Reactions between 1,8-dichloroanthracenes with substituents in position 10 and ortho-chloroaryne afford mixtures of 1,8,13-(syn) and 1,8,16-trichlorotriptycenes (anti). The syn/anti ratio is dependent on these substituents. Electropositive substituents like SiMe$_3$ and GeMe$_3$ lead to preferred formation of the syn-isomer, whereas CMe$_3$ groups exclusively afford the anti-isomer. Different quantum chemical calculations including location of transition states give conflicting results, but indicate the importance of dispersion forces for an at least qualitative prediction of results. The syn-trichlorotriptycenes with SiMe$_3$ and GeMe$_3$ substituents were characterized by using NMR spectroscopy, mass spectrometry, and X-ray diffraction experiments.

Triptycene represents one of a few rigid organic frameworks of $D_{3h}$ symmetry without any (Lewis-basic) heteroatoms. It was first synthesized by Bartlett et al. in 1942 using a multi-step procedure starting from anthracene and $p$-benzoquinone.$^{[1]}$ In 1956, Wittig and Ludwig reported a more efficient access to triptycene in one step from anthracene by reacting it with in situ-formed benzylene.$^{[2]}$ The symmetry and rigidity of triptycene have inspired a plethora of applications in fundamental and applied chemical research.$^{[3–5]}$ Substituted triptycenes are widely used, for example, as building blocks for fluorescent or non-fluorescent organic macromolecules, polymers, and liquid crystals$^{[5,6]}$ as rigid spacers in several Pd complexes used for cross coupling reactions,$^{[7]}$ as devices in molecular machines,$^{[8]}$ in crystal engineering processes,$^{[9,10]}$ and as a basis for the design of highly porous organic materials with numerous applications.$^{[11]}$

Although the chemistry of triptycenes and their functionalization is generally in an advanced state, the 1,8,13-trisubstitution motif remains a challenge for synthesis. However, exactly this pattern is interesting to introduce three functionalities oriented in the same direction. We try to make use of such 1,8,13-trisubstituted triptycenes (also called syn-triptycenes) as rigid organic frameworks for constructing directed polydentate Lewis acids,$^{[12,13]}$ but many other applications might be envisioned.

Scheme 1. a) Proposed steric interactions of 10-substituted 1,8-dichloroanthracenes and chloroaryne; b) structural data for a tert-butyl derivative.

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Scheme 1. a) Proposed steric interactions of 10-substituted 1,8-dichloroanthracenes and chloroaryne; b) structural data for a tert-butyl derivative.
stituents. However, the predicted partial charges depend very much on the quantum-chemical method employed. Although in a recent theoretical study the charge distribution of chlorobenzene has been given as $+0.11$ (C-2) and $-0.04$ e (C-3) [NBO charges, B3LYP/6-311 + G(dp)], we find contradictory results between natural bond orbital (NBO) ($C(2) - 0.02$, $C(3) + 0.10$ e) and atoms in molecules (AIM) ($C(2) - 0.01$, $C(3) - 0.21$ e) charges [B3LYP/6-31G(d,p)] [further details can be found in the Supporting Information, and electrostatic potentials (ESP) are also reported therein]. This demonstrates that the charge argument is less clear-cut than suggested. More unambiguous are charges predicted for a range of 10-substituted anthracene molecules: although the charge at C-9 is virtually invariant for all molecules ($R = SiMe_3$, CMe$_3$, Ph, Cy, iPr, Me, H) (NBO $-0.18$ to $-0.17$, AIM $+0.01$ e for all), the charge at C-10 is clearly more negative (NBO $-0.44$, AIM $-0.65$ e) for $R = SiMe_3$ than for all carbon substituents (NBO $+0.03$ to $+0.04$, AIM 0 to $-0.02$ e). This distinction is clear, such that a SiMe$_3$ group was likely to exert the desired regiochemical effect.

The limited number of available electropositive functions compatible with the other reactive groups in the systems restricts the choice of possibilities. However, 1,8-dichloroanthracenes with EMe$_3$ (E = Si, Ge) substituents in position 10 were accessible from earlier projects: 10-bromo-1,8-dichloroanthracene can selectively be metalled with nBuLi and the carbonion reacted with Me$_3$ECI reagents. The 10-EMe$_3$-1,8-dichloroanthracenes with E = Si (1) and Ge (2) were then reacted with in situ-generated chloroaryne to afford the corresponding trichlorotriptycenes (Scheme 2), which were then used to test the validity of the predictions.

