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1,8,10-Substituted Anthracenes – Hexafunctional Frameworks via *Head*-to-*Tail* Photodimerisation

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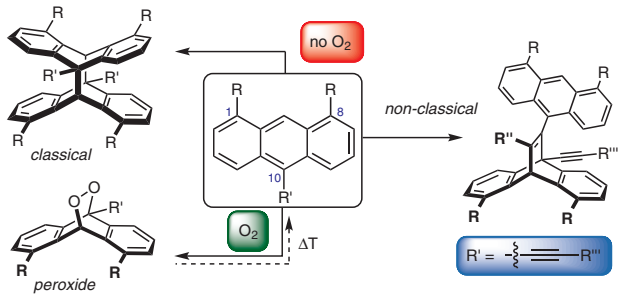

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Abstract Several 1,8,10-functionalised anthracene derivatives and a couple of 1,8,9-functionalised anthracene analogous, bearing alkynyl substituents at positions 1 and 8 were synthesised and their photochemistry investigated in UV irradiation experiments. Almost all compounds could be converted into their 9,10:10′,9′-*head*-to-*tail* photodimers completely excluding the formation of the corresponding *head*-to-*head* isomers. Working under non-inert conditions led to formation of endoperoxides in some cases. Furthermore, a non-classical [4π+2π] photodimer was obtained from 1,8,10-tris[(trimethylsilyl)ethynyl]anthracene with one of the alkynyl substituents involved in the photoreaction. The ^{1}H and ^{13}C NMR spectra of all classical and non-classical photodimers were compared with those of the endoperoxides identifying characteristic shifts for the atoms at positions 9 and 10. Moreover, solid-state structures were determined for one or more of each representative.

Key words anthracenes, photodimerisation, endoperoxides, non-classical photodimers, solid-state structures

First reports on the photodimerisation of anthracene stem from Fritzsche in 1866, who obtained colourless crystals by irradiating a saturated anthracene solution with sunlight.[1] This species was later gradually proven to be the dimeric 9,10:9′,10′-photoproduct, formed by [4π+4π] cycloaddition of the central rings.[2] In the 1950s, the interest in organic photochemistry had increased significantly and since then the photochemical reactions of anthracenes have been extensively studied.[3] In general, photodimerisation of anthracenes provides the advantage of doubling the number of directed functionalities.

During our research in the field of poly-Lewis acids, we started investigating the use of anthracene photodimers as rigid functionalisable frameworks.[4] In this contribution, we synthesised a series of 1,8,10-functionalised anthracene monomers. In general, irradiation of these compounds with UV light might lead to the formation of two possible photoisomers *head*-to-*head* **A** and *head*-to-*tail* **B** (Figure 1). However, we noticed that the use of alkynyl substituents at positions 9 and 10 inhibits any appearance of the *head*-to-*head* isomer and the *head*-to-*tail* isomer is formed quantitatively in most cases. Recently, Klajn et al. demonstrated that the selectivity of such photodimerisation can be influenced by performing the reaction in the presence of nanoflasks.[5] Notwithstanding, in our case, the selective *anti*-dimerisation enables an easy and efficient access to non-flexible Janus-like frameworks with three functionalities on both sides of the anthracene dimer.

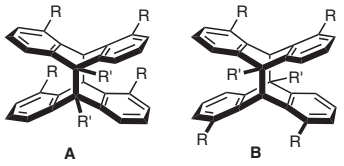
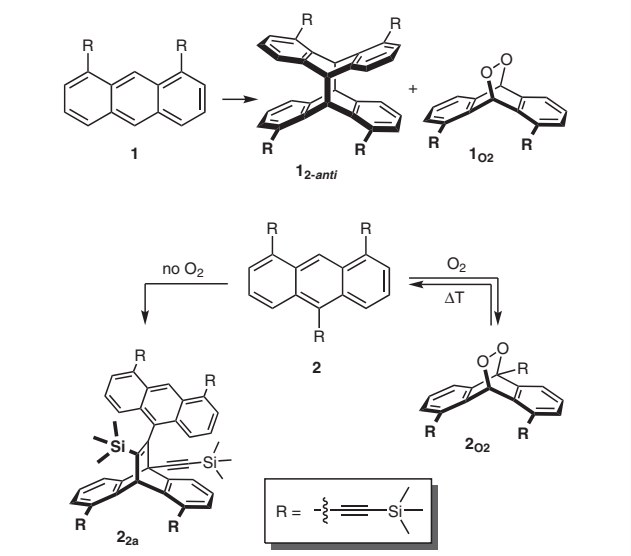


Figure 1 Photodimers **A** (*head*-to-*head*) and **B** (*head*-to-*tail*) might be obtained upon irradiating 1,8,10-trisubstituted anthracenes with UV light.

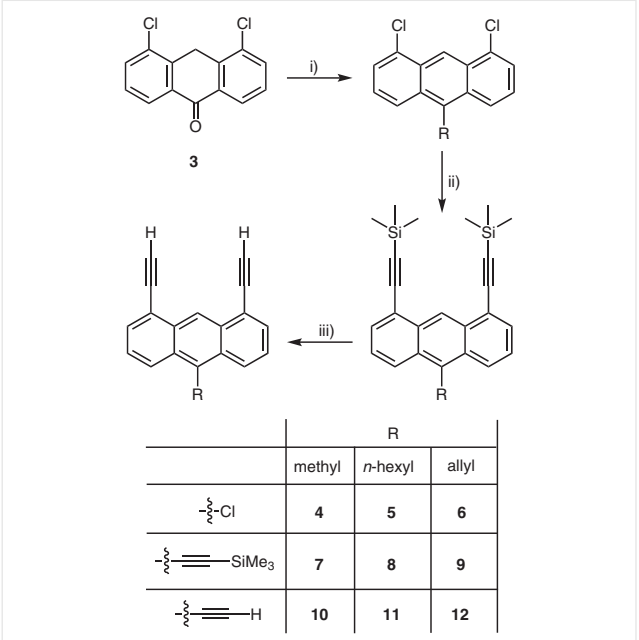
Recently, we reported the syntheses of several 1,5-, 1,8-, and 1,8,10-substituted anthracenes and their behaviour towards UV irradiation.[4] For 1,8-bis[(trimethylsilyl)ethynyl]anthracene (**1**) the formation of two compounds has been observed, which were described as *syn*- and *anti*-isomer. However, our recent studies disproved the existence of the *syn*-compound and instead provided evidence for the presence of the corresponding 9,10-epidioxyanthracene $\mathbf{1}_{O2}$ (Scheme 1). The photodimer $\mathbf{1}_{2\text{-}anti}$ is formed exclusively by using strictly oxygen-free solvents. Similar results were found by reinvestigating the photodimerisation experiments of 1,8,10-tris[(trimethylsilyl)ethynyl]anthracene (**2**). Instead of the reported *head*-to-*tail* photoproduct, the cor-

responding endoperoxide $\mathbf{2_{O2}}$ was obtained. We then found that complete exclusion of oxygen led to the formation of the non-classical photodimer $\mathbf{2_{2a}}$ as a product of [4π+2π] cycloaddition. The mentioned misinterpretations resulted from the poor NMR spectroscopic differentiability of photodimers and endoperoxides. Generally, a comparison of the reactivities of the anthracene derivatives **1** and **2** shows that a substituent at position 10 can have a decisive influence on the photodimerisation (as it has been shown to have on the regiochemistry of the addition of arynes[6]). In order to study this effect in more detail, we herein describe the syntheses of various 1,8,10-functionalised anthracenes by verifying their photodimerisability.



Scheme 1 *Head*-to-*tail* photodimer $\mathbf{1_{2\text{-}anti}}$ and the endoperoxide $\mathbf{1_{O2}}$ are formed in UV-light-induced reactions of 1,8-bis[(trimethylsilyl)-ethynyl]anthracene (**1**). The irradiation of 1,8,10-tris[(trimethylsilyl)-ethynyl]anthracene (**2**) under inert conditions leads to formation of the non-classical photodimer $\mathbf{2_{2a}}$. In the presence of oxygen, the thermally labile endoperoxide $\mathbf{2_{O2}}$ is generated instead.

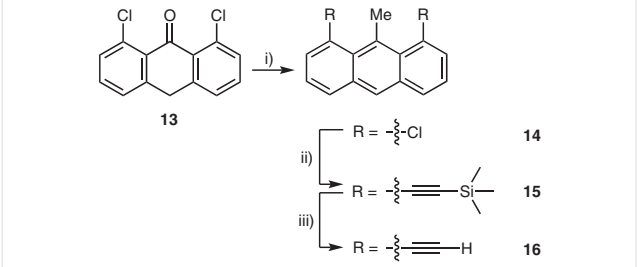
A common strategy for the preparation of 1,8-dichloroanthracenes modified with hydrocarbon substituents at the 10-position is the conversion of 1,8-dichloroanthracen-10(9*H*)-one (**3**) with Grignard or organolithium reagents.[7] Usually, the elimination of water and the subsequent aromatisation has to be induced in a second step either by addition of concentrated hydrochloric acid or heating the crude products with phosphorus pentoxide in toluene. A series of such compounds have been reported in one of our previous works.[6a] Besides the literature-known methyl and allyl derivatives **4** and **6**, the novel 1,8-dichloro-10-hexylanthracene (**5**) was synthesised for our current investigations (Scheme 2). The chloro substituents in compounds **4**–**6** were replaced in double Kumada cross-coupling reactions by rigid (trimethylsilyl)ethynyl functions. Deprotection of the protecting groups using potassium carbonate in methanol subsequently afforded the terminal alkynes **10**–**12**. All new compounds were characterised by multinuclear NMR spectroscopy and high-resolution mass spectrometry. Furthermore, single crystals of compounds **4**, **5**, and **9**–**12** were grown and their solid-state structures were determined in X-ray diffraction studies [Figures S12–S17, Supporting Information (SI)].



