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Synthesis of Pyridylanthracenes and their Reversible Reaction with Singlet Oxygen to Endoperoxides

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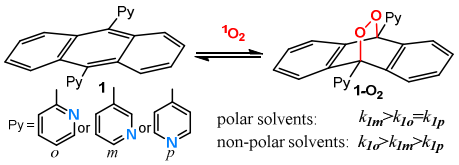


ABSTRACT: The *ortho, meta* and *para* isomers of 9,10-dipyridylanthracene **1** have been synthesized and converted into their endoperoxides **1–O$_2$** upon oxidation with singlet oxygen. The kinetics of this reaction can be controlled by the substitution pattern and the solvent: In highly polar solvents the *meta* isomer is the most reactive, whereas the *ortho* isomer is oxidized fasted in non-polar solvents. Heating of the endoperoxides afforded the parent anthracenes by release of singlet oxygen.

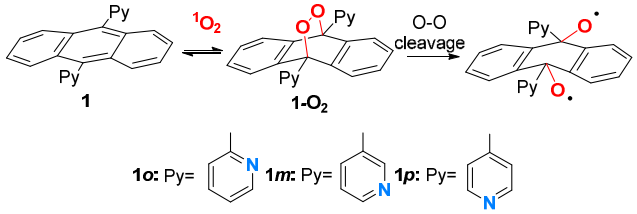
Singlet oxygen ($^1O_2$) is a powerful reagent used for the syntheses of organic peroxides from alkenes, such as in the Schenck Ene reaction, the [2+2] and the [4+2] cycloaddition.[1-3] Of particular interest is the oxygenation of acenes to give aromatic endoperoxides (EPOs), as in some cases it can proceed reversibly with the regeneration of the parent acene and oxygen, partly in its exited state.[4,5] Acene photooxygenations have been harnessed, for example, for lithographic applications,[6] the design of luminescent $^1O_2$–response polymers,[7] for oxygen storage,[8] or for molecular rotors.[9] It is therefore of great importance to predict reactivities of acenes towards their oxygenation and the degree of the reversibility of this reaction.

We have recently shown that the reactivity of substituted diarylanthracenes with $^1O_2$ correlates in a positive linear fashion with their HOMO energies and their redox potentials.[10] Various substituents on phenyl groups have been investigated. However, reversible photooxygenations of anthracenes with heterocycles at the 9,10-position have not been reported until now. Pyridylanthracenes seem to be especially attractive, since pyridine is inert towards reaction with $^1O_2$,[11] whereas thiophene or imidazole are not suitable because of their oxidation lability.[12] Additionally, the nitrogen atom of the pyridines might be placed in the *ortho-, meta-,* or *para*-position, with the possibility to distinguish between electronic and steric influences. Interestingly, pyridylanthracenes are known to possess important luminescence properties,[13] and have been used to construct coordination polymers,[14] but their reaction with $^1O_2$ was hitherto unknown.

Herein, we report on the synthesis of three isomeric 9,10-dipyridylanthracenes **1** where the nitrogen atom is placed in *o-, m-* or *p*-position (**1*o–p***) and their photooxygenation to the corresponding EPOs. The electronic effects of the pyridine substituents are quantified. Furthermore, the reversibility of this

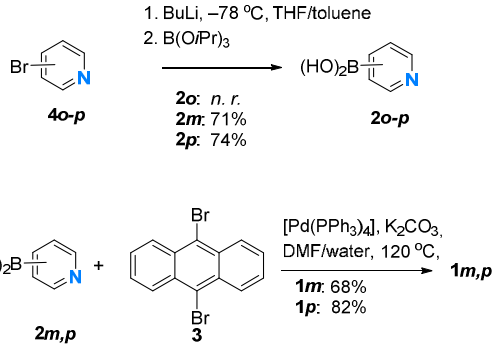
reaction is investigated, whether thermolysis affords either the starting species upon cleavage of the two C–O bonds or causes decomposition as a result of an O–O bond cleavage (Scheme 1).

