Synthesis, Fluorescence Properties, and Head-to-Tail Regioselectivity in the Photodimerization of a Donor–Acceptor-Substituted Anthracene

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Dedicated to Professor Armin de Meijere on the occasion of his 60th birthday

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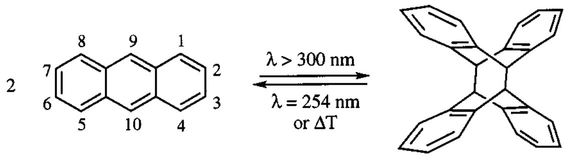
The novel 2,6-donor–acceptor-substituted anthracene, namely 6-methoxy-2-anthracene carboxylic acid (**7**), was synthesized. The emission of this compound exhibits significant solvatochromism. The fluorescence band position and intensity are also remarkably sensitive to H^+. Irradiation of the anthracene **7** in solution yields the *syn* and *anti* head-to-tail dimers exclusively. A synergistic electronic effect between the donor and acceptor substituents is proposed to operate on the photophysical and photochemical properties of anthracene **7**.

Introduction

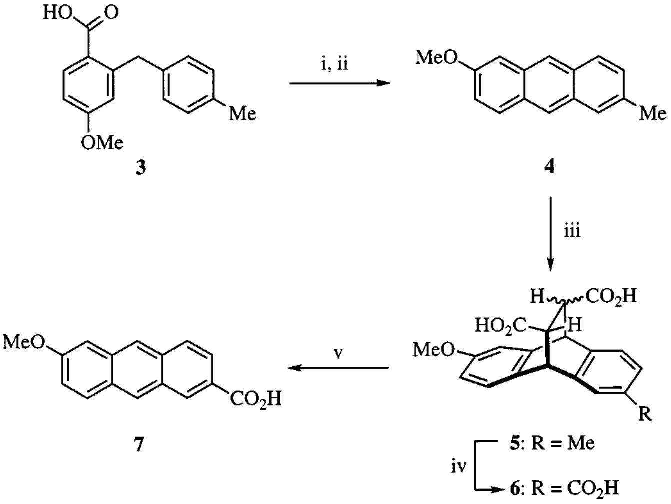
Anthracene and its derivatives are among the most useful polycyclic aromatic compounds.[1] In view of their fluorescent properties, they are of practical interest as sensors and markers in biological or supramolecular systems.[2] Furthermore, anthracenes are efficient photochromic systems: They dimerize upon irradiation in a [4 + 4] cycloaddition, and the dimer reverts back to its monomers on photolysis at lower wavelength or on thermolysis (Scheme 1).[3] Since the fluorescence of anthracenes can be reversibly modulated through the cycloaddition-cycloreversion reaction, such photochromic systems are useful candidates for the application in data storage and processing on a molecular level.[3a,4] Thus, there exist many investigations of the influence of substituents on the photophysical and photochemical properties of anthracenes;[1,5] however, most of the anthracenes studied so far are substituted at the C-9 and/or C-10 positions, presumably due to the ready availability of these compounds. In contrast, 2,6-donor−acceptor-substituted anthracenes are quite rare[6] and for this reason their photocyclization has to date been neglected.[7] Nevertheless, these anthracenes may be useful targets since the conjugated π-electrons constitute a push-pull system, and the electronic interaction between the two conjugated substituents may lead to new photophysical and photochemical properties of such polarized anthracenes. Herein, the synthesis of the 2,6-donor−acceptor-substituted 6-methoxyanthracene-2-carboxylic acid (**7**) is reported, and its photophysical and photochemical properties will be described.



Scheme 1. The dimerization of anthracenes

Results

Anthracene **7** was synthesized from the known benzylbenzoic acid **3**, which was obtained in 68% overall yield from anisic acid by a modification of the reported procedure (Scheme 2).[8]



Scheme 2. i: PPA, 80°C, 4 h; ii: $NaBH_4$, diglyme, methanol, room temp. (ca. 20°C), 15 h; iii: fumaric acid, 1,4-dioxane, 101°C, 3 d; iv: $KMnO_4$, NaOH, H_2O, 70°C, 14 h; v: Ph_2O, 254 °C, 4 h

Benzoic acid **3** was cyclized with polyphosphoric acid, and the intermediate anthrone was subsequently reduced to 2-methoxy-6-methylanthracene (**4**).[9] The C-9 and C-10 atoms were then protected against oxidation by Diels−Alder reaction with fumaric acid to give the ethanoanthracene **5**, and subsequent oxidation by potassium permanganate led to the tricarboxylic acid **6**. The