	R		
	methyl	*n*-hexyl	allyl
-Cl	4	5	6
$-SiMe_3$	7	8	9
-H	10	11	12

Scheme 2 Syntheses of the 1,8,10-trifunctionalised anthracenes **4**–**12**. *Reagents and conditions*: i) RMgBr, THF, r.t., overnight, 19% (**5**); ii) $Me_3Si–C≡C–MgBr$, $Ni(acac)_2$, PPh_3, THF, reflux, 3–4 d, 92% (**7**), 91% (**8**), 55% (**9**); iii) K_2CO_3, MeOH, 1 h–3 d, quant (**10**), 95% (**11**), 76% (**12**).

In order to distinguish between the influences of functionalities at positions 9 and 10, the 9-methyl-substituted anthracene derivatives **14**–**16** were also synthesised (Scheme 3). Starting from anthrone **13**,[8] three synthetic steps were performed in analogy to the procedures described above. The solid-state structure of **14** is depicted in

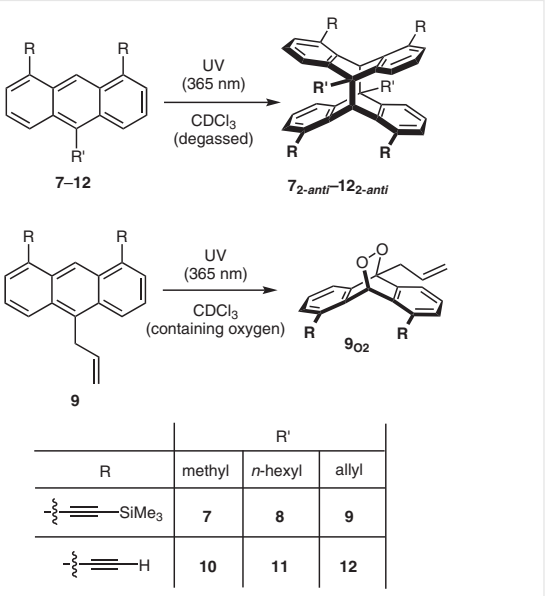


Scheme 3 Syntheses of the 1,8,9-functionalised anthracenes **14**–**16**. *Reagents and conditions*: i) MeLi, toluene, –70 °C to r.t., overnight, 66%; ii) $Me_3Si–C≡C–MgBr$, $Ni(acac)_2$, PPh_3, THF, reflux, 1 d, 60%; iii) K_2CO_3, MeOH, 1 h, 87%.

Figure S18 (SI). Significant differences between the 1,8,9- and the 1,8,10-substituted anthracene derivatives are found in the ^{1}H NMR spectra, where the resonances of the protons at position 9 are located at 9.3–9.5 ppm and those of the protons at position 10 at 8.2–8.3 ppm. The assignment of these signals was verified by means of NOESY NMR experiments for compounds **14**–**16** in the form of correlations between the protons at position 10 and those at positions 4 and 5.

As already mentioned, under strict exclusion of oxygen, the *head*-to-*tail* photodimer $\mathbf{1}_{2\text{-}anti}$ is formed quantitatively from 1,8-bis[(trimethylsilyl)ethynyl]anthracene (**1**), whereas UV irradiation of the corresponding 1,8,10-trialkynylanthracene **2** leads to a complete conversion into the non-classical photodimer $\mathbf{2}_{2a}$. The alkynyl-substituted anthracenes **7**–**12** were investigated in analogous experiments. All compounds undergo [4π+4π] cycloaddition reactions and the corresponding *head*-to-*tail* photodimers $\mathbf{7}_{2\text{-}anti}$–$\mathbf{12}_{2\text{-}anti}$ are formed (Scheme 4). In the case of the hexyl-substituted anthracenes **8** and **11**, a change of the colour from pale yellow to red or brown during the UV irradiation indicates slight decomposition, which can also be detected by NMR spectroscopy. Indications for the formation of neither the *head*-to-*head*- nor any non-classical photodimers were found. However, structures like compound $\mathbf{2}_{2a}$ have been observed before and seem to be the favourable products for substrates with alkynyl moieties at positions 9 or 10 of the anthracene.[9] Apparently, these functionalities prevent the classical [4π+4π] cycloaddition in general, probably due to their participation in the conjugated system. Aliphatic substituents like methyl or hexyl do not take such an effect and cannot take part in the photoreaction. The formation of endoperoxides by irradiating anthracenes in the presence of oxygen is well known. In order to promote the oxygenation reaction, a solution of the allyl-substituted anthracene **9** was irradiated in an open round-bottomed flask under vigorous stirring. As already reported for trialkynylanthracene **2**, the addition of oxygen takes place preferentially, affording the 9,10-epidioxyanthracenes $\mathbf{9}_{O2}$ quantitatively after one day (Scheme 4).

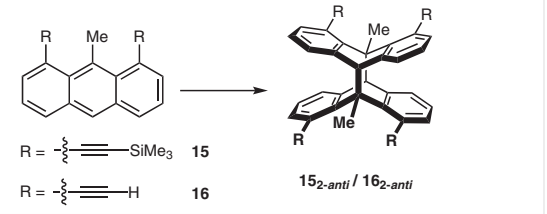
The general reversibility of endoperoxide formation has been extensively studied in the past.[10] The epidioxyanthracene $\mathbf{9}_{O2}$ was found to be thermally stable at room temperature, in contrast to compound $\mathbf{2}_{O2}$. Thus, the anthracene reactant **2** can be slowly recovered from a solution of $\mathbf{2}_{O2}$ by deoxygenation. The addition and elimination of oxygen was monitored by ^{1}H NMR spectroscopy in $CDCl_3$. After two days of irradiating (365 nm) the anthracene reactant, the ratio between $\mathbf{2}_{O2}$ and **2** was found to be 91:9. Upon storing the sample in the dark, the ratio was slowly decreased to 66:34 after three days, 48:52 after five days, and 23:77 after ten days. The elimination was accomplished by removing the solvent under reduced pressure and drying the residue in vacuo for six hours at 45 °C.



R	R' methyl	*n*-hexyl	allyl
SiMe$_3$	7	8	9
H	10	11	12

Scheme 4 Photodimerisation of the 1,8,10-substituted anthracenes **7**–**12** to the *head*-to-*tail* photodimers $\mathbf{7}_{2\text{-}anti}$–$\mathbf{12}_{2\text{-}anti}$. The endoperoxide $\mathbf{9}_{O2}$ is obtained by UV irradiation of anthracene **9** in the presence of oxygen.

For the 1,8,9-trisubstituted anthracene derivatives **15** and **16**, similar results were obtained, as for the 1,8,10-substituted derivatives **7**–**12**. Apart from traces of possible decomposition products, only the *head*-to-*tail* photodimers $\mathbf{15}_{2\text{-}anti}$ and $\mathbf{16}_{2\text{-}anti}$ were formed (Scheme 5).



Scheme 5 Photodimerisation of the 1,8,9-substituted anthracenes **15** and **16** to the *head*-to-*tail* photodimers $\mathbf{15}_{2\text{-}anti}$ and $\mathbf{16}_{2\text{-}anti}$.

Generally, the NMR spectroscopic distinction between 9,10:10′,9′-anthracene photodimers and 9,10-epidioxyanthracenes is not straightforward, due to their similar 9,10-dihydroanthracene structures. Therefore, we took a closer look at the ^{1}H and ^{13}C NMR spectra of all products, generated by UV irradiation. Particularly, the signals of the hydrogen and carbon atoms at positions 9 and 10 are noteworthy and can be used to distinguish the different species (Table 1).

Table 1 ^{1}H and ^{13}C NMR Spectroscopic Shifts of the Resonances at Positions 9 and 10 of all Photodimers and Endoperoxides in $CDCl_3$ [500 MHz (^{1}H); 125 MHz (^{13}C), 298 K][a]

Entry	H9	H10	C9	C10
$\mathbf{1}_{2\text{-}anti}$	5.54	4.54	48.8	52.2
$\mathbf{7}_{2\text{-}anti}$	5.24	–	57.2	52.3
$\mathbf{8}_{2\text{-}anti}$	5.18	–	57.7	58.2
$\mathbf{9}_{2\text{-}anti}$	5.19	–	57.1	56.4
$\mathbf{10}_{2\text{-}anti}$	5.51	–	56.4	52.6
$\mathbf{11}_{2\text{-}anti}$	5.47	–	57.0	58.4
$\mathbf{12}_{2\text{-}anti}$	5.47	–	56.6	56.4
$\mathbf{15}_{2\text{-}anti}$	–	4.13	57.2	68.5
$\mathbf{16}_{2\text{-}anti}$	–	4.17	57.0	68.3
$\mathbf{2}_{O2}$	6.82	–	75.7	78.6
$\mathbf{9}_{O2}$	6.87	–	75.0	80.0
$\mathbf{2}_{2a}$	9.29 (a) 6.51 (b)	– –	123.9 (a) 50.1 (b)	n.a.[b] 59.9 (b)

[a] For NMR spectroscopic assignments (a) and (b), see Figure 5 (vide infra).
[b] n.a.: Not assigned.