Scheme 1. Oxygenation of pyridylanthracenes 1 and reconversion/decomposition of the EPOs.



From our previous experience in the syntheses of diarylanthracenes we envisaged that the Suzuki-Miyaura cross-coupling reaction between pyridineboronic acids **2** and 9,10-dibromoanthracene (**3**) is a valuable method to provide the pyridylanthracenes **1**.[9] Therefore, the pyridineboronic acids **2** were prepared by lithium–halogen exchange of the corresponding bromopyridines **4** followed by transmetalation with triisopropylborate (Scheme 2).

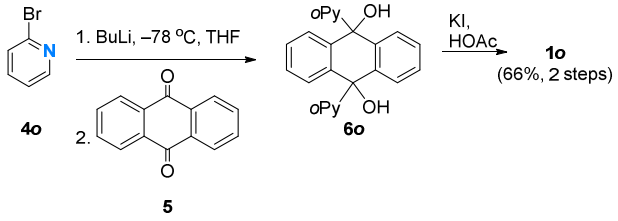
Scheme 2. Synthesis of 9,10-dipyridylanthracenes 1*o*,*m* by Suzuki-Miyuara cross-coupling (method A).



While the *meta* and *para* pyridineboronic acids **2*m*** and **2*p*** could be prepared in moderate yields (~70%),[15] the *ortho* derivative could not be isolated. Upon inspection of literature reports, 2-pyridineboronic acids are labile towards hydrolysis due to cleavage of the C–B bond and therefore, only specifically modified synthetic protocols are suitable.[16] For example, other borates than alkyl borates were employed,[17] and the intermittent boronic ester was isolated prior to hydrolysis requiring an additional step.[18] As this instability of the boronic acid **2*o*** is reported to further cause diminished yields in the following cross-coupling reaction,[19] we switched to an alternative procedure to obtain **1*o***. Thus, after *in situ* generation of 2-pyridyllithium (two equivalents) from the bromopyridine **4o** using n–butyl lithium (BuLi) at −78 °C, its reaction with anthraquinone (**5**) lead to the intermediary coupling product, 9,10-dihydro-9,10-dipyridinyl-9,10-anthracenediol (**6*o***), which was in turn reduced to the anthracene **1*o*** with potassium iodide in glacial acetic acid under reflux in moderate overall yield (Scheme 3, method B).

Owing to the good water solubility of all pyridylanthracenes **1** at pH<3, mono-coupled products and starting materials could be easily removed by extractions at low pH into the organic phase, followed by precipitation of the product which remained in the aqueous phase.

Scheme 3. Synthesis of 9,10-*o*-dipyridylanthracene (1*o*) from 2-pyridyllithium and anthraquinone (method B).



Sensitized photooxygenations were carried out by irradiation of solutions of pyridylanthracenes **1** in the presence of tetraphenylporphyrin as sensitizer under oxygen atmosphere. All three isomers delivered exclusively 9,10-EPOs (**1–O_2)** with nearly quantitative yields as characterized by NMR and mass spectroscopy (see supporting information).

To evaluate the reactivities of the pyridylanthracenes **1**, their rates of photooxygenations were determined and compared with the rate of 9,10-diphenylanthracene (DPA) in dichloromethane (DCM) as standard (Table 1, details of measurement and evaluation of experimental errors are given in the SI). As expected, the reactivity relative to DPA is strongly reduced by a factor of ~3–4, owing to the electron withdrawing character of the pyridine rings. The pyridine ring itself is chemically inert towards its photooxygenation, and causes a slightly stronger physical deactivation of $^1O_2$ as compared to benzene (for example, $t_{½}$ for $^1O_2$ is 13–20 µs in pyridine and 20–30 µs in benzene).[20] Thus, our pyridylanthracenes are attractive substrates for reactions with $^1O_2$. The absolute second order rate constant k_r can be derived from these data based on a literature value for DPA (k_{rDPA}=4.2x10^6 M^{-1}s^{-1}) and by assuming that singlet oxygen is quenched only chemically by the substrate and physically by the solvent, thus, neglecting the physical deactivation by the substrate.

