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Why Triple Bonds Protect Acenes from Oxidation and Decomposition

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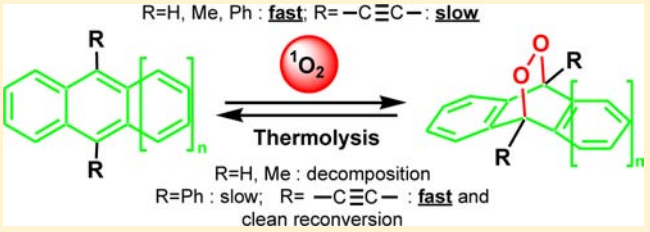
Supporting Information

ABSTRACT: An experimental and computational study on the impact of functional groups on the oxidation stability of higher acenes is presented. We synthesized anthracenes, tetracenes, and pentacenes with various substituents at the periphery, identified their photooxygenation products, and measured the kinetics. Furthermore, the products obtained from thermolysis and the kinetics of the thermolysis are investigated. Density functional theory is applied in order to predict reaction energies, frontier molecular orbital interactions, and radical stabilization energies. The combined results allow us to describe the mechanisms of the oxidations and the subsequent thermolysis. We found that the alkynyl group not only enhances the oxidation stability of acenes but also protects the resulting endoperoxides from thermal decomposition. Additionally, such substituents increase the regioselectivity of the photooxygenation of tetracenes and pentacenes. For the first time, we oxidized alkynylpentacenes by using chemically generated singlet oxygen ($^1O_2$) without irradiation and identified a 6,13-endoperoxide as the sole regioisomer. The bimolecular rate constant of this oxidation amounts to only 1×10^5 s^{-1} M^{-1}. This unexpectedly slow reaction is a result of a physical deactivation of $^1O_2$. In contrast to unsubstituted or aryl-substituted acenes, photooxygenation of alkynyl-substituted acenes proceeds most likely by a concerted mechanism, while the thermolysis is well explained by the formation of radical intermediates. Our results should be important for the future design of oxidation stable acene-based semiconductors.

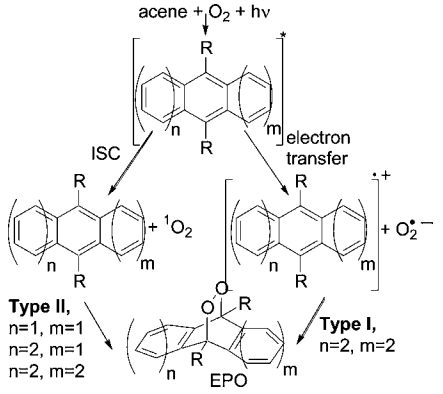


INTRODUCTION

Functionalized oligoacenes have attracted enormous interest because of their applications as luminescent and semiconducting materials.[1] Anthracenes and tetracenes have been employed as fluorophores for ion sensing and as electroluminescent devices,[2,3] whereas the larger pentacenes are widely utilized as organic field effect transistors showing exceptionally high charge transport properties.[4] It is a great challenge to develop compounds of this class with higher stability against oxidation. When exposed to light and air, acenes undergo a reaction with oxygen to give endoperoxides (EPOs).[5] This reaction is not only the key step in the mechanism of photodegradation of semiconducting materials but also serves in the design of oxygen fluorophores.[6] A very important aspect is that the photooxidations of some acenes are reversible, as the EPOs react back to the parent acenes and oxygen under thermolysis.[7] We applied this reversible photooxidation of acenes for erasable photopatterning.[8] To a varying extent the evolved oxygen can be in its excited state, and such EPOs were used as oxygen carriers.[9,10] Extensive research has been devoted to elucidate the mechanisms of the photooxidation and the thermolysis in order to control the reactivity toward oxygen and the reversibility.[7,11]

In a photooxidation, singlet oxygen ($^1O_2$) is initially formed by sensitization which reacts with acenes to afford EPOs. This process is denoted as Type II photooxidation, but its mechanism (concerted vs stepwise) is still a matter of debate (Scheme 1).[11b,d] Typically, a triplet sensitizer is required with a triplet energy greater than the energy barrier between $^3O_2$ and $^1O_2$ (22.5 kcal/mol). This is fulfilled with anthracenes and tetracenes, which generate $^1O_2$ in the first step and undergo cycloaddition in the second step. However, a photooxidation is also observed if the triplet energy is too low to generate $^1O_2$, which is operative for some substituted pentacenes. It was

Scheme 1. Formation of EPOs from Oligoacenes by Type I and Type II Mechanisms



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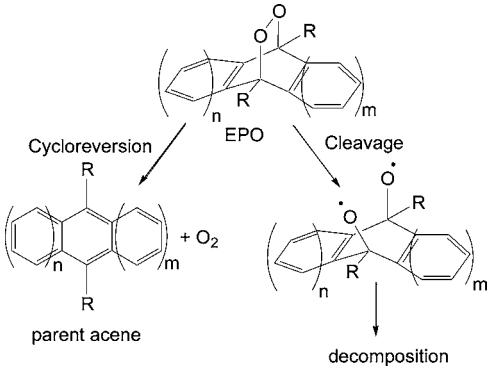
extensively discussed that in this case the EPO is formed by a reaction where the acene is first excited by light and subsequently transfers an electron to $^3O_2$ (Type I reaction, Scheme 1).[12] Type I and Type II reactions are believed to operate simultaneously whenever the acene is excited by irradiation. At present the only available kinetic data for the oxidation result from superimpositions of these two competing processes. Moreover, there is still ongoing discussion about the possible pathways of a Type II reaction: the reaction between the acene and $^1O_2$ can proceed along either a concerted or a stepwise pathway. Theoretical calculations from Bendikov have shown that pentacene exclusively reacts along the stepwise path, whereas anthracene reacts via both concerted and stepwise biradical pathways.[11d] However, very recently we found experimental evidence for a stepwise path with ionic intermediates.[13]

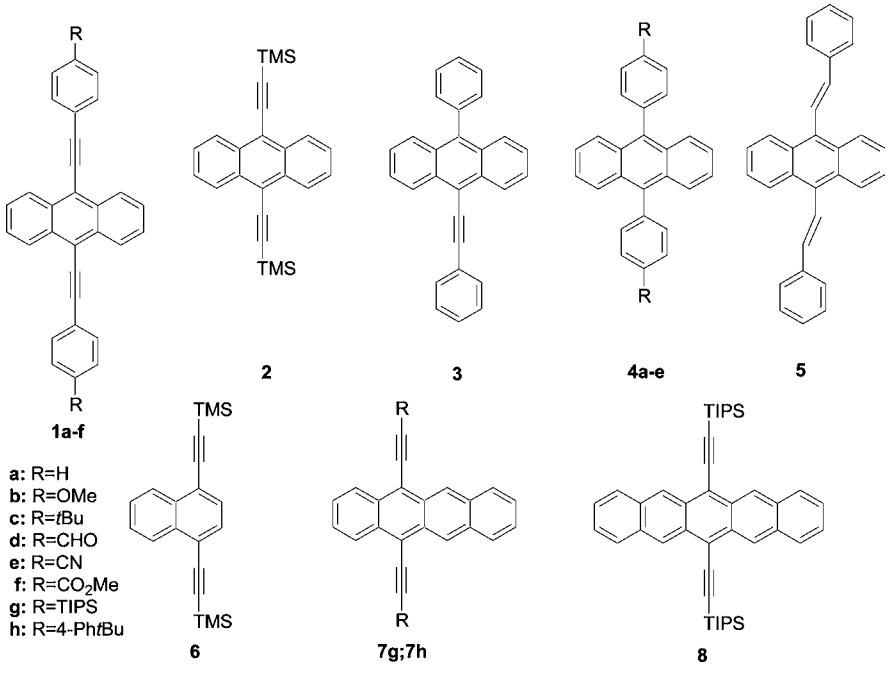
The retro-reaction of an EPO to the parent acene competes with rearrangement to diepoxides or decomposition to quinones (Scheme 2).[14] Decisive for this competition is the difference between the dissociation energies of the C−O versus C−C bonds.[15]