In the ^{1}H NMR spectra, the proton resonances of the classical [4π+4π] photodimers $\mathbf{X}_{2\text{-}anti}$ are located between 5.2 and 5.5 ppm for H9 and between 4.1 and 4.5 ppm for H10. The corresponding singlets of the endoperoxides $\mathbf{Y}_{O2}$ for H9 are shifted to considerably lower field (6.8–6.9 ppm). A clear distinction between photodimers and endoperoxides can also be made by comparing the ^{13}C NMR spectra. The signals of the carbon atoms at positions 9 and 10 are found at 49–57 ppm for the 1,8,10-substituted photodimers $\mathbf{7}_{2\text{-}anti}$–$\mathbf{12}_{2\text{-}anti}$ and at 57–69 ppm for the 1,8,10-substituted derivatives $\mathbf{15}_{2\text{-}anti}$ and $\mathbf{16}_{2\text{-}anti}$. The signals resulting from the endoperoxides $\mathbf{Y}_{O2}$ are located at 75–80 ppm. The non-classical photodimer $\mathbf{2}_{2a}$ gives two sets of signals in each spectrum, one for the anthracene [labelled (a) in Table 1] and one for the dihydroanthracene moiety [labelled (b)].

In addition to NMR spectroscopy, X-ray diffraction analysis is a suitable method for the characterisation of anthracene photoproducts. We were able to crystallise several of the *head*-to-*tail*-photodimers, as well as one of the endoperoxides and the non-classical [4π+2π] photodimer $\mathbf{2}_{2a}$. Its molecular structure is depicted in Figure 2. Recently, we reported the formation of an analogous derivative by unforeseen [4π+2π] photodimerisation of 1,8-bis[(trimethylsilyl)ethynyl]-10-(oct-1-ynyl)anthracene.[9e] All structural parameters of both compounds are identical within experimental error. For $\mathbf{2}_{2a}$ the bond lengths between the bridgehead atoms are 1.554(3) Å for C(3)–C(55) and 1.575(3) Å for C(10)–C(54). The C=C bond C(54)–C(55) is notably elongated with 1.333(4) Å, compared to all of the C≡C bonds, for instance C(25)–C(26) with only 1.202(4) Å.

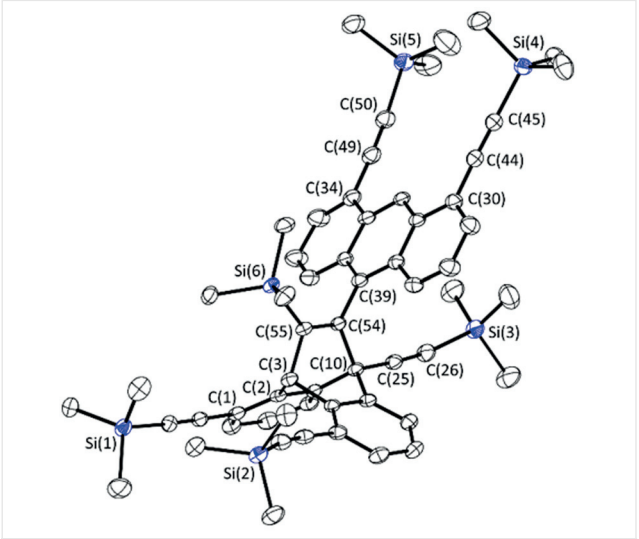


Figure 2 Molecular structure of $\mathbf{2}_{2a}$ in the crystalline state. Displacement ellipsoids are drawn at 50% probability level, hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.394(4), C(2)–C(3) 1.519(3), C(3)–C(55) 1.554(3), C(10)–C(25) 1.460(4), C(10)–C(54) 1.575(3), C(25)–C(26) 1.202(4), C(26)–Si(3) 1.841(3), C(39)–C(54) 1.493(3), C(54)–C(55) 1.333(4), C(55)–Si(6) 1.882(2); C(1)–C(2)–C(3) 127.2(2), C(2)–C(3)–C(55) 106.5(2), C(3)–C(55)–C(54) 112.4(2), C(3)–C(55)–Si(6) 117.2(2), C(10)–C(25)–C(26) 174.8(3), C(10)–C(54)–C(39) 117.8(2), C(10)–C(54)–(C55) 114.8(2), C(25)–C(10)–C(54) 112.7(2), C(25)–C(26)–Si(3) 169.9(3), C(39)–C(54)–C(55) 127.3(2), C(54)–C(55)–Si(6) 130.4(2).

In the case of all classical photodimers $\mathbf{X}_{2\text{-}anti}$, the bonds between the bridgehead atoms are apparently longer than those of the non-classical species $\mathbf{2}_{2a}$. For compounds $\mathbf{12}_{2\text{-}anti}$ and $\mathbf{16}_{2\text{-}anti}$ (Figure 3) these bond lengths were determined to be 1.63 Å, which is considerably elongated compared to standard C–C single bond values (1.52 Å[11]) and characteristic for 9,10:10′,9′-photodimers[2e,4,12] (actually this length is comparable to recently studied diamantoid dimers like diamantyl-diamantane[13]). Compared to each other, $\mathbf{16}_{2\text{-}anti}$ shows stronger distortions of the ethynyl substituents than $\mathbf{12}_{2\text{-}anti}$, indicated by the bond angles at C(15): 177.2(2)° for $\mathbf{12}_{2\text{-}anti}$ and 171.5(2)° for $\mathbf{16}_{2\text{-}anti}$. Obviously, the methyl group of $\mathbf{16}_{2\text{-}anti}$ leads to significantly stronger steric repulsion of the ethynyl substituents than the hydrogen atom of $\mathbf{12}_{2\text{-}anti}$ (similar distortions have been investigated in detail for 1,8-dialkynylanthracenes in the gaseous and solid phase and demonstrated that these are inherent effects and not imposed by crystal packing[14]). This repulsion also leads to a larger space between the upper and lower benzene rings, exemplarily demonstrated by the distance between C(14) and C(7′) of 4.42(1) Å for $\mathbf{12}_{2\text{-}anti}$ and 4.87(1) Å for $\mathbf{16}_{2\text{-}anti}$.

The class of endoperoxides is well known and solid-state structures have so far been determined not only for epidioxyanthracenes,[15] but also for some tetracene and pentacene derivatives.[16] The molecular structure of $\mathbf{9}_{O2}$

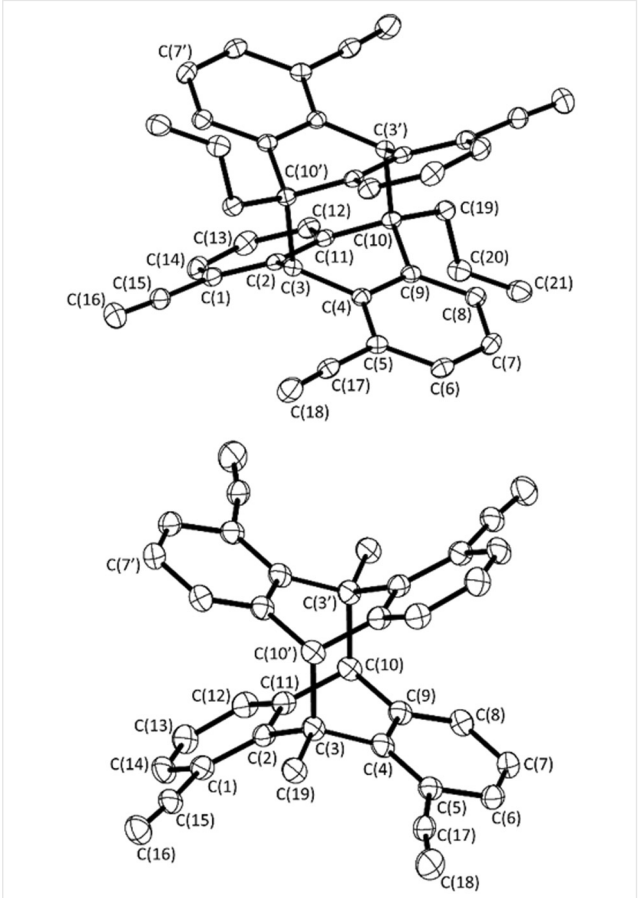


Figure 3 Molecular structures of $\mathbf{12}_{2\text{-}anti}$ (above) and $\mathbf{16}_{2\text{-}anti}$ (below) in the crystalline state. Displacement ellipsoids are drawn at 50% probability level, hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for $\mathbf{12}_{2\text{-}anti}$/$\mathbf{16}_{2\text{-}anti}$: C(1)–C(2) 1.404(2)/1.405(3), C(1)–C(15) 1.440(2)/1.458(3), C(2)–C(3) 1.511(2)/1.541(3), C(2)–C(11) 1.399(2)/1.409(3), C(3)–C(10′) 1.634(2)/1.628(3), C(3)–C(19) –/1.528(3), C(10)–(C11) 1.530(2)/1.502(3), C(10)–C(19) 1.545(2)/–, C(15)–C(16) 1.190(2)/1.174(4), C(19)–C(20) 1.508(2)/–, C(20)–C(21) 1.316(2)/–; C(1)–C(2)–C(3) 121.9(1)/128.0(2), C(1)–C(2)–C(11) 119.9(1)/116.9(2), C(1)–C(15)–C(16) 177.2(2)/171.5(2), C(2)–C(3)–C(4) 108.6(1)/107.5(2), C(2)–C(3)–C(10′) 112.2(1)/109.2(2), C(2)–C(3)–C(19) –/113.3(2), C(2)–C(11)–C(10) 117.4(1)/118.5(2), C(3′)–C(10)–C(11) 108.9(1)/115.0(2), C(3′)–C(10)–C(19) 106.5(1)/–, C(10′)–C(3)–C(19) –/104.8(2), C(10)–C(19)–C(20) 115.7(1)/–, C(19)–C(20)–C(21) 124.7(1)/–.