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ethanoanthracenes **5** and **6** were obtained as 1:1 mixtures of the corresponding (11*R*,12*R*) and (11*S*,12*S*) diastereomers, but since the carbon atoms will lose their chirality in the following step, no attempts were made to separate and structurally assign the isomers. The retro Diels−Alder reaction of ethanoanthracene **6** in refluxing diphenyl ether[10] afforded 6-methyl-2-anthracenecarboxylic acid (**7**) in 77% yield. Anthracene **7**, a yellow solid, is reasonably soluble in dimethyl sulfoxide, acetone, acetonitrile, and tetrahydrofuran. The structural assignment of anthracene **7** is based on its NMR-spectroscopic and mass-spectrometric data.

The absorption spectrum of anthracene **7** in methanol shows an intense, broad β band (S_0-S_3 transition) at λ_{max} = 265 nm and a broad p band (S_0-S_1 transition), whose tail extends to 425 nm, with a maximum at λ = 374 nm. Its emission is solvent- and concentration-dependent (Table 1): Whereas in methanol and THF two emission bands were observed, in solvents such as dimethyl sulfoxide, acetonitrile and benzene one broad band at λ_{fl} = 454, 453, and 448 nm, respectively, was obtained (Figure 1). However, more concentrated solutions of anthracene **7** (> 10^{-4} M) in THF or methanol also displayed only one emission band; furthermore, an additional band appeared at λ_{fl} = 423 nm on dilution of the acetonitrile solution. The fluorescence quantum yield (ϕ_{fl}) in methanol was determined to be 0.69 (relative to anthracene; 0.27[11]).

Table 1. Emission data of anthracene **7**

Solvent[a]	Concentration [mol × L^{-1}] × 10^{-6}	Fluorescence λ [nm]
MeOH	500	456
MeOH	7.9	429[b], 447
THF	7.9	438[b], 455
DMSO	7.9	454
DMSO (+ 0.1 mL 0.1 N NaOH)	7.9	429[b], 444
CH_3CN	7.9	453
CH_3CN	0.8	423[b], 447
Benzene	7.9	448

[a] λ_{ex} = 375 nm; fluorescence experiments were performed in 2 mL of degassed solvent. − [b] Fluorescence maximum.

The fluorescence of anthracene **7** exhibits a significant pH dependence. On acidification of a methanol solution (10^{-5} M) with diluted hydrochloric acid, the fluorescence bands at λ = 447 and 429 nm disappeared. A new band at λ = 457 nm was observed, which decreased significantly on addition of concentrated acid (Figure 2). Moreover, another weak band at λ = 555 nm appeared. The original emission spectrum of anthracene **7** was restored on neutralization. A slight increase of the emission intensity was found on treatment of **7** in methanol with 2 N NaOH. In contrast to 2-anthracenecarboxylic acid,[12] no wavelength shift and shape change of the emission band occurred for anthracene **7**. However, basification of anthracene **7** in DMSO or acetonitrile resulted in a change of the emission spectrum from the broad unstructured band to one with two maxima similar to the fluorescence band of **7** in methanol. Unlike during acidification, the absorption spectrum of anthracene **7** changed in intensity and shape on addition of NaOH solution. For comparison, the fluorescence intensity of anthracene **4** in methanol (λ = 412_{max}, 436) did not significantly change on acidification. The observed slight decrease is presumably due to dilution effects; however, addition of 2 N NaOH resulted in a notable increase of the emission band.

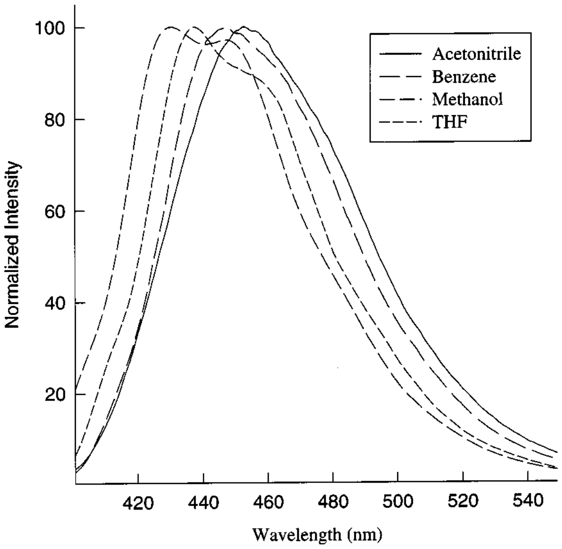


Figure 1. Normalized fluorescence spectra of anthracene **7** in different solvents (λ_{ex} = 365 nm; *T* = 20°C; *c* = 7.9 × 10^{-5} M)

