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Steric and Electronic Substituent Effects Influencing Regioselectivity of Tetracene Endoperoxidation

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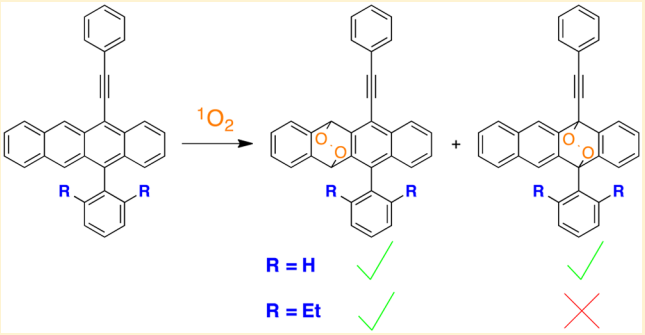
Supporting Information

ABSTRACT: This paper describes the influence of steric and electronic factors in the regioselectivity of endoperoxide formation of tetracene derivatives using $^1O_2$. A combination of kinetics experiments and product distributions resulting from these photosensitized oxidations demonstrates that, while the steric effect of *o*-alkyl groups on aryl substituents is highly localized to the substituted ring, the resistance to oxidation based on phenylethynyl substituents is more evenly distributed between the two reactive rings. These results are important for the rational design of highly persistent acenes.



Acenes are key compounds in a host of applications, including luminescent chemical sensors and solid-state optoelectronics.[1−4] In addition to the importance of their physical properties, their cycloaddition reactions are important as well. Especially important, in part because of the ubiquity of light and O_2, is the formation of acene endoperoxides through cycloaddition with singlet oxygen ($^1O_2$), which is generated through photosensitization.[5,6] This reaction is key in a number of sensing and dosimetry strategies for $^1O_2$, as the interruption of acene conjugation that results from this oxidation can change the observed relaxation pathways of coupled fluorophores.[7−12] In the context of optoelectronic applications such as transistors, this facile oxidation of, for example, pentacene or rubrene, is undesirable from the perspective of device performance and stability. A number of known approaches based on the effects of substituents on the core acenes, particularly alkynyl substitution of acene cores, increase acene persistence under photooxidative conditions.[13−21]

Rooted in our interest in understanding the effects of substituents on acene reactivity with $^1O_2$,[22] our group recently reported that highly persistent pentacene derivatives are available by combining on the central 6- and 13-positions (i) the steric effects from *ortho*-alkyl groups on an aryl ring substituent and (ii) the electronic effects of an ethynyl substituent, resulting from destabilization of radical or ionic intermediates of cycloaddition.[13] In contrast to the pentacene core, for which the central 6,13-site is the most reactive based on both frontier molecular orbital (FMO) and aromaticity analyses, the unsubstituted tetracene core has two central rings with equal reactivity. Therefore, the influence of differential substitution of these two sites on the regioselectivity of $^1O_2$ addition can give important information regarding the localized substituent effects on reactivity.[14,23] In this study, we probe both electronic effects of popular substituents of acenes—aryl and ethynyl substituents—as well as steric effects of *ortho*-ethyl groups on aryl substituents, on both the overall rate of tetracene−$^1O_2$ addition as well as their local effects on reactivity of the rings to which they are attached.

We designed a series of five tetracene derivatives, each of which is disubstituted in the 5- and 12-positions, in order to determine the impact of ethynyl and aryl substitution on the rates of endoperoxidation across the substituted 5,12-positions and unsubstituted 6,11-positions (Figure 1). As is well-known, symmetrically substituted diarylacenes were available by addition of excess phenyllithium (**1**) or 2,6-diethylphenyllithium (**2**) to 5,12-tetracenequinone, followed by reduction of the resulting dialkoxide. We prepared unsymmetrically substituted aryl-ethynyl tetracenes **3**−**5** by selective formation of the γ-hydroxyketone from 1 equiv of lithium phenylacetylide and tetracenequinone,[22,24,25] followed by addition of excess aryllithium reagent and reduction of the dialkoxide with $SnCl_2$ in aqueous HCl. Compounds **2**, **4**, and **5** are heretofore unreported in the open literature.