Scheme 2. Possible Pathways of EPO Transformations



The oxidation stability of an acene increases with decreasing number of fused rings. For applications of anthracenes as semiconductors, the disadvantage of their low charge carrier mobilities is compensated by their high stability toward oxidation as compared to tetracenes and pentacenes, which decompose already in the presence of visible light and air.[16] Additionally, the substituents in the *peri*-positions contribute to the stability by their steric demand and conjugation. Maliakal reported that the oxidation stability of pentacene can be significantly enhanced by a factor of 50 when alkynyl substituents are introduced at the periphery.[12] Theoretical studies of a series of 6,13-substituted pentacenes revealed that the alkynyl group causes a decrease of the LUMO energy while the level of the HOMO does not differ much from that of unsubstituted pentacene. Based on these studies, Maliakal et al. explained the abnormal photostability of alkynylpentacenes by the extremely low LUMO energy: If a Type I pathway is operative, the excited state is stabilized and the electron transfer to $^3O_2$ proceeds rather slowly.[12] This explanation would not match with a Type II reaction in which the levels of the HOMOs determine the reactivity toward $^1O_2$. Since the HOMOs of pentacene and alkynylpentacenes are similar, the difference in their reactivities evokes a Type I reaction for alkynylpentacenes.[17] However, at present it is not clear how such reactants behave toward $^1O_2$ when the Type II pathway is enforced. Experimental conditions of "dark" reactions, where $^1O_2$ is generated from a chemical source, would give fruitful hints and allow determining a bimolecular rate constant originating only from a Type II reaction.[18] Introduction of a deactivating substituent opens also the important question about the regioselectivity of the photooxygenation of higher acenes, which was recently shown on tetracenes by Thomas.[19] Oxygen should attack the ring with the highest electron density. Recently, our group found that the triple bond has also a strong impact on the thermolysis. EPOs of 9,10-alkynylanthracenes quantitatively reconvert to the parent acene and $^1O_2$ faster than all other EPOs.[20] Before, cycloaddition of anthracenes with

Chart 1. Structures of Variously Substituted Oligoacenes



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quantitative reconversion was only known for arylanthracenes, while alkyl- or mono-substituted anthracenes decomposed.[7,14] For EPOs of higher acenes like tetracenes and pentacenes, a quantitative reconversion is not even possible with phenyl groups at the *meso*-positions.[21,22] The reversibility of the photooxidation of alkynyl-substituted acenes is important for their applications as semiconductors,[23] since oxygenated material could be reconverted to the acene by simple thermolysis.

Herein we describe, on experimental and computational bases, the impact of the alkynyl group on the reactivity of acenes toward oxygen and on the propensity to reconvert back from the EPO to the parent acene. For this purpose we synthesized anthracenes, tetracenes, and pentacenes with various types of alkynyl substituents and investigated the kinetics of their oxidation and thermolysis of the EPOs. Interesting influences of the substituents and the number of acene rings on the bimolecular rate constants and the activation parameters have been found. We verified these experimental data by theoretical *ab initio* calculations and concluded different reaction pathways for the oxidations and the subsequent thermolysis. Our studies point preferentially to the abnormal role of the triple bond in the stability and reactivity of acenes. The results described herein should be interesting for understanding the mechanisms of acene oxidations and the thermolysis of the formed EPOs. Furthermore, the remarkable influence of alkyne substituents might be useful to improve the oxidation stability of organic semiconductors.

RESULTS AND DISCUSSION

Syntheses of Alkynyl Acenes. The synthetic procedure is described in detail in the Supporting Information.

Photooxidations. Alkynyl-substituted acenes used in this study were first photooxygenated under typical preparative conditions for product isolation and characterization (Chart 1). Solutions of $(1-2) \times 10^{-2}$ M of the acene and 5×10^{-4} M of the sensitizer methylene blue (MB) in $CHCl_3$ were irradiated with a sodium lamp (600 W) while oxygen was bubbled through the solution at −20 °C until complete conversion of starting material. The products were identified by ^1H and ^{13}C NMR spectroscopy and isolated by chromatography. Only the naphthalene derivative **6** was completely inert toward photooxygenation. All other compounds afforded EPOs in moderate to good yields after isolation (Table 1).

The addition of $^1O_2$ to higher acenes can lead to the formation of regioisomers. Thomas et al. previously studied the products obtained from photooxygenation of compound **7g** and found that $^1O_2$ attacks preferentially the unsubstituted 6,11-positions with a 2:1 selectivity (Scheme 3).[19b] This prompted us to employ tetracenes with other alkynyl substituents in order to direct the product distribution toward the 5,12-EPO. Indeed, photooxygenation of the *tert*-butylphenylalkylphenyl derivative **7h** afforded a product mixture with a 6:4 ratio in favor of the 5,12-EPO which could be isolated by chromatography (Figure 1).

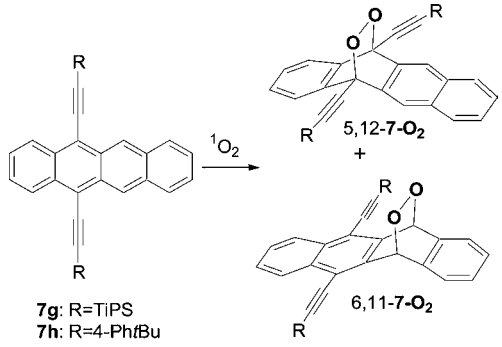
In contrast to the product mixtures resulting from alkynyltetracenes **7**, photooxygenation of alkynylpentacene **8** proceeded regioselectively and afforded only the 6,13-EPO in 78% yield after chromatography (Scheme 4, Figure 2). A trace of a byproduct containing a full anthracene unit was confirmed by the typical absorption pattern of anthracenes in the UV−vis spectrum (Supporting Information, Figure S1).

Table 1. Photooxygenations of Alkynyl-Substituted Acenes

entry	acene	substituent	yield (%)[a]
1	**1a**	Ph	89
2	**1b**	4-PhOMe	86
3	**1c**	4-Ph*t*Bu	88
4	**1d**	4-PhCHO	50
5	**1e**	4-PhCN	<5[b]
6	**1f**	4-PhCO$_2$Me	45
7	**2**	TMS	89
8	**3**	−	76
9	**4a−e**	R	>90[d]
10	**5**	Ph	98
11	**6**	TMS	0
12	**7g**	TIPS	80
13	**7h**	4-Ph*t*Bu	48[c]
14	**8**	TIPS	78

[a]Yield after isolation by chromatography. [b]Very slow conversion and decomposition at longer irradiation time. [c]Yield of isolated major 5,12-EPO. [d]See ref 13c.

Scheme 3. Distribution of the Two Possible Regioisomers Formed upon Photooxygenation of Acetylenyltetracenes 7



Previously, formation of a dimer as a result of a [4+4] cycloaddition was reported when oxygen-free solutions were irradiated with UV light of 300 nm.[24] Under our conditions using the 589 nm light of a sodium lamp, no such dimer was detected in the crude NMR spectrum of **8-O$_2$**. When a higher diluted sample of **8** was irradiated in the absence of oxygen, a negligible reaction was observed, probably due to remaining traces of oxygen (see Supporting Information, Figure S2). Since alkynylpentacenes are known to be photooxidized even without a sensitizer, we carried out the photooxygenation of acene **8** without MB under otherwise identical conditions. Again, only the angular 6,13-EPO could be isolated in 74% yield.

Dark Oxygenations. Oxygenations of acenes could also be carried out in the dark using chemical sources of $^1O_2$.[25] Such conditions allow us to rule out oxidation via a Type I mechanism. We therefore treated pentacene **8** with a mixture of MoO_4^-/H_2O_2 in a water/oil microemulsion.[25] Comparison of the crude products formed under "dark" and irradiation conditions showed that for both reactions the 6,13-EPO is the main product (Supporting Information, Figures S3 and S4).

