mandard-Cazin, M. Rougee and R. V. Bensasson, J. Am. Chem. Soc., 1995, 117, 9159.
- (4) B. Monroe, J. Phys. Chem., 1978, 82, 15.
- (5) W. Fudickar, D. Zehm, A. Kelling, U. Schilde, T. Linker, unpublished work.
- (6) H.-D. Becker, V. Langer, J. Sieler and H.-C. Becker, J. Org. Chem., 1992, 57, 1883.