Table 1 summarizes the absorbance and steady-state fluorescence properties of **1**−**5** in dichloromethane. The general shapes and extinction coefficients (roughly 10^4 M^{-1} s^{-1}) of all five molecules are consistent with the absorbance spectra reported for other similar tetracene derivatives.[22] The greater conjugation imparted by phenylethynyl substituents relative to twisted aryl substituents causes the lowest energy electronic transitions of **3**−**5** to have an ∼30 nm bathochromic shift from **1** and **2**. The fluorescence spectra of these compounds also reflect this trend, with a bathochromic shift of approximately 35−40 nm upon substitution of a phenylethynyl group for an aryl group. Finally, all the tetracenes are

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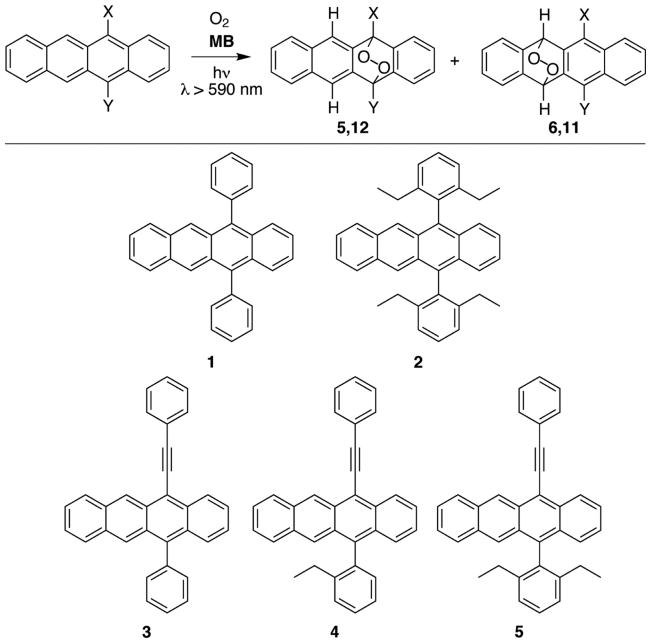

Figure 1. Top: Synthesis of regioisomeric mixtures of tetracene endoperoxides through selective irradiation of the photosensitizer methylene blue (**MB**). Bottom: Structures of tetracenes **1**–**5** studied in this work.

Table 1. Absorbance and Fluorescence Properties of 1–5 in CH_2Cl_2

	λ_{max} (abs) [nm][a]	log(ε)	λ_{max} (em) [nm]	Φ_F[b]
1	493	3.9	503	0.97
2	495	4.2	501	0.56
3	522	4.1	541	0.79
4	522	4.2	537	0.38
5	523	4.0	538	0.57

[a]Maximum of the 0,0 transition of the lowest energy vibronic band. [b]Determined relative to fluorescein in 0.1 M NaOH (aq).

strongly fluorescent, with ethyl substitution lowering the quantum yields of fluorescence relative to nonethylated derivatives, presumably due to the "loose bolt" effect through enhanced transfer of excited state energy to vibrations involving the alkyl groups.[26]

To determine the effect of substituents on the rates of endoperoxidation of the substituted and unsubstituted rings, we subjected each tetracene to singlet oxygen using the dye methylene blue (**MB**) as photosensitizer in $CHCl_3$ and followed the disappearance of each acene as a function of irradiation time by UV/vis spectrophotometry. We chose **MB** as photosensitizer because it has a strong absorbance at wavelengths greater than 600 nm, where the tetracenes under investigation here do not absorb, allowing our results to remain free of complications by differences in reactivity between the acenes in their excited states, such as [4 + 4] dimerization, or by potential differences in $^1O_2$ sensitization by excited state acenes. To determine the relative rates of photooxidation of each of the tetracenes, we used a 9,10-diphenylanthracene (DPA) as a standard, as it has a known rate constant of reaction with $^1O_2$ ($\sim 3 \times 10^6$ M^{-1} s^{-1}).[27] Comparing the reactivity of tetracenes **1**–**5** to DPA experimentally allows us to estimate the observed rate of reaction for each tetracene, using the common approximation that the steady-state concentration of $^1O_2$ does not vary significantly with different acenes.[27] Table 2 lists the bimolecular rate constants for **1**–**5**, determined by back-to-back comparison to the rate of disappearance of DPA.

Table 2. Rate Constants ($\times 10^6$ M^{-1} s^{-1}) and Regioselectivity of 1–5 in $CHCl_3$

	k_{tot}	EPO ratio (6,11:5,12)	$k_{5,12}$	$k_{6,11}$
1	63	25:75	47	16
2	22	>95:5	<1.1	21
3	28	35:65	18	10
4	18	75:25	4.6	14
5	9	>95:5	<0.5	8.6

Figure 2 shows representative spectral data for the disappearance of acene **4** during irradiation of **MB**, as well as