(Figure 4) explicitly shows, that the oxygenation of anthracene **9** took place at the middle ring at positions 9 and 10. Compared to literature data, the O–O bond [1.492(2)] and the C–O bonds [1.463(2) for C(3)–O(1) and 1.476(2) for C(10)–O(2)] are in the normal range for these kinds of compounds.[15,16] The structural parameters of the carbon backbone are in good agreement with those of the classical *head*-to-*tail* photodimers or the dihydroanthracene moiety of compound $\mathbf{2}_{2a}$.

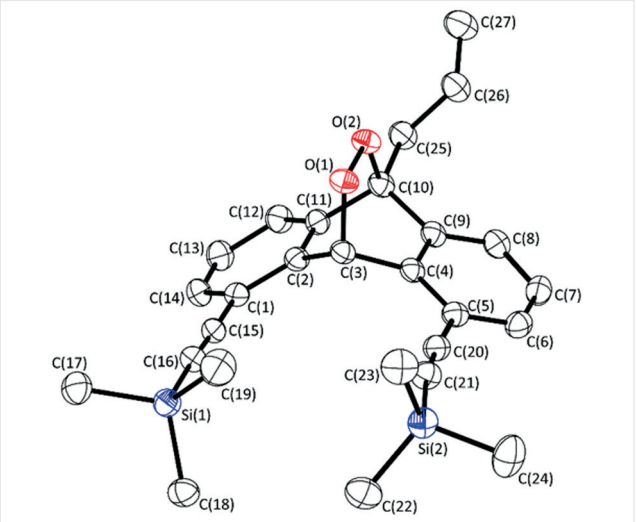


Figure 4 Molecular structure of $\mathbf{9}_{O2}$ in the crystalline state. Displacement ellipsoids are drawn at 50% probability level, hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–C(2) 1.399(2), C(1)–C(14) 1.406(2), C(1)–C(15) 1.435(2), C(2)–C(3) 1.500(2), C(2)–C(11) 1.395(2), C(3)–O(1) 1.463(2), C(10)–C(11) 1.517(2), C(10)–C(25) 1.519(2), C(10)–O(2) 1.476(2), C(15)–C(16) 1.204(2), C(16)–Si(1) 1.848(2), C(17)–Si(1) 1.861(2), C(25)–C(26) 1.508(2), C(26)–C(27) 1.314(3), O(1)–O(2) 1.492(2); C(1)–C(2)–C(3) 126.9(1), C(1)–C(2)–C(11) 120.6(1), C(1)–C(15)–C(16) 177.8(2), C(2)–C(1)–C(15) 121.1(1), C(2)–C(1)–C(14) 118.1(1), C(2)–C(3)–O(1) 106.8(1), C(3)–O(1)–O(2) 109.6(1), C(9)–C(10)–C(11) 108.5(1), C(9)–C(10)–C(25) 116.2(1), C(10)–C(25)–C(26) 114.2(1), C(10)–O(2)–O(1) 111.7(1), C(15)–C(16)–Si(1) 176.5(1), C(16)–Si(1)–C(17) 109.6(1), C(25)–C(26)–C(27) 124.4(2), C(25)–C(10)–O(2) 103.5(1).

In contrast to NMR spectroscopy and X-ray diffraction, the applicability of mass spectrometry for the analysis of photodimers is highly restricted. Generally, only the molecular peak of the corresponding monomer is detected.[3b] However, mass spectrometry is a convenient method to demonstrate the formation of endoperoxides, since their molecular peaks can be usually detected by common electron impact ionisation at 70 eV.

In conclusion, a series of 1,8,10- and 1,8,9-functionalised anthracenes were synthesised and investigated with special regards to their photodimerisation. All derivatives, except 1,8,10-tris[(trimethylsilyl)ethynyl]anthracene (**2**), undergo 9,10:10′,9′-cycloaddition reactions, affording the corresponding *head*-to-*tail* photodimers. The formation of the complementary *head*-to-*head* isomers was not observed. It was further proven that anthracenes with alkynyl substituents at position 10 prefer a non-classical [4π+2π] photodimerisation upon UV irradiation, as has been observed before. Under atmospheric conditions, namely in the presence of oxygen, two endoperoxides were obtained. Depending on the substituent at position 10, they were found to be either thermally stable or to slowly eliminate oxygen, reforming the anthracene reactant. Detailed NMR studies

revealed that the signals of the hydrogen and carbon atoms at positions 9 and 10 provide diagnostic information for the different species.

1,8-Bis[(trimethylsilyl)ethynyl]anthracene (**1**),[17] 1,8,10-tris[(trimethylsilyl)ethynyl]anthracene (**2**),[4] 1,8-dichloroanthracene-10-(9*H*)-one (**3**)[8], 1,8-dichloro-10-methylanthracene (**4**),[6a] 10-allyl-1,8-dichloroanthracene (**6**),[18] and 1,8-dichloroanthracene-9-(10*H*)-one (**13**)[8] were synthesised according to literature protocols. 1-Bromohexane, MeLi (1.6 M in Et_2O), EtMgBr (3.0 M in Et_2O) and Ni(acac)$_2$ (all purchased from Acros Organics), trimethylsilylacetylene (from fluorochem), Mg turnings (from Merck), anhyd $CeCl_3$ (from Strem Chemicals), and PPh_3 (from Fluka) were used without further purification. All reactions using organometallic reagents, as well as Kumada cross-coupling reactions were carried out under a dry inert atmosphere of N_2 using standard Schlenk techniques in anhydrous solvents (THF dried over potassium; Et_2O dried over $LiAlH_4$; toluene dried over Na, all solvents were freshly distilled before use). Column chromatography was performed on silica gel 60 (0.04–0.063 mm). NMR spectra were recorded on a Bruker DRX 500, a Bruker Avance III 500, and a Bruker Avance III 500 HD at ambient temperature (298 K). The chemical shifts (δ) were measured in ppm with respect to the solvent ($CDCl_3$: ^{1}H NMR δ = 7.26, ^{13}C NMR δ = 77.16) or referenced externally (^{29}Si: $SiMe_4$). EI mass spectra were recorded using an Autospec X magnetic sector mass spectrometer with EBE geometry (Vacuum Generators, Manchester, UK) equipped with a standard EI source. Exact mass measurements were performed in the high-resolution mode with PFK as internal standard. MALDI experiments were performed using a Q-IMS-TOF mass spectrometer Synapt G2Si (Waters, Manchester, UK) in resolution mode, interfaced to a MALDI ion source. The numbering scheme for NMR assignments of the substituted anthracenes (Figure 5) is based on IUPAC guidelines.

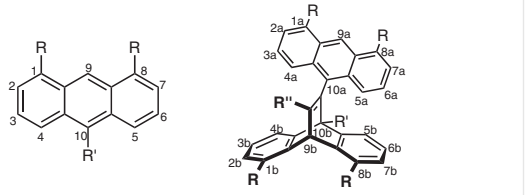


Figure 5 Numbering scheme for NMR spectroscopic assignments

1,8-Dichloro-10-hexylanthracene (5)

n-Hexylmagnesium bromide was freshly prepared by adding a solution of 1-bromohexane (1.1 mL, 7.9 mmol) in Et_2O (7 mL) to Mg turnings (219 mg, 9.0 mmol) in Et_2O (13 mL) and heating the mixture to reflux for 2 h. The Grignard suspension was slowly added to a solution of 1,8-dichloroanthracen-10(9*H*)-one (**3**; 469 mg, 1.78 mmol) and anhyd $CeCl_3$ (404 mg, 1.64 mmol) in THF (80 mL) at 0 °C. After stirring the mixture at r.t. overnight, H_2O (20 mL) was added and the suspension was filtered. The aqueous layer was extracted with CH_2Cl_2 (2 × 30 mL), the combined organic phases were washed with brine, and dried ($MgSO_4$). After evaporation of the solvent, the crude product was filtered over silica gel with *n*-pentane as eluent. Small amounts of by-products were removed by sublimation (75 °C/ $5\cdot10^{-3}$ mbar, 12 h) affording **5** as a yellow solid; yield: 110 mg (19%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.26, (s, 1 H, H9), 8.20 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H, H4/H5), 7.63 (d, $^3J_{H,H}$ = 7.1 Hz, 2 H, H2/H7), 7.44 (dd, $^3J_{H,H}$ = 8.7, 7.4 Hz, 2 H, H3/H6), 3.55–3.61 (m, 2 H, ArCH_2), 1.74–1.83 (m, 2 H, $ArCH_2CH_2$), 1.52–1.61 (m, 2 H, $ArCH_2CH_2CH_2$), 1.31–1.43 (m, 4 H, $CH_2CH_2CH_3$), 0.92 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 137.3 (C10), 133.4, 130.7, 129.4, 125.7 (C2/C7), 125.5 (C3/C6), 123.9 (C3/C6), 119.9 (C9), 31.9 (CH_2), 31.7 ($ArCH_2CH_2$), 30.1 ($ArCH_2CH_2CH_2$), 29.0 (ArCH_2), 22.8 (CH_2), 14.3 (CH_3).