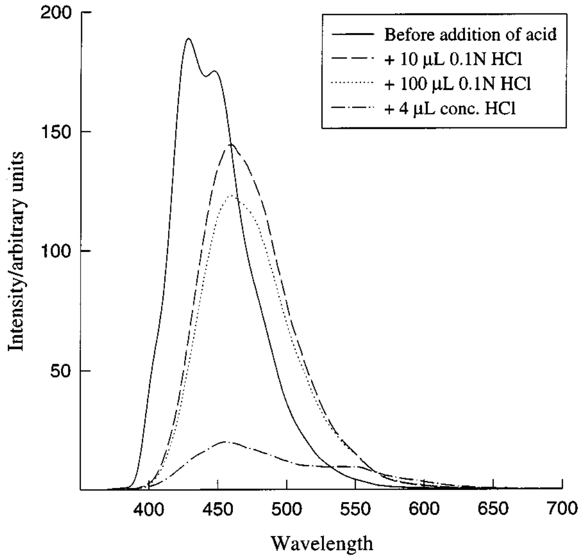
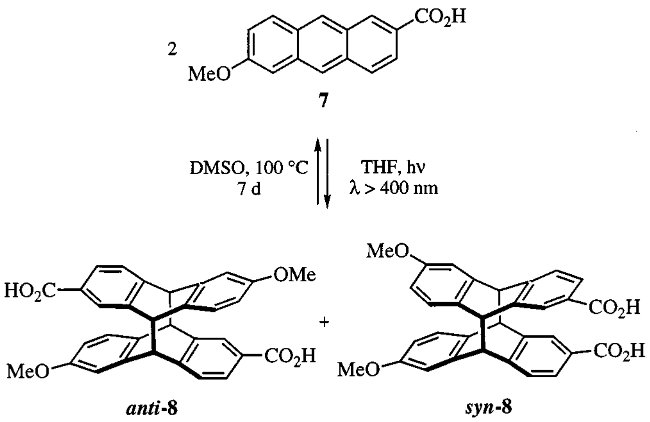


Figure 2. Fluorescence spectrum of anthracene **7** upon acidification (λ_{ex} = 365 nm; *T* = 20°C; *c* = 10^{-5} M, *V* = 2 mL of methanol)

Irradiation of anthracene **7** in degassed [D_6]DMSO for 3 d at λ > 400 nm led to the head-to-tail photodimers ***syn*-8** and ***anti*-8** in a 1:1 ratio (50% conversion) without any by-product, as determined by ^{1}H-NMR spectroscopy (Scheme 3). In tetrahydrofuran, the photoreaction was complete after 16 h and also gave a mixture of the head-to-head dimers along with small amounts of unidentified by-products. One of the dimers was isolated in low yield from the reaction mixture by crystallization. Solid samples of anthracene

7, crystallized from tetrahydrofuran, showed no reaction on irradiation. The photodimers were transformed quantitatively to the monomers on heating at 100 °C in DMSO; irradiation of the dimers ***syn*-8** and ***anti*-8** in this solvent at $\lambda > 300$ nm smoothly led to a mixture of anthracene **7** and its photodimers.



Scheme 3

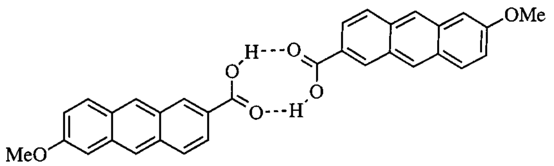
The head-to-tail structure of the two dimers was deduced from the characteristic signal of the bridgehead protons in the ^{1}H-NMR spectrum: Whereas these protons appear as AB systems (δ = 4.69, 4.71, J = 11 Hz[13]) for the head-to-tail dimers, the corresponding protons of the head-to-head isomers should give singlets, which were not observed in the ^{1}H-NMR spectrum of the reaction mixture. The isolated regioisomer was determined to be the dimer ***anti*-8**.