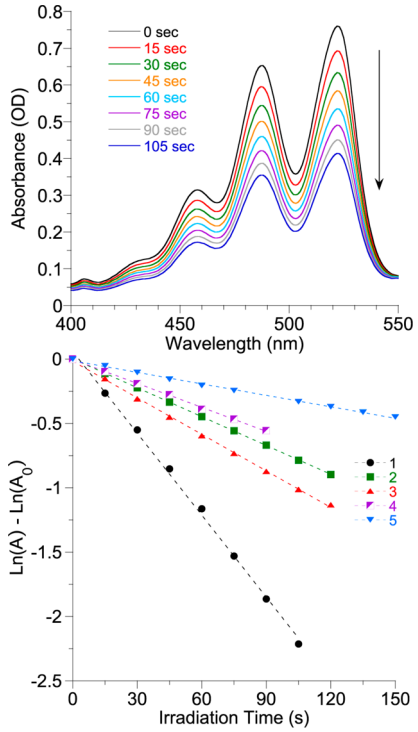

Figure 2. Top: Disappearance of compound **4** upon irradiation of **MB** (OD = 0.88 at λ_{max} of 653 nm) in $CHCl_3$ monitored by UV/vis spectrophotometry. Bottom: Fits of kinetics of disappearance to pseudo-first-order kinetic models for tetracenes **1**–**5**.

the kinetic data for each acene represented as a pseudo-first-order kinetic plot. The kinetic data for each tetracene fit well to a pseudo-first-order rate law model. As expected, all the tetracene derivatives investigated reacted faster than DPA, due to the decreased loss of aromatic stabilization upon reaction of longer acenes compared to shorter acenes. Consistent with reported observations of acene derivatives, substitution of one phenylethynyl substituent for an aryl substituent (comparing **1** to **3**) results in a decrease in reaction rate with $^1O_2$.[13,14,22] Moreover, further substitution with ethyl groups in the *ortho* positions of aryl groups directly bound to the acene core also slows oxidation, with one ethyl group on an aryl substituent decreasing the rate of oxidation by one-third (comparing **3** to **4**), and two ethyl groups (comparing **3** and **5**) decreasing the rate of oxidation by two-thirds. We attribute this pattern to each ethyl group hindering one face of the acene. As Miller and

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co-workers reported for analogous pentacene derivatives,[17] double substitution with 2,6-diethylaryl substituents slowed the oxidation of tetracene **2** relative to **1**, although, for this tetracene, it reduced the rate by only two-thirds. Quantitatively, therefore, both the use of steric shielding with alkyl groups and electronic deactivation with phenylethynyl groups imparts less protection against oxidation with $^1O_2$ for tetracenes than pentacenes, relative to the diphenyl derivatives.

To determine how these substituents affect the regiochemistry of addition (5,12 or 6,11), we determined the distribution of products of $^1O_2$-mediated endoperoxidation of **1**–**5** by ^{1}H NMR analysis of unpurified oxidation mixtures. Identification of the regiochemistry of endoperoxides was based on the chemical shift of the resonance assigned to hydrogen atoms on the 6- and 11-positions, which differ by up to 2 ppm for the two regioisomers (see Figure 3). The ^{1}H NMR spectra of

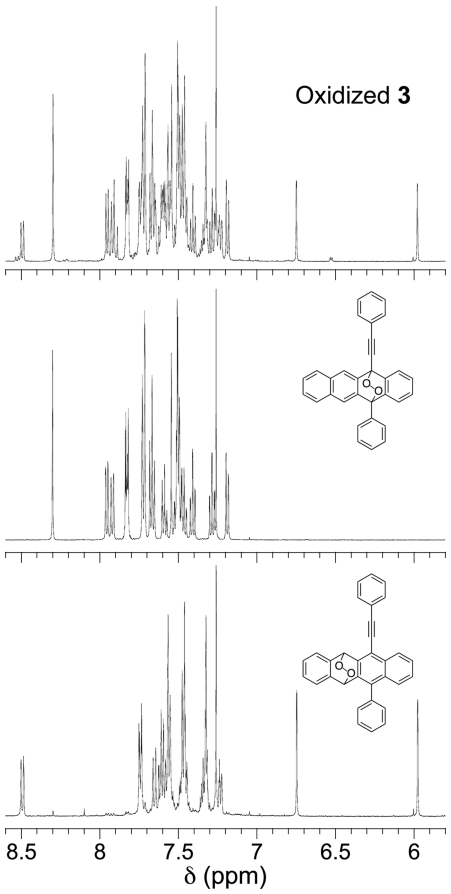

Figure 3. ^{1}H NMR spectra of crude mixture of $^1O_2$-mediated oxidation of **3** (top) and of each of the purified endoperoxides.