With respect to the earlier experiments with $R = H$, Me and CMe$_3$, we observed a drastic increase in the syn/anti ratio of the triptycene product with $R = SiMe_3$. Instead of 0:100 for $R = CMe_3$, we now observe a strong preference for the syn-isomer (for $R = SiMe_3$, syn/anti mixture 84:16). A similar observation was made with $R = GeMe_3$, but the preference for the syn-isomer was less pronounced (syn/anti mixture 70:30). As both, Si and Ge, are more electropositive atoms than carbon, the original prediction by the calculations seemed to have proven true, and even the higher electronegativity of germanium compared to silicon seems to be reflected in the experimental results. Comparable results—a favored formation of syn-Diels–Alder cycloaddition products—are observed when, for example, SiMe$_3$- instead of CMe$_3$-substituted furane derivatives are converted with haloarynes.

The isomers in the product mixtures of 3 and 4 could be separated by sublimation and were characterized by $^1H$, $^{13}C$ and $^{29}Si$ NMR spectroscopy as well as high-resolution mass spectrometry. In the case of anti-3, the rotation about the C$_9$–Si axis is found to be hindered, as is indicated by two resonances at 0.99 (6H) and 0.55 ppm (3H), induced by the protons of the SiMe$_3$ substituent. A similar splitting has been observed earlier for the tert-butyl analogue of anti-4.

Characteristic for the two different isomers, syn and anti, are the singlet resonances of the bridgehead proton H9. That of syn-isomer (syn-4) experiences a larger downfield shift than that of the anti-isomer (anti-4) ($d = 7.12$ vs. 6.49 ppm).

The molecular structures of syn-3 and syn-4, as determined by single-crystal X-ray diffraction, are shown in Figure 1. Both compounds are isostructural. The molecules are of $C_3$ symmetry (close to $C_1$) and exhibit paddlewheel configurations. Benzene and methyl substituents are arranged in a staggered conformation. The C–C bonds in the benzene rings vary by about 0.03 Å in length around that of benzene (1.395 Å.$^{[20]}$). Longer are the distances C(2)–C(3) and C(4)–C(5) (1.517(2), 1.548(2) Å (syn-3); 1.519(2), 1.545(2) Å (syn-4)). The bonds C(4)–E(1) are significantly elongated compared to the corresponding standard C(sp$^3$)–E distances (1.922(2) Å (syn-3) vs. 1.87 Å and
1.994(3) Å (syn-4) vs. 1.96 Å.\textsuperscript{[22]} This indicates intramolecular repulsion between the hydrogen atoms at C(6) and the methyl groups.

The fact that electronic parameters dominate the regioselectivity of the reactions combined with the inability of charges to predict the reaction prompted us to gain a more detailed view of this aryne [44-2] cycloaddition reaction. The most direct way of theoretical investigation of reactions and their product distribution is the calculation of structures and energies of the corresponding transition states. We performed such calculations for a series of reactions by using different approximations. To establish a benchmark and to find the most suitable level of theory, we calculated the barriers of activation for the simplest system first: the reaction of 1,8-dichloroanthracene with chlorobenzene (for details, see Table S4). It turned out that the best and still affordable method is DFT using the B3LYP functional with the 6-31G(d,p) basis set including corrections for basis-set superposition error. The optimized transition-state structures are shown in Figure 2.

**Figure 2.** Optimized [B3LYP/6-31G(d,p)] transition-state structures for the formation reaction of 1,8,13-trichlorotriptycene (syn, above) and 1,8,16-trichlorotriptycene (anti, below).

AIM and interacting quantum atoms (IQA) techniques\textsuperscript{[23]} revealed interesting aspects for these transition-state structures (Figures S4 and S5). Bond critical points (BCP) appear during bond formation in the reactions, with their properties being those of weakly stabilizing closed-shell interactions. Natural energy decomposition analysis (NEDA) in NBO theory\textsuperscript{[24]} shows better stabilization for the transition states of anti-trichlorotriptycene than for the syn-isomer (Table S6). The lower activation barrier makes anti-trichlorotriptycene the preferred product in the corresponding reaction. Detailed analysis reveals the importance of the electronic component (sum of electrostatic, polarization, and self-energies) in this better stabilization. Relating the relative energies for the transition states for syn- and anti-isomers to the corresponding experimentally observed syn/anti product ratios in reactions of chlorobenzene with 1,8-dichloroanthracene (Table 1), the B3LYP/6-31G(d,p) results so far supported at least qualitatively the observations.