MS (EI, 70 eV): *m*/*z* = 330.0 [M]$^+$, 259.0 [M – C_5H_{11}]$^+$, 225.0 [M – C_5H_{11} – Cl]$^+$, 189.0 [M – C_5H_{11} – 2Cl]$^+$.

HRMS (EI): *m*/*z* calcd for $C_{20}H_{20}Cl_2^+$: 330.09366; found: 330.09367; dev. [ppm]: 0.04, dev. [mmu]: 0.01.

1,8-Dichloro-9-methylanthracene (14)

A solution of MeLi (1.6 M in Et_2O; 4 mmol, 2.5 mL) was added dropwise to a solution of 1,8-dichloroanthracen-9(10*H*)-one (**13**; 501 mg, 1.90 mmol) in toluene (18 mL) at −70 °C. The mixture was allowed to warm to r.t. and stirred overnight. Aq 10% HCl (7 mL) was added and the mixture was heated to reflux for 40 min. After extraction of the aqueous layer with toluene (3 × 10 mL), the combined organic phases were washed with brine (10 mL), and dried ($MgSO_4$). The solvent was evaporated. Column chromatography (*n*-pentane, ∅ = 3 cm, *l* = 12 cm) afforded **14** as a bright yellow solid; yield 328 mg (66%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.22 (s, 1 H, H10), 7.838 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, H4/H5), 7.59 (d, $^3J_{H,H}$ = 7.0 Hz, 2 H, H2/H7), 7.30 (dd, $^3J_{H,H}$ = 8.2 Hz, $^3J_{H,H}$ = 7.3 Hz, 2 H, H3/H6), 3.39 (s, 3 H, CH_3).

MS (EI, 70 eV): *m*/*z* = 259.9 [M]$^+$, 225.1 [M – Cl]$^+$, 190.1 [M – 2Cl]$^+$.

Kumada Cross-Coupling Reactions; General Procedure

[(Trimethylsilyl)ethynyl]magnesium bromide was obtained by adding trimethylsilylacetylene to a solution of EtMgBr in THF at 0 °C. The mixture was stirred overnight at r.t. observing a gas evolution. The freshly prepared [(trimethylsilyl)ethynyl]magnesium bromide (adjusted to 1 M in THF) was added to a solution of the 1,8-dichloroanthracene, Ni(acac)$_2$, and PPh_3 in THF at r.t. and the mixture was heated to reflux for several days. After quenching with sat. aq NH_4Cl and extraction of the aqueous layer with CH_2Cl_2, the combined organic phases were dried ($MgSO_4$). The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography on silica gel.

1,8-Bis[(trimethylsilyl)ethynyl]-10-methylanthracene (7)

Synthesis according to the general procedure for Kumada cross-coupling reactions using 1,8-dichloro-10-methylanthracene (**4**; 1.01 g, 3.87 mmol), [(trimethylsilyl)ethynyl]magnesium bromide (1 M in THF, 15.5 mL, 15.5 mmol), PPh_3, and Ni(acac)$_2$ (one spatula tip of each compound), reflux for 3 d. Column chromatography [*n*-pentane/CH_2Cl_2 (15:1), ∅ = 5 cm, *l* = 5 cm, R_f = 0.6] afforded **7** as a yellow solid; yield: 1.37 g (92%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.32 (s, 1 H, H9), 8.28 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H, H4/H5), 7.79 (d, $^3J_{H,H}$ = 6.9 Hz, 2 H, H2/H7), 7.45 (dd, $^3J_{H,H}$ = 8.9 Hz, $^3J_{H,H}$ = 6.9 Hz, 2 H, H3/H6), 3.09 (s, 3 H, ArCH_3), 0.38 [s, 18 H, Si(CH_3)$_3$].

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 132.2 (C2/C7), 131.5 (C10), 131.1, 130.0, 126.0 (C4/C5), 124.9 (C3/C6), 122.8 (C9), 122.1, 104.1 (C≡C–Si), 99.9 (C≡*C*–Si), 14.6 (ArCH_3), 0.6 [Si(CH_3)$_3$].

^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$): δ = −17.5.

MS (EI, 70 eV): *m*/*z* = 384.2 [M]$^+$, 281.1 [M – Si(CH_3)$_3$ – (CH_3)$_2$]$^+$.

HRMS (MALDI-TOF): *m*/*z* calcd for $C_{25}H_{28}Si_2^+$: 384.17241; found: 384.1719, dev. [ppm]: 1.33, dev. [mmu]: 0.51.

1,8-Bis[(trimethylsilyl)ethynyl]-10-hexylanthracene (8)

Synthesis according to the general procedure for Kumada cross-coupling reactions using 1,8-dichloro-10-hexylanthracene (**5**; 310 mg, 0.94 mmol), [(trimethylsilyl)ethynyl]magnesium bromide (1 M in THF; 10.2 mL, 10.2 mmol), PPh_3, and $Ni(acac)_2$ (one spatula tip of each compound), reflux for 4 d. Column chromatography [*n*-pentane/CH_2Cl_2 (8:1), ⌀ = 3 cm, *l* = 15 cm, R_f = 0.6] afforded **8** as a yellow solid; yield: 389 mg (91%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.31, (s, 1 H, H9), 8.25 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H, H4/H5), 7.78 (d, $^3J_{H,H}$ = 7.1 Hz, 2 H, H2/H7), 7.42–7.47 (m, 2 H, H3/H6), 3.54–3.59 (m, 2 H, ArC*H*$_2$), 1.72–1.81 (m, 2 H, ArCH$_2$C*H*$_2$), 1.50–1.60 (m, 2 H, ArCH$_2$CH$_2$C*H*$_2$), 1.29–1.42 (m, 4 H, C*H*$_2$C*H*$_2$CH$_3$), 0.91 (t, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH_3), 0.38 [s, 18 H, Si(CH_3)$_3$].

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 136.9, 132.1 (C2/C7), 131.3, 129.4, 125.7 (C4/C5), 124.9 (C3/C6), 122.9 (C9), 122.2, 104.1 (*C*≡C–Si), 99.9 (C≡*C*–Si), 31.9 (CH_2), 31.7 (ArCH$_2$CH$_2$), 30.1 (ArCH$_2$CH$_2$C*H*$_2$), 28.5 (ArC*H*$_2$), 22.9 (CH_2), 14.3 (CH_2CH_3), 0.6 [Si(CH_3)$_3$].

^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$): δ = –17.5.

MS (EI, 70 eV): *m*/*z* = 454.3 [M]$^+$, 383.2 [M – C_5H_{11}]$^+$.

HRMS (MALDI-TOF): *m*/*z* calcd for $C_{30}H_{38}Si_2^+$: 454.25066; found: 454.2505, dev. [ppm]: 0.35, dev. [mmu]: 0.16.

10-Allyl-1,8-bis[(trimethylsilyl)ethynyl]anthracene (9)

Synthesis according to the general procedure for Kumada cross-coupling reactions using 10-allyl-1,8-dichloroanthracene (**6**; 300 mg, 1.04 mmol), [(trimethylsilyl)ethynyl]magnesium bromide (1 M in THF; 12 mL, 12 mmol), PPh_3, and $Ni(acac)_2$ (one spatula tip of each compound), reflux for 4 d. Column chromatography [*n*-pentane/CH_2Cl_2 (8:1), ⌀ = 3 cm, *l* = 22 cm, R_f = 0.8] afforded **9** as bright yellow crystals; yield: 236 mg (55%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.40 (s, 1 H, H9), 8.22 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, H4/H5), 7.81 (d, $^3J_{H,H}$ = 6.5 Hz, 2 H, H2/H7), 7.46 (dd, $^3J_{H,H}$ = 9.0 Hz, $^3J_{H,H}$ = 6.9 Hz, 2 H, H3/H6), 6.20 (ddt, $^3J_{H,H}$ = 17.0 Hz, $^3J_{H,H}$ = 10.5 Hz, $^3J_{H,H}$ = 5.4 Hz, 1 H, CH$_2$C*H*=CH$_2$), 5.08 (dd, $^3J_{H,H}$ = 10.2 Hz, $^2J_{H,H}$ = 1.6 Hz, 1 H, CH$_2$CH=C*H*$_{cis}$), 4.85 (dd, $^3J_{H,H}$ = 17.2 Hz, $^2J_{H,H}$ = 1.6 Hz, 1 H, CH$_2$CH=C*H*$_{trans}$), 4.36 (d, $^3J_{H,H}$ = 5.4 Hz, 2 H, C*H*$_2$CH=CH$_2$), 0.42 [s, 18 H, Si(CH_3)$_3$].

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 136.4 (CH$_2$*C*H=CH$_2$), 132.8, 132.2 (C2/C7), 131.2, 129.9, 125.8 (C4/C5), 125.2 (C3/C6), 123.6 (C9), 122.2, 116.5 (CH$_2$CH=*C*H$_2$), 104.0 (*C*≡C–Si), 100.0 (C≡*C*–Si), 32.3 (*C*H$_2$CH=CH$_2$), 0.6 [Si(CH_3)$_3$].

^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$): δ = –17.5.

MS (EI, 70 eV): *m*/*z* = 410.2 [M]$^+$, 337.1 [M – Si(CH_3)$_3$]$^+$, 307.1 [M – Si(CH_3)$_3$ – 2(CH_3)]$^+$.

HRMS (EI): *m*/*z* calcd for $C_{34}H_{30}Cl_4Si_2$: 410.18806; found: 410.18712, dev. [ppm]: 2.28, dev. [mmu]: 0.94.