Thermolysis. The EPOs of alkynylanthracenes **1** reconvert quantitatively to the parent species without any decomposition upon warming (Figure 3A−C). Like arylanthracenes **4**, whose reversible reaction with $^1O_2$ is already known,[13] their reconversion at room temperature is so fast that the storage

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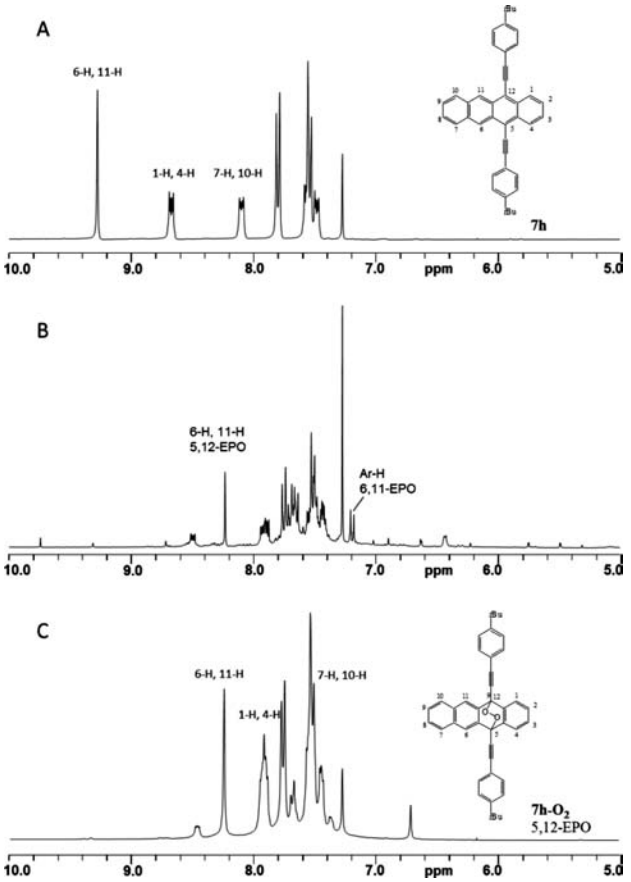
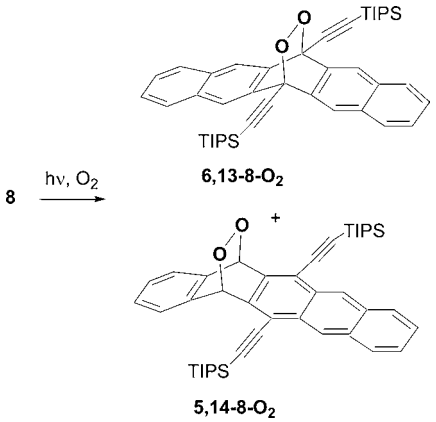


Figure 1. ^{1}H NMR spectra monitoring the photooxygenation of arylalkynyltetracene **7h**: (A) starting material, (B) crude product mixture after photooxygenation under standard conditions, and (C) isolated 5,12-EPO.

Scheme 4. Photooxygenation of the Acetylenylpentacene 8 to the 6,13-EPO 8-O_2



in a freezer is required. Since this unexpected behavior was just recently observed by our group,[20] we extended the scope of compounds to the mixed form, namely the 9-aryl-10-alkynylanthracene **3** and the bis-alkenylanthracene **5**. While heating of the EPO **3**-O_2 gave the parent species **3** quantitatively (Figure 4A–C), the alkenyl group exhibited no stabilization, and **5**-O_2 decomposed without reconversion.

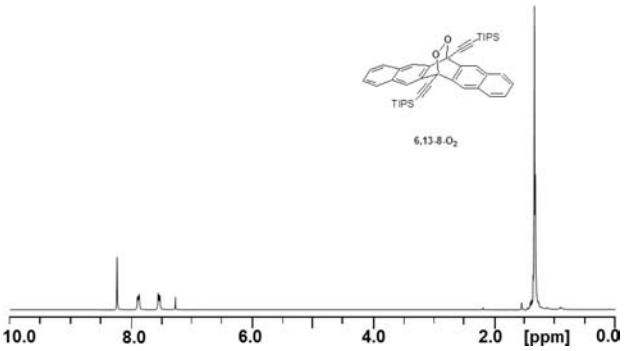


Figure 2. ^{1}H NMR spectrum of the isolated 6,13-EPO of **8**.

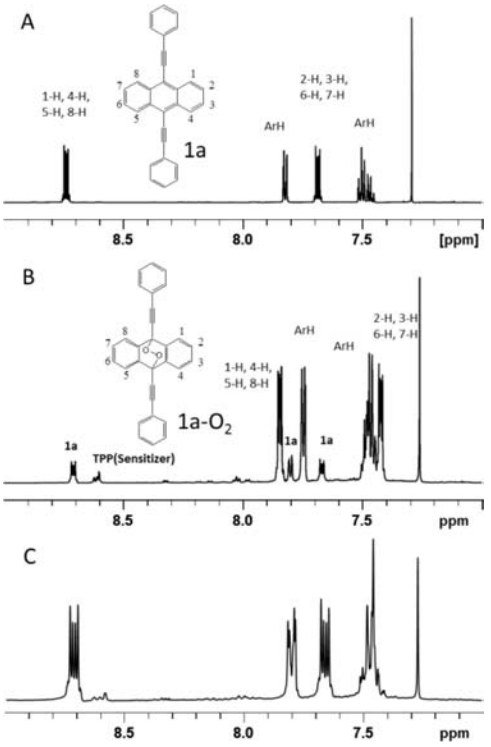


Figure 3. ^{1}H NMR spectra monitoring the reversible photooxygenation of alkynylanthracene **1a**: (A) before irradiation, (B) directly after the photooxygenation, and (C) after 1 day at room temperature.

Interestingly, the EPOs of tetracenes **7**-O_2 and the pentacene EPO **8**-O_2 also undergo clean thermolysis (Figure 5). This is the first example for a pentacene EPO which reacts back to the parent pentacene quantitatively by simple warming.[22] It is important to note that this cycloreversion to the acenes is only possible with the EPO regioisomers where oxygen is bound to the carbon atoms substituted by the triple bonds (5,12-**7**-O_2 and 6,13-**8**-O_2), whereas the other regioisomers decompose on warming.[14] Moreover, the thermolysis of the alkynylpentacene EPO exhibited an exceptional behavior: In contrast to all other EPOs, a clean thermolysis required a tedious exclusion of oxygen. When a 0.1 M solution of the EPO was heated in an inert atmosphere, a full reconversion to the parent species **8** occurred, as confirmed by ^{1}H NMR spectroscopy (Figure 5). On the other hand, heating of a 2.3×10^{-5} M solution of **8**-O_2 at 80 °C under air afforded the reconversion of less than 50% of the parent species, as compared to heating of the same solution

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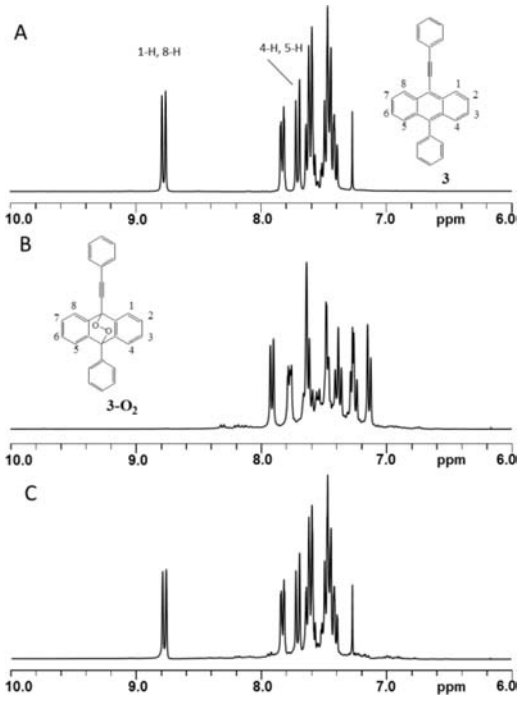


Figure 4. ^{1}H NMR spectra monitoring the reversible photooxygenation of alkynylanthracene **3**: (A) before irradiation, (B) directly after completion of the photooxygenation, and (C) after 1 week at room temperature.

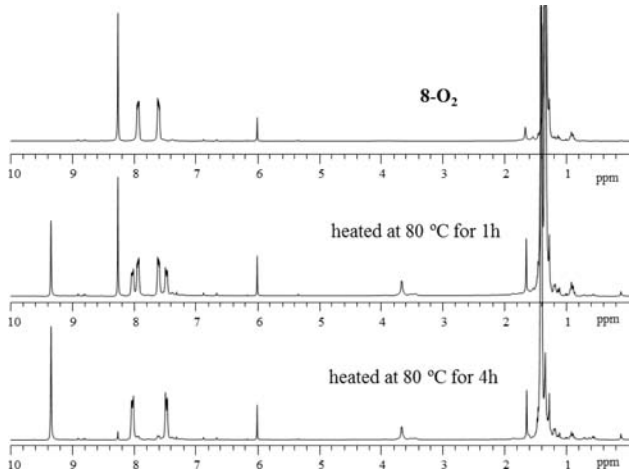


Figure 5. ^{1}H NMR spectra of a 0.1 M solution of **8-O$_2$** during heating at 80 °C under exclusion of air.

under exclusion of air (Supporting Information, Figures S5 and S6). Byproducts could not be identified under these conditions.

This finding is important for the application of higher acenes as electronic devices: Oxidation is reversible, and oxygenated material which was considered to be not useful can be partially regenerated by heating in an inert atmosphere.

Influence of Substituents on the Kinetics of the Photooxygenations. For kinetic analysis, solutions of 1×10^{-5} M of the acene and 1×10^{-6} M of the sensitizer tetraphenylporphin (TPP) in $CHCl_3$ were irradiated at room temperature under air (see Supporting Information for a detailed description).