Table 1. Rate constants, oxidation potentials, and calculated HOMO energies of the photooxygenation of pyridylanthracenes 1 in DCM.

acene	k_{obs} / s^{-1}	k_r / 10^6 $M^{-1}s^{-1}$	E_{Ox} [c] / V	E_{HOMO} [d] / eV
1*o*	0.83±0.02[a]	1.01[b]	+1.47	−6.55
1*m*	1	1.21[b]	+1.43	−6.61
1*p*	0.66±0.03[a]	0.80[b]	+1.46	−6.63
DPA	3.45±0.11[a]	4.20	+1.38	−6.67

[a]Observed rate relative to the *meta* isomer **1*m***. Experimental errors determined from four independent photooxygenations. [b]Absolute values based on literature data for DPA (4.2x10^6 M^{-1}s^{-1}). [c]Measured by cyclic voltammetry. [d]Calculated by Gaussian 09.

The kinetic data summarized in Table 1 show a reactivity bias according to the position of the nitrogen atom: The *meta* isomer **1*m*** reacts faster than the other two isomers, where the nitrogen atoms are in conjugation with the bridgehead carbon atoms C9 and C10. The redox potentials of the three pyridylanthracene isomers were experimentally determined by cyclic voltammetry in DCM (see supporting information Figure S1). In contrast to DPA, the pyridylanthracenes showed irreversible waves, with one anodic peak according to the generation of the anthracene cation radical.[21] The irreversibility might be the result of a chemical reaction following the oxidation, that is, the attack of the nucleophilic lone pair of the pyridine nitrogen at the cationic species (EC mechanism). However, the measured potentials resemble the reactivity order, which is in agreement with our previous studies on the reactivity of substituted arylanthracenes (Table 1).[10] On the other hand, HOMO energies obtained from density functional theory (DFT) calculations in DCM using a self-consistent reaction field method (see supporting information) were not consistent with the reactivities, where the *ortho* isomer has the highest HOMO energy level. This could be explained by a comparison of the optimized calculated structures: In contrast to the other two isomers, **1*o*** has a smaller acene-pyridine twist angle (70° for **1*o***, ~82° for **1*m***/**1*p***) due to less steric hindrance, which affects its orbital energies (see Figure S2 supporting information). Thus, the value of the HOMO energy of **1*o*** cannot fit into the expected order.

To prove whether the reactivity order is controlled by either electronic effects *via* conjugation or by steric effects arising from the less space requiring nitrogen atom compared to the CH-group, we investigated the photooxygenations of the three pyridylanthracenes in less polar solvents. Interestingly, when performing the reaction in toluene, the order changed from k_{meta}>k_{ortho}>k_{para} to k_{ortho}>k_{meta}>k_{para}. This trend is even more remarkable in hexane (Table 2 and Figures S3 and S4 supporting information). Even though the *para* isomer is still the least reactive as a result of conjugation, the strikingly high reactivity of the *ortho* compound is owed to the reduced steric demand of the nitrogen atom. Moreover, calculated HOMO energies in hexane ($E_{HOMO/1o}$> $E_{HOMO/1m}$>$E_{HOMO/1p}$) fit nicely to this trend (see Table S1 supporting information). This confirms the surpassing of steric over electronic effects in non-polar solvents, which was hitherto not discussed in photooxygenations of acenes.

Table 2. Relative reactivity of the three isomeric pyridylanthracenes compared to the reactivity of DPA in various solvents.

solvent	toluene	hexane	DCM	acetonitrile	methanol
k_{1o}/k_{DPA}	0.56	0.55	0.24	0.21	0.14
k_{1m}/k_{DPA}	0.43	0.25	0.28	0.24	0.20
k_{1p}/k_{DPA}	0.35	0.19	0.18	0.22	0.14