The structural differentiation between the *anti* and *syn* structure is based on ^{1}H-NMR-spectroscopic data. The ROESY-NMR spectrum of the the isolated isomer ***anti*-8** showed a very small NOE effect between the 1-H and 5′-H protons, but no such effect between the 4-H and 8′-H protons. PM3 calculations confirm a smaller separation between the 1-H and 5′-H protons (375 pm) than between the 4-H and 8′-H pair (380 pm). In the case of the *syn* dimer, a possible NOE effect between the 1-H/4′-H and the 5-H/8′-H pairs cannot be distinguished from the through-bond *para* coupling of the aromatic protons; the latter coupling was confirmed by COSY-NMR experiments. Fortunately, the methoxy protons serve as useful probe to distinguish the *anti* and *syn* dimers by ROESY-NMR experiments directly on the mixture of the two isomers: In the case of dimer ***syn*-8**, a small NOE effect was observed between the methyl and 5-H protons, whereas in the regioisomer ***anti*-8**, a similar effect is found between the methyl and the 1-H protons.

The dimer ***anti*-8** absorbs at λ = 238 and 275 nm, of which the latter absorption band is broad and extends to 310 nm. In the emission spectrum, weak fluorescence is observed at λ = 315, 348, and 369 nm; however, during the measurement, the irradiation induced the reversion to the monomer **7**, as evidenced by the appearance of the strong fluorescence band of anthracene **7**.

Discussion

The solvent and concentration dependence of the fluorescence spectra of anthracene **7** may be explained by the formation of a hydrogen-bonded dimer **9** whose absorption is red-shifted relative to that of the monomer **7**. In a more concentrated solution, dimer formation is favored, and the amount of monomer increases upon dilution. In methanol and THF, the dimerization is to some degree suppressed by hydrogen bonding with the solvent. Such behavior has already been reported for 2-anthracenecarboxylic acid.[14] However, it remains unclear, why dimer formation is not suppressed in DMSO. Presumably, the formation of dimer **9** is favored by better solvation than for the monomer in DMSO.



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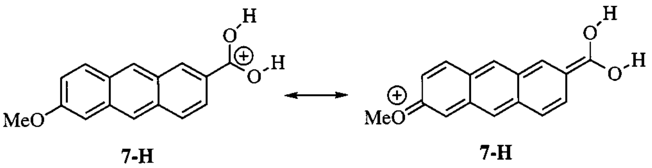
On slight acidification of anthracene **7** in methanol, the hydrogen bonds of the carboxy functionality with methanol are disrupted by the acid and emission of the monomer, which is hydrogen-bonded to a proton, is observed. Further acidification leads to protonation of anthracene **7** in its first excited state to give the conjugate acid **7-H**, whose emission is significantly red-shifted compared to anthracene **7** (Scheme 4). The photo-protonation of carboxylic acids is known to be accompanied by a bathochromic shift and by quenching of the fluorescence intensity;[15] however, it was reported that the 2-anthracenecarboxylic acid does not exhibit such an emission until its ground state is protonated, i.e. under strongly acidic conditions (pH < −6).[15b] In contrast, fluorescence of the protonated excited state of anthracene **7** is observed at the moderately acidic conditions of pH ≈ 4 (4 μL of 36% HCl in 2 mL of methanol solution). Since the absorption spectrum of the anthracene **7** does not change under these acidic conditions, the protonation solely occurs in the excited state. It seems reasonable to assume that this difference from 2-anthracenecarboxylic acid is due to the additional stabilizing donating effect of the methoxy group (Scheme 4).



