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The Effect of Bulky Substituents on the Formation of Symmetrically Trisubstituted Triptycenes

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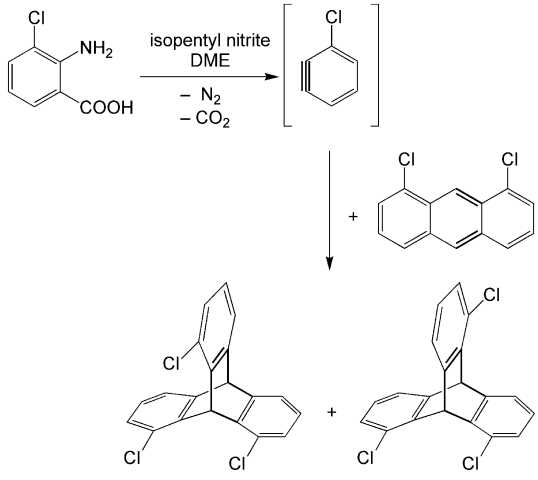
A series of 1,8-dichloroanthracene precursor molecules with substituents in C-10 position of different steric demand (cyclohexyl, *tert*-butyl, methyl, isopropyl, *n*-butyl, phenyl, benzyl, trimethylsilylethinyl) were synthesised and subjected to electrocyclic cycloadditions with chlorobenzyne generated from 3-chloroanthranilic acid. The aim was to steer the regioselectivity of the addition reaction by the steric repulsion between this C-10 substituent and the chlorine substituent at the benzyne intermediate. With H as C-10 substituent the reaction leads to 23 % *syn* and 77 % *anti* form. With the small methyl group a *syn*/*anti* ratio of 37:63 was achieved. Contrary to our expectations the large C-10 substituent *tert*-butyl leads to 100 % selectivity for the *anti* form. The best results were achieved for the C-10 substituent *n*-butyl with a *syn*/*anti* ratio of 40:60. The crystal structures of five 1,8-dichloroanthracenes with C-10 substituents were determined, namely those with *tert*-butyl, cyclohexyl, *n*-butyl and phenyl groups. As expected the backbone of the *tert*-butyl compound shows marked distortion of the planarity. Additionally, the crystal structures of three triptycenes were determined, namely those of the *syn* compound 1,8,13-trichlorotriptycene and those of the *anti* compounds 10-*tert*-butyl-1,8,16-trichlorotriptycene and 1,8,16-trichloro-10-methyltriptycene.

Introduction

In 1942 the first triptycene was obtained by Bartlett et al.[1] by Diels–Alder cycloaddition of anthracene and *p*-benzoquinone. Due to its structure the [2.2.2] bridgehead system keeps the angle between the planes of the aromatic rings at about 120°. Triptycenes are useful in the generation of rigid backbones and for creating structures with well-defined geometries.[2] One example is the preparation of cage compounds for potential applications such as storage[3] and recognition,[4] inspired by nano-sized compounds in biological systems.[5] Some of these self-assembled supramolecular cages use the ability of a coordination bond or a hydrogen bond for a direct orientation of the desired components.[6]

We became interested in functionalised triptycenes through a project for the synthesis of new poly-Lewis-acids[7] with defined positions of the acceptor sites. Poly-Lewis-acids are an active field of research,[8] but there is a distinct paucity of suitable rigid hydrocarbon backbones with defined structures capable of tolerating strong Lewis-acidic functionalities. In order to achieve selectivity in association with Lewis-bases, host molecules were synthesized with Lewis-acid functions in suitably close proximity and oriented such that they can act simultaneously.[9] These systems could serve for the recognition of anions and bases in general and for the activation of small molecules.[10]

A rigid backbone of C_3-symmetry would be perfectly given by a triptycene with functional groups at the 1-, 8-, and 13-positions.[11] The introduction of chloro functions in these positions offers various ways of derivatisation, e.g. their direct replacement by Lewis-acids or rigid spacer-units like alkynes via Kumada coupling reactions.[12] Scheme 1 illustrates the synthesis of trisubstituted triptycenes by the Diels–Alder cycloaddition of disubstituted anthracenes



Scheme 1. General outline for the synthesis of trisubstituted triptycenes.

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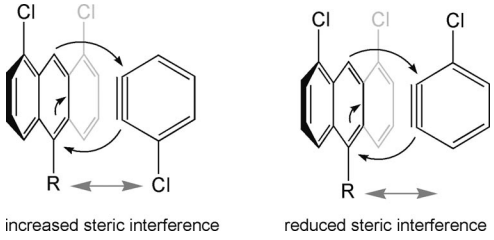
(diene) with a monosubstituted benzyne (dienophile).[13] The disubstituted anthracenes employed in the reactions are accessible from the commercially available 1,8-dichloroanthraquinone. Benzyne itself can be generated in situ by addition of the monosubstituted anthranilic acid (dissolved in DME) to a solution of disubstituted anthracene and isoamyl nitrite in DME with elimination of N_2 and CO_2.[14]

Herein we describe the syntheses of eight modified anthracenes and investigations of their influence on the formation of *syn*- and *anti*-trichlorotriptycenes.

Results and Discussion

Syntheses of the Modified Anthracenes

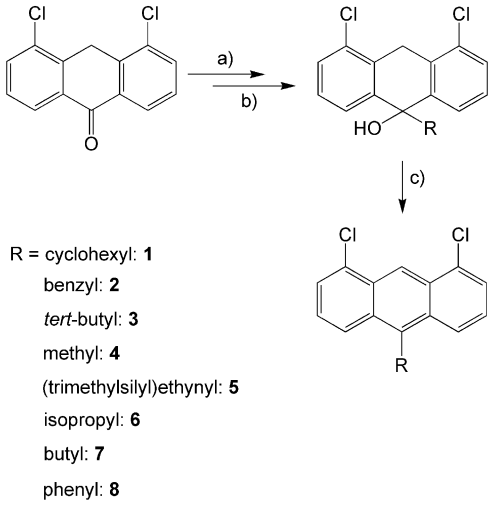
As a prerequisite for exploring the triptycene-formation reactions, we first prepared a series of 1,8-dichloroanthracenes modified by substituents of different steric demand at C-10. We found that individual protocols for the introduction of substituents in C-10 position had to be developed (Scheme 2).



Scheme 2.

For instance the 10-*tert*-butyl-1,8-dichloroanthracene (**3**) could only be synthesised by the reaction of the corresponding anthrone with the *tert*-butyl-Grignard reagent. The reaction with *tert*-butyllithium did not lead to the expected product, but to a complicated mixture of products difficult to separate and identify. Moreover, in the case of anthracenes with a bulky substituent in C-10 position, the elimination of water and the subsequently initiated aromatisation of the anthrone reaction products with metal alkyls could only be achieved by heating these compounds several times with P_2O_5 in toluene or tetrachloromethane (Scheme 3). Care has to be applied to find the right reaction conditions for each case, because the reaction with P_2O_5 does not only result in dehydration, but may also lead to rearrangements in the substituent substructures.

After hydrolytic work-up the resulting alcohol from the reaction of 1,8-dichloroanthrone with *tert*-BuMgBr undergoes decay reactions upon treatment with P_2O_5. We observed the formation of 1,8-dichloro-10-methyl-10-(prop-1-en-2-yl)-9,10-dihydroanthracene (**16**), which was identified by crystal structure determination (Figure 1). This is obviously a by-product of a Wagner–Meerwein-type rearrangement of one methyl-group from the *tert*-butyl substituent to a carbocation resulting from water elimination of the OH



Scheme 3. For compounds **1**, **2** and **3**: a) RMgBr, THF/Ether, b) 3 M HCl, c) toluene P_2O_5; for compounds **4** and **5**: a) RMgBr, ether, b) and c) NH_4Cl; for compound **6**: a) RMgBr, ether, b) NH_4Cl, c) P_2O_5; for compounds **7** and **8**: a) RLi, toluene, b) and c) 3 M HCl.

group under acidic conditions. Subsequently, a proton is abstracted from another methyl-group to form a propylenyl substituent at C-10.