endoperoxides of compounds **2**, **4**, and **5** show splitting of resonances of the ethyl groups consistent with either (i) the presence of ethyl groups that are both *syn* and *anti* to the endoperoxide (**2** and **5**) or (ii) a mixture of *syn* and *anti* stereoisomers (**4**). As shown in Table 2, the presence or absence of alkyl groups on the *ortho* positions of aryl substituents has a large influence on the regioselectivity of the addition. Tetracenes that had either one or two 2,6-diethylphenyl substituents (**2** and **5**) showed no more than trace quantities of endoperoxides formed at the substituted 5- and 12-positions. We attribute this high degree of regioselectivity to steric hindrance in the transition state of $^1O_2$ addition to the substituted ring from the ethyl groups on twisted aryl substituents blocking both faces of the acene. Decreasing the number of *ortho*-ethyl groups on aryl substituents reduced the preference for addition to the unsubstituted ring: **4** showed only a modest 3:1 ratio favoring the 6,11 isomer, and both **1** and **3**, which lack any *ortho*-alkyl groups on pendant aryl substituents, reacted with $^1O_2$ preferentially at the substituted ring. We were able to separate the mixtures of endoperoxides derived from **1** and **3** by flash chromatography for independent characterization.

Combining the kinetic and product distribution results allows for a deeper level of quantitative analysis by calculating the effect of substituents on the rates of addition to each of the nominally reactive central rings using eqs 1 and 2

$$k_{5,12} = \chi_{5,12} \cdot k_{tot} \quad (1)$$

$$k_{6,11} = \chi_{6,11} \cdot k_{tot} \quad (2)$$

in which $X_{x,y}$ is the mole fraction of the endoperoxide at either the 5,12- or 6,11-positions derived from NMR analysis. This model assumes that the formation of each endoperoxide follows a pseudo-first-order rate law, and the reactions are not reversible. The Supporting Information contains a derivation of the conclusion that, in such a situation, the ratio of products will equal the ratio of rate constants. From comparing **1** to **2** and **3** to either **4** or **5**, it is clear that the steric effect imparted by *ortho*-alkyl groups on aryl substituents is highly localized to the substituted ring; the reduction in overall rate comes entirely from decreased reactivity of the substituted 5,12 ring. In contrast, the overall reduction in rate of oxidation of phenylethynylated **3** relative to **1**, attributable to a decrease in stability of a radical or zwitterionic intermediate of oxidation, is more evenly distributed between the two rings. This is consistent with the results of Fudickar and Linker, who showed that the major oxidation product of 5,12-bis(4-*tert*-butylphenylethynyl)tetracene was also the disubstituted ring.[14]

In conclusion, we have shown that analysis of the kinetics and regioselectivity of tetracene oxidation by photochemically generated $^1O_2$ reveals details about the nature of different substituent effects that promote increased resistance to oxidation. Steric shielding of one ring enables high levels of regioselectivity of oxidation of tetracene, which otherwise has similar reactivity for the two inner rings. We believe that the value of these studies will be especially important in the rational design of highly persistent acenes with multiple groups of substituents, such as rubrene derivatives and acenes longer than pentacene, for preventing reactions observed to cause decomposition.

EXPERIMENTAL SECTION

General Information. All synthetic experiments were performed under standard air-free and under an argon gas atmosphere with magnetic stirring unless otherwise mentioned. Crude products were purified using silica gel (230–400 mesh) as stationary phase. NMR spectra were acquired on either a 500 MHz or a 300 MHz spectrometer. Chemical shifts were reported relative to residual protonated solvent (7.26 ppm for $CHCl_3$). High-resolution mass spectra (HRMS) were obtained using a Fourier transform ion cyclotron resonance mass spectrometer.

Electronic absorbance spectra were acquired with a double-beam spectrophotometer. Emission spectra were obtained using a spectrometer equipped with a double excitation monochromator and single emission monochromator, a photomultiplier tube for detection of emitting photons, and a 75 W Xe lamp for sample excitation at a

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90° angle from the incident irradiation. Fluorescence quantum yields were determined relative to fluorescein in 0.1 M aqueous NaOH. Pseudo-first-order kinetics of acenes were determined using methylene blue sensitizer to generate singlet oxygen with a 200 W Hg/Xe lamp equipped with a condensing lens, water filter, and manual shutter, with a 590 nm long-pass filter.

Tetracene 1. Phenyllithium (2.41 mL, 4.82 mmol, 2.0 M) was dissolved in 30 mL of dry THF and cooled to −78 °C in a reaction flask. Tetracen-6,12-dione (0.178 g, 0.689 mmol) was added to the flask. It was allowed to slowly warm to room temperature and stirred overnight. The reaction was quenched by adding 6 mL of NH_4Cl aqueous solution, and the THF was removed *in vacuo*. The organics were extracted with dichloromethane and dried over $MgSO_4$, and solvent was removed *in vacuo*. Then, the crude diol product was reduced by adding 7.5 mL of 10% H_2SO_4 aqueous solution saturated with tin(II) chloride dihydrate and stirred overnight at room temperature. Work up procedure was repeated as for diol. The crude product was purified by silica gel flash column chromatography using hexanes/CH_2Cl_2 (3:1, v/v) as eluent and recrystallized from hexanes and CH_2Cl_2 to yield the desired product (0.036 g, 24%) as a red powder. ^{1}H NMR (500 MHz, THF): δ 8.32(s, 2H), 7.80−7.77 (m, 2H), 7.67−7.63 (m, 6H), 7.62−7.60 (m, 2H), 7.55−7.53 (m, 4H), 7.30−7.26 (m, 2H), 7.24−7.22(m, 2H). Our NMR spectra of this compound agree with the literature.[28] HRMS (DART) calcd for $C_{30}H_{20}$ $[M + H]^+$, 381.1638, found, 381.1646