The bimolecular rate constants of the photooxygenation of a series of anthracenes are compiled in Table 2. The data reveal a strong influence of the substituents on the reactivity. Anthracenes **1** which carry ethynyl groups react significantly more slowly to give the corresponding EPOs than all other types of substituted anthracenes. The strongest activation is caused by alkenyl or alkyl groups, i.e., for anthracene **5** and 9,10-dimethylanthracene (DMA). A combination of aryl and alkynyl substituents, which is represented by the 9-aryl-10-ethynylphenylanthracene **6**, exhibits a reactivity which can be considered as superimposition of the effects arising from the two functional groups. The reactivity of **3** ranges in between the reactivities of alkynylanthracenes **1** and arylanthracenes **4**.

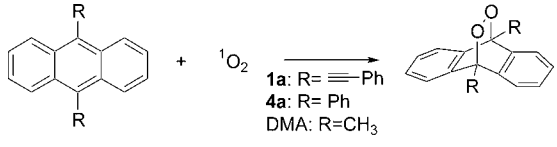
Table 2. Kinetic Data of the Photooxygenation of Various Anthracenes with Substituents in the 9,10-Positions in $CHCl_3$

acene	bimolecular rate constant, $k_r \times 10^6$ s^{-1} M^{-1}
1a	0.13
1b	0.36
1c	0.24
1d	0.052
1e	0.045
3	1.23
4a	3[a]
4b	5.44
4c	4
4e	0.74
5	10
anthracene	0.52 (0.54)[a]
DMA	12 (27)[a]

[a]Literature value from ref 26.

For a theoretical evaluation of the energy changes resulting from the oxygenations of anthracenes, B3LYP/6-311G* calculations of total energies including ZPE corrections at 25 °C were carried out (a detailed description is found in the Supporting Information).[27] It is important to note that the calculation of the energy of $^1O_2$ requires higher levels of theory.[28] Our value of −150.2355 hartrees might be underestimated since the calculated energy for the reaction from **1a** to **1a-O$_2$** is positive. However, the data resulting from reactions between acenes and $^1O_2$ as shown in Table 3 reflect a good relative relation between the highly reactive DMA and the slowly reacting alkynylanthracene **1a**. In other words, the reaction of ethynylphenyl-substituted acenes is thermodynamically most disfavored, whereas methyl-substituted acenes are most favored.

Table 3. Total Energies (in hartrees) of the Anthracenes 1a, 4a, and DMA and the Resulting Reaction Energies (in hartrees)



	E_{acene}	E_{EPO}	$E_{EPO} - E_{acene}$	ΔE[a]
1a	−1152.7415	−1302.9710	−150.2295	+0.006
4a	−1000.5086	−1150.7891	−150.2805	−0.045
DMA	−617.3903	−767.6915	−150.3011	−0.065

[a]$\Delta E = E_{EPO} - E_{acene} - E^1_{O_2}$; $E^1_{O_2} = -150.2355$ hartree.

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Both the phenyl and the ethynylphenyl groups further promote remote substituent effects, as the reactivity decreases from **1b**/**4b** carrying electron-donating groups to **1e**/**4e** with electron-withdrawing groups. To elucidate these substituent effects, we determined the HOMO and LUMO energies of aryl- and alkynylanthracenes experimentally by measuring oxidation potentials by cyclic voltammetry and theoretically by B3LYP/6-311G* calculations (Table 4).[27] Indeed, we found that

Table 4. Frontier Orbital Levels of Aryl- and Arylethynylanthracenes

	E_{HOMO} (eV)		E_{LUMO} (eV)	
acene	expt[a]	theory[b]	expt[c]	theory[b]
1a	−5.50	−5.11	−2.99	−2.44
1b	−5.30	−5.03	−2.80	−2.42
1c	−5.40	−4.97	−2.89	−2.36
1d	−5.56	−5.49	−3.12	−3.02
1e	−5.62	−5.55	−3.14	−3.10
4a	−5.56	−5.22	−2.48	−1.63
4b	−5.47	−5.11	−2.44	−1.68
4c	−5.54	−5.14	−2.52	−1.71
4e	−5.71	−5.79	−2.68	−2.36

[a]Determined by cyclic voltammetry from the onset of oxidation relative to ferrocene/ferroceneium with a known HOMO energy level of 4.8 eV. Oxidation potential measured in CH_2Cl_2 with Bu_4NClO_4 as supporting electrolyte. [b]Obtained from B3LYP/6-311G* calculations. [c]Determined from $E_{HOMO} + E_{gap}$, where E_{gap} is the energy gap between HOMO and LUMO, determined from the UV/vis spectra.

electron-donating substituents raise the HOMO energy and the electron density of the central benzene ring (at the 9,10-position), even transmitted through many bonds. The deviations of the energy levels between electron-donating and electron-withdrawing groups resulting from theoretical calculations are greater than for the experimental values, but both methods reveal a similar trend. Within the row of *para*-substituted arylethynylanthracenes **1a**−**e** and arylanthracenes **4a**−**e**, the HOMO levels correlate well with the reactivities toward the cycloaddition (Figure 6).

Influence of the Acene Type on the Kinetics of the Photooxygenations. Due to the strong increase in oxidation stability caused by the triple bond attached to the acene system,

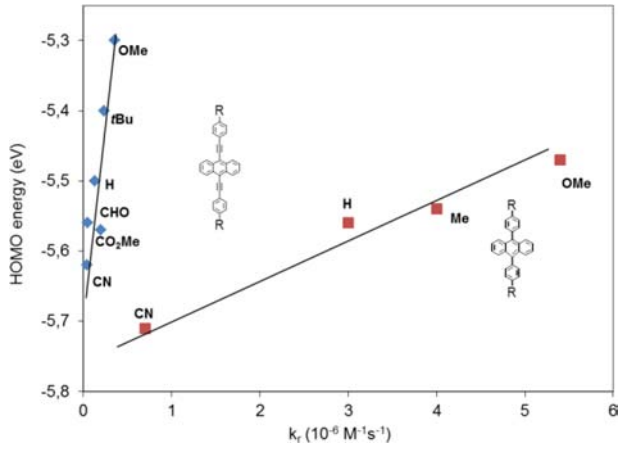


Figure 6. Correlation of HOMO energies (experimental values) of arylethynylanthracenes **1** and arylanthracenes **4** with the rates of the photooxygenations.

we investigated the reactivities of silylacetylenyl-substituted oligoacenes toward $^1O_2$ (Chart 1, Table 5). With higher acenes

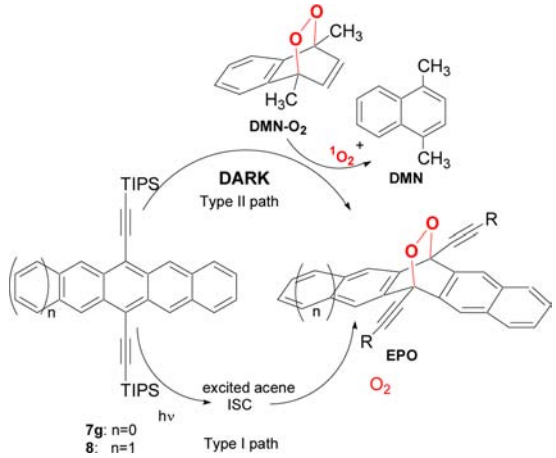
Table 5. Kinetic Data of Oxygenations of Alkynyl-Substituted Oligoacenes in $CHCl_3$

entry	acene	bimolecular rate constant, $k_r \times 10^6$ s^{-1} M^{-1}
1	**6**	no conversion
2	anthracene	0.52 (0.54)[a]
3	**2**	0.1 (irradiation[a])
4	tetracene	23 (18)[a]
5	**7g**	12 (irradiation[b]) 7.5
6	**7g**	(dark[c])
7	**7h**	15 (irradiation[b])
8	pentacene	420[a]
9	**8**	0.98 (irradiation[b])
10	**8**	0.1 (dark[c])

[a]Taken from refs 26 and 29. [b]Steady-state photolysis using MB as sensitizer and a red LED as light source. [c]Oxygenation by continuous release of $^1O_2$ from 1,4-dimethylnaphthaleneendoperoxide.

the conventional measurement of the kinetics under continuous irradiation becomes problematic since their spectral range is too far red-shifted and overlaps with the absorption spectra of the sensitizer. Thus, to avoid a possible photoexcitation of the substrate, measurements of the kinetics of tetracenes **7** and pentacene **8** were carried out with light from a red LED (635 nm). In addition, kinetic measurements of oxygenations of **7g** and **8** were performed in the dark by using a chemical source of singlet oxygen, namely 1,4-dimethylnaphthaleneendoperoxide (**DMN-O$_2$**), which generates $^1O_2$ at defined concentrations (Scheme 5). These conditions are especially important to avoid excitation of the acene, which would in turn cause an electron transfer from the T1 state to oxygen.