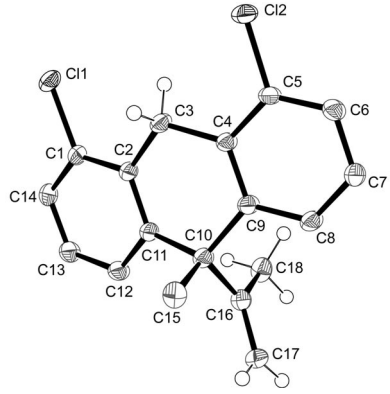


Figure 1. Crystal structure of 1,8-dichloro-10-methyl-10-(prop-1-en-2-yl)-9,10-dihydroanthracene (**16**). Only some selected hydrogen-atoms are pictured for a better overview. Selected bond lengths [Å] and angles [°]: C(2)–C(3) 1.503(2), C(3)–C(4) 1.503(2), C(9)–C(10) 1.547(2), C(10)–C(11) 1.531(2), C(10)–C(15) 1.556(3), C(10)–C(16) 1.524(2), C(2)–C(11) 1.394(2), C(4)–C(9) 1.392(2), C(4)–C(5) 1.401(2), C(11)–C(12) 1.400(2), C(1)–C(2)–C(3) 120.1(2), C(2)–C(3)–C(4) 114.6(2), C(4)–C(5)–C(6) 123.4(1), C(7)–C(8)–C(9) 121.3(2), C(9)–C(10)–C(11) 112.3(1).

Syntheses of the Triptycenes

Based on the work of Rogers and Averill,[15] we repeated the attempt to prepare the symmetrically substituted trichlorotriptycene by reaction of 1,8-dichloroanthracene with 6-chloroanthranilic acid. Analogous to their report, the trichlorotriptycene was obtained in a mixture of 21% *syn* and 79% *anti* form. They found that the isomeric ratio depends on the substituents of the diene and dienophile and investigated different substituents at the anthranilic acid in 6-posi-

tion and different 1,8-substituents at the anthracene. It turned out that in particular the functionalities at the intermediate benzyne are important in dictating the observed regiochemistry. With methyl as substituent the formation of the *syn* isomer is found to be preferred, but with chloro substitution, the *anti* isomer is the preferably formed one.

Considering this information we started studying the *syn*/*anti* ratio of similar reactions of C-10-substituted 1,8-dichloroanthracene with 6-chloroanthranilic acid and found that these C-10 substituents have indeed an effect on the isomeric ratio. A summary of the results of these experiments is provided in Table 1.

Table 1. Ratio of *syn*- and *anti*-triptycene formed in the reaction between with 6-chloroanthranilic acid and C-10-substituted 1,8-dichloroanthracenes depending on the C-10 substituent.

	R at C-10	% *anti*	% *syn*	% Yield[a]
9	H	79	21	16
10	*c*-C_6H_{11}	79	21	60
11	Me_3C–	100	0	43
12	Me	63	37	42
13	Me_2CH–	70	30	40
14	*n*-C_4H_9	60	40	22
15	Ph	75	25	28
	$PhCH_2$–	–	–	0
	Me_3Si–C≡C–	–	–	0

[a] All yields are given for the mixture of *syn*- and *anti*-triptycene.

The relatively low yields in most cases can be explained by the fact that 3-chlorobenzyne is not easily produced via aprotic diazotization of 3-chloroanthranilic acid. The high contribution of 75% *anti*-structure in the case of the trichlorophenyltriptycene (**15**) can be rationalised by additional intramolecular interactions between the π-system and the chloro function (of the benzyne) as reported by Öki.[16]

Astonishing are the results of the Diels–Alder reactions with the benzyl- and (trimethylsilyl)ethynyl-substituted anthracenes. They led only to trace amounts of the expected triptycenes, barely detectable by NMR spectroscopy. Even the application of longer reaction times and different work-up procedures (column chromatography) resulted almost exclusively in the recovery of starting material.

Except for the entry with the *tert*-butyl group, the results in Table 1 indicate, that a C-10 substituent induces only little influence on the isomeric ratio to a slightly increased amount of the *syn* product. However, this influence is accompanied by other factors like polarity, which explains the non-linear behaviour of the *syn*-amount in relation to the steric demand of the C-10 substituent. Nevertheless, we expected to take the most pronounced influence on the addition reaction by using the sterically most demanding substituent, which was the *tert*-butyl group in our series of experiments. However, this assumption was disproved by the formation of 100% *anti*-10-*tert*-butyl-1,8,16-trichlorotriptycene (**11**). Clearly, the exclusive formation of the *anti* structure indicates that electronic factors override the steric ones.

In order to rationalise these findings we performed quantumchemical calculations on an exploratory level (HF/STO3G), the results of which can be summarised as follows. As argued earlier by others,[17] the regiochemistry of the addition of arynes depends on the nature of substituents, which may influence their polarities. In the case of 3-chlorobenzyne, we calculated a small negative charge on C-2 and a neutral charge at C-1, i.e. the negative end of the dienophil at C-2 or towards the chlorine substituent. In the parent diene (1,8-dichloroanthracene), C-9 and C-10 have almost the same charges, so that an equal preference for *syn* and *anti* orientation of the resulting triptycene could be predicted, with the repulsive steric interaction between the chlorine atoms favouring slightly the *anti* form. This is what the experiments of Rogers and Averill have shown.[15] Methyl substitution at C-10 makes the C-10 position more positive, i.e. this should preferably interact with 3-chlorobenzyne to result in *anti*-triptycenes, but here the Cl–Me repulsion is also increased. An even more pronounced charge distribution δ^+(C-10) and δ^-(C-9) is achieved by *tert*-butyl substitution, which seems to be sufficiently regio-directing to override any steric argument.

The calculations predict that the situation could be changed by substitution at C-9, but this would be accompanied by an intolerable increase in synthetic complexity. The most promising prediction is the effect of silylation at C-10, as this reverses the polarity compared to above-mentioned cases.

NMR Studies on the Isomeric Mixture of Substituted Triptycenes

The exact classification of *syn*- and *anti*-triptycenes and their ratio could be achieved by using two-dimensional NMR spectroscopy, NOESY and HMQC (Figure 2). Rogers and Averill reported[15] that "the most effective way to differentiate the isomeric pairs of triptycenes was by ^{1}H NMR spectra". They described the typical patterns for the aromatic protons as well as the two singlets generated by

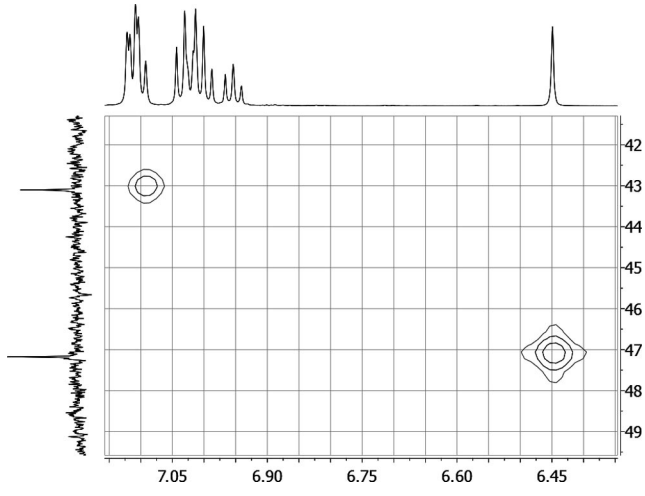


Figure 2. Section of the HMQC spectrum of a mixture of 1,8,13-trichloro-10-methyltriptycene (*syn*-**12**) and 1,8,16-trichloro-10-methyltriptycene (*anti*-**12**) showing the signals of the bridgehead positions.

the bridgehead protons. It is also mentioned by Kidd et al.[18] that the shifts of these singlets depend on the aromatic substituents and that the bridgehead proton of the *syn*-isomer experiences a larger shift $\Delta\delta$ than that of the *anti*-isomer. In general we approve these results, but found in addition that in the case of the modified 1,8,13-trichlorotriptycenes, due to the close arrangement of three chloro functions, the corresponding bridgehead proton, pointing to the same side as the chloro substituents, is so strongly deshielded that its signal overlaps with the proton signals of the aromatic system. A clear assignment in these cases can therefore only be achieved by two-dimensional NMR spectroscopy.

The *syn*/*anti* mixture of the methyl-substituted trichlorotriptycene **12** can serve as a representative example for all synthesised triptycene systems. Its ^{13}C NMR spectrum contains signals for the aromatic ring at 149.25–119.22 ppm and signals corresponding to the methyl substituents at δ = 17.48 and 13.51 ppm. Resonances at δ = 51.88 and 50.23 ppm (C-10) and 46.90 and 42.82 ppm (C-9) correspond to the bridgehead carbon atoms, respectively. In a ^{1}H-^{13}C HMQC experiment these carbon atoms induce cross peaks with the directly bonded bridgehead protons of the *syn*- and *anti*-triptycene at δ = 7.08 and 6.43 ppm. For a proper assignment of these proton signals of the triptycene isomers, we carried out NOESY experiments: only the bridgehead proton of the *anti*-isomer shows a through-space interaction with one of the aromatic protons leading to a cross-peak in the corresponding spectra.