5,12-Endoperoxide of Tetracene 1. A solution of **1** (0.020 g) and methylene blue (0.0015 g) in $CHCl_3$ was irradiated at $\lambda > 590$ nm in a quartz cuvette with a stir bar while bubbling the solution with air. The oxidation completed at around 1 h, as determined by TLC and NMR spectroscopy. The solvent was removed *in vacuo*, and the crude product was purified using silica gel column chromatography with hexanes/CH_2Cl_2 (1:1, v/v) to yield the product as a colorless powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81−7.79 (m, 2H), 7.71−7.68 (m, 3H), 7.62−7.59 (m, 2H), 7.43−7.41 (m, 1H), 7.246(s, 2H). ^{13}C NMR (500 MHz, $CDCl_3$): δ 140.0, 137.2, 133.1, 132.3, 128.4, 128.3, 128.2, 127.9, 127.6, 126.6, 123.7, 122.9, 84.0. HRMS (DART) calcd for $C_{30}H_{20}O_2$ $[M + H]^+$, 413.1536, found, 413.1534.

6,11-Endoperoxide of Tetracene 1. Isolated as a second fraction from the flash column for the separation of endoperoxides of **1** as a light yellow powder. ^{1}H NMR (500 MHz, C_6D_6): δ 7.73−7.72 (m, 1H), 7.72−7.41 (m, 2H), 7.23−7.20 (m, 6H), 7.15−7.14(m, 2H), 7.03−7.02(m, 2H), 6.95−6.94 (m, 2H), 6.85−6.84 (m, 2H), 6.11 (s, 2H). ^{13}C NMR (500 MHz, C_6D_6): δ 139.2, 137.1, 134.8, 133.6, 132.3, 131.0, 130.7, 129.0, 128.6, 127.3, 126.6, 123.6, 77.4. HRMS (ESI) calcd for $C_{30}H_{20}O_2$ $[M + Na]^+$, 435.1356, found, 435.1369.

1-Iodo-2,6-diethylbenzene. *para*-Tolunesulfonic acid (10.4 g, 0.060 mol) was dissolved in 80 mL of *t*-BuOH at 25 °C. While stirring this solution in the flask, 3.0 g (3.31 mL, 0.020 mol) of 2,6-diethylaniline was added dropwise. A solution of $NaNO_2$ (2.81 g, 0.040 mol) and KI (8.34 g, 0.050 mol) in 12 mL of deionized water was added and stirred for an hour. The reaction mixture was poured into 250 mL of water, and 1 M $NaHCO_3$ was added until the pH > 8, after which 40 mL of saturated aqueous $Na_2S_2O_3$ was added. The reaction was extracted with ether and dried over $MgSO_4$. The solvent was removed *in vacuo* to yield the product (2.5 g, 48%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21 (t, J = 7.5, 1H), 7.11 (d, J = 7.5 Hz, 2H), 2.83 (q, J = 7.5 Hz, 4H), 1.24 (t, J = 5.5 Hz, 2H).[29]

Tetracene 2. *n*-Butyllithium (2.1 mL, 3.3 mmol, 1.6 M) in hexanes was added to a solution of 1-iodo-2,6-diethylbenzene (1.02 g, 0.81 mmol) in 30 mL of dry THF, and the mixture was stirred for 5 h at −78 °C. 5,12-Tetracenequinone (0.18 g, 0.69 mol) was added, and the reaction mixture was allowed to warm to room temperature slowly and was stirred for 5 h. Then, the product in the reaction mixture was reduced by adding 6 mL of 10% H_2SO_4 aqueous solution saturated with tin(II) chloride dihydrate and stirred overnight at room temperature. The reaction was quenched with 4 mL of a saturated aqueous solution of NH_4Cl, and the THF was removed by rotary evaporation. The organics were extracted with dichloromethane, washed with brine, and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the crude product was purified by silica gel flash chromatography using hexanes/CH_2Cl_2 (4:1, v/v) as the eluent and recrystallized from hexanes/CH_2Cl_2 to yield **2** (0.25 g, 73%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (s, 2H), 7.80 (m, 2H), 7.57 (t, J = 8.0 Hz, 2H), 7.50−7.48 (m, 2H), 7.42(d, J = 7.5 Hz, 4H), 7.29−7.27 (m, 2H), 7.23−7.21 (m, 2H), 2.12 (q, J = 7.5 Hz, 8H), 7.50−7.42 (t, J = 7.5 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.8, 137.1, 135.0, 131.2, 129.7, 129.2, 128.5, 128.2, 126.9, 125.8, 125.3, 125.0, 124.9, 26.6, 14.8. HRMS (DART) calcd for $C_{38}H_{36}$ $[M + H]^+$, 493.2890, found, 493.2905. mp = 210−211 °C.