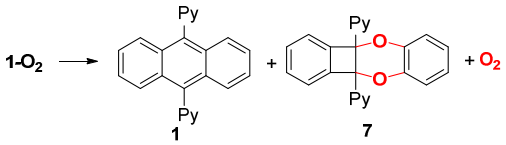
To further prove the strong effect of solvents on the reactivity of pyridylanthracenes **1** with $^1O_2$, we investigated highly polar acetonitrile and methanol next. Indeed, now not only the *meta* isomer was the most reactive as above reported for DCM, but also the *ortho* isomer reacts as slowly as the *para* isomer (Table 2 and Figures S6 and S7 supporting information). This indicates that the sterical benefit from the less space requiring nitrogen atom in *ortho* position is extinguished in polar solvents. The strongest effect

and slowest reactivity for the *ortho* isomer was observed in methanol. This can be well explained by the existence of hydrogen bonds between pyridine and methanol.[22] Coordination of the nitrogen to the solvent reduced the reactivity of **1*o*** and **1*p*** because of the partly positive charge at the nitrogen. Thus, we could trigger the photooxygenation of pyridylanthracenes by change of the substitution pattern and solvents.

Finally, we investigated the thermolysis of our EPOs **1–O$_2$**, and therefore, heating was performed at 90 °C in toluene (Table 3). The *para* and *meta* isomers both afforded quantitatively the parent forms **1*m*** and **1*p*** within 24 h, which could be isolated after chromatography in 90% yield. The chemical rate constants of thermolysis are within the range of the rate of thermolysis of **DPA–O$_2$** (Table 3 and Figure S8). Both EPOs also released $^1O_2$ upon heating. The amount of this reactive species was quantified by trapping experiments and is in the range of $^1O_2$ released by DPA–O_2 (see NMR spectra, Figures S9–11, supporting information).[23] In contrast, the EPO **1*o*–O$_2$** showed no conversion at the same temperature even after 7 days. Eventually, treatment at 135 °C afforded a mixture of the parent form **1*o*** in 62% yield and tetracyclic compound **7** in 30% yield (Table 3, entry 1). The side product **7** is a result of the cleavage of the O–O bond followed by rearrangement.[5]

This interesting behavior can be explained again by steric interactions. For the *m*-, *p*-isomers and DPA as well, a C–H group is always in close proximity to the C–O bond. This steric hindrance weakens this bond, leading to homolysis during heating and a clean back-reaction to the parent anthracenes. On the other hand, for the *o*-isomer this unfavorable interaction is not operative and cleavage of the O–O bond can compete. Thus, we found another remarkable effect of the three isomers on their ability to release $^1O_2$.

Table 3. Thermolyses of EPOs 1–O$_2$ and DPA–O$_2$.



entry	EPO	**1** (%)	**7** (%)	$^1O_2$ (%)	k (s^{-1})
1	**1*o*–O$_2$**	62[a]	30[a]	-	-
2	**1*m*–O$_2$**	90[b]	0	36	$4{,}6\times10^{-5}$
3	**1*p*–O$_2$**	92[b]	0	39	$1{,}9\times10^{-5}$
4	DPA–O_2	95[b]	0	37	3.4×10^{-5}

[a]Thermolysis carried out at 135 °C in xylene. [b]At 90 °C in toluene.

In conclusion, we found that pyridylanthracenes **1** can be synthesized in only few steps and react reversibly with singlet oxygen to the EPOs **1–O_2**, with kinetics depending on their substitution pattern. Their reactivity, however, is lower and less diverse as compared to other arylanthracenes. In less polar solvents, the *ortho* isomer reacts significantly faster owing to a reduced steric demand of the nitrogen atom, whereas reactivity depends exclusively on conjugation effects in polar solvents. An unexpected behavior is also observed for their retro-reactions, where the EPO **1*o*–O_2** is significantly more stable than the two other isomers. Thus, we could control the reversible reaction with $^1O_2$ by the substitution pattern and the solvents. Therefore, pyridylanthracenes are important precursors for photooxygenations, which offer additional interesting features as luminescent and metal coordinating materials in future work.