For all compounds, the ratio of *syn*- and *anti*-triptycene was either determined by integration of the bridgehead proton signals or by integration of the signals induced by the C-10 substituent. The NMR spectra of compounds **10**, **11**, **13**, **14** and **15** show almost identical chemical shifts and splittings.

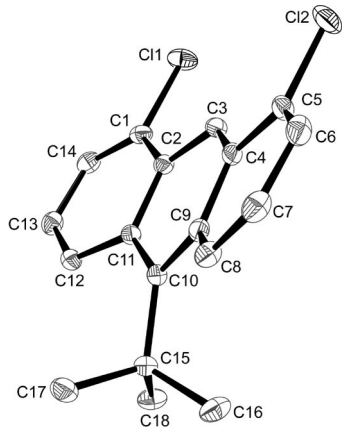


Figure 3. Molecular structure of 10-*tert*-butyl-1,8-dichloroanthracene (**3**).

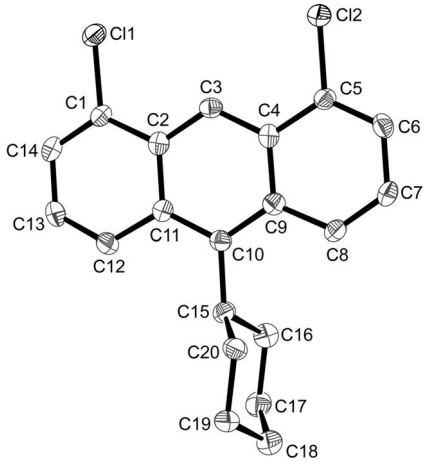


Figure 4. Molecular structure of 1,8-dichloro-10-cyclohexylanthracene (**1**).

Molecular Structures of Modified Dichloroanthracenes

Single crystals of compounds **1**, **5**, **7** and **8** suitable for X-ray diffraction were obtained by slow evaporation of the solvent from the solutions obtained in the preparative procedures described above. Crystals of 10-*tert*-butyl-1,8-dichloroanthracene (**3**) were obtained from a pentane/dichloromethane mixture at room temperature as yellow plates.

The molecular structures of compounds **1**, **3**, **5**, **7** and **8** were determined by single-crystal X-ray diffraction and are displayed in Figures 3, 4, 5, 6, and 7. Some selected structural parameter values are compiled in Table 2 for comparison. Compounds **1**, **3**, **5**, **7** and **8** show two different structural motifs of the anthracene backbone depending on the substituent in C-10 position. **1**, **5**, **7** and **8** have in common a planar anthracene skeleton.

In contrast, the anthracene backbone of 10-*tert*-butyl-1,8-dichloroanthracene (**3**) shows a butterfly-like deformation caused by the steric bulk of the *tert*-butyl group. In this respect the structure is concordant with the known

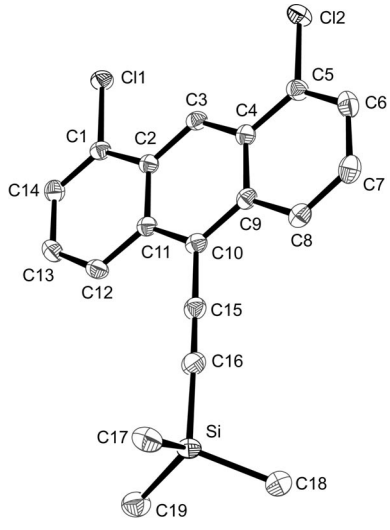


Figure 5. Molecular structure of 1,8-dichloro-10-[(trimethylsilyl)-ethynyl]anthracene (**5**).

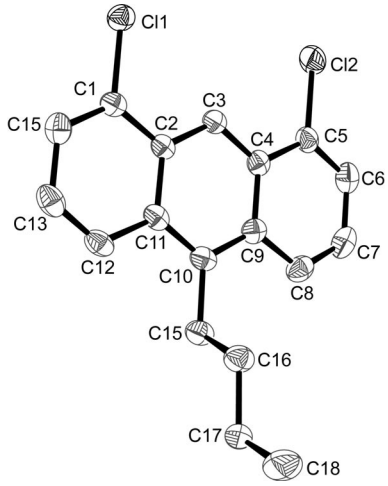


Figure 6. Molecular structure of 10-butyl-1,8-dichloroanthracene (**7**).

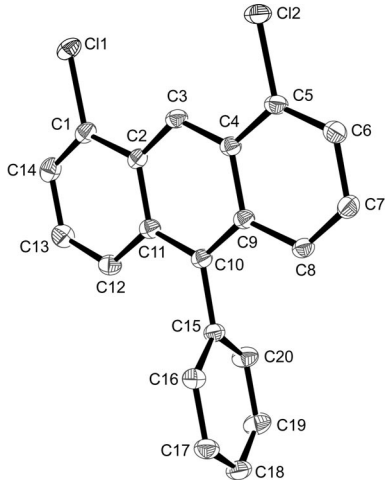


Figure 7. Molecular structure of 1,8-dichloro-10-phenylanthracene (**8**).

Table 2. Selected bond lengths [Å] and angles [°] of **1**, **3**, **5**, **7** and **8**.

	1	**3**	**5**	**7**	**8**
Cl(1)–C(1)	1.745(3)	1.741(1)	1.744(2)	1.739(2)	1.748(2)
C(2)–C(3)	1.388(4)	1.393(2)	1.394(2)	1.393(2)	1.391(2)
C(2)–C(11)	1.444(4)	1.440(2)	1.436(2)	1.437(3)	1.443(2)
C(10)–C(11)	1.418(4)	1.425(2)	1.416(2)	1.409(3)	1.407(2)
C(10)–C(15)	1.532(4)	1.561(2)	1.437(2)	1.518(3)	1.505(2)
Cl(1)–C(1)–C(2)	119.2(2)	118.9(1)	118.8(2)	118.9(1)	118.6(1)
Cl(1)–C(1)–C(14)	118.1(2)	118.3(1)	118.8(2)	118.5(1)	118.7(1)
C(1)–C(2)–C(3)	122.0(3)	121.9(1)	123.1(2)	122.1(2)	122.6(1)
C(2)–C(3)–C(4)	121.4(3)	119.9(1)	121.3(2)	120.7(2)	121.3(1)
C(10)–C(11)–C(12)	123.9(3)	123.0(1)	121.9(2)	122.5(2)	122.5(1)
C(9)–C(10)–C(11)	119.7(3)	116.9(1)	121.2(2)	119.9(2)	120.7(1)
C(9)–C(10)–C(15)	121.2(2)	122.1(1)	119.3(2)	120.1(1)	118.8(1)
C(11)–C(10)–C(15)	119.0(2)	120.9(1)	119.4(2)	120.0(2)	120.5(1)

crystal structure of 9-*tert*-butylanthracene.[19] As both chloro functions are located at the opposite side of the anthracene system relative to the *tert*-butyl group, the influence of the latter is small and the Cl atoms are found in plane with the almost planar side rings they are bonded to. The bond C(10)–C(15) connecting the *tert*-butyl group to anthracene is 1.561(2) Å long, i.e. longer than standard C–C bonds. Also compared to 10-butyl-1,8-dichloroanthracene (**7**) this bond is 0.043 Å longer, which can be attributed to the steric repulsion between the hydrogen atoms in 4- and 5-position of the anthracene system and those of the *tert*-butyl group. The *tert*-butyl group itself seems to be only little affected, as the bond lengths of 1.549(2) Å and the angles around C(15) of 109.1(1)° [C(17)–C(15)–C(16)], 110.2(1)° [C(17)–C(15)–C(18)] are indicating no distortions, and only a somewhat compressed angle of 102.7(1)° [C(16)–C(15)–C(18)] indicates some influence by repulsive interactions.

The structural parameter values of compounds **1**, **5**, **7** and **8** can be described together due to the fact that the anthracene backbone is undistorted regarding planarity. The C–Cl distances are 1.745(3) Å (cyclohexyl), 1.744(2) Å (trimethylsilylethynyl), 1.738(2) Å (butyl) and 1.748(2) Å (phenyl) and agree well with the value 1.749 Å reported for 1,8-dichloro-10-methylanthracene[20] and are just slightly shorter than in 1,8-dichloroanthracene [1.751(3) Å].[21] The Cl atoms of the structures are in plane with the anthracene backbone. The bond lengths for the aromatic system of **1**, **5**, **7** and **8** vary from the common C–C bond length in benzene (1.398 Å) but show trends comparable to literature known anthracene structures, such as the parent non-substituted anthracene (1.37 to 1.43 Å).[22] In all four structures, the bonds of C(1)–C(14), C(2)–C(3) and C(12)–C(13) are shorter (average bond length of 1.37 Å) than the other bonds of the aromatic system (average bond length of 1.42 Å). The C(10)–C(15) distances between the different substituents and the anthracene are 1.532(4) Å (cyclohexyl), 1.437(2) Å (trimethylsilylethynyl), 1.518 Å (butyl) and 1.505(2) Å (phenyl).