1,8-Bis[(trimethylsilyl)ethynyl]-9-methylanthracene (15)

Synthesis according to the general procedure for Kumada cross-coupling reactions using 1,8-dichloro-9-methylanthracene (**14**; 330 mg, 1.26 mmol), [(trimethylsilyl)ethynyl]magnesium bromide (1 M in THF; 11.0 mL, 11.0 mmol), PPh_3, and $Ni(acac)_2$ (one spatula tip of each compound), reflux for 1 d. Column chromatography [*n*-pentane/CH_2Cl_2 (8:1), ⌀ = 3 cm, *l* = 15 cm, R_f = 0.5] afforded **15** as a yellow solid; yield: 292 mg (60%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.23 (s, 1 H, H10), 7.89 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, H4/H5), 7.82 (dd, $^3J_{H,H}$ = 6.9 Hz, $^4J_{H,H}$ = 1.2 Hz, 2 H, H2/H7), 7.34 (dd, $^3J_{H,H}$ = 8.3 Hz, $^3J_{H,H}$ = 7.0 Hz, 2 H, H3/H6), 3.79 (s, 3 H, ArC*H*$_3$), 0.32 [s, 18 H, Si(CH_3)$_3$].

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 135.9 (C2/C7), 135.0, 132.0, 132.0, 130.4 (C4/C5), 127.1 (C10), 124,4 (C3/C6), 120.4, 108.1 (*C*≡C–Si), 101.0 (C≡*C*–Si), 24.7 (Ar*C*H$_3$), 0.0 [Si(CH_3)$_3$].

^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$): δ = –18.0.

MS (EI, 70 eV): *m*/*z* = 383.9 [M]$^+$, 311.1 [M – Si(CH_3)]$^+$.

HRMS (MALDI-TOF): *m*/*z* calcd for $C_{25}H_{28}Si_2^+$: 384.17241; found: 384.1722, dev. [ppm]: 0.55, dev. [mmu]: 0.21.

Deprotection of the Trimethsilyl Protecting Groups; General Procedure

K_2CO_3 was added to a suspension of the 1,8-bis[(trimethylsilyl)ethynyl]anthracene in MeOH and the mixture was stirred at r.t. for various periods of time. The solvent was evaporated and the crude product was purified by either filtration or column chromatography on silica gel.

1,8-Diethynyl-10-methylanthracene (10)

Synthesis according to the general procedure for deprotection of the trimethsilyl protecting groups using 1,8-bis[(trimethylsilyl)ethynyl]-10-methylanthracene (**7**; 200 mg, 0.52 mmol) and K_2CO_3 (218 mg, 1.58 mmol), stirring at r.t. for 1 h. Filtration over silica gel with CH_2Cl_2 afforded **10** in quantitative yield as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.45 (s, 1 H, H9), 8.31 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, H4/H5), 7.79 (d, $^3J_{H,H}$ = 6.8 Hz, 2 H, H2/H7), 7.48 (dd, $^3J_{H,H}$ = 9.0 Hz, $^3J_{H,H}$ = 6.8 Hz, 2 H, H3/H6), 3.61 (s, 2 H, 2 × C≡CH), 3.10 (s, 3 H, CH_3).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 131.7, 131.5, 131.3 (C2/C7), 130.0, 126.2 (C4/C5), 124.9 (C3/C6), 122.6 (C9), 121.1, 82.7 (C≡CH), 82.2 (*C*≡CH), 14.4 (CH_3).

MS (EI, 70 eV): *m*/*z* = 240.1 [M]$^+$.

HRMS (MALDI-TOF): *m*/*z* calcd for $C_{19}H_{12}^+$: 240.09335; found: 240.0933, dev. [ppm]: 0.21, dev. [mmu]: 0.05.

1,8-Diethynyl-10-hexylanthracene (11)

Synthesis according to the general procedure for deprotection of the trimethsilyl protecting groups using 1,8-bis[(trimethylsilyl)ethynyl]-10-hexylanthracene (**8**; 362 mg, 0.80 mmol) and K_2CO_3 (384 mg, 2.78 mmol), stirring at r.t. overnight. Column chromatography [*n*-pentane/CH_2Cl_2 (8:1), ⌀ = 3 cm, *l* = 15 cm, R_f = 0.4] afforded **11** as a yellow solid; yield: 273 mg (95%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.45, (s, 1 H, H9), 8.28 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, H4/H5), 7.79 (d, $^3J_{H,H}$ = 6.7 Hz, 2 H, H2/H7), 7.47 (dd, $^3J_{H,H}$ = 9.0 Hz, $^3J_{H,H}$ = 6.8 Hz, 2 H, H3/H6), 3.61 (s, 2 H, 2 × C≡CH), 3.55–3.60 (m, 2 H, ArC*H*$_2$), 1.73–1.82 (m, 2 H, ArCH$_2$C*H*$_2$), 1.53–1.61 (m, 2 H, ArCH$_2$CH$_2$C*H*$_2$), 1.31–1.43 (m, 4 H, C*H*$_2$C*H*$_2$CH$_3$), 0.92 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 137.0, 131.6, 131.3 (C2/C7), 129.3, 126.0 (C4/C5), 125.0 (C3/C6), 122.7 (C9), 121.2, 82.7 (C≡CH), 82.1 (*C*≡CH), 31.9 (CH_2), 31.8 (ArCH$_2$CH$_2$), 30.1 (ArCH$_2$CH$_2$C*H*$_2$), 28.4 (ArC*H*$_2$), 22.8 (CH_2), 14.3 (CH_3).

MS (EI, 70 eV): *m*/*z* = 310.2 [M]$^+$, 239.1 [M – C_5H_{11}]$^+$.

HRMS (MALDI-TOF): *m*/*z* calcd for $C_{24}H_{22}^+$: 310.17160; found: 310.1717, dev. [ppm]: 0.32, dev. [mmu]: 0.10.

10-Allyl-1,8-diethynylanthracene (12)

Synthesis according to the general procedure for deprotection of the trimethsilyl protecting groups using 10-allyl-1,8-bis[(trimethylsilyl)ethynyl]anthracene (**9**; 1.00 g, 2.44 mmol) and K_2CO_3 (1.77 g, 12.8 mmol), stirring at r.t. for 3 d. Column chromatography (*n*-pentane, ⌀ = 6 cm, *l* = 12 cm, R_f = 0.2) afforded **12** as a yellow solid; yield: 496 mg (76%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.50 (s, 1 H, H9), 8.25 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, H4/H5), 7.79 (d, $^3J_{H,H}$ = 6.9 Hz, 2 H, H2/H7), 7.48 (dd, $^3J_{H,H}$ = 9.0 Hz, $^3J_{H,H}$ = 6.9 Hz, 2 H, H3/H6), 6.18 (ddt, $^3J_{H,H}$ = 17.3 Hz, $^3J_{H,H}$ = 10.5 Hz, $^3J_{H,H}$ = 5.5 Hz, 1 H, CH_2CH=CH_2), 5.07 (d, $^3J_{H,H}$ = 10.2 Hz, 1 H, CH_2CH=CH_{cis}), 4.87 (d, $^3J_{H,H}$ = 17.3 Hz, 1 H, CH_2CH=CH_{trans}), 4.36 (d, $^3J_{H,H}$ = 5.5 Hz, 2 H, CH_2CH=CH_2), 3.61 (s, 2 H, 2 × C≡CH).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 136.3 (CH_2CH=CH_2), 133.0, 131.6, 131.3 (C2/C7), 129.9, 126.1 (C4/C5), 125.3 (C3/C6), 123.6 (C9), 121.3, 116.6 (CH_2CH=CH_2), 82.8 (C≡CH), 82.0 (C≡CH), 32.2 (CH_2CH=CH_2).

MS (EI, 70 eV): *m*/*z* = 266.0 [M]$^+$, 239.0 [M – C_2H_3]$^+$.

HRMS (EI): *m*/*z* calcd for $C_{34}H_{30}Cl_4Si_2$: 266.10900; found: 266.10859, dev. [ppm]: 1.54, dev. [mmu]: 0.41.

1,8-Diethynyl-9-methylanthracene (16)

Synthesis according to the general procedure for deprotection of the trimethsilyl protecting groups using 1,8-bis[(trimethylsilyl)ethynyl]-9-methylanthracene (**15**; 200 mg, 0.52 mmol) and K_2CO_3 (218 mg, 1.58 mmol), stirring at r.t. for 1 h. Filtration over silica gel with CH_2Cl_2 afforded **16** as a yellow solid; yield: 109 mg (87%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.25 (s, 1 H, H10), 7.93 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, H4/H5), 7.85 (d, $^3J_{H,H}$ = 6.9 Hz, 2 H, H2/H7), 7.36 (dd, $^3J_{H,H}$ = 8.3 Hz, $^3J_{H,H}$ = 7.0 Hz, 2 H, H3/H6), 3.78 (s, 3 H, CH_3), 3.60 (s, 2 H, 2 × C≡CH).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 136.3 (C2/C7), 134.7, 132.0, 132.0, 130.7 (C4/C5), 127.1 (C10), 124,4 (C3/C6), 119.4, 86.4 (C≡CH), 84.0 (C≡CH), 24.6 (CH_3).

MS (EI, 70 eV): *m*/*z* = 240.0 [M]$^+$.

HRMS (MALDI-TOF): *m*/*z* calcd for $C_{19}H_{12}^+$: 240.09335; found: 240.0928, dev. [ppm]: 2.29, dev. [mmu]: 0.55.