**Table 1.** Results of the trichlorotriptycene syntheses by conversion of the corresponding 1,8-dichloroanthracene derivatives 1 and 2 with in situ-generated chloroaryne. The data for other 10-substituted 1,8-dichloroanthracenes (R-10 = CMe\textsubscript{3}, Me, H) are given for comparison.\textsuperscript{[25]} The reactions have also been investigated by quantum-chemical calculations (see the main text and the Supporting Information). All yields are given for isolated mixtures of syn- and anti-trichlorotriptycenes.

| Compound | R-10 | Syn [%] | Anti [%] | Yield [%] | Product |
|----------|------|---------|----------|-----------|---------|
| H        | 21   | 79      | 16       |           |         |
| Me       | 37   | 63      | 42       |           |         |
| CMe\textsubscript{3} | 0    | 100     | 43       |           |         |
| SiMe\textsubscript{3} | 84   | 16      | 55       | 3         |         |
| GeMe\textsubscript{3} | 70   | 30      | 45       | 4         |         |

However, we could not achieve even a qualitatively correct prediction of the product ratio for the reaction with R = SiMe\textsubscript{3} (Scheme 2). Consequently, a substantial series of additional calculations was performed (Table S7) to find more reliable transition-state energies for this reaction. All attempts of expanding the basis set, using different DFT functionals and modeling in solution, did not improve the calculated energies: the barriers to the formation of the syn-isomer (with R = SiMe\textsubscript{3}) were still predicted higher than those for the corresponding anti-isomer. Attempts to account for static correlation with the CASSCF method did either not give results compatible with the experimental findings. However, single-point MP2 and XMCQDPT2 energies\textsuperscript{[26]} for the transition-state structures from the respective RHF and CASSCF calculations indicated that dynamic correlation plays a significant role in these reactions. To test this hypothesis further, we carried out very time-consuming MP2/def2-SVP(P) optimizations for the transition states. These revealed that the transition states for the formation of syn- and anti-trichloro-10-(trimethylsilyl)triptycene (3) can have completely different structures (Figure 3: TS to the syn-isomer) to those predicted by DFT calculations. The validity of this transi-

**Figure 3.** Different views of the optimized [MP2/def2-SVP(P)] transition-state structure of the formation of syn-1,8,13-trichloro-10-(trimethylsilyl)triptycene (syn-3).
tion-state structure for the syn-isomer on this particular level of theory has beenverified by computing the full reaction path.

Figure 3 shows the structure of the transition state of the reaction of 1 with chloroaryne to syn-1,8,13-trichloro-10-(tri-methylsilyl)triphylene (2). Surprisingly, we see that it is likely stabilized by π-stacking of the benzene ring with the anthracene molecule. Unfortunately, all our attempts to find computationally and to fully prove the existence of a transition state to the anti-isomer of 3 were not successful.

Despite its seeming simplicity, the formation of triptycenes from the reaction of arynes with anthracenes turns out to be a highly complex system governed by many parameters that require a subtle balance. The finding of a distinct contribution of dispersion in the transition state sheds new light on such reactions. We will now examine further tailormade reference systems experimentally and theoretically in order to gain an increasingly valid description of the multiple factors that determine the regioselectivity of such reactions.

Acknowledgements

This work was supported by Deutsche Forschungsgemeinschaft [DFG, Priority Program SPP 1807 "Control of London dispersion interactions in molecular chemistry" (MI477/28-1)]. We thank Klaus-Peter Mester for recording NMR spectra, Heinze-Werner Patruck for measuring mass spectra, Regionales Rechenzentrum Köln (RRZK) for providing computing time (supercomputer CHEOPS), and Johanna Grote for designing the graphical abstract layout. We also acknowledge support for the Article Processing Charge from the DFG and the Open Access Publication Fund of Bielefeld University.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: anthracenes · cycloaddition · dispersion · solid-state structures · triptycenes

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