In 1,8-dichloro-10-cyclohexylanthracene (**1**), the cyclohexyl substituent adopts the expected chair conformation and is nearly orthogonal to the anthracene backbone thus minimising the steric interferences of the hydrogen atoms.

In the case of 1,8-dichloro-10-[(trimethylsilyl)ethynyl]-anthracene (**5**), the angle of C(10)–C(15)–C(16) is 177.8(2)° and the C(15)–C(16)–Si angle is, i.e. the acetylene unit is almost perfectly linear. It is also nearly in plane with the anthracene system. The silicon atom adopts a tetrahedral coordination with C–Si–C angles ranging from 108.2(1)° to 111.2(1)°.

The butyl group in compound **7** shows no significant deformations or structural characteristics. The C–C bond lengths of the substituent are 1.511(3) to 1.528(3) Å and the C–C–C angles 111.6(2) to 113.9(2)°.

The C–C bond lengths of the phenyl substituent in 1,8-dichloro-10-phenylanthracene (**8**) are 1.394(2) to 1.387(2) Å, which fits well with C–C bond lengths of benzene. With respect to steric interactions with the *peri*-disposed C–H groups in the anthracene backbone, the phenyl substituent resides at a dihedral angle of 76.9° and 81.1° (because of two independent molecules in the asymmetric

unit) relative to the plane of the anthracene core. In the similar 6-phenylpentacene, this angle is 81.1° and 89.6°.[23]

Molecular Structure of 1,8,13-Trichlorotriptycene (9)

1,8,13-Trichlorotriptycene (**9**) crystallises in the monoclinic system in the space group $P2_1/m$. The molecule is close to threefold rotational symmetry,[24] but does only contain a mirror plane as crystallographical element of symmetry. The dihedral angles between the planes of the benzene rings are 121.5 and 117.0°. All three chlorine atoms point to the same direction and are oriented nearly parallel to each other. The average C(sp^2)–Cl bond length in aromatic compounds is 1.76 Å[25] and the two C–Cl bond lengths in **9** are 1.743(2) and 1.739(1) Å. The average C–C bond length in the benzene rings is 1.39 Å. All three rings are parallel to the C(3)–C(10) axis and the eight-membered cage shows no significant distortion. The bonds to the atoms C(3) and C(10) have nearly the same length (1.52 Å). In addition, all angles about the atoms C(3) and C(10) are close to 105°: C(2)–C(3)–C(4) 105.5(1)°, C(4′)–C(3)–C(4) 105.1(1)° and all C–C–C angles around C(10) are 105.8(1)°.

Molecular Structure of Modified *anti*-Trichlorotriptycenes

In general triptycene has a paddlewheel configuration with a structure close to D_{3h} symmetry, which is lowered by substitution. The maximum possible symmetry for an *anti*-trisubstituted triptycene is C_s. Steric interactions between the chloro function at C(19) and the substituent at C(10) lead to a small distortion of the eight-membered cage of the triptycene.[26] We determined the structures of two such *anti*-trichlorotriptycenes, **11** and **12** (see Figures 8 and 9). For comparison, the structural parameter values for compounds **11** and **12** are listed together in Table 3.

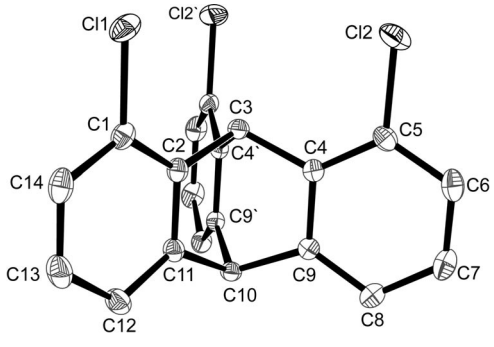


Figure 8. Molecular structure of 1,8,13-trichlorotriptycene (**9**). Selected bond lengths [Å] and angles [°]: Cl(1)–C(1) 1.743(2), Cl(2)–C(5) 1.739(1), C(1)–C(14) 1.395(2), C(2)–C(3) 1.521(2), C(3)–C(4) 1.522(1), C(4)–C(5) 1.385(2), C(4)–C(9) 1.402(2), C(9)–C(10) 1.525(1), C(10)–C(11) 1.522(2), Cl(1)–C(1)–C(2) 120.3(1), Cl(1)–C(1)–C(14) 118.8(2), C(14)–C(1)–C(2) 120.9(2), C(2)–C(3)–C(4) 105.5(1), C(09)–C(10)–C(11) 105.8(1).

In compounds **11** and **12** (Figures 9 and 10), the bond lengths C(10)–C(20) are 0.076 Å (**11**) and 0.040 Å (**12**) longer than the C(3)–C(15) bond. This may be rationalised

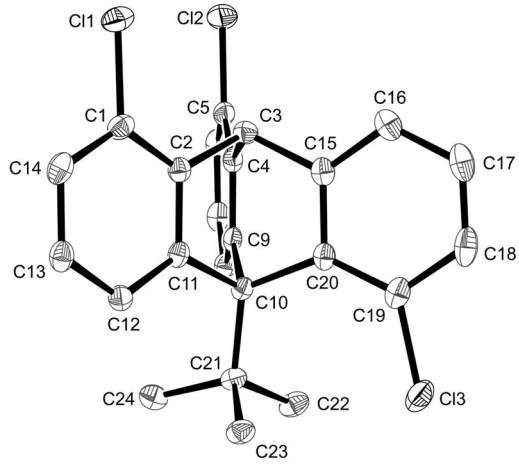


Figure 9. Molecular structure of 10-*tert*-butyl-1,8,16-trichlorotriptycene (**11**).

Table 3. Selected bond lengths [Å] and angles [°] of structures **11** and **12**.

	11	**12**
Cl(1)–C(1)	1.742(2)	1.742(4)
Cl(2)–C(5)	1.746(1)	1.739(4)
Cl(3)–C(19)	1.740(2)	1.739(5)
C(3)–C(4)	1.507(2)	1.530(5)
C(3)–C(15)	1.514(2)	1.516(6)
C(4)–C(9)	1.404(2)	1.395(6)
C(9)–C(10)	1.574(2)	1.536(6)
C(10)–C(20)	1.590(2)	1.556(6)
C(15)–C(20)	1.419(2)	1.402(6)
C(10)–C(21)	1.575(2)	1.526(6)
Cl(1)–C(1)–C(14)	118.9(1)	118.6(3)
Cl(2)–C(5)–C(6)	119.0(1)	118.5(3)
Cl(3)–C(19)–C(20)	127.1(1)	124.1(3)
Cl(3)–C(19)–C(18)	111.6(1)	115.8(3)
C(18)–C(19)–C(20)	121.4(2)	120.1(4)
C(4)–C(3)–C(15)	105.4(1)	105.1(3)
C(4)–C(9)–C(10)	114.4(1)	114.3(3)
C(15)–C(20)–C(10)	111.2(1)	112.6(4)
C(9)–C(10)–C(20)	102.7(1)	102.8(3)
C(9)–C(10)–C(21)	113.1(1)	112.2(3)
C(20)–C(10)–C(21)	118.4(1)	118.1(4)

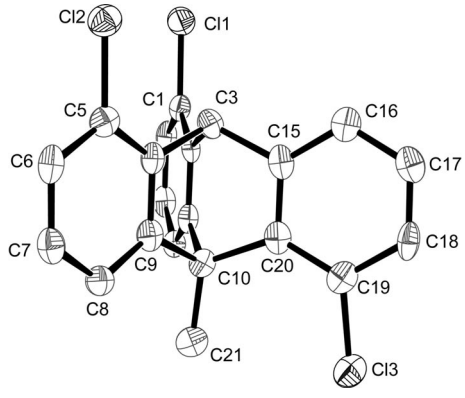


Figure 10. Molecular structure of 1,8,16-trichloro-10-methyltriptycene (**12**).

by the steric repulsion between Cl(3) and the substituent at C(10). In addition, the angles C(20)–C(10)–C(21) are expanded to 118.4(1)° (**11**) and 118.1(4)° (**12**), whereas the C(9)–C(10)–C(21) angles are compressed to 113.1(1)° (**11**) and 112.2(3)° (**12**).