Photodimerisation Reactions; General Procedure

In an NMR tube small amounts (3–5 mg) of the respective anthracene derivative were dissolved in anhyd and degassed $CDCl_3$ (0.5 mL). The mixtures were irradiated with UV light (365 nm) until no more signals of the reactant could be observed in the ^{1}H NMR spectrum.

***anti*-Photodimer of 1,8-Bis[(trimethylsilyl)ethynyl]anthracene ($\mathbf{1}_{2\text{-}anti}$)**

Synthesis according to the general procedure for photodimerisation reactions.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.05 (d, $^3J_{H,H}$ = 7.3 Hz, 4 H, H4/H5), 6.97 (d, $^3J_{H,H}$ = 7.7 Hz, 4 H, H2/H7), 6.79 (t, $^3J_{H,H}$ = 7.6 Hz, 4 H, H3/H6), 5.54 (s, 2 H, H9), 4.54 (s, 2 H, H10), 0.38 [s, 36 H, $Si(CH_3)_3$].

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 144.2, 143.4, 130.3 (C2/C7), 126.4 (C4/C5), 125.8 (C3/C6), 121.8, 104.5 (C≡C–Si), 98.2 (C≡C–Si), 52.2 (C10), 48.8 (C9), 0.6 [$Si(CH_3)_3$].

^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$): δ = –17.8.

Non-Classical [4π+2π] Photodimer of 1,8,10-Tris[(trimethylsilyl)ethynyl]anthracene ($\mathbf{2}_{2a}$)

Synthesis according to the general procedure for photodimerisation reactions.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.29 (s, 1 H, H9a), 7.66 (d, $^3J_{H,H}$ = 6.9 Hz, 2 H, H2b/H7b), 7.55 (d, $^3J_{H,H}$ = 7.4 Hz, 2 H, H4a/H5a), 7.34 (dd, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.1 Hz, 2 H, H2a/H7a), 7.08 (t, $^3J_{H,H}$ = 7.7 Hz, 2 H, H3a/H6a), 7.00 (dd, $^3J_{H,H}$ = 8.8 Hz, $^3J_{H,H}$ = 6.9 Hz, 2 H, H3b/H6b), 6.79 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, H4b/H5b), 6.51 (s, 1 H, H9b), 0.37 {s, 18 H, $[Si(CH_3)_3]_2$}, 0.35 {s, 18 H, $[Si(CH_3)_3]_2$}, –0.43 [s, 9 H, $Si(CH_3)_3$], –0.45 [s, 9 H, $Si(CH_3)_3$].

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 158.8, 148.7, 145.4, 144.9, 136.0, 132.2 (C2b/C7b), 130.8, 130.4 (C2a/C7a), 128.1 (C4b/C5b), 126.3, 124.8 (C3a/C6a), 124.5 (C3b/C6b), 123.9 (C9a), 123.0 (C4a/C5a), 121.3, 118.3, 104.1, 103.5, 100.2, 99.5, 98.0, 96.7, 59.9 (C10b), 50.1 (C9b), 0.6 {$[Si(CH_3)_3]_2$}, 0.5 {$[Si(CH_3)_3]_2$}, –0.6 [$Si(CH_3)_3$], –1.9 [$Si(CH_3)_3$].

^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$): δ = –5.6 [$Si(CH_3)_3$], –17.6 {$[Si(CH_3)_3]_2$}, –17.7 {$[Si(CH_3)_3]_2$}, –18.2 [$Si(CH_3)_3$].

***anti*-Photodimer of 1,8-Bis[(trimethylsilyl)ethynyl]-10-methylanthracene ($\mathbf{7}_{2\text{-}anti}$)**

Synthesis according to the general procedure for photodimerisation reactions.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.24–7.26 (m, 4 H, H4/H5), 7.00 (dd, $^3J_{H,H}$ = 7.7 Hz, $^4J_{H,H}$ = 1.0 Hz, 4 H, H2/H7), 6.84 (t, $^3J_{H,H}$ = 7.7 Hz, 4 H, H3/H6), 5.24 (s, 2 H, H9), 2.47 (s, 6 H, CH_3), 0.37 [s, 36 H, $Si(CH_3)_3$].

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 146.3, 144.5, 130.7 (C2/C7), 125.5 (C3/C6), 123.4 (C4/C5), 121.6, 105.7 (C≡C–Si), 98.1 (C≡C–Si), 57.2 (C9), 52.3 (C10), 25.3 ($ArCH_3$), 0.5 [$Si(CH_3)_3$].

^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$): δ = –18.0.

***anti*-Photodimer of 1,8-Bis[(trimethylsilyl)ethynyl]-10-hexylanthracene ($\mathbf{8}_{2\text{-}anti}$)**

Synthesis according to the general procedure for photodimerisation reactions.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.14 (d, $^3J_{H,H}$ = 8.0 Hz, 4 H, H4/H5), 6.99 (d, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.0 Hz, 4 H, H2/H7), 6.80 (t, $^3J_{H,H}$ = 7.7 Hz, 4 H, H3/H6), 5.18 (s, 2 H, H9), 3.11–3.17 (m, 4 H, $CH_2(CH_2)_4CH_3$), 1.46–1.54 (m, 4 H, CH_2), 1.21–1.31 [m, 12 H, 3 × CH_2], 0.87 (t, $^3J_{H,H}$ = 6.9 Hz, 6 H, 2 × CH_3), 0.37 [s, 36 H, $Si(CH_3)_3$].

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 144.7, 143.4, 130.9 (C2/C7), 126.0 (C4/C5), 125.0 (C3/C6), 121.8, 105.9 (C≡C–Si), 97.9 (C≡C–Si), 58.2 (C10), 57.7 (C9), 37.2 [$CH_2(CH_2)_4CH_3$], 32.1 (CH_2), 30.8 (CH_2), 25.6 (CH_2), 22.8 (CH_2), 14.1 (CH_3), 0.6 [$Si(CH_3)_3$].

^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$): δ = –18.1.

***anti*-Photodimer of 10-Allyl-1,8-bis[(trimethylsilyl)ethynyl]anthracene ($\mathbf{9}_{2\text{-}anti}$)**

Synthesis according to the general procedure for photodimerisation reactions.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.18 (d, $^3J_{H,H}$ = 7.7 Hz, 4 H, H4/H5), 7.00 (d, $^3J_{H,H}$ = 7.7 Hz, 4 H, H2/H7), 6.80 (t, $^3J_{H,H}$ = 7.7 Hz, 4 H, H3/H6), 5.46 (ddt, $^3J_{H,H}$ = 17.2 Hz, $^3J_{H,H}$ = 10.5 Hz, $^3J_{H,H}$ = 5.2 Hz, 2 H, CH_2CH=CH_2), 5.27 (d, $^3J_{H,H}$ = 17.5 Hz, 2 H, CH_2CH=CH_{trans}), 5.19 (s, 2 H, H9), 5.05 (dd, $^3J_{H,H}$ = 10.5 Hz, $^2J_{H,H}$ = 1.3 Hz, 2 H, CH_2CH=CH_{cis}), 4.14 (d, $^3J_{H,H}$ = 5.1 Hz, 4 H, CH_2CH=CH_2), 0.39 [s, 36 H, $Si(CH_3)_3$].

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 144.6, 143.4, 136.8 (CH_2CH=CH_2), 130.8 (C2/C7), 126.1 (C4/C5), 125.2 (C3/C6), 121.8, 116.5 (CH_2CH=CH_2), 105.8 (C≡C–Si), 98.3 (C≡C–Si), 57.1 (C9), 56.4 (C10), 39.6 (CH_2CH=CH_2), 0.6 [$Si(CH_3)_3$].

^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$): δ = –17.9.

anti-Photodimer of 1,8-Diethynyl-10-methylanthracene ($10_{2\text{-}anti}$)

Synthesis according to the general procedure for photodimerisation reactions.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31 (d, $^3J_{H,H}$ = 7.7 Hz, 4 H, H4/H5), 7.03 (d, $^3J_{H,H}$ = 7.7 Hz, 4 H, H2/H7), 6.87 (t, $^3J_{H,H}$ = 7.7 Hz, 4 H, H3/H6), 5.51 (s, 2 H, H9), 3.36 (s, 4 H, 4 × C≡CH), 2.44 (s, 6 H, 2 × CH_3).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 146.3, 145.4, 130.0 (C2/C7), 125.8 (C3/C6), 124.0 (C4/C5), 120.4, 83.5 (*C*≡CH), 80.9 (C≡*C*H), 56.4 (C9), 52.6 (C10), 25.4 (CH_3).

anti-Photodimer of 1,8-Diethynyl-10-hexylanthracene ($11_{2\text{-}anti}$)

Synthesis according to the general procedure for photodimerisation reactions.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.17 (d, $^3J_{H,H}$ = 7.7 Hz, 4 H, H4/H5), 7.02 (d, $^3J_{H,H}$ = 7.6 Hz, 4 H, H2/H7), 6.83 (t, $^3J_{H,H}$ = 7.7 Hz, 4 H, H3/H6), 5.47 (s, 2 H, H9), 3.37 (s, 4 H, 4 × C≡CH), 3.08–3.14 [m, 4 H, $CH_2(CH_2)_4CH_3$], 1.44–1.52 [m, 4 H, $CH_2(CH_2)_2CH_3$], 1.26–1.33 (m, 8 H, $CH_2CH_2CH_3$), 1.18–1.25 [m, 4 H, $CH_2(CH_2)_3CH_3$], 0.89 (t, $^3J_{H,H}$ = 6.9 Hz, 6 H, 2 × CH_3).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 145.8, 143.5, 129.9 (C2/C7), 126.4 (C4/C5), 125.2 (C3/C6), 120.5, 83.7 (*C*≡CH), 80.8 (C≡*C*H), 58.4 (C10), 57.0 (C9), 37.3 [$CH_2(CH_2)_4CH_3$], 31.9 (CH_2), 30.5 [$CH_2(CH_2)_2CH_3$], 25.2 [$CH_2(CH_2)_3CH_3$], 22.8 (CH_2), 14.3 (CH_3).