Scheme 4

The [4 + 4] photocycloaddition of 9-substituted anthracenes is well known and usually gives the head-to-tail dimers as main product along with the less stable head-to-head dimers.[3a,16] Also, the photochemistry of 2-alkoxy-substituted anthracenes and 1- and 2-anthracenecarboxylic acids and their derivatives has been investigated. In each case, all of the four possible regioisomeric dimers were formed on solution photolysis.[17] Although, a preference for the head-to-tail dimers was observed, the factors that govern this regioselectivity have not been discussed in detail.[18] The photodimerization of 2,6-disubstituted anthracenes is rather rare: The only example is the photoreaction of a 2,6-dialkoxyanthracene which yields the 1,4−9′,10′ photodimer, along with the two possible symmetric photodimers; however, because of the dimer symmetry, the head-to-head and head-to-tail products cannot be distinguished.[7] Thus, the dimerization of anthracene **7** is the first example for a head-to-tail-selective photodimerization of 2,6-substituted anthracenes in solution. This selectivity cannot be explained by steric interactions between the substituents, because in that case, the *anti*-head-to-head dimer should be formed rather than the actually observed *syn* one. Since the *anti*-head-to-head dimer is not formed, an *anti*-directing electrostatic attraction between a methoxy-substituted phenyl ring and a benzoic acid moiety negligibly affects the regiochemistry. The molecular-orbital coefficients as well as the net atomic charges of the reactive sites C-9 and C-10 in the ground and excited state did not satisfactorily explain the observed regioselectivity. Quite the contrary, according to PM3 calculations, the head-to-head dimers should form in the photodimerization. Thus, the regiochemistry of the photoreaction is not influenced by factors such as steric and orbital interactions, which usually determine the geometry of the initially formed excimer. These observations resemble those of the [2 + 2] photodimerization of some substituted alkenes, for which it has been shown by theoretical studies that a conical intersection with an energy minimum for a head-to-tail arrangement determines the regioselectivity of the reaction.[19] Moreover, on the same theoretical basis, the head-to-tail-directing electronic influence of substituents has been demonstrated by the application of the two-electron-two-orbital model,[19] which was also applied to explain (without any steric reasons!) the preference of 9-substituted anthracenes for a head-to-tail photocyclization.[20]

The same explanation may be used to rationalize the regioselectivity of the photodimerization of anthracene **7**. In fact, a conical intersection has been found recently for the [4 + 4] photocyclization of 1,3-butadiene on the basis of CASSCF calculations.[21] This model should also be valid for other laterally mono-substituted anthracenes; however, such anthracenes do not show such a distinct selectivity.[17] It may be concluded that the conjugated donor and acceptor functionalities in anthracene **7** have a synergistic effect on the regiocontrol of the photoreaction. Such synergism has already been shown to direct the photodimerization of a push-pull-based acridizinium salt towards exclusive head-to-tail dimerization.[22] Also the photodimerization of the lower homologue of anthracene **7**, namely methyl 6-methoxy-2-naphthoate, was reported to proceed in an *anti*-head-to-tail fashion.[23] However, to show that the regioselective [4 + 4] photodimerization of push-pull-substituted chromophores is a general phenomenon and to fully understand the regioselectivity of the photodimerization of substituted anthracenes, more experimental and theoretical work will be necessary.

In summary, a 2,6-disubstituted anthracene with unusual photophysical and photochemical properties was synthesized, which are mainly governed by the combined electronic effects of π-conjugated donor and acceptor substituents. Due to its remarkable fluorescence properties, this compound may also serve as a useful fluorescence sensor in biological, polymeric or supramolecular systems.

Experimental Section

^{1}H and ^{13}C NMR: Bruker AC 200 (^{1}H: 200 MHz; ^{13}C: 50.3 MHz); Bruker DMX 600 (^{1}H: 600 MHz). C_q, CH, CH_2, and CH_3 were determined by using the DEPT pulse sequence. ^{1}H-NMR chemical shifts refer to $\delta_{TMS} = 0.0$. ^{13}C-NMR chemical shifts refer to solvent signals ($CDCl_3$: δ = 77.0; [D$_6$]DMSO: δ = 39.5). − UV: Hitachi U-3200 spectrophotometer. − Fluorescence: Perkin−Elmer LS50 spectrometer. − MS: Finnigan MAT 90. − Melting points (uncorrected): Büchi B-545. − Elemental analyses were performed by Mikroanalytisches Laboratorium der Universität Würzburg. − Photoreactions were performed with a high-pressure mercury lamp (150 W, Heraeus TQ 150) at room temp. (ca. 20°C); the sample was placed 5 cm in front of the cooling mantle of the light source. Absorption and emission spectra were recorded in deoxygenated spectral-grade solvents (Fluka). The relative fluorescence quantum yield was determined by the usual method[24] using anthracene as reference (0.27[11]). Solution photolyses were carried out in deoxygenated solvents. The solutions were purged with argon gas for at least 30 min prior to use.