Scheme 5. Pathways of Oxygenations of Higher Acenes in the Dark and by Irradiation



Continuous irradiation over a period of 24 h of naphthalene **6** caused no conversion (Table 5, entry 1). Even after irradiation with a 400 W sodium lamp over a period of 7 days at −20 °C, no EPO was detected. The oxygenation of the ethynylanthracene **2** was measurable but notably (factor of 5) slower (entry 3) than the oxygenation of anthracene (entry 2). The rate constant of the reaction between **7g** and $^1O_2$ was measured using standard conditions of irradiation and in the "dark" by measuring the initial rates of the disappearance of **7a**

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from a stock solution after addition of the donor **DMN-O$_2$** at different concentrations (the experimental procedure is described in detail in the Supporting Information).[18] The value obtained from measurement in the "dark" (7.5×10^6 s^{-1} M^{-1}) is slightly diminished compared to that measured from irradiation (12×10^6 s^{-1} M^{-1}, entries 5 and 6), which might be due to weak absorption of the excitation light at the upper edge of the absorption spectrum of **7g**. Under this circumstance a self-sensitization is possible. In contrast to anthracenes, the measured rate constant for substituted tetracenes is a superimposition of those of the reactions forming the 5,12- and the 6,11-EPO. Due to the regiochemical preference of the unsubstituted 6,11-position of **7g** (Scheme 3), the rate constant for the formation of the sole 5,12-EPO is smaller than the observed rate. Thus, in analogy with the trend found with anthracenes, alkynyl substitution reduces the reactivity as compared to that of unsubstituted tetracene by at least a factor of 2 (23×10^6 s^{-1} M^{-1}, entry 4). The reaction of the *tert*-butylphenylalkylphenyl derivative **7h** proceeds slightly faster with a 6:4 ratio of 5,12- and 6,13-EPOs (15×10^6 s^{-1} M^{-1}, entry 7). This indicates that an arylalkynyl group has a weaker influence on the reactivity (compare entries 7 and 4).

Surprisingly, photooxygenation of the silynylethynylpentacene **8** proceeded significantly more slowly than the reaction of tetracenes **7** (Table 5, entry 9). It is important to note that the measured rate of the oxygenation of **8** under irradiation is a superimposition of both Type I and Type II reactions. Thus, the rate constant of the oxygenation of **8** was also determined in the "dark" by using **DMN-O$_2$** as $^1O_2$ donor.[18] This bimolecular rate constant of the "dark" reaction (0.1×10^6 s^{-1} M^{-1}) is an order of magnitude smaller than the rate derived from measurement under irradiation (0.98×10^6 s^{-1} M^{-1}). This result reveals that alkynylpentacenes can react via both a Type I photooxygenation (slow) and a $^1O_2$-based Type II reaction (very slow). Table 5 presents for the first time the rate constants for the Type II oxygenation of alkynylpentacenes. Under irradiation, the Type I reaction which proceeds via electron transfer is faster than the $^1O_2$-based Type II reaction. These observations are in accordance with the interpretation of Maliakal et al., who claimed a preference for Type I reaction for acenes which have low-lying LUMO orbitals, like alkynylpentacenes.[12] However, both values of the rate of oxygenation are much smaller than the rate of the oxygenation of the tetracenes **7**. On the other hand, the unsubstituted pentacene reacts faster by a factor of >20 (4.2×10^8 s^{-1} M^{-1}) than tetracenes **7** (Table 5, entries 5–8).[29] This abnormal behavior prompted us to measure the kinetics of the Type II photooxygenation of a highly reactive acene in the presence of alkynylpentacene **8**. Surprisingly, during irradiation of a 1:1 mixture of **8** and **4a** in the presence of a sensitizer, the less reactive acene **8** reacted first (Figure 7). The rapid reaction of **4a** started immediately after **8** had disappeared. Under the conditions of a "dark" oxygenation using the $^1O_2$ donor **DMN-O$_2$**, the same behavior was found, indicating that the effect does not result from sensitizer quenching (Figure S7). Thus, $^1O_2$ is first consumed by alkynylpentacene **8**. Since this reaction proceeds more slowly than the oxygenation of **4a** in the absence of **8**, $^1O_2$ must be deactivated without the formation of **8-O$_2$**. This explains why **8** reacts more slowly.

In summary, the impacts of the triple bond on the reactivity of acenes vary strongly with the number of fused rings. As shown in Figure 8, for unsubstituted acenes (R = H) the reactivity increases with increasing number of rings remarkably.

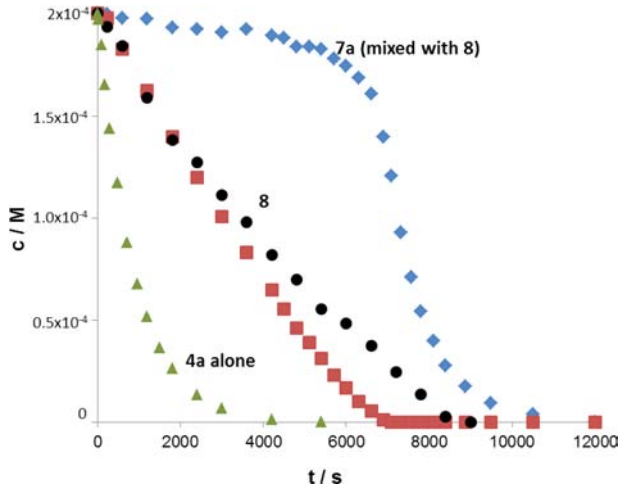

Figure 7. Decay of the concentrations in a mixture of **4a** and **8** in the presence of TPP during irradiation measured by UV–vis spectroscopy. The blue curve shows the concentration of **4a** and the red curve the concentration of **8** in the mixture. The green curve shows the decay of **7a** alone and the black curve the decay of **8** alone in the presence of TPP.

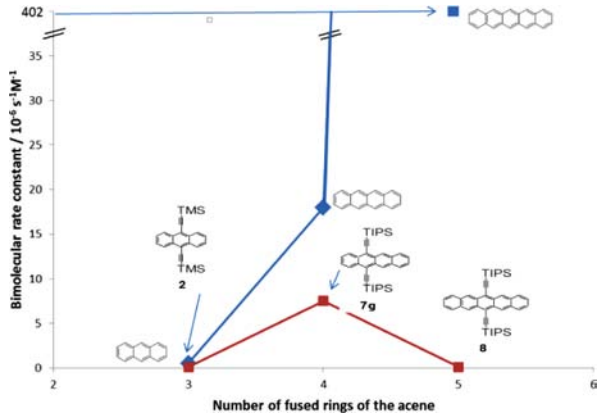

Figure 8. Dependence of the reactivities of unsubstituted and alkynyl-substituted acenes toward $^1O_2$ on the number of rings.

The reactivity of alkynyl-substituted acenes exhibits a maximum for tetracenes. Alkynylpentacenes react more slowly than the corresponding tetracenes. These findings might be interesting for the design of new acene-based semiconductors or LEDs with higher oxidation stabilities.

Mechanistic Discussion of the Photooxygenations. The reactivity and regioselectivity of [4+2] cycloadditions of unsubstituted acenes and singlet oxygen was previously explained by Li and van den Heuvel et al. on the basis of the frontier molecular orbital (FMO) theory.[11a,c] In the FMO theory the second-order perturbation energy ΔE of a Diels–Alder reaction results from an atom orbital overlap between the "termini" of the diene and the dienophile.[30] The coefficients of the atom orbitals and the energy of the HOMO of the diene correlate with ΔE (detailed information about the calculation of ΔE can be found in the Supporting Information). The FMO theory predicts well that the reactivity increases with increasing number of rings and that in higher acenes the addition of $^1O_2$ is preferred at the innermost ring where the atom orbitals have the largest coefficients.[11d] It has to be noted that the FMO theory is applicable only at the initial stage of a reaction where it can disclose a relation between aromaticity and reactivity.[31]

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Substituents which lift the HOMO energy would enhance the reactivity. Tables 2 and 4 and Figure 6 clearly demonstrate this relation if the two rows of alkynylanthracenes **1** and arylanthracenes **4** are inspected separately. However, this good correlation does not fit for the direct comparison of alkynyl- (**1**) with aryl- (**4**) substituted anthracenes. Thus, despite their having similar HOMO energies and even orbital coefficients at the central carbon atoms (e.g., **1a** versus **4a**, Figure 9), their reactivity toward singlet oxygen differs by a factor of 25. The reactivity of anthracene falls between the reactivities of **1a** and **4a**, which also does not fit with the calculated HOMO energy and coefficients (Figure 9). This remarkable behavior can only be rationalized by a change in the mechanism of the photooxygenations.