Experimental Section

General Experimental Procedures. All 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 aluminum foils (0.25 mm thick, 60 F254, Merck, Germany). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer at 300 MHz and 75 MHz, respectively. Chemical shifts are referenced to TMS (0 ppm) and the solvent signals of deuterochloroform (δ = 7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C) and D_2O (4.79 ppm for ^{1}H) were used as standards. The elemental analyses were performed with a Vario EL III elemental analyzer. High resolution mass spectra were obtained using ESI-Q-TOF techniques.

General procedure for the synthesis of boronic acids 2*m* and 2*p*. The corresponding bromopyridine (3.16 g, 20 mmol) and triisopropylborate (5.64 g, 30 mmol) were dissolved in absolute THF (40 mL) and the solution was cooled to −78 °C. Under cooling BuLi (2M THF solution, 20 mmol) was added during 3h by using a syringe pump. The reaction was left over night and allowed to warm to room temperature. Hydrochloric acid (1 M aqueous solution, 40 mL) was carefully added followed by addition of chloroform (100 mL). The organic phase was removed and the aqueous phase was neutralized using potassium hydroxide (1 M aqueous solution). Water was evaporated to dryness and the residue was treated with hot ethanol. After filtration, ethanol was evaporated giving the neat boronic acid.

*3-Pyridylboronic acid (**2m**):*[17,24] white solid (1.74 g, 14.2 mmol, 71%); mp: >310 °C; ^{1}H NMR (300 MHz, D_2O) δ=8.5 (s, 1H), 8,34 (d, *J*=5.2 Hz, 1H), 8.28 (d, *J*=7.6 Hz, 1H), 7.57 (dd, *J*=5.2 Hz, 7.6Hz, 1H); ^{13}C NMR (60 MHz, D_2O) δ=148.0, 148.0, 143.9, 127.3.

*4-Pyridylboronic acid (**2p**):*[25] white solid (1.81 g, 16.1 mmol, 74%); mp:>310 °C; ^{1}H NMR (300 MHz, D_2O/d-TFA) δ=8.56 (d, *J*=5.67 Hz, 2H), 8.12 (d, *J*=5.67 Hz, 2H); ^{13}C NMR (60 MHz, D_2O/d-TFA) δ=139.1, 130.5.

Procedure for the synthesis of the anthracenediol 6*o*. A solution of 2-bromopyridine (1.58 g, 10 mmol) in absolute THF (20 mL) was cooled to −78 °C and BuLi (2M in THF, 10 mmol) was added over a period of 15 min. After 30 min, while cooling was maintained, anthraquinone (832 mg, 4 mmol) was added in several portions. The reaction mixture was allowed to warm to room temperature and left over night.

Water (30 mL) was added carefully followed by addition of ethyl acetate (70 mL). The organic phase was separated washed two times with water (30 mL) and dried over sodium sulfate. The crude product was directly used for the next step with no further purification.

*9,10-Dihydro-9,10-dipyridinyl-9,10-anthracenediol (**6o**):* brown solid (1.8 g yield of crude material); ^{1}H NMR (300 MHz, $CDCl_3$) δ=8.56 (d, *J*=3.2 Hz, 2H), 7.83 (d, *J*=3.2 Hz, 2H), 7.64 (dd, *J*=3.1 Hz, 3.2 Hz, 2H), 7.37 (dd, *J*=3.3 Hz, 6.0 Hz, 4H), 7.23 (dd, *J*=3.3 Hz, 6.0 Hz, 4H), 7.18 (dd, *J*=3.1 Hz, 3.2 Hz, 2H), 5.95 (s, 2H, OH); ^{13}C NMR (60 MHz, $CDCl_3$) δ=165.5, 147.6, 139.7, 137.1, 128.7, 128.4, 122.3, 73.2; HRMS (EI+): m/z: calcd for $C_{24}H_{18}O_2N_2$: 366.1368 [M]; found 366.1375 [M].