2-Methoxy-6-methylanthracene (4): To 15 g of polyphosphoric acid (84%) was added 1.40 g (5.5 mmol) of benzylbenzoic acid **3** at 60°C. The viscous solution was stirred for 4 h at 80°C. After careful addition of water, the solution was stirred for a further 30 min at 80 °C. On cooling and three times extracting with 50 mL of dichloromethane, the combined organic phases were subsequently washed with 50 mL of 10% aq. NaOH and 50 mL of water. After drying with $MgSO_4$, filtration, evaporation of the solvent and washing with 10 mL of methanol, 930 mg of a brown solid was obtained. The solid was dissolved in 20 mL of deoxygenated diglyme and after addition of 500 mg (13.21 mmol) of solid $NaBH_4$, the solution was stirred for 30 min at room temperature under argon. The reaction mixture was then cooled to 0°C and 10 mL of methanol was carefully added, followed by 250 mg (6.61 mmol) of $NaBH_4$. The solution was stirred for 14 h at room temperature. Acetic acid was added until pH ≈ 4−5 and the solution was stirred for 1 h at room temperature. On addition of 100 mL of water with vigorous stirring, a brown solid precipitated. After washing the residue three times with 40 mL of water and twice with 20 mL of methanol, 400 mg of anthracene **4** was obtained as a yellow solid. Evaporation of the methanol from the filtrate and crystallization from diethyl ether/*n*-hexane yielded additionally 230 mg of anthracene **4** (total amount: 630 mg, 2.83 mmol, 51% from **3**). An analytical sample was obtained by sublimation (120°C/10 mbar), followed by crystallization from dichloromethane/methanol, m.p. 197−198 °C. − UV (*n*-hexane): λ (log ε) = 392 (3.64), 371 (3.60), 346 (3.63), 328 (3.65), 313 (3.45), 259 (4.52), 254 (4.51), 246 (4.52). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.51 (s, 3 H, CH_3), 3.94 (s, 3 H, OCH_3), 7.13 (dd, ^3J = 9 Hz, ^4J = 2 Hz, 1 H, ar-H), 7.15 (s, 1 H, ar-H), 7.26 (dd, ^3J = 9 Hz, ^4J = 2 Hz, 1 H, ar-H), 7.69 (br. s, 1 H, ar-H), 7.83 (d, ^3J = 9 Hz, 1 H, ar-H), 7.84 (d, ^3J = 9 Hz, 1 H, ar-H), 8.21 (br. s,[25] 2 H, ar-CH). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.9 (CH_3), 55.2 (OCH_3), 103.6 (ar-CH), 120.3 (ar-CH), 123.9 (ar-CH), 125.2 (ar-CH), 126.4 (ar-CH), 127.4 (ar-CH), 128.3 (ar-CH), 129.7 (ar-CH), 130.6 (ar-C_q), 130.8 (ar-C_q), 132.1 (ar-C_q), 132.1 (ar-Cq), 133.9 (ar-C_q), 156.6 (ar-C_q). − MS (EI, 70 eV); *m*/*z* (%): 222 (82) [M^+], 179 (100) [$M^+ - C_2H_3O$]. − $C_{16}H_{14}O$ (222.3): calcd. C 86.45, H 6.35; found C 86.06, H 5.89.

2-Methoxy-6-methyl-9,10-dihydro-9,10-ethanoanthracene-*trans*-11,12-dicarboxylic Acid (5): A solution of 2.64 g (12.0 mmol) of anthracene **4** and 2.80 g (24.1 mmol) of fumaric acid in 75 mL of deoxygenated 1,4-dioxane was kept at reflux for 3 d under argon. After evaporation of the solvent, the remaining solid was extracted with 50 mL of chloroform. The insoluble fumaric acid was removed by filtration and the residue was washed with another 50 mL of chloroform. The solution was extracted with 200 mL of 10% aqueous NaOH and the water layer was acidified with concentrated hydrochloric acid and extracted twice with 50 mL of chloroform. The solution was dried with $MgSO_4$, filtered and concentrated to give 3.24 g (8.0 mmol, 66%) of ethanoanthracene **5** as a dark-yellow solid, m.p. 128−129°C (dec.). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.26 (s, 3 H, CH_3), 2.28 (s, 3 H, CH_3), 3.32 (m, 4 H, 11-H, 12-H), 3.73 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 4.60 (m, 4 H, 9-H, 10-H), 6.57−6.63 (m, 2 H, ar-H), 6.84−6.90 (m, 4 H, ar-H), 7.06−7.21 (m, 6 H, ar-H). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.3 (CH_3), 21.3 (CH_3), 47.5 (CH), 47.5 (CH), 49.9 (CH), 55.7 (OCH_3), 55.8 (OCH_3), 110.9 (CH), 111.7 (CH), 112.3 (CH), 124.3 (CH), 125.0 (CH), 125.1 (CH), 125.5 (CH), 126.3 (CH), 126.4 (CH), 127.4 (CH), 127.6 (CH), 134.1 (C_q), 136.3 (C_q), 137.0 (C_q), 138.8 (C_q), 140.9 (C_q), 142.3 (C_q), 143.6 (C_q), 144.6 (C_q), 145.7 (C_q), 159.5 (C_q), 159.7 (C_q), 175.9 (CO). − MS (EI, 70 eV); *m*/*z* (%): 338 (6) [M^+], 222 (100) [$M^+ - C_4H_4O_4$], 179 (58) [$M^+ - C_4H_4O_4 - C_2H_3O$]. − $C_{20}H_{18}O_5$ (338.4): calcd. C 71.00, H 5.36; found C 70.13, H 5.89.