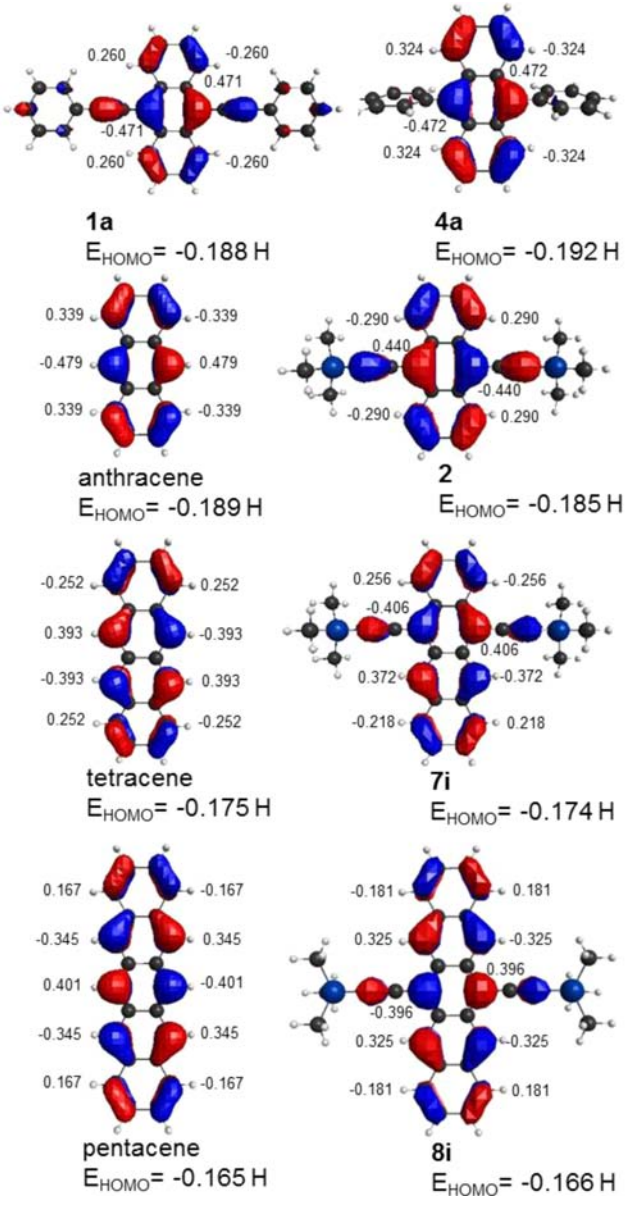
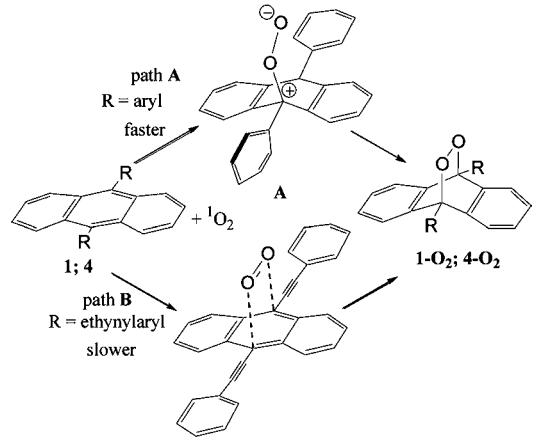


Figure 9. Calculated (B3LYP 6-31*) atom orbital coefficients and energies (hartrees) of the HOMOs of unsubstituted and alkynyl-substituted acenes.

For $^1O_2$-based [4+2] cycloadditions, either a concerted or a stepwise addition of oxygen to the acene is possible (Scheme 6).[11b,d,13b] It was previously shown that the stepwise pathway of the oxygenation of anthracene lies energetically ca. 4 kcal/mol below the concerted one.[11d] The preference for the stepwise path is common for higher acenes which exhibit an increasing disjoint biradical nature.[32] The contribution of the biradical character can be quantified by a comparison between restricted closed-shell B3LYP and open-shell B3LYP solutions of the singlet ground states.[32] Therefore, we calculated the differences between restricted open-shell and closed-shell energies at the singlet B3LYP/6-31* level of theory for anthracene (−0.03 kcal/mol), **1a** (−0.006 kcal/mol), and **4a** (<−0.001 kcal/mol). The singlet biradical state of the open-shell solution for anthracene is energetically below that of the closed-shell solution, which explains why a stepwise biradical process is preferred. The biradical ground state of arylanthracene **4a** gains no stabilization, and the energetic preference for a path proceeding via radicals is smaller. However, the addition of oxygen to anthracenes **4** could also proceed stepwise via the formation of a zwitterionic intermediate A (Scheme 6, pathway A). In this pathway a positive charge is stabilized by a substituent as the benzene rings can rotate into the plane of the acene system, causing full conjugation along the biaryl axis, in accordance with our previous studies on molecular switches.[13] This ionic pathway is energetically favored, which explains the higher reactivity of arylanthracenes as compared to unsubstituted anthracene. Moreover, the good correlation between reactivities and HOMO energies of differently substituted arylanthracenes **4** (Figure 6) fits well to a mechanism with ionic—rather than radical—intermediates.

Scheme 6. Proposed Mechanistic Pathways of the Addition of $^1O_2$ to Acenes 4 (Path A) and 1 (Path B)[a]



[a]Anthracene was used for simplification.

On the other hand, the formation of a zwitterionic intermediate during oxygenation of alkynylanthracenes **1** becomes less likely due to the low stability of a propargyl cation.[33] Additionally, the biradical ground state of **1a** is not stabilized. In consequence, both stepwise pathways are energetically disfavored, forcing the oxygenation of the alkynylanthracene **1a** to a slower concerted mechanism (Scheme 6, pathway B). This explains why anthracenes with triple bonds have the smallest affinity toward $^1O_2$ and are well protected from oxidation. A concerted mechanism also explains the good reactivity/HOMO energy correlation of differently substituted alkynylanthracenes (Figure 6).

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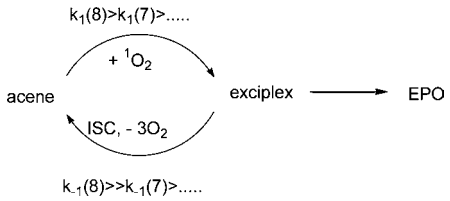
Thus, from our calculations it becomes evident that the differences in the reactivities of **1a**, **4a**, and anthracene do not originate from the nature of the frontier orbitals of the reactants. Rather the stabilizing effects of transition states and intermediates, resulting in a change of the reaction pathways, are responsible for these remarkable oxidation kinetics.

This mechanistic consideration also applies for tetracenes (for less time-consuming calculations we used the trimethylsilyl- (TMS) substituted acenes instead of triisopropyl- (TIPS) substituted acenes): B3LYP calculations result in similar HOMO energy levels for the faster reacting tetracene and TMS-ethynyltetracene **7i** (Figure 9), which evokes a concerted reaction in the case of alkynyl substitution. Unsubstituted tetracene should undergo a stepwise reaction due to its strong biradical character in analogy to pentacene.[11d,33] Thus, again the triple bond has a strong influence on the kinetics and the mechanism of the $^1O_2$ reaction, protecting the acene from fast oxidation.