Procedure for the synthesis of the *ortho*-pyridylanthracene 1*o*. 9,10-dihydro-9,10-dipyridinyl-9,10-anthracenediol (**6*o***, 1.8 g, crude material) was dissolved in glacial acetic acid (100 mL). To this solution were added potassium iodide (6g, 33 mmol) and NaH_2PO_2 (6g, 68 mmol) and heating at 110 °C was maintained with stirring overnight. After cooling to room temperature, the solution was carefully neutralized by addition of potassium hydroxide (2M aqueous solution) followed by extraction between chloroform and water and drying over sodium sulfate. To the crude product was added hydrochloric acid (1 M) until a pH of 1 was reached. During acidification a part of the residue dissolved in the water phase, which gave a yellow color. The organic phase was removed and discarded. To the aqueous phase was added potassium hydroxide (1M solution) until a pH of 8 was reached. The product was then isolated by extraction into chloroform (2x 80 mL) and evaporation of the solvent. The procedure of acidification-extraction-neutralization was repeated until the product was pure.

*9,10-Bis(2-pyridyl)anthracene (**1o**)*; yellow solid (871 mg, 2.64 mmol, 66% over two steps); mp: 304−307 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ=8.98 (d, *J*=6.1Hz, 2H, Ar3), 7.96 (dd, *J*=7.6 Hz, 7.7 Hz, 2H, HAr5), 7.56−7.66 (m, 6H, H1, H4, H5, H8, HAr4), 7.51 (d, *J*=7.6 Hz, HAr6, 2H), 7.37 (dd, *J*=6.8 Hz, 3.8 Hz, 4H, H2, H3, H6, H7); ^{13}C NMR (60 MHz, $CDCl_3$) δ=158.5 (s, CAr1), 150.0 (d, CAr3), 136.3 (d, CAr5), 136.1 (s, C-9, C-10), 129.7 (s, C-11, C-12, C-13, C14), 126.9 (d, CAr4), 126.2 (d, C-1, C-4, C-5, C-8), 125.5 (d, C-2, C-3, C-6, C-7), 122.4 (d, CAr6); IR (cm^{-1}, ATR) ũ=3032, 2590, 1540, 1438, 1401, 1390, 1196, 1063, 1031, 990, 882, 806, 770. Elemental analysis calcd (%) for $C_{24}H_{16}N_2$ (332.39): C 86.74, H 4.81, N 8.43; found: C 86.44, H 4.90, N 8.48.

General procedure for the synthesis of 9,10-dipyridylanthracenes 1*m* and 1*p* by Suzuki coupling of the corresponding boronic acid to 9,10-dibromoanthracene. 9,10 Dibromoanthracene (672 mg, 2mmol), the boronic acid **2** (615 mg, 5 mmol), K_2CO_3 (2.72 g, 20 mmol) and *tetrakis*(triphenylphosphine)palladium(0) (231 mg, 0.2 mmol) were dissolved in DMF (80 mL) and water (10 mL). Nitrogen was bubbled through the solution for 10 min, after which the gas flow was stopped and a temperature of 100 °C was adjusted under stirring. After keeping for 12h at this temperature, the solvents were removed under vacuum and the residue was re-dissolved in a mixture of chloroform and water. The two phases were separated and the organic layer was twice washed with water. Finally, to the last portion of water (80 mL) hydrochloric acid (1 M) was added until a pH of 1 was reached. During acidification, a part of the residue dissolved in the water phase, which gave a yellow color. The organic phase was removed and discarded. To the aqueous phase was added potassium hydroxide (1M solution) until a pH of 8 was reached. The product was then isolated by extraction into chloroform (2x 80 mL) and evaporation of the solvent. The procedure of acidification-extraction-neutralization was repeated until the product was pure.