Further proof for this repulsion stems from the dissymmetry of the angles about C(19) as the chlorine atom Cl(3) at this position is dislocated from an "ideal" bonding situation at an arene core. Though the sum of angles about C(19) at 360.0(2)° show it expectedly to be planar, Cl(3) is bent away from the substituent at C(10). The angles Cl(3)–C(19)–C(20) are drastically widened at 127.1(1)° (**11**) and 124.1(3)° (**12**), while the angles Cl(3)–C(19)–C(18) are found to be compressed at 111.6(1)° (**11**) and 115.8(3)° (**12**). This result thus gives an idea of the high degree of steric repulsion build up during the triptycene formation by electrocyclic reactions and clearly demonstrates electronic effects to be more important than steric repulsion.

The bond lengths in the benzene rings partly vary about 0.02 Å from the standard bond length of benzene (1.398 Å), which is the same result as reported for triptycene itself.[27] The C–C(Cl)–C angles involving the chlorine-substituted carbon atom are nearly 120° [120.4(1)° (**11**), 121.4(2)° (**12**)]. This distortion can be rationalised by the steric interference between the *tert*-butyl group and the chloro atom.

The C–Cl bond lengths are 1.740(2) to 1.746(1) Å for **11** and 1.739(4) to 1.742(4) for **12**. This is not in line with the results on 10-*tert*-butyl-1,2,3,4-tetrachlorotriptycene (1.716, 1.723, 1.725 and 1.743 Å) which is in good agreement with the C(sp^2)–Cl bond length in trichlorobenzene [1.719(5) Å].[28,29]

Conclusions

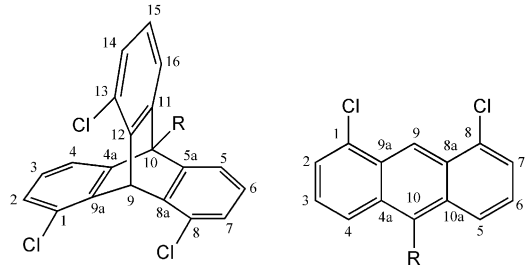
Influence on the selectivity of *syn*- and *anti*-forms of trichlorotriptycenes can be taken by varying the substituents in C-10 position of the 1,8-dichloroanthracene precursor molecules. Without substituents the reaction of 1,8-dichloroanthracene with in situ generated chlorobenzyne leads to 23% *syn* and 77% *anti* form. With smaller C-10 substituents at the 1,8-dichloroanthracene like methyl the relation of *syn* and *anti* triptycenes changes to 37% *syn* and 63% *anti*. Contrary to expectations the relatively large C-10 substituent *tert*-butyl leads to 100% selectivity for the *anti* form of 10-*tert*-butyl-trichlorotriptycene (**11**).

The crystal structures of the 10-*tert*-butyl-1,8,16-trichlorotriptycene (**12**), 1,8,16-trichloro-10-methyltriptycene (**12**) demonstrate that there is a severe repulsive steric interaction between these C-10 substituent and the chloro function introduced by the chlorobenzyne. This interaction must also be present during the electrocyclic reaction between the chlorobenzyne and the C-10-substituted 1,8-dichloroanthracenes. Calculations show on the other hand, that C-10 substituents always change the orbital coefficients in a way to favour the *anti* over the *syn* form, and the experiments demonstrate that such electronic effects clearly override steric repulsion effects during the reaction.

Future work will be directed to alternative strategies for a selective 1,8,13-substitution of the triptycene framework. Such strategies could include templated metallation.

Experimental Section

General Remarks: NMR spectra were recorded with a Bruker DRX 500 and a Bruker Avance 600 instrument at room temperature; the chemical shifts (δ) were measured in ppm with respect to the solvent ($CDCl_3$, ^1H NMR δ = 7.26 ppm, ^{13}C NMR δ = 77.13 ppm). MS were recorded with a Shimadzu GCIMS-QP2010S mass spectrometer. Melting points (m.p.) were determined on Büchi melting point B-545 melting point apparatus. Crystallographic structure determinations were carried out with Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares cycles programs SHELXS-97 and SHELXL-97. Column chromatography was performed on silica gel 60 (0.04–0.063 mm mesh). Methylmagnesiumbromide solution (3 M in diethyl ether), *n*-butyllithium solution (1.6 M in hexane), isoamyl nitrite and 1-chloroanthranilic acid were commercially available. 4,5-Dichloro-9-anthrone was prepared by a published procedure.[30] 1,8-Dichloro-10-cyclohexylanthracene (**1**), 10-benzyl-1,8-dichloroanthracene (**2**), 10-*tert*-butyl-1,8-dichloroanthracene (**3**), 1,8-dichloro-10-methylanthracene (**4**) and 1,8-dichloro-10-isopropylanthracene (**6**) were synthesized by a modified procedure of Toyota et al.[31] 10-Butyl-1,8-dichloroanthracene (**7**) and 1,8-dichloro-10-phenylanthracene (**8**) were also synthesized by a modified procedure of Toyota et al.[32] All triptycenes were synthesised by the method described by Rogers and Averill[15] with a variation in work-up depending on the substituents. The reactions were carried out by using freshly distilled and dry solvents from solvent stills. The numbering scheme for NMR assignments (Scheme 4) is based on IUPAC and Hellwinkel guidelines.



Scheme 4. Numbering scheme for NMR assignments.

General Procedure for the Syntheses of 1,8-Dichloro-10-cyclohexylanthracene (1), 10-Benzyl-1,8-dichloroanthracene (2) and 10-*tert*-Butyl-1,8-dichloroanthracene (3): The Grignard reagent was prepared by the reaction of magnesium and alkyl bromide in diethyl ether in the ordinary manner. The resulting mixture was added dropwise to a cooled solution of 4,5-dichloro-9-anthrone (1 equiv. anthrone to 5 equiv. Grignard reagent) in THF and stirred overnight at room temperature. For the following work up 3 M HCl was used to quench the reaction. The organic layer was separated and the aqueous layer was extracted with dichloromethane. Afterwards the combined organic solution was washed with aq. NaCl, dried with $MgSO_4$ and the solvents evaporated. For the complete elimination of water, the residue was dissolved in little amount of toluene and heated to 80 °C in the presents of P_2O_5. The solid was removed by filtration, and the filtrate was washed with water and the solvents evaporated. The crude product was purified by

chromatography on silica gel with eluents depending on the different fragments.

1,8-Dichloro-10-cyclohexylanthracene (1): The desired product was obtained by chromatography on silica gel with pentane; bright yellow solid; yield 191 mg (33%); m.p. 167.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 9.33 (s, 1 H, *H*9), 8.61–8.36 (2br. s, 2 H), 7.62 (d, $^3J_{H,H}$ = 6.9 Hz, 2 H, *H*2/*H*7), 7.40 (br. s, 2 H), 4.10 (tt, $^3J_{H,H}$ = 3.6, 12.7 Hz, 1 H, *H*15), 2.50 (m, 2 H), 2.04–1.92 (m, 4 H), 1.57 (m, 4 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.36, 133.66, 128.18, 127.71, 125.62, 120.69, 41.39 (*C*15), 32.34 (*C*16/*C*20), 28.07 (*C*17/*C*19), 26.49 (*C*18) (signals missing due to overlap or broadening) ppm. MS (EI, 70 eV): *m*/*z* = 328.1 [M$^+$], 293.1 [M$^+$ – Cl], 259.0 [M$^+$ – 2 Cl], 83.1 [C_6H_{10}], 35.0 [Cl]. HRMS: calculated for $C_{20}H_{18}Cl_2$: 328.0786; measured: 328.0778.

10-Benzyl-1,8-dichloroanthracene (2): The product was purified by column chromatography with pentane/toluene, 1:1 as eluent; bright yellow solid; yield 280 mg (40%); m.p. 162.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 9.37, (s, 1 H, *H*9), 8.15 (d, $^3J_{H,H}$ = 9.1 Hz, 2 H, *H*2/*H*7), 7.64 (d, $^3J_{H,H}$ = 7.1 Hz, 2 H, *H*4/*H*5), 7.41 (dd, $^3J_{H,H}$ = 7.7, 8.5 Hz, 2 H, *H*3/*H*6), 7.22–7.16 (m, 3 H, *m*-*H* and *p*-*H*), 7.06 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, *o*-*H*), 5.00 (s, 2 H, benzyl-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.15, 133.48, 133.30, 131.64, 129.37, 128.59, 127.98, 126.23, 126.01, 125.74, 124.08, 120.89, 34.16 (*C*-benzyl) ppm. MS (EI, 70 eV): *m*/*z* = 336.1 [M$^+$], 301.1 [M$^+$ – Cl], 266.2 [M$^+$ – 2 Cl], 91.1 [$CH_2 - C_6H_5$]. HRMS: calculated for $C_{21}H_{14}Cl_2$: 336.0473; measured: 336.0446.