2-Methoxy-9,10-dihydro-9,10-ethanoanthracene-6-*trans*-11,12-tricarboxylic Acid (6): A solution of 264 mg (0.78 mmol) ethenoanthracene **5** and 316 mg (0.20 mmol) of $KMnO_4$ in 8 mL of 0.5 M aqueous NaOH was stirred for 14 h at 70°C. After cooling of the suspension, the MnO_2 was removed by filtration and the remaining solid was washed with 5 mL of hot water. The combined filtrates were acidified with hydrochloric acid (concd.) and the resulting suspension was extracted three times with diethyl ether. The combined organic phases were dried with $MgSO_4$ and concentrated to dryness to give 220 mg (0.57 mol, 73%) of a 1:1 mixture of the regioisomeric tricarboxylic acids **6** as pale yellow solid. For an analytical sample, the solid was recrystallized from ethyl acetate, m.p. 161−162°C (dec.). − ^{1}H NMR (200 MHz, [D_6]DMSO): δ = 3.22 (m, 4 H, 11-H, 12-H), 3.78 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 4.87 (m, 4 H, 9-H, 10-H), 6.71−6.79 (m, 2 H, ar-H), 6.97 (s, 1 H, ar-H), 7.15 (s, 1 H, ar-H), 7.27 (d, ^3J = 8 Hz, 1 H, ar-H), 7.42 (d, ^3J = 9 Hz, 1 H, ar-H), 7.46 (d, ^3J = 8 Hz, 1 H, ar-H), 7.60 (d, ^3J = 8 Hz, 1 H, ar-H), 7.78−7.87 (m, 3 H, ar-H), 8.01 (s, 1 H, ar-H). − ^{13}C NMR (50.3 MHz, [D_6]DMSO): δ = 44.9 (CH), 46.0 (CH), 46.7 (CH), 46.8 (CH), 47.3 (CH), 55.0 (OCH_3), 55.1 (OCH_3), 110.1 (CH), 11.7 (CH), 110.9 (CH), 111.5 (CH), 123.8 (CH), 124.0 (CH), 124.8 (CH), 125.0 (CH), 125.5 (CH), 127.3 (C_q), 127.5 (C_q), 128.3 (C_q), 128.5 (C_q), 132.0 (C_q), 134.2 (C_q), 141.0 (C_q), 143.1 (C_q), 143.5 (C_q), 145.6 (C_q), 147.5 (C_q), 157.6 (C_q), 157.7 (C_q), 167.1 (CO), 167.1 (CO), 172.9 (CO), 173.0 (CO), 173.1 (CO), 173.2 (CO). − MS (EI, 70 eV); *m*/*z* (%): 382 (3) [M^+], 252 (100) [$M^+ - C_4H_4O_4$]. − $C_{20}H_{16}O_7 \cdot 0.5\ H_2O$ (386.3): calcd. C 63.66, H 4.54; found C 63.67, H 4.70.