6,11-Endoperoxide of Tetracene 2. The oxidation was executed using the same procedure as followed for tetracene **1**. The crude product was purified using silica gel column chromatography with eluent hexanes/CH_2Cl_2 (1:1, v/v) to yield the product as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (t, J = 7.50 Hz, 2H), 7.32−7.30 (m, 2H), 7.28−7.26 (m, 4H), 7.25−7.23 (m, 2H), 5.63 (s, 2H), 2.34−2.27 (m, 4H), 1.97 (t, J = 7.5 Hz, 2H), 1.87 (q, J = 7.5 Hz, 2H), 0.93 (t, J = 7.5 Hz, 6H), 0.71 (t, J = 7.5 Hz, 6H). ^{13}C NMR (500 MHz, $CDCl_3$): δ 144.1, 143.7, 138.8, 134.9, 133.9, 132.6, 129.1, 127.1, 126.9, 126.7, 126.0, 124.0, 77.5, 27.3, 27.1, 15.1, 15.1. HRMS (DART) calcd for $C_{38}H_{36}O_2$ $[M + H]^+$, 525.2788, found, 525. 2803.

12-Hydroxy-12-phenylethynyltetracen-5-one. *n*-Butyllithium (1.0 mL, 1.6 mmol, 1.6 M) in hexanes was added to a solution of 0.21 mL (2.0 mmol) of phenylacetylene in 9 mL of dry THF dropwise at −78 °C, and the mixture was stirred vigorously for 30 min. The reaction mixture was slowly added to a solution of 0.500 g (1.96 mmol) of 5,12-tetracenequinone in 6 mL dry THF at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was filtered through a fritted funnel, and the solid was washed with 100 mL of THF/H_2O (1:1, v/v). The filtrate was mixed with 100 mL of a saturated aqueous solution of NH_4Cl and stirred at room temperature for 30 min. The suspension was then extracted with 150 mL of ether and dried over $MgSO_4$. The solvent was removed *in vacuo*, and the crude ketoalcohol was purified by flash chromatography on silica gel using hexanes/ethyl acetate (5:1, v/v) to yield 0.43 g (69%) of the product. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.83 (s, 1H), 8.65 (s, 1H), 8.34−8.25 (m, 2H), 8.03 (d, J = 8.0 Hz, 1H), 8.00(d, J = 8.0 Hz, 1H), 7.79−7.75 (m, 1H), 7.66−7.63 (m, 1H), 7.61−7.55 (m, 2H), 7.46−7.44 (m, 2H), 7.73−7.28 (m, 3H), 3.14 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 183.6, 144.2, 139.5, 136.0, 134.4, 132.8, 132.0, 130.06, 130.0, 129.6, 129.3, 129.06, 129.0, 128.43, 128.36, 128.19, 127.81, 127.57, 127.44, 127.26, 122.1, 91.3, 86.7, 67.3. HRMS (ESI) calcd for $C_{26}H_{16}O_2$ $[M + Na]^+$, 383.1048, found, 383.1061.

Tetracene 3. 12-Hydroxy-12-phenylethynyltetracen-5-one (0.10 g, 0.28 mmol) was dissolved in 6 mL of dry THF and cooled to −78 °C. Phenyllithium (0.56 mL, 1.1 mmol, 2.0 M) in dibutylether was added dropwise. The reaction was allowed to slowly warm to room temperature and stirred overnight. Reduction was achieved by adding 4.5 mL of 10% HCl aqueous solution saturated with tin(II) chloride dihydrate and stirring overnight at room temperature. The reaction mixture was then extracted with CH_2Cl_2 and dried over $MgSO_4$. The solvent was removed *in vacuo*, and the crude product was purified by silica gel flash chromatography using hexanes/CH_2Cl_2 (3:1, v/v) as eluent and recrystallized from hexanesCH_2Cl_2 to yield the desired product (0.070 g, 69%) as a red powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.36 (s, 1H), 8.74 (d, J = 8.5 Hz,1H), 8.31 (s, 1H), 8.12 (d, J = 8.50 Hz, 2H), 7.88 (d, J = 7 Hz, 1H), 7.82 (d, J = 8.5, 1H), 7.68−7.61 (m, 4H), 7.57−7.51 (m, 5H), 7.50−7.42 (m, 2H), 7.41−7.31 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.8, 138.5, 132.6, 131.8, 131.7, 131.5, 131.4, 130.3, 129.5, 129.0, 128.6, 128.6, 128.5, 128.4, 127.8, 127.5, 127.1, 126.5, 126.2, 125.9, 125.5, 125.4, 125.3, 123.9, 117.2. HRMS (DART) calcd for $C_{32}H_{20}$ $(M + H)^+$, 405.1638, found, 405.1656. mp = 128−129 °C.