10-*tert*-Butyl-1,8-dichloroanthracene (3): Purification of the product was carried out by column chromatography with pentane; bright yellow solid; yield 69 mg (12%); m.p. 156.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 9.28 (s, 1 H, *H*9), 8.46 (d, $^3J_{H,H}$ = 9.2 Hz, 2 H, *H*2/*H*7), 7.57 (d, $^3J_{H,H}$ = 7.1 Hz, 2 H, *H*4/*H*5), 7.26 (dd, $^3J_{H,H}$ = 6.9, 7.2 Hz, 2 H, *H*3/*H*6), 1.90 (s, 9 H, methyl-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.72–122.62, 35.42 (*C*15), 28.67 (*C*-methyl) ppm. MS (EI, 70 eV): *m*/*z* = 302.1 [M$^+$], 287.1 [M$^+$ – Me], 276.1 [M$^+$ – Cl], 232.1 [M$^+$ – 2 Cl], 57.1 [C_4H_9]. HRMS: calculated for $C_{18}H_{16}Cl_2$: 302.0629; measured: 302.0616.

General Procedure for the Syntheses of 1,8-Dichloro-10-methylanthracene (4), 1,8-Dichloro-10-[(trimethylsilyl)ethynyl]anthracene (5) and 1,8-Dichloro-10-isopropylanthracene (6): The Grignard reagents were either available commercially or synthesized by the way described before. To a solution of alkyl-Grignard in diethyl ether was added 4,5-dichloro-9-anthrone (1 equiv. anthrone to 3 equiv. Grignard reagent). The mixture was stirred overnight and quenched by the addition of aq. NH_4Cl. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layers have been washed with aq. NaCl, dried with $MgSO_4$ and concentrated.

1,8-Dichloro-10-methylanthracene (4): Purification of the product was carried out by column chromatography with pentane. A previously elimination of water by heating the residue with P_2O_5 was not necessary; bright yellow solid; yield 248 mg (63%); m.p. 156.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 9.24 (s, 1 H, *H*9), 8.22 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, *H*2/*H*7), 7.63 (d, $^3J_{H,H}$ = 7.1 Hz, 2 H, *H*4/*H*5), 7.46 (dd, $^3J_{H,H}$ = 7.2, 7.3 Hz, 2 H, *H*3/*H*6), 3.10 (s, 3 H, methyl-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 133.21, 131.88, 133.16, 129.13, 125.64, 125.33, 123.97, 119.59, 29.74 (*C*-methyl) (one signal missing due to overlapping or broadening) ppm. MS (EI, 70 eV): *m*/*z* = 259.9 [M$^+$], 224.9 [M$^+$ – Cl], 189.0 [M$^+$ – 2 Cl]. HRMS: calculated for $C_{15}H_{10}Cl_2$: 260.0160; measured: 260.0139.

1,8-Dichloro-10-[(trimethylsilyl)ethynyl]anthracene (5): Purification of the product was carried out by column chromatography with pentane. A previously elimination of water by heating the residue with P_2O_5 was not necessary; bright yellow solid; yield 288 mg (56%); m.p. 154.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 9.29 (s, 1 H, *H*9), 8.51 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H, *H*2/*H*7), 7.67 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, *H*4/*H*5), 7.53 (dd, $^3J_{H,H}$ = 7.7, 7.2 Hz, 2 H, *H*3/*H*6), 0.42 (s, 9 H, methyl-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 133.80, 132.94, 128.94, 126.79, 126.37, 126.12, 123.89, 122.02, 107.67 (*C*≡C-Si), 100.75 (C≡*C*-Si), 0.13 (*C* methyl) ppm. ^{29}Si NMR (99 MHz, $CDCl_3$): δ = –17.0 ppm. MS (EI, 70 eV): *m*/*z* = 341.8 [M$^+$], 326.8 [M$^+$ – Me], 97.1 [C≡CSiMe_3].

1,8-Dichloro-10-isopropylanthracene (6): According to the literature, treatment of the intermediate with P_2O_5 in toluene for 1 h at 85 °C resulted in water elimination and aromatisation. Purification of the product was carried out by column chromatography with pentane; bright yellow solid; yield 202 mg (39%). Analytical studies were published by Toyota et al.[31]

General Procedure for the Syntheses of 10-Butyl-1,8-dichloroanthracene (7) and 1,8-Dichloro-10-phenylanthracene (8): The lithiated species (5 mmol) in toluene was cooled to –78 °C and 4,5-dichloro-9-anthrone (2 mmol) in toluene was slowly added. After warmed to room temp. and stirred overnight, the mixture was quenched by the addition of 3 M hydrochloric acid. After the compound was refluxed for 30 min, the organic materials were extracted with toluene and the toluene solution was washed with aq. NaCl, dried with $MgSO_4$ and concentrated. The crude product was purified by chromatography on silica gel with hexane as eluent.

10-Butyl-1,8-dichloroanthracene (7): Bright yellow solid; yield 339 mg (59%); m.p. 77.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 9.26 (s, 1 H, *H*9), 8.21 (d, $^3J_{H,H}$ = 8.9 Hz, 2 H, *H*2/*H*7), 7.64 (d, $^3J_{H,H}$ = 7.1 Hz, 2 H, *H*4/*H*5), 7.44 (dd, $^3J_{H,H}$ = 7.1, 7.2 Hz, 2 H, *H*3/*H*6), 3.59 (t, $^3J_{H,H}$ = 8.2 Hz, 2 H, *H*15), 1.78 (m, 2 H, *H*16), 1.60 (m, 2 H, *H*17), 1.03 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, methyl-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.16, 133.30, 130.62, 129.31, 125.59, 125.42, 123.74, 119.74, 33.64 (*C*15), 28.50 (*C*16), 23.34 (*C*17), 14.02 (*C*-methyl) ppm. MS (EI, 70 eV): *m*/*z* = 301.9 [M$^+$], 258.9 [M$^+$ – $CH_2CH_2CH_3$], 245.8 [M$^+$ – $CH_2CH_2CH_2CH$]. HRMS: calculated for $C_{18}H_{16}Cl_2$: 302.0629; measured: 302.0618.

1,8-Dichloro-10-phenylanthracene (8): Bright yellow solid; yield 371 mg (59%); m.p. 172.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 9.43 (s, 1 H, *H*9), 7.63–7.26 (m, 11 H, aryl-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.97, 138.24, 132.65, 131.04, 128.50, 127.91, 127.29, 126.28, 125.83, 125.41, 122.26, 121.01 ppm. MS (EI, 70 eV): *m*/*z* = 321.8 [M$^+$], 285.9 [M$^+$ – Cl], 251.9 [M$^+$ – 2 Cl]. HRMS: calculated for $C_{20}H_{12}Cl_2$: 322.0316; measured: 322.0291.

General Procedure for the Syntheses of Triptycenes: All triptycenes were synthesized by the method published by Rogers and Averill.[15] To enhance the yields the reaction time and the amount of anthranilic acid and isoamyl nitrite was modified. All triptycenes were purified by sublimation (120 °C, 0.007 mbar). The isomers were not separated by column chromatography. All yields and NMR-data reference to a mixture of *syn* and *anti* isomer. Only the classifiable NMR-signals are described in detail.

1,8,13-Trichlorotriptycene and 1,8,16-Trichlorotriptycene (9):[15] White solid; yield 260 mg (23%); m.p. 350.3 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 7.44 (m, 3 H, *H*4/*H*5/*H*16 *syn*), 7.39 (d, $^3J_{H,H}$ = 7.5 Hz, 1 H, *H*13 *anti*), 7.34 (d, $^3J_{H,H}$ = 7.3 Hz, 2 H, *H*4/*H*5 *anti*), 7.08 (m, 3 H, *H*2/*H*7/*H*15 *anti*), 7.02 (m, 4 H, *H*3/*H*6/*H*9/*H*15 *syn*), 6.99 (m, 6 H, *H*2/*H*7/*H*14 *syn*, *H*3/*H*6/*H*14 *anti*), 6.44 (s, 1 H, *H*9 *anti*), 5.93 (s, 1 H, *H*10 *anti*), 5.91 (s, 1 H, *H*10 *syn*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.28–122.09 (*C*-aryl *syn* and *anti*), 51.02 (*C*10 *anti*), 50.21 (*C*10 *syn*), 47.42 (*C*9 *anti*), 43.39

(*C*9 *syn*) ppm. MS (EI, 70 eV): *m*/*z* = 355.9 [M$^+$], 321.0 [M$^+$ – Cl], 286.0 [M$^+$ – 2 Cl], 250.0 [M$^+$ – 3 Cl].