6-Methoxy-2-anthracenecarboxylic Acid (7): A deoxygenated solution of 208 mg (0.61 mmol) of ethanoanthracene **6** in 4 mL of deoxygenated diphenyl ether was stirred at 254°C under argon for 4 h. The solution was allowed to cool to ca. 100°C and the fumaric acid, which had sublimed on the upper flask wall, was removed. *n*-Hexane was added and the precipitated solid was separated and washed subsequently with *n*-hexane, tetrachloromethane, and ethyl acetate to give 119 mg (0.47 mmol, 77%) of anthracene **7** as a dark-yellow solid. Further purification was achieved by sublimation at 180°C/10 mbar) to yield a bright yellow solid, m.p. 288−289°C. − UV (MeOH): λ_{max} (log ε) = 265 (4.16), 358 (3.36), 374 (3.40), 390 (3.32). − ^{1}H NMR (200 MHz, [D_6]DMSO): δ = 4.03 (s, 3 H, OCH_3), 7.33 (dd, ^3J = 8 Hz, 9 Hz, ^2J = 2 Hz, 1 H, ar-H), 7.52 (d, ^3J = 2 Hz, ar-H), 7.99 (dd, ^3J = 9 Hz, ^2J = 2 Hz, 1 H, ar-H), 8.14 (d, ^3J = 9 Hz, 1 H, ar-H), 8.17 (d, ^3J = 9 Hz, 1 H, ar-H), 8.55 (s, 1 H, ar-H), 8.81 (s, 1 H, ar-H), 8.83 (s, 1 H, ar-H). − ^{13}C NMR (50.3 MHz, [D_6]DMSO): δ = 55.3 (OCH_3), 103.6 (CH), 120.9 (CH), 123.7 (CH), 124.2 (CH), 126.5 (C_q), 127.8 (CH), 128.1 (CH), 128.5 (CH), 128.5 (C_q), 130.1 (CH), 131.7 (CH), 132.6 (C_q), 134.0 (C_q), 157.6 (C_q), 167.5 (CO). − MS (EI, 70 eV); *m*/*z* (%): 252 (100) [M^+], 209 (93) [$M^+ - CO_2H$]. − $C_{16}H_{12}O_3$ (252.3): calcd. C 76.18, H 4.97; found C 76.12 H 4.70.

Photodimer of 6-Methoxy-2-anthracenecarboxylic Acid (7): A solution of 33 mg (0.13 mmol) of anthracene **7** in 5 mL of tetrahydrofuran was irradiated for 16 h at λ > 400 nm (Schott GG 385). After evaporation of the solvent (40°C, 10 mbar), the remaining solid was crystallized from tetrahydrofuran/ethyl acetate to give 10 mg (0.02 mmol, 30%) of dimer ***anti*-8** as a white solid, m.p. 270−285°C (dec.). − UV (THF): λ_{max} = 238, 275. − ^{1}H NMR (600 MHz, [D_6]DMSO): δ = 3.55 (s, 6 H, OCH_3), 4.69, 4.71 (AB system, *J* = 11 Hz, 4 H, bridgehead H), 6.34 (dd, ^3J = 8 Hz, ^2J = 3 Hz, 2 H, 7-H), 6.60 (d, ^2J = 3 Hz, 2 H, 5-H), 6.86 (d, ^3J = 8 Hz, 2 H, 8-H), 7.05 (d, ^3J = 8 Hz, 2 H, 4-H), 7.41 (dd, ^3J = 8 Hz, ^2J = 2 Hz, 2 H, 3-H), 7.53 (d, ^2J = 2 Hz, 2 H, 1-H). − Dimer ***syn*-8** (data determined from the mixture with the dimer ***anti*-8**): ^{1}H NMR (600 MHz, [D_6]DMSO): δ = 3.58 (s, 6 H, OCH_3), 4.69, 4.71 (AB system, *J* = 11 Hz, 4 H, bridgehead H), 6.37 (dd, ^3J = 8 Hz, ^2J = 3 Hz, 2 H, 7-H), 6.59 (d, ^2J = 3 Hz, 2 H, 5-H), 6.88 (d, ^3J = 8 Hz, 2 H, 8-H), 7.06 (d, ^3J = 8 Hz, 2 H, 4-H), 7.37 (dd, ^3J = 8 Hz, ^2J = 2 Hz, 2 H, 3-H), 7.50 (d, ^2J = 2 Hz, 2 H, 1-H). Due to the low solubility of the dimers, ^{13}C-NMR spectra could not be recorded.

Thermal Cycloreversion of the Photodimer: A 1:1 mixture of the photodimers ***syn*-8** and ***anti*-8** was heated at 100°C in deoxygenated [D_6]DMSO and the reaction progress monitored by ^{1}H-NMR spectroscopy. After 7 d, the dimer was quantitatively transformed to the monomer.

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