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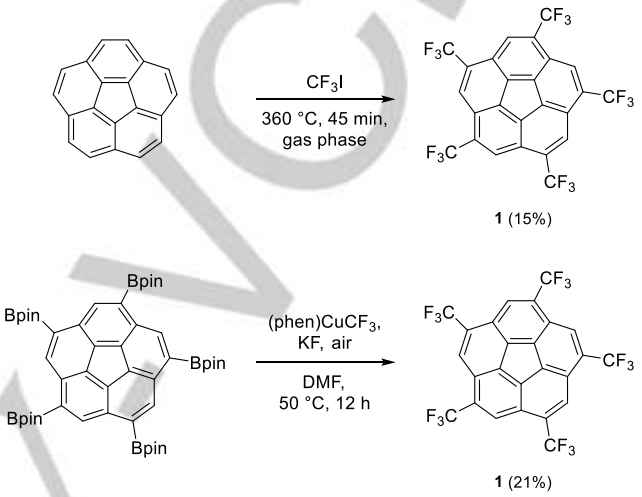
Selective Synthesis of Perfluoroalkylated Corannulenes and Investigation of their Structural, Dynamic and Electrochemical Behavior

Axel Haupt,[a] Lisa-Marie Keller[a], Maximilian Kutter[a] and Dieter Lentz*[a]

Abstract: Herein we report general methods allowing the synthesis of various perfluoroalkylated corannulenes with a specific substitution pattern. Variable temperature NMR spectroscopic investigations revealed dynamic behavior which was analyzed by line shape analysis. The activation parameters of these dynamic processes were determined. For a tetrasubstituted compound it was possible to observe through space scalar coupling. The packing motifs were elucidated by X-ray crystallography, showing that the substitution pattern as well as the size of substituents strongly influence intermolecular π-stacking. The reduction potentials of the perfluoroalkylated compounds were determined by cyclic voltammetry.

Introduction

The introduction of fluorine or perfluoroalkyl groups into a molecule strongly influences its properties.[1-3] This fact has led to numerous applications of fluorinated molecules and materials during the last decades. As demonstrated by us and others before, the electron affinity of the bowl shaped polycyclic aromatic hydrocarbon corannulene increases with the number of perfluoroalkyl groups introduced.[4] By now there have been several synthetic approaches towards the selective preparation of this type of compound. However, only 1,2-*bis*(trifluoromethyl) corannulene can be prepared on a larger scale using hexafluorobutyne as building block.[4c-e] For example, the C_5-symmetric 1,3,5,7,9-*pentakis*-(trifluoromethyl) corannulene **1** was first prepared by the group of Boltalina using an unselective gas phase reaction on mg scale, that yields complicated product mixtures and hence requires subsequent purification by HPLC (Scheme 1).[4a, 4b] Recently, Siegel and coworkers published an optimized synthetic protocol for this compound starting from the respective pinacolboronic ester (Scheme 1).[5] Despite its selectivity, this method still requires some extra steps to prepare the starting material using precious metal catalysts.[6] For this reason, one could think about synthetic protocols using readily available starting materials, e. g. aryl halides. The kilogram scale synthesis of corannulene published by Siegel some years ago affords such a halogenated compound as synthetic intermediate, which was already described earlier by the group of Sygula.[7]
Countless different methods are described in literature concerning the monosubstitution of aromatic moieties with perfluoroalkyl groups.[8] However, there exist only very few examples for the introduction of two of these substituents, especially in neighboring positions. Copper coupling of perfluorinated cycloalkenes yields substituted benzenes or cyclooctatetraenes.[9] Another approach is the coupling of aryl bromides with copper bronze and perfluoroalkyl iodides which is rather limited to the long chained, liquid R^FI.[10]
Furthermore, the supramolecular chemistry and the crystal packing of corannulene can be changed by introducing trifluoromethyl substituents.[4] In its solid-state X-ray structure, the orientation of unsubstituted corannulene molecules is dominated mainly by σ–π-interactions resulting in intermolecular edge to bowl contacts.[11] This significantly changes, when CF_3 groups are introduced. Here one can observe solid state structures that are dominated by π–π-interactions resulting in one dimensional, columnar stacking of the corannulene moieties.[4]
Scott could already show more than 25 years ago by NMR experiments, that corannulene is not a rigid molecule, but can invert its bowl shape quite readily even at low temperatures.[12] Some correlation of substituents attached to corannulene and the observed inversion barrier of the bowl was published some years later by Siegel.[13] Further, Mislow and coworkers could show, that various alkylbenzenes, e. g. *hexakis*(isopropyl) benzene, can be analyzed concerning their conformational behavior.[14] The rotational barriers of neighboring alkyl groups are high enough to make dynamic processes visible by variable temperature NMR spectroscopy. This also allows a



Scheme 1. Previously reported synthesis of 1,3,5,7,9-*pentakis*-(trifluoromethyl) corannulene **1** by gas phase reaction and coupling of pinacolboronic ester.[4a, 4b, 5]