As mentioned before, alkynylpentacene **8** can react via either a Type I (electron transfer) or Type II ($^1O_2$) pathway. In the case of the Type II mechanism, alkynylpentacene **8** deactivates singlet oxygen, causing an abnormally slow reaction. This can be best explained by the reversible formation of an exciplex between $^1O_2$ and **8** (Scheme 7). An exciplex is strongly

Scheme 7. Proposed Mechanism of Oxygenation of an Acene via the Formation of an Encounter Complex to the EPO



supported by zero or negative activation energies during the reactions of acenes with $^1O_2$.[34] Indeed, the photooxygenation of **8** showed little temperature dependence, indicating a very small activation energy (see Supporting Information, Figure S12). The exciplex can either proceed to the EPO or dissociate with intersystem crossing (ISC) to the parent acene and triplet oxygen. In the case of the alkynyl derivative **8**, the rate of dissociation under ISC is faster and deactivation dominates. Such a mechanism for the physical quenching of singlet oxygen by a reversible charge transfer is known for amines and was also reported for aromatic compounds like methoxybenzenes. In fact, some methoxybenzenes are persistent toward oxygenation due to dominant physical quenching.[35] Thus, in our competition experiment with a mixture of **4a** and **8** (Figure 7), $^1O_2$ is mainly deactivated by pentacene **8** and cannot reach and react with anthracene **4a**. Only a small amount of singlet oxygen or a Type I processes can oxidize pentacene **8** slowly. After 2 h and almost complete conversion of pentacene **8** to the EPO, the quenching is no longer possible and the anthracene **4a** starts to react (Figure 7). Therefore, alkynylpentacenes can be used to protect anthracenes from oxidation. These results are not only interesting for the mechanism of singlet oxygen reactions, but should be important for the design of semiconductors. Since alkynyl-substituted acenes are more slowly oxidized, they should be superior materials compared with aryl-substituted systems.

The regioselectivity can be well explained by application of the FMO theory: A comparison with the unsubstituted acenes shows that, in general, the atom orbital coefficients of the carbon atoms of the neighboring ring are reduced relative to those of the atoms of the substituted ring. This effect is strong for the anthracene and pentacene systems, resulting in selective formation of the central EPOs. In view of the FMO theory, the center rings in **1** and **8** have a higher electron density relative to that of the neighboring ring. In the case of the tetracene, the difference in the atom orbital coefficients of the substituted 5,12 and the unsubstituted 6,11 positions is smaller, which explains the formation of two regioisomers. The preference of the 6,11-EPO for the oxygenation of **7g** reported by Thomas is not in accordance to the FMO theory, while the 5,12-EPO preference for **7h** fits well.[19b] The change in the isomer ratio of **7g** could originate from the silyl groups which are known to quench or interact with singlet oxygen.[36]

Kinetics of the Thermolysis. For those EPOs which quantitatively afforded the parent acenes under cleavage of oxygen, their reappearance was monitored at different temperatures by UV−vis measurements. The obtained data were used to calculate the activation enthalpies and entropies for the dissociation (Table 6).

As expected, the EPOs of anthracene and DMA decomposed on warming.[14] The first striking effect revealed from Table 6 is that alkynyl-substituted EPOs **1-O$_2$**, **2-O$_2$**, **3-O$_2$**, **7-O$_2$**, and **8-O$_2$** cleanly cleave off oxygen and reconvert to the acenes quantitatively. Thus, such functional groups protect EPOs of all types of acenes from decomposition.

Also surprising is the fast thermolysis observed for this class of EPOs. The rates of cycloreversion of the EPOs of **1** are much higher than for all literature-known anthracenes or naphthalenes. For example, the rate of the reconversion of the well-known $^1O_2$ donor **DMN-O$_2$** at 25 °C is $k = 3.3 \times 10^{-5}$ s^{-1}. In contrast, the rate of the cycloreversion of the most extreme case, **1e-O$_2$**, at 25 °C is 6.7×10^{-4} s^{-1}. Only EPOs of alkylated imidazoles, as reported by Foote, reconvert to the parent form already at <−30 °C.[37] Anthracene EPO **3-O$_2$**, which carries both a phenyl and an ethynylphenyl substituent, reconverts more slowly than the EPOs **1-O$_2$** but still much faster than diarylanthracene EPOs **4-O$_2$**.

The extremely fast reconversion of alkynylanthracene EPOs correlates with the low activation enthalpies $\Delta H^{\#}$. Compared to EPOs of arylanthracenes, the activation enthalpies of EPOs **1-O$_2$** are lower by ca. 40 kJ/mol. Activation entropies of EPOs of **1** are negative, which is in accordance to relatively high yields of $^1O_2$ compared to EPOs **4** with positive entropies as previously reported.[20] Table 6 also shows that the rate of the thermolysis depends only on the substituent that is directly attached to the anthracene core; remote substituents in the *p*-position of the phenyl or phenylacetylenyl substituents, which control the rate of the photooxygenation, have no influence.

On the other hand, we found an interesting dependence of the rate of the thermolysis on the type of the acene. Thus, this rate decreases gradually from alkynylanthracene EPO **5** to the tetracene EPOs **7a** and **7b** and finally to the pentacene EPO of **8**.

The exceptional behavior of the pentacene EPO **8-O$_2$** to decompose by heating under air might be explained by the low ionization potential of pentacene **8**, which allows it to react with triplet oxygen at elevated temperatures by an electron transfer or by a radical process.[38] However, we demonstrate herein that it is possible to reconvert oxidized pentacenes

Table 6. Kinetic Data of the Thermolysis of Acene EPOs

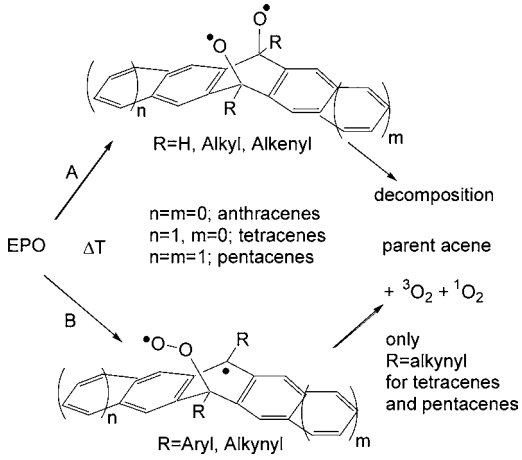
EPO	$t_{1/2}$ EPO[a]	range	thermolysis, k^{-1}/s^{-1}	$\Delta H^{\#}$,[b] kJ/mol	ΔS,[b] J/K·mol
1a-O_2	23 min (25 °C)	2 °C	3.3×10^{-5}	87	−12
		25 °C	5.0×10^{-4}		
		40 °C	4.0×10^{-3}		
1b-O_2	31 min (25 °C)	2 °C	2.8×10^{-5}	83	−27
		25 °C	3.6×10^{-4}		
		40 °C	2.8×10^{-3}		
1c-O_2	33 min (25 °C)	2 °C	2.8×10^{-5}	88	−12
		25 °C	3.6×10^{-4}		
		50 °C	2.8×10^{-3}		
1d-O_2	15 min (25 °C)	2 °C	2.1×10^{-5}	83	−25
		25 °C	7.6×10^{-4}		
1e-O_2	17 min (25 °C)	25 °C	6.7×10^{-4}	90	−23
		40 °C	4.4×10^{-3}		
2-O_2	70 min (25 °C)	25 °C	1.6×10^{-4}	–	–
3-O_2	4.6 h (50 °C)	50 °C	4.1×10^{-5}	–	–
4a-O_2	2.1 h (100 °C)	70 °C	2.5×10^{-6}	129	+21
		80 °C	0.9×10^{-5}		
		100 °C	0.9×10^{-4}		
4b-O_2	1.6 h (100 °C)	70 °C	5.0×10^{-6}	124	+12
		80 °C	2.6×10^{-5}		
		100 °C	1.2×10^{-4}		
4c-O_2	2.7 h (100 °C)	80 °C	1.0×10^{-5}	124	+9
		100 °C	0.7×10^{-4}		
4e-O_2	1.1 h (100 °C)	70 °C	3.3×10^{-6}	131	+33
		80 °C	1.3×10^{-5}		
		100 °C	1.7×10^{-4}		
5-O_2	decomposition	–	–	–	–
ANT-O_2	decomposition	–	–	–	–
$DMAO_2$	decomposition	–	–	–	–
$DMNO_2$	350 min (25 °C)	25 °C	3.3×10^{-5}	101[c]	+8[c]
7a-O_2 (5,12)	31 h (25 °C)	25 °C	6.2×10^{-6}	113	+37
	43 min (60 °C)	60 °C	2.7×10^{-4}		
7a-O_2 (6,11)	decomposition	–	–	–	–
7b-O_2 (5,12)	23 min (60 °C)	60 °C	5.0×10^{-4}	83	−57
8-O_2	200 min (60 °C)	60 °C	5.6×10^{-5}	97	−33
		70 °C	1.7×10^{-4}		
		80 °C	4.4×10^{-4}		

[a]Half-life of the EPO measured at the given temperature in toluene. [b]Activation parameters estimated from the Arrhenius plot. [c]See ref 15.

cleanly to the parent acene by simple heating under an inert atmosphere. This finding should have an important meaning for the application of semiconducting pentacene films, since oxygenated material was previously considered as not useful.