5,12-Endoperoxide of Tetracene 3. The oxidation was executed using the same procedure as followed for tetracene **1**. The crude product was purified using silica gel column chromatography with hexanes/CH_2Cl_2 (1:1, v/v) to yield the product as a reddish powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31 (s, 1H), 7.95(d, J = 7.5,1H), 7.92 (d, J = 8.0 Hz, 1H), 7.83−7.82 (m, 2H), 7.72 (d, J = 8.0 Hz 3H), 7.66 (t, J = 8.0 Hz, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.54 (s, 1H), 7.52−7.45

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(m, 5H), 7.42−7.40 (m, 1H), 7.30−7.27 (m, 1H), 7.19 (d, J = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.2, 138.3, 136.2, 135.3, 132.8, 132.6, 132.5, 129.8, 128.6, 128.5, 128.4, 128.3, 128.18, 128.16, 127.5, 127.0, 126.7, 123.5, 122.9, 121.9, 121.5, 95.0, 83.9, 79.0. HRMS (DART) calcd for $C_{32}H_{20}O_2$ $[M + H]^+$, 437.1536, found, 437.1527.

6,11-Endoperoxide of Tetracene 3. Obtained by the same procedure as the 5,12-endoperoxide of **1**, as a second fraction during chromatographic purification as a colorless powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.50−8.49 (m, 1H), 7.75−7.73 (m, 2H), 7.66 (d, J = 8.5 Hz, 1H), 7.63−7.61 (m, 2H), 7.60−7.55 (m, 4H), 7.49−7.44 (m, 4H), 7.34−7.32 (m, 3H), 7.25−7.21 (m, 1H), 6.75 (s, 1H), 5.98 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.1, 137.6, 136.8, 136.0, 135.1, 132.9, 132.3, 131.8, 131.5, 130.9, 130.4, 128.9, 128.8, 128.6, 128.5, 128.3, 128.2, 127.2, 127.1, 126.9, 124.1, 123.4, 123.0, 115.8, 98.9, 83.7, 77.8, 77.1. HRMS (DART) calcd for $C_{32}H_{20}O_2$ $[M + H]^+$, 437.1536, found, 437.1530.

Tetracene 4. 1-Bromo-2-ethylbenzene (0.51 g, 2.8 mmol) was dissolved in 5 mL of dry THF and cooled to −78 °C. *n*-Butyllithium (1.7 mL, 2.7 mmol, 1.6 M) in hexanes was slowly added to the flask, and the mixture was stirred for 5 h at the same temperature. 12-Hydroxy-12-phenylethynyltetracen-5-one (0.25 g, 0.69 mmol) was added, and the reaction was allowed to warm to room temperature slowly and was stirred overnight. The following day, 6 mL of 10% HCl aqueous solution saturated with tin(II) chloride dihydrate was added, and the reaction was stirred overnight at room temperature. After addition of 5 mL of saturated aqueous NH_4Cl solution and removal of THF by rotary evaporation, the organics were extracted with dichloromethane and dried over $MgSO_4$. The solvent was removed *in vacuo*, and the crude product was purified by silica gel flash chromatography using hexanes/CH_2Cl_2 (2:1, v/v) as the eluent and recrystallized from hexanes/CH_2Cl_2 to yield the desired product (0.086 g, 28%) as a red solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.37 (s, 1H), 8.75−8.74 (m, 1H), 8.18(s, 1H), 8.21−8.12 (m, 1H), 7.89−7.87 (m, 2H), 7.82 (d, J = 8.5 Hz, 1H), 7.61−7.56 (m, 2H), 7.55−7.50 (m, 4H), 7.48−7.42 (m, 3H), 7.37−7.34 (m, 1H), 7.33−7.30 (m, 2H), 2.2 (q, J = 7.5 Hz, 2H), 0.86 (t, J = 7.8 Hz, 3H). ^{13}C NMR (500 MHz, $CDCl_3$): δ 144.0, 138.1, 137.7, 132.8, 132.0, 131.9, 131.7, 131.6, 130.5, 129.7, 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 127.6, 127.2, 126.5, 126.4, 126.1, 126.0, 125.7, 125.5, 125.5, 124.0, 117.2, 101.9, 87.2, 26.5, 15.1. HRMS (DART) calcd for $C_{34}H_{24}$ $[M + H]^+$, 433.1951, found, 433.1957. mp = 121−122 °C