*9,10-Bis(3-pyridyl)anthracene (**1m**):* yellow solid (451 mg, 1.35 mmol, 68 % yield); mp: 292−294 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ=8.87 (d, *J*=3.97 Hz, 2H, HAr4), 8.77 (s, 2H, HAr2), 7.86 (m, 2H, HAr6), 7.57-7,71 (m, 6H, H1, H4, H5, H8, HAr5), 7.42 (dd, *J*=3.3 Hz, 6.8 Hz, 4H, H2, H3, H6, H7); ^{13}C NMR (60 MHz, $CDCl_3$) δ=151.7 (d, CAr2), 149.11 (d, CAr4), 138.8 (d, CAr6), 134.6 (s, C11, C12, C13, C14), 133.7 (s, C9, C10), 130.1 (s, C11, C12, C13, C14), 126.4 (d, C1, C4, C5, C8), 125.7 (d, C2, C3, C6, C7), 123.4 (d, CAr5); IR (cm^{-1}, ATR): ũ=3028, 1562, 1479, 1385, 1025, 940, 799, 765. Elemental analysis calcd (%) for $C_{24}H_{16}N_2$ (332.39): C 86.74, H 4.81, N 8.43; found: C 86.23, H 4.94, N 8.72.

*9,10-Bis(3-pyridyl)anthracene (**1p**):*[14b] white solid (554 mg, 1.64 mmol, 82 % yield); mp: 363 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ=8.91 (d, *J*=4.2 Hz, 4H), 7.64 (dd, *J*=3.3 Hz, 6.8 Hz), 7.47 (d, *J*=4.2 Hz, 4H), 7.42 (dd, 3.3 Hz, 6.8 Hz, 4H); ^{13}C NMR (60 MHz, $CDCl_3$) δ=150.0, 147.4, 134.7, 129.0, 126.4, 126.2, 125.9; IR (cm^{-1}, ATR) ũ=3032, 1590, 1540, 1438, 1401, 1193, 806, 770. Elemental analysis calcd (%) for $C_{24}H_{16}N_2$ (332.39): C 86.74, H 4.81, N 8.43; found: C 86.49, H 4.82, N 8.48.

Procedure for the Photooxygenations of Pyridylanthracenes 1*o*−*m*. In a 20 cm long Pyrex glass vial the anthracene (160 mg, 0.5 mmol) and 5,10,15,20-tetraphenylporphyrin (5 mg, 8 µmol) were dissolved in dichloromethane (10 mL). The solution was cooled to −20 °C and a slow steam of oxygen was continuously passed through while the vial was irradiated with a sodium lamp (400 W) for 12 h. The solvent was then evaporated and the product was isolated by column chromatography.

*9,10-Bis(2-pyridyl)-9,10-dihydro-9,10-epidioxidoanthracene (**1o-O$_2$**):* white solid (171 mg, 0.48 mmol, 95%); R_f = 0.30 (chloroform/ethyl acetate 95:5); mp: 199−205 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ=8.99 (d, *J*=4.8 Hz, 2H, HAr3), 7.96 (dd, *J*=7.8 Hz, 7.9 Hz, 2H, HAr5), 7.84 (d, *J*=7.9 Hz, 2H, HAr6), 7.50 (dd, *J*=4.8 Hz, 7.8 Hz, 2H, HAr4), 7.21 (br, 8H, H1, H2, H3, H4, H5, H6, H7, H8); ^{13}C NMR (60 MHz, $CDCl_3$) δ=154.5 (s, CAr1), 149.1 (d, CAr3), 140.3 (s, C11, C12, C13, C14), 137.7 (d, CAr5), 127.8 (d, C1, C4, C5, C8), 123.4 (d, CAr4), 123.5 (d, C2, C3, C5, C8), 122.7 (d, CAr6), 84.5 (s, C9, C10); IR (cm^{-1}, ATR) ũ=3066, 1588, 1571, 1457, 1434, 1215, 1157, 1099, 1049, 997, 918, 751; HRMS (ESI+): m/z: calcd for $C_{24}H_{16}N_2O_2$: 364.1212 [M]; found 364.1220 [M].