1,8,13-Trichloro-10-cyclohexyltriptycene and 1,8,16-Trichloro-10-cyclohexyltriptycene (10): White solid; yield 154 mg (58%); m.p. 298.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 8.07 (d, $^3J_{H,H}$ = 8.0 Hz), 7.32 (d, $^3J_{H,H}$ = 7.1 Hz), 7.30 (d, $^3J_{H,H}$ = 7.1 Hz, 1 H, *H*13 *anti*), 7.25 (d, $^3J_{H,H}$ = 7.4 Hz, 3 H, *H*4/*H*5/*H*16 *syn*), 7.19 (d, $^3J_{H,H}$ = 8.0 Hz), 7.11 (s, 1 H, *H*9 syn), 6.98 (m), 6.92 (dd, $^3J_{H,H}$ = 7.8, 7.9 Hz, *H*3/*H*6/*H*15 *syn*), 6.85 (dd, $^3J_{H,H}$ = 7.6 Hz, 1 H, *H*14 *anti*), 6.39 (s, 1 H, *H*9 *anti*), 3.70 (t, $^3J_{H,H}$ = 11.5 Hz, cyclohexyl-H *anti*), 2.99 (t, $^3J_{H,H}$ = 11.4 Hz, cyclohexyl-H *syn*), 2.66–1.54 (m, cyclohexyl-H *syn* and *anti*) (signals missing due to overlapping or broadening) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.91–121.97 (*C*-aryl *syn* and *anti*), 60.51 (*C*10 *anti*), 58.19 (*C*10 syn), 48.12 (*C*9 *anti*), 43.95 (*C*9 syn), 39.57–27.38 (*C*-cyclohexyl) ppm. MS (EI, 70 eV): *m*/*z* = 438.1 [M$^+$], 403.1 [M$^+$ – Cl], 367.1 [M$^+$ – 2 Cl], 320.0 [M$^+$ – Cl – C_6H_{10}]. HRMS: calculated for $C_{26}H_{21}Cl_3$: 438.0709; measured: 438.0700.

10-*tert*-Butyl-1,8,16-trichlorotriptycene (11): White solid; yield 85 mg (41%); m.p. 283.7 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 7.84 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, *H*4/*H*5), 7.40 (d, $^3J_{H,H}$ = 7.0 Hz, 1 H, *H*13), 7.16 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, *H*15), 7.11 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, *H*2/*H*7), 6.96 (m, 3 H, *H*3/*H*6/*H*14), 6.53 (s, 1 H, *H*9), 2.29 (s, 6 H, methyl-H), 2.01 (s, 3 H, methyl-H) ppm. ^{13}C NMR (125 MHz, [D$_8$]THF): δ = 150.39–124.18 (*C*-aryl), 70.07, 48.91 (*C*9), 38.35 (*C*-methyl), 32.67 (*C*-methyl), 32.60 [$C(CH_3)_3$] ppm. MS (EI, 70 eV): *m*/*z* = 412.0 [M$^+$], 397.0 [M$^+$ – CH_3], 377.1 [M$^+$ – Cl], 355.0 [M$^+$ – C_4H_9]. HRMS: calculated for $C_{24}H_{19}Cl_3$: 412.0552; measured: 412.0552.

1,8,13-Trichloro-10-methyltriptycene and 1,8,16-Trichloro-10-methyltriptycene (12): White solid; yield 228 mg (42%); m.p. 350.4 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 7.39 (d, $^3J_{H,H}$ = 7.1 Hz, 1 H, *H*13 *anti*), 7.33 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, *H*4/*H*5 *anti*), 7.26 (d, $^3J_{H,H}$ = 7.5 Hz, 3 H, *H*4/*H*5/*H*16 *syn*), 7.10 (m, 5 H, *H*2/*H*7/*H*14 *syn*, *H*2/*H*7 *anti*), 7.08 (s, 1 H, *H*9 *syn*), 7.03 (m, 6 H, *H*3/*H*6/*H*15 *syn*, *H*3/*H*6/*H*15 *anti*), 6.94 (dd, $^3J_{H,H}$ = 7.5, 7.8 Hz 1 H, *H*14 *anti*), 6.43 (s, 1 H, *H*9 *anti*), 2.72 (s, 3 H, methyl-H *anti*), 2.38 (s, 3 H, methyl-H *syn*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.25–119.22 (*C*-aryl *syn* and *anti*), 51.88 (*C*10 *anti*), 50.23 (*C*10 *syn*), 46.90 (*C*9 *anti*), 42.82 (*C*9 *syn*), 17.48 (*C*-methyl *anti*), 13.51 (*C*-methyl *syn*) ppm. MS (EI, 70 eV): *m*/*z* = 370.0 [M$^+$], 354.9 [M$^+$ – CH_3], 335.0 [M$^+$ – 2 Cl], 266.1 [M$^+$ – 3 Cl].

1,8,13-Trichloro-10-isopropyltriptycene and 1,8,16-Trichloro-10-isopropyltriptycene (13): White solid; yield 80 mg (40%); m.p. 317.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 7.78 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, *H*4 *anti*), 7.62 (d, $^3J_{H,H}$ = 7.7 Hz), 7.40 (d, $^3J_{H,H}$ = 7.2 Hz, 1 H, *H*5 *anti*), 7.33 (d, $^3J_{H,H}$ = 7.3 Hz, 4 H, *H*4/*H*5/*H*16 *syn*, *H*13 *anti*), 7.20 (m), 7.11 (s, 1 H, *H*9 *syn*), 7.03 (m, *H*3/*H*6/*H*15 *anti*), 6.91 (dd, $^3J_{H,H}$ = 7.8, 7.9 Hz, 1 H, *H*14 *anti*), 6.86 (dd, $^3J_{H,H}$ = 7.4, 7.6 Hz, 3 H, *H*3/*H*6/*H*15 *syn*), 6.41 (s, 1 H, *H*9 *anti*),

Table 4. Crystallographic data for **1**, **3**, **5**, **7**, **8**, **9**, **11**, **12** and **16**.