6,11-Endoperoxide of Tetracene 4. Formation of endoperoxide followed the same exact procedure as described for **1**. Only one of the endoperoxide regioisomers, however, could be obtained pure through flash chromatography as a light yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.49 (d, J = 8.0, 1H), 7.75−7.73 (m, 2H), 7.62−7.58(m, 1H), 7.56 (d, J = 7.0, 1H), 7.52−7.48 (m, 1H), 7.48−7.45 (m, 4H), 7.44−7.38 (m, 3H), 7.36−7.32 (m, 2H), 7.30−7.26 (m, 1H), 7.22(d, J = 7.0 Hz, 1H), 6.74(s, 1H), 5.76 (s, 1H), 2.13−2.04 (m, 2H), 0.79 (t, J = 7.5, 3H).

Tetracene 5. 1-Iodo-2,6-diethylbenzene (0.57 g, 2.2 mmol) was dissolved in 10 mL of dry THF and cooled to −78 °C. *n*-Butyllithium (1.1 mL, 1.6 mmol, 1.6 M) in hexanes was slowly added to the flask, and the mixture was stirred for 5 h at the same temperature. 12-Hydroxy-12-phenylethynyltetracen-5-one (0.22 g, 0.61 mmol) was added, and the reaction was allowed to slowly warm to room temperature and stirred overnight. The diol product was then reduced by adding 6 mL of 10% HCl aqueous solution saturated with tin(II) chloride dihydrate and stirred overnight at room temperature. 5 mL of saturated aqueous NH_4Cl solution was added, and the reaction was extracted with dichloromethane and dried over $MgSO_4$. The solvent was removed *in vacuo*, and the crude product was purified by silica gel flash chromatography using hexanes/CH_2Cl_2 (2:1, v/v) as eluent and recrystallized from hexanes/CH_2Cl_2 to yield the desired product (0.086 g, 31%) as a red powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.37 (s, 1H), 8.74 (d, J = 8.5 Hz, 1H), 8.14−8.11 (m, 2H), 7.89−7.87 (m, 2H), 7.82 (d, J = 8.5 Hz, 1H), 7.58−7.46 (m, 6H), 7.46−7.34 (m, 4H), 7.32−7.28 (m, 1H), 2.04 (q, J = 7.5 Hz, 4H), 0.81 (t, J = 8.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.9, 137.4, 136.7, 133.0, 132.3, 132.12, 132.05, 131.9, 130.7, 130.0, 129.2, 129.0, 128.93, 128.88, 128.82, 128.74, 127.5, 126.8, 126.15, 126.12, 126.10, 126.02, 125.77, 125.72, 124.1, 117.2, 102.1, 87.4, 26.8, 15.2. HRMS (DART) calcd for $C_{36}H_{28}$ $[M + H]^+$, 461.2264, found, 461.2265. mp = 110−111 °C

6,11-Endoperoxide of Tetracene 5. The oxidation was executed using the same procedure as followed for tetracene **3**. The crude endoperoxide was purified using silica gel chromatography with eluent hexanes/CH_2Cl_2 (1:1, v/v) to yield the product as a light yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.50−8.48 (m, 1H), 7.75−7.73 (m, 2H), 7.61−7.58 (m, 1H), 7.56 (d, J = 7.0 Hz, 1H), 7.51−7.45(m,, 4H), 7.43−7.40 (m, 1H), 7.37−7.29 (m, 5H), 6.75 (s, 1H), 5.66 (s, 1H), 2.34−2.27 (m, 2H), 1.97 (t, J = 7.5 Hz, 1H), 1.87 (q, J = 7.5 Hz, 1H), 1.00 (t, J = 7.5 Hz, 3H), 0.75 (t, J = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.6, 143.4, 138.0, 137.7, 137.4, 133.7, 133.6, 133.1, 132.5, 131.9, 129.0, 128.9, 128.8, 128.4, 128.3, 127.5, 127.3, 127.1, 127.0, 126.1, 125.7, 124.2, 124.0, 123.1, 115.5, 98.9, 83.8, 78.0, 26.8, 26.6, 15.1, 15.0. HRMS (DART) calcd for $C_{36}H_{28}O_2$ $[M + H]^+$, 493.2162, found, 493.2171.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01692.

NMR spectra of all unreported tetracenes and endoperoxidation mixtures, UV/vis absorbance spectra from kinetics experiments, and derivation of eqs 1 and 2 (PDF)

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Notes

The authors declare no competing financial interest.

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