*9,10-Bis(3-pyridyl)-9,10-dihydro-9,10-epidioxidoanthracene (**1m-O$_2$**):* white solid (175 mg, 0.48 mmol, 97%); R_f = 0.33 (chloroform/ethyl acetate 95:5); mp: 285−288 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ=9.02 (s, 2H, HAr2), 8.86 (d, *J*=4.8 Hz, 2H, HAr6), 8.09 (d, *J*=6.1 Hz, 2H, HAr4), 7.62 (dd, *J*=4.8 Hz, 6.1 Hz, 2H, HAr5), 7.30 (dd, *J*=4.9 Hz, 8.0 Hz, 4H, H1, H4, H5, H8), 7.15 (dd, *J*=4.9 Hz, 8.0 Hz, 4H, H2, H3, H6, H7); ^{13}C NMR (60 MHz, $CDCl_3$) δ=149.7 (d, CAr2), 149.0 (d, CAr4), 139.2 (s, C11, C12, C13, C14), 134.7 (d, CAr4), 129.0 (s, CAr1), 128.9 (d, C1, C4, C5, C8), 125.2 (d, Ar5), 123.2 (d, C2, C3, C5, C8), 82.9 (s, C9, C10); IR (cm^{-1}, ATR) ũ=3034, 1514, 1412, 1267, 1155, 1099, 1021, 997, 758; HRMS (ESI+): m/z: calcd for $C_{24}H_{16}N_2O_2$: 364.1212 [M]; found 364.1215 [M].

*9,10-Bis(4-pyridyl)-9,10-dihydro-9,10-epidioxidoanthracene (**1p-O$_2$**):* white solid (173 mg, 0.48 mmol, 96%); R_f = 0.25 (chloroform/ethyl acetate 95:5); mp: 358−360 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ=8.94 (d, *J*=4.6 Hz, 4H, HAr3), 7.55 (d, *J*=4.6 Hz, 4H, HAr2), 7.30 (dd, *J*=3.2 Hz, 5.6 Hz, 4H, H1, H4, H5, H8), 7.16 (dd, *J*=3.2 Hz, 5.6 Hz, 4H, H2, H3, H6, H7); ^{13}C NMR (60 MHz, $CDCl_3$) δ=150.1 (d, CAr3), 141.4 (s, CAr1), 138.7 (s, C11, , C12, C13, C14), 128.2 (d, C1, C4, C5, C8), 123.2 (d, C2, C3, C5, C8), 122.3 (d, CAr2), 83.4 (s, C9,

C10); IR (cm^{-1}, ATR): ũ=3042, 1595, 1459, 1409, 1323, 1216, 918, 808, 757; HRMS (ESI+): m/z: calcd for $C_{24}H_{16}N_2O_2$: 364.1212 [M]; found 364.1208 [M].

Procedures for the Thermolyses of EPOs 1*o*–O_2-1*p*–O_2. The EPOs **1*m*–O_2** and **1*p*–O_2** (0.4 mmol) were heated at 110 °C in refluxing toluene for 24 h and the EPO **1*o*–O_2** was heated in chlorobenzene at 135 °C for 48 h. The solvent was evaporated and the crude product was chromatographed using the same eluent that was used for the starting material.

*4b,10a-Dihydro-4b,10a-di(2-pyridyl)-benzo[b]benzo[3,4]cyclobuta[1,2-e][1,4]dioxin (**7o**):* yellow solid (42 mg, 0.12 mmol, 30 %); R_f = 0.15 (chloroform/ethyl acetate 95:5); mp: 194–195 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ=8.3 (d, *J*=4.3 Hz, 2H), 7.52 (m, 6H), 7.29 (m, 2H), 7.21 (m, 2H), 6.99 (m, 2H), 6.91 (m, 2H); ^{13}C NMR (60 MHz, $CDCl_3$) δ=156.5, 148.9, 144.9, 144.5, 136.4, 132.0, 127.5, 124.3, 123.5, 123.2, 122.8, 118.9, 97.0; HRMS (ESI+): m/z: calcd for $C_{24}H_{16}N_2O_2$: 364.1212 [M]; found 364.1222 [M].

Associated Content

Supporting Information

NMR spectra of all compounds, determination of chemical rate constants of photooxygenations in various solvents and thermolysis, cyclic voltammograms, theoretical calculations, description of the $^1O_2$ trapping experiments. This material is available free of charge via the Internet at http://pubs.acs.org

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