	1	**3**	**5**	**7**	**8**	**9**	**11**	**12**	**16**
Empirical formula	$C_{20}H_{18}Cl_2$	$C_{18}H_{16}Cl_2$	$C_{19}H_{16}Cl_2Si$	$C_{18}H_{16}Cl_2$	$2C_{20}H_{12}Cl_2$ $0.5CH_2Cl_2$	$C_{20}H_{11}Cl_3$	$C_{24}H_{19}Cl_3$	$C_{21}H_{13}Cl_3$	$C_{18}H_{16}Cl_2$
M_r	329.24	303.21	343.31	303.21	688.86	357.64	413.74	371.66	303.21
F(000)	688	316	712	632	2824	364	856	380	632
Colour	colourless	yellow	colourless	pale yellow	yellow	colourless	colourless	colourless	colourless
Crystal form	fragment	plate	needles	needles	fragment	needle	fragment	plate	fragment
Crystal system	orthorhombic	triclinic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic	triclinic	orthorhombic
Space group	$P2_12_12$	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$	$C2/c$	$P2_1/m$	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$
a [Å]	11.323(1)	9.533(1)	15.162(1)	4.700(1)	40.109(1)	7.891(1)	8.395(1)	7.963(1)	7.313(1)
b [Å]	19.812(1)	9.641(1)	14.855(1)	12.194(2)	8.221(1)	13.523(1)	11.070(1)	8.089(1)	10.154(1)
c [Å]	6.944(1)	9.929(1)	7.402(1)	25.929(3)	23.058(1)	7.972(1)	19.908(1)	13.391(2)	19.752(1)
α [°]	90	115.59(1)	90	90	90	90	90	79.57(1)	90
β [°]	90	105.28(1)	94.55(1)	90	124.87(1)	112.42(1)	95.15(1)	89.20(1)	90
γ [°]	90	104.49(1)	90	90	90	90	90	74.89(1)	90
V [Å^3]	1557.7(2)	721.1(1)	1662.0(2)	1486.0(3)	6237.0(2)	786.4(1)	1842.4(1)	818.5(2)	1466.7(1)
Z	4	2	4	4	8	2	4	2	4
$\rho_{calcd.}$ [g cm^{-3}]	1.404	1.397	1.372	1.355	1.467	1.510	1.492	1.508	1.373
μ [mm^{-1}]	0.410	0.436	0.456	0.423	0.497	0.578	0.504	0.558	0.429
θ_{max} [°]	25	30	27.47	30.03	30	30	27.46	24.99	30
Index ranges h	$-13 \le h \le 13$	$-13 \le h \le 13$	$-19 \le h \le 19$	$-6 \ge h \ge 6$	$-55 \le h \le 56$	$-11 \le h \le 11$	$-10 \le h \le 10$	$0 \le h \le 9$	$-10 \le h \le 10$
Index ranges k	$-23 \le k \le 23$	$-13 \le k \le 13$	$-19 \le k \le 18$	$-17 \ge k \ge 17$	$-11 \le k \le 11$	$-18 \le k \le 19$	$-14 \le k \le 14$	$-8 \le k \le 9$	$-14 \le k \le 14$
Index ranges l	$-8 \le l \le 8$	$-13 \le l \le 13$	$-9 \le l \le 8$	$-36 \ge l \ge 36$	$-32 \le l \le 32$	$-11 \le l \le 11$	$25 \le l \le 25$	$-15 \le l \le 15$	$-27 \le l \le 27$
Refl. collected	14682	29376	19114	17144	79833	9269	44475	9322	39724
Independent refl.	2750	4207	3667	4346	9089	2380	4204	2881	4279
R_{int}	0.089	0.034	0.056	0.043	0.052	0.016	0.041	0.071	0.034
Observed refl., $I > 2\sigma(I)$	2198	3546	2867	3639	6945	2144	3611	2069	4003
Parameters	199	184	202	182	411	118	247	218	184
R_1, $I > 2\sigma(I)$	0.0403	0.0330	0.0375	0.0431	0.0340	0.0283	0.0353	0.0593	0.0360
wR_2, $I > 2\sigma(I)$	0.0813	0.0849	0.0894	0.0884	0.0837	0.0802	0.0942	0.1371	0.0927
R_1 (all data)	0.0613	0.0418	0.0544	0.0567	0.0522	0.0319	0.0424	0.0934	0.0395
wR_2 (all data)	0.0888	0.0896	0.0967	0.0931	0.0905	0.0838	0.0983	0.1552	0.0949
GoF	1.027	1.036	1.025	1.045	1.045	1.045	1.043	1.031	1.025
ρ_{max} [e Å^{-3}]	0.199	0.361	0.236	0.365	0.398	0.503	0.745	0.911	0.869
ρ_{min} [e Å^{-3}]	–0.230	–0.288	–0.339	–0.253	–0.390	–0.215	–0.382	–0.375	–0.237
Flack parameter	0.52(8)	–	–	0.02(6)	–	–	–	–	0.56(5)
CCDC numbers	768539	768540	768541	768542	768543	768544	768545	768546	768547

4.29 (m, 1 H, C*H*CH$_3$ *anti*), 3.55 (m, 1 H, C*H*CH$_3$ *syn*), 1.92 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, methyl-H *anti*), 1.85 (d, $^3J_{H,H}$ = 6.7 Hz, 6 H, methyl-H *syn*), 1.74 (d, $^3J_{H,H}$ = 6.7 Hz, 3 H, methyl-H *anti*) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 149.90–122.13 (*C*-aryl *syn* and *anti*), 71.61 (*C*HCH$_3$ *syn*), 62.87 (*C*10 *anti*), 59.07 (*C*10 *syn*), 48.04 (*C*9 *anti*), 43.55 (*C*9 *syn*), 25.83 (*C*HCH$_3$ *anti*), 24.55 (*C*-methyl *anti*), 21.71 (*C*-methyl *syn*), 21.40 (*C*-methyl *anti*) ppm. MS (EI, 70 eV): *m*/*z* = 398.0 [M$^+$], 363.1 [M$^+$ – Cl], 321.0 [M$^+$ – Cl – C$_3$H$_7$], 250.0 [M$^+$ – 3 Cl – C$_3$H$_7$]. HRMS: calculated for $C_{23}H_{17}Cl_3$: 398.0396; measured: 398.0392.

10-Butyl-1,8,13-trichlorotriptycene and 10-Butyl-1,8,16-trichlorotriptycene (14): White solid; yield 103 mg (22%); m.p. 284.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 7.41 (d, $^3J_{H,H}$ = 7.3 Hz, 2 H, *H*4/*H*5 *anti*), 7.29 (m, 4 H, *H*4/*H*5/*H*16 *syn*, *H*13 *anti*), 7.12 (m, 7 H, *H*2/*H*7/*H*9/*H*14 *syn*, *H*2/*H*7/*H*15 *anti*), 7.03 (dd, $^3J_{H,H}$ = 7.7 Hz, 2 H, *H*3/*H*6 *anti*), 6.98 (dd, $^3J_{H,H}$ = 7.7, 7.8 Hz, 4 H, *H*3/*H*6/*H*15 *syn*, *H*14 *anti*), 6.39 (s, 1 H, *H*9 *anti*), 3.45 (br. s, 2 H, C*H*$_2$CH$_2$CH$_2$CH$_3$ *anti*), 2.89 (t, $^3J_{H,H}$ = 7.7 Hz, 2 H, C*H*$_2$CH$_2$CH$_2$CH$_3$ *syn*), 2.07 (m, 2 H, C*H*$_2$CH$_2$CH$_3$ *syn*), 1.81 (m, 6 H, C*H*$_2$CH$_3$ *syn* and *anti*, C*H*$_2$CH$_2$CH$_3$ *anti*), 1.15 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, methyl-H *syn*), 1.11 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, methyl-H *anti*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.13–123.28 (*C*-aryl *syn* and *anti*), 55.03 (*C*10), 47.56 (*C*9 *anti*), 43.34 (*C*9 *syn*), 28.26 (*C*H$_2$CH$_2$CH$_2$CH$_3$ *syn*), 27.32 (*C*H$_2$CH$_2$CH$_3$ *syn*) 24.78 (*C*H$_2$CH$_3$ and *C*H$_2$CH$_2$CH$_2$CH$_3$ *anti*), 24.55 (*C*H$_2$CH$_3$ *syn*), 14.30 (*C*-methyl) (signals missing due to overlapping or broadening) ppm. MS (EI, 70 eV): *m*/*z* = 412.0 [M$^+$], 377.1 [M$^+$ – Cl], 356.9 [M$^+$ – C$_4$H$_9$], 342.1 [M$^+$ – 2 Cl]. HRMS: calculated for $C_{24}H_{19}Cl_3$: 412.0552; measured: 412.0531.

1,8,13-Trichloro-10-phenyltriptycene and 1,8,16-Trichloro-10-phenyltriptycene (15): White solid; yield 136 mg (27%); m.p. 297.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 8.02 (d, $^3J_{H,H}$ = 7.9 Hz, 3 H, *H*4/*H*5/*H*16 *syn*), 7.88 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, *H*4/*H*5 *anti*), 7.66 (dd, $^3J_{H,H}$ = 7.6 Hz, 3 H, *H*3/*H*6/*H*15 *syn*), 7.55 (m, 5 H, *H*2/*H*7/*H*14 *syn*, *H*3/*H*6 *anti*), 7.52 (d, $^3J_{H,H}$ = 7.1 Hz, 2 H, *H*2/*H*7 *anti*), 7.43 (d, $^3J_{H,H}$ = 7.1 Hz, 1 H, *H*13 *anti*), 7.22 (s, 1 H, *H*9 *syn*), 7.16 (d, $^3J_{H,H}$ = 7.9 Hz), 7.11 (m, phenyl-H), 7.04 (d, $^3J_{H,H}$ = 7.9 Hz, 1 H, *H*15 *anti*), 6.97 (dd, $^3J_{H,H}$ = 7.3, 7.8 Hz 1 H, *H*14 *anti*), 6.90 (m, phenyl-H), 6.52 (s, 1 H, *H*9 *anti*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.88–122.96 (*C*-aryl *syn* and *anti*), 61.59 (*C*10), 48.04 (*C*9 *anti*), 43.76 (*C*9 *syn*) (one signal missing due to overlap or broadening) ppm. MS (EI, 70 eV): *m*/*z* = 432.0 [M$^+$], 397.0 [M$^+$ – Cl], 362.1 [M$^+$ – 2 Cl], 326.1 [M$^+$ – 3 Cl]. HRMS: calculated for $C_{26}H_{15}Cl_3$: 432.0239; measured: 432.0216.

Crystallographic Structure Determinations: Selected single crystals suitable for X-ray diffraction measurement were suspended in a paratone-N/paraffin oil mixture, mounted on a glass fibre and transferred onto the goniometer of the diffractometer. The measurements were carried out with Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares cycles (program SHELX-97[33]). The structure-plot in this article were generated using the program ORTEP-III.[34]

The CCDC numbers given in Table 4 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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