anti-Photodimer of 10-Allyl-1,8-diethynylanthracene ($12_{2\text{-}anti}$)

Synthesis according to the general procedure for photodimerisation reactions.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.23 (d, $^3J_{H,H}$ = 7.8 Hz, 4 H, H4/H5), 7.03 (dd, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 0.9 Hz, 4 H, H2/H7), 6.83 (t, $^3J_{H,H}$ = 7.7 Hz, 4 H, H3/H6), 5.47 (s, 2 H, H9), 5.42 (ddt, $^3J_{H,H}$ = 16.1 Hz, $^3J_{H,H}$ = 10.7 Hz, $^3J_{H,H}$ = 5.4 Hz, 2 H, CH_2CH=CH_2), 5.27 (dd, $^3J_{H,H}$ = 17.8 Hz, $^2J_{H,H}$ = 1.8 Hz, 2 H, CH_2CH=CH_{trans}), 5.05 (dd, $^3J_{H,H}$ = 10.4 Hz, $^2J_{H,H}$ = 1.9 Hz, 2 H, CH_2CH=CH_{cis}), 4.07 (d, $^3J_{H,H}$ = 5.6 Hz, 4 H, CH_2CH=CH_2), 3.41 (s, 4 H, 4 × C≡CH).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 145.5, 143.4, 136.3 (CH_2CH=CH_2), 130.1 (C2/C7), 126.7 (C4/C5), 125.4 (C3/C6), 120.5, 117.3 (CH_2CH=CH_2), 83.6 (*C*≡CH), 81.1 (C≡*C*H), 56.6 (C10), 56.4 (C9), 40.1 (CH_2CH=CH_2).

anti-Photodimer of 1,8-Bis[(trimethylsilyl)ethynyl]-9-methylanthracene ($15_{2\text{-}anti}$)

Synthesis according to the general procedure for photodimerisation reactions.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.07 (dd, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.4 Hz, 4 H, H2/H7), 6.96 (dd, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,H}$ = 1.3 Hz, 4 H, H4/H5), 6.75 (t, $^3J_{H,H}$ = 7.5 Hz, 4 H, H3/H6), 4.13 (s, 2 H, H10), 3.13 (s, 6 H, 2 × CH_3), 0.28 [s, 36 H, $Si(CH_3)_3$].

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 145.6, 143.5, 135.0 (C2/C7), 128.1 (C4/C5), 125.6 (C3/C6), 120.1, 107.4 (*C*≡C–Si), 98.9 (C≡*C*–Si), 68.5 (C10), 57.2 (C9), 31.8 (ArCH_3), 0.0 [$Si(CH_3)_3$].

^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$): δ = –18.3.

anti-Photodimer of 1,8-Diethynyl-9-methylanthracene ($16_{2\text{-}anti}$)

Synthesis according to the general procedure for photodimerisation reactions.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.12 (dd, $^3J_{H,H}$ = 7.7 Hz, $^4J_{H,H}$ = 1.4 Hz, 4 H, H2/H7), 7.02 (dd, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,H}$ = 1.3 Hz, 4 H, H4/H5), 6.82 (t, $^3J_{H,H}$ = 7.5 Hz, 4 H, H3/H6), 4.17 (s, 2 H, H10), 3.32 (s, 4 H, 4 × C≡CH), 3.15 (s, 6 H, 2 × CH_3).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 145.7, 143.5, 135.6 (C2/C7), 128.4 (C4/C5), 125.8 (C3/C6), 119.1, 85.5 (*C*≡CH), 82.4 (C≡CH), 68.3 (C10), 57.0 (C9), 31.8 (ArCH_3).

9,10-Endoperoxide of 1,8,10-Tris[(trimethylsilyl)ethynyl]anthracene (2_{O2})

A vigorously stirred solution of 1,8,10-tris[(trimethylsilyl)ethynyl]anthracene (**2**; 30 mg, 64 µmol) in $CHCl_3$ (6 mL) was irradiated with UV light (365 nm) in an open round-bottomed flask for 2 d. After evaporation of the solvent under reduced pressure, $\mathbf{2_{O2}}$ (91%) was obtained as a yellow solid, contaminated with 9% of the reactant **2**.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.63 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, H4/H5), 7.45 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, H2/H7), 7.28 (t, $^3J_{H,H}$ = 7.6 Hz, 2 H, H3/H6), 6.82 (s, 1 H, H9), 0.37 [s, 9 H, $Si(CH_3)_3$], 0.30 {s, 18 H, $[Si(CH_3)_3]_2$}.

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 138.4, 137.5, 133.2 (C2/C7), 127.7 (C3/C6), 22.8 (C4/C5), 119.2, 102.1 (C≡*C*–Si), 101.3 [(*C*≡C–Si)$_2$], 99.7 [(C≡*C*–Si)$_2$], 93.3 (*C*≡C–Si), 78.6 (C10), 75.7 (9), 0.3 {$[Si(CH_3)_3]_2$}, –0.1 $[Si(CH_3)_3]$.

^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$): δ = –15.4 $[Si(CH_3)_3]$, –17.1 {$[Si(CH_3)_3]_2$}.

9,10-Endoperoxide of 10-Allyl-1,8-bis[(trimethylsilyl)ethynyl]anthracene (9_{O2})

A vigorously stirred solution of 10-allyl-1,8-bis[(trimethylsilyl)ethynyl]anthracene (**9**; 253 mg, 0.62 mmol) in $CHCl_3$ (50 mL) was irradiated with UV light (365 nm) in an open round-bottomed flask for 12 h. After evaporation of the solvent under reduced pressure, $\mathbf{9_{O2}}$ was quantitatively obtained as yellow crystals.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, H2/H7), 7.38 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, H4/H5), 7.21 (t, $^3J_{H,H}$ = 7.8 Hz, 2 H, H3/H6), 6.87 (s, 1 H, H9), 6.14 (ddt, $^3J_{H,H}$ = 16.8 Hz, $^3J_{H,H}$ = 10.4 Hz, $^3J_{H,H}$ = 6.4 Hz, 1 H, CH_2CH=CH_2), 5.44 (dd, $^3J_{H,H}$ = 17.2 Hz, $^2J_{H,H}$ = 1.3 Hz, 1 H, CH_2CH=CH_{trans}), 5.31 (dd, $^3J_{H,H}$ = 10.3 Hz, $^2J_{H,H}$ = 1.2 Hz, 1 H, CH_2CH=CH_{cis}), 3.46 (d, $^3J_{H,H}$ = 6.5 Hz, 1 H, CH_2CH=CH_2), 0.37 [s, 18 H, $Si(CH_3)_3$].

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 140.2, 139.1, 132.2 (C2/C7) 131.4 (CH_2CH=CH_2), 127.2 (C3/C6), 121.8 (C4/C5), 119.2, 119.1 (CH_2CH=CH_2), 101.5 (C≡C–Si), 99.4 (C≡*C*–Si), 80.0 (C10), 75.0 (C9), 32.7 (CH_2CH=CH_2), 0.3 $[Si(CH_3)_3]$.

^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$): δ = –17.1.

MS (EI, 70 eV): m/z = 442.0 $[M]^+$, 410.0 $[M - 2O]^+$.

HRMS (EI): m/z calcd for $C_{27}H_{30}O_2Si_2$: 442.17789; found: 442.17714, dev. [ppm]: 1.70, dev. [mmu]: 0.75.

Crystal Structure Determination

Suitable crystals of compounds **4**, **5**, **9**, **10**, **11**, **12**, **14**, $\mathbf{2_{2a}}$, $\mathbf{4_{2\text{-}anti}}$, $\mathbf{8_{2\text{-}anti}}$, $\mathbf{9_{2\text{-}anti}}$, $\mathbf{10_{2\text{-}anti}}$, $\mathbf{12_{2\text{-}anti}}$, $\mathbf{16_{2\text{-}anti}}$ and $\mathbf{9_{O2}}$ were obtained by slow evaporation of saturated solutions in benzene (**4**, **5**, **11**, $\mathbf{2_{2a}}$, $\mathbf{4_{2\text{-}anti}}$, $\mathbf{16_{2\text{-}anti}}$), $CHCl_3$ (**10**, $\mathbf{8_{2\text{-}anti}}$, $\mathbf{9_{2\text{-}anti}}$, $\mathbf{10_{2\text{-}anti}}$, $\mathbf{12_{2\text{-}anti}}$, $\mathbf{9_{O2}}$), *n*-pentane/CH_2Cl_2 (8:1) mixture (**9**), CH_2Cl_2 (**12**), or *n*-pentane (**14**). They were selected, coated with paratone-N oil, mounted on a glass fibre, and transferred onto the goniometer of the diffractometer into a cold stream of N_2 gas solidifying the oil. Data collections were performed on a Rigaku SuperNova diffractometer or a Bruker AXS X8 with an APEX II diffractometer. The structures were solved by direct methods and refined by full-matrix least-squares cycles (program SHELXL).[19] Crystal and refinement details, as well as CCDC numbers, are provided in Tables S1 and S2 (SI).[20]

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Supporting Information

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