Mechanism of the Thermolysis: Competition between Reconversion and Decomposition. Understanding the process of decomposition of acenes is important for the prediction of the stability of an electronic device.[1,4,12] A quantitative reconversion is given only for EPOs of anthracenes substituted with aryl or alkynyl groups, while EPOs of tetracenes and pentacenes gave quantitative reconversion only with alkynyl substituents. Thus, we investigated the mechanism of the thermolysis of EPOs by measurement of activation energies in combination with theoretical calculations. In general, cleavage of the C−O bond, leading to the parent acene and oxygen, competes with homolysis of the O−O bond, resulting in decomposition (Scheme 8). Experimental values of

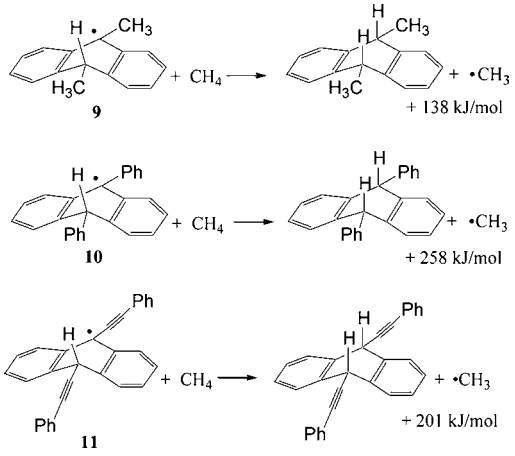
Scheme 8. Competition between Decomposition and Reconversion of Acene EPOs



the bond dissociation energy (BDE) of the C−O bond of ethers (ca. 80 kcal/mol) are significantly higher than the BDE of the O−O bond of peroxides (ca. 34 kcal/mol).[39] Since it is accepted that BDEs are derived experimentally from the activation energies $\Delta E^{\#}$ of thermal decomposition,[39a] we have determined the activation energy for the thermolysis of the EPO of DMA from NMR measurements. The obtained value of 24.7 kcal/mol is even lower than the activation energy of acyclic alkyl peroxides. Homolytic cleavage of the C−O bond (pathway B) can therefore occur only if the corresponding carbon-centered radical is sufficiently stabilized by the two adjacent phenyl rings and the bridging substituent R.

The strength of the stabilization of a carbon-centered radical by a substituent R can be quantified relative to the stability of the methyl radical by a formal hydrogen-transfer process between the carbon-centered radical species and methane in an isodesmic reaction (Scheme 9).[40] The reaction enthalpy

Scheme 9. Isodesmic Reactions To Determine RSE of Related Compounds



corresponds to the radical stabilization energy (RSE) of the substituent. A positive value would imply a stabilizing effect of R. Thus, we calculated the enthalpies of isodesmic reactions of anthracene model systems with substituents R, which transfer a hydrogen atom to the methyl radical. The relative energy changes of the two radical species and the corresponding hydrocarbons were estimated theoretically by UB3LYP/6-

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311G* calculations including zero-point corrections and adaption to 298 K.[27] From our results on the thermolysis shown in Table 6, anthracenes, tetracenes, and pentacenes exhibit a similar dependence on the substituent R. We therefore chose the anthracene system as representative example which required a minimum on calculation time.

Monoradical **9** with a methyl substituent exhibits an RSE of 138 kJ/mol, which is higher than the RSE of a simple methyl group (13 kJ/mol). This is understandable because the radical is also substituted with two benzene rings which belong to the acene system. On the other hand, the RSE of radical species **10** is significantly higher, and the intermediate from pathway B in Scheme 8 is well stabilized. Since the thermolysis of arylanthracenes is endothermic (Table 3), the intermediate can also react back to the more stable EPO, causing a very slow formation of the acene and oxygen (Figure 10).[15] This

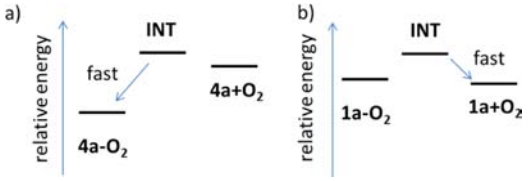

Figure 10. Reaction energy profiles of the thermolysis of aryl- and arylalkynylanthracenes (estimated from data in Table 3 and the activation energies in Table 6).

reversible opening and closing of a C−O bond is in accordance with our previous studies on molecular rotors, where the long lifetime of an intermediate allowed even a rotation of the adjacent phenyl ring (Scheme 8, R = Ph).[13a] With the alkynyl substituent present in radical **11**, the RSE of 201 kJ/mol is still sufficiently high for radical stabilization, and the thermolysis should proceed again by pathway B. However, the calculated energy changes of the reaction from the EPO to the acene and $^1O_2$ point at an exothermic reaction (Table 3), and thus, the intermediate converts more rapidly to the starting materials, namely the parent acene and oxygen (Figure 10b). This explains well why alkynyl-substituted acenes reconvert fast whereas arylanthracenes reconvert slowly. Moreover, it becomes clear why all other types of substituents cause decomposition.

Although a concerted retro-reaction with release of singlet oxygen as discussed by Turro cannot be completely ruled out,[15] the striking difference between aryl- vs alkynylanthracenes found herein can be best rationalized by a stepwise process. The formation of radical intermediates is in accordance with our previous studies on *para*-substituted arylanthracenes as well.[13b]

CONCLUSIONS

We have synthesized anthracenes, tetracenes, and pentacenes with silylalkynyl or arylalkynyl substituents at the periphery. For the anthracene system the impact of the alkynyl groups on the reactivity with singlet oxygen was compared with that of other substituents such as H, methyl, ethenyl, or phenyl. We found that the bimolecular rate of the photooxygenation decreases in the order from methyl/ethenyl, to phenyl, to H, and finally to alkynyl. Thus, the rates between DMA and **1a** differ by 2 orders of magnitude. The impact of the triple bond was investigated with the tetracene and the pentacene systems as well. It was revealed that the influence is slightly weaker for tetracenes but very strong for the pentacene system. For the first time, a 6,13-EPO of an alkynyl-substituted pentacene was isolated and characterized. The oxygenation of 6,13-TIPS-alkynylpentacene **8** was also carried out in the "dark" by the use of a chemical source of $^1O_2$. Under this condition a Type I photooxidation with the excited pentacene and $^3O_2$ is switched off. We obtained a very small rate constant of 1×10^5 s^{-1} M^{-1} for the Type II reaction of **8**. Interestingly, a competitive photooxygenation of **8** and **4a** revealed that $^1O_2$ is physically quenched by **8**. The regioselectivities of photooxygenations of tetracenes and pentacenes are strongly influenced by the alkynyl substituent, which directs oxygen to the two substituted carbon atoms. This fits well with the FMO theory, since the differences in the orbital coefficients increase upon alkynyl substitution. FMO studies showed that the reactivity correlates with the HOMO energy only within rows of acenes carrying phenyl groups with various *para*-substituents. On the other hand, the FMO theory cannot explain the influence of different substituents on the reactivity with $^1O_2$. This gives strong evidence for a change in the mechanism of the photooxygenations. We propose radical pathways for unsubstituted acenes, zwitterionic intermediates for aryl-substituted acenes, and a concerted reaction for alkynyl-substituted acenes. Thus, the triple bond switches the mechanism remarkably, explaining the very slow oxidation of such acenes.

Additionally, alkynyl substituents of all types of acenes protect their EPOs from decomposition and promote a clean reconversion of the EPOs to the parent acenes. This very fast reaction can be well explained by the calculated energy differences between **1a**-O_2 and **1a** compared with **4a**-O_2 and **4a**. The ease of the cleavage of oxygen caused by the triple bond by the formation of biradical intermediates was strongly supported by calculations of isodesmic reaction energies. The phenyl group provides the highest RSE, which results in C−O cleavage. The RSE of alkynyl-substituted radical intermediates is smaller but still sufficient to favor a C−O cleavage, which as a consequence proceeds faster. Thus, the triple bond causes a clean reconversion to acenes without decomposition.

Overall, the protection of acenes by triple bonds is remarkably strong. Oxidations proceed very slowly compared to those of alkyl-, phenyl-, or unsubstituted acenes. Furthermore, if EPOs are formed with alkynyl substituents, they cleanly reconvert to the parent acene by simple heating. Since oligo- and polyacenes are important compounds for applications as electronic or luminescent devices, their substitution with triple bonds provides the basis for the design of more stable materials.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures and analytical data; UV−vis spectra of the oxygenation products of **8** and the thermolysis of **8**-O_2 under aerobic conditions; procedure and product spectra of the "dark" oxygenation of **8** and determination of k_r; cyclic voltammograms of anthracenes **1**; and details about theoretical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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