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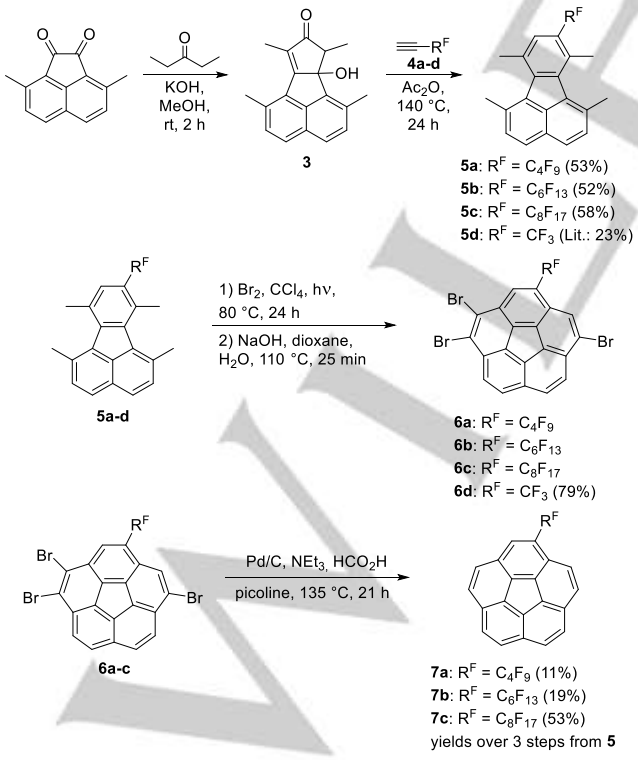
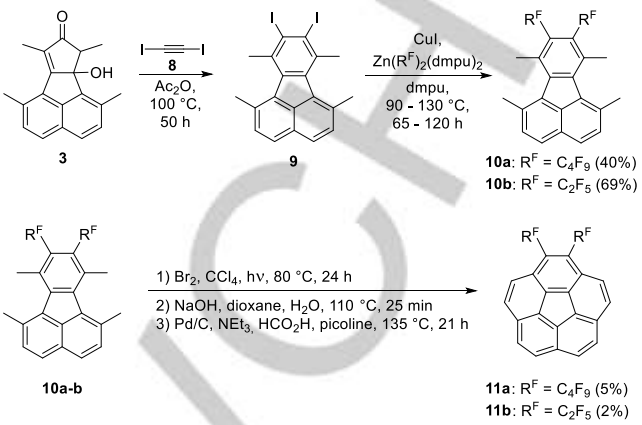
quantification of the rotational barriers.[14a] Finally, the presence of energetically favored conformers could be proven by X-ray crystallography.[14c] Such investigations have not been described for perfluoroalkylated compounds by now. Despite its first synthesis more than 50 years ago, *hexakis*-(pentafluoroethyl) benzene has never been characterized by variable temperature NMR or X-ray crystallography.[15] Other examples contain the crystallographic analysis of ortho-perfluoroalkylated polyaromatics.[10] However, to the best of our knowledge, there were no investigations concerning the conformational analysis of such type of compound based on variable temperature NMR.

Results and Discussion

Synthesis of mono perfluoroalkylated corannulenes.
The substitution of monoiodocorannulene by a perfluorooctyl group described by the group of Siegel is a low yield reaction.[5] Thus we looked for an alternative synthesis which introduces the perfluoroalkyl group by a Diels-Alder cycloaddition reaction during the construction of the respective fluoranthene derivative **5a-d** (Scheme 2). The cyclopentadienone precursor **3** was reacted with mono perfluoroalkylated acetylenes **4a-d**. In case of trifluoromethyl derivative **5d** this was already described earlier in literature.[16] The dienophiles **4a-c** could be prepared by a slightly optimized literature procedure.[17, 18] The subsequent cyclization and bromination steps follow in general the procedure that is also used for the synthesis of unsubstituted corannulene. This protocol has the advantage that the intermediate tribromocorannulene derivates **6** can be used as



Scheme 2. Synthesis of monoperfluoroalkylated corannulenes.



Scheme 3. Preparation of double perfluoroalkylated corannulenes.

starting materials for the synthesis of tetrasubstituted corannulenes with a 1,2,4,6-substitution pattern (see Scheme 5). The derivatives **7a-c** could be obtained in acceptable yields, but the necessity to perform several reaction steps for each compound was not too attractive for further investigations.

Synthesis of double perfluoroalkylated corannulenes.
To introduce two trifluoromethyl groups in 1,2-position of corannulene hexafluorobutyne can be used as dienophile.[4c-e] The limited access to other *bis*(perfluoroalkyl) acetylenes inspired us to use diiodoacetylene **8** as dienophile and subsequently replace the iodo substituents of diiodofluoranthene **9**.[19] This could be achieved using a method adapted from the general perfluoroalkylation of aryl iodides by Mikami and coworkers (Scheme 3).[20] Due to the steric congestion of the disubstituted compounds **10a-b** (see also Fig. 1) and to suppress the amount of monosubstituted side products **5a** and **5e** an excess of zinc reagent and copper iodide is needed.[21] Using these conditions the perfluoroalkylated fluoranthene derivatives can be obtained in acceptable yields. The mono- and disubstituted compounds can be separated by column chromatography on silica. The yields of the conversion of the fluoranthene derivatives **10a-b** into the respective corannulenes **11a-b** are rather low but no attempts have been made to optimize the procedures for the cyclization and debromination reactions.

Synthesis of fourfold perfluoroalkylated corannulenes. 1,2,5,6-Tetrabromocorannulene **2** is a synthetic intermediate in Siegel's large scale synthesis of corannulene.[7a] Thus, one can obtain multigram amounts of this compound in hand, having an ideal starting material for further functionalization. Usually, perfluoroalkylation reactions start from aryl iodides or even more activated arene compounds. The use of aryl bromides is only very scarcely described.[8, 22] This fact can be a major obstacle when a fourfold substitution is desired.

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Although aryliodides were mainly used as starting materials in Mikami's perfluoroalkylation method we were able to substitute compound **2** by pentafluoroethyl groups. 1,2,5,6-*Tetrakis*(pentafluoroethyl) corannulene **12** along with the trisubstituted side products 1,2,6-tris(pentafluoroethyl) corannulene **13a** and 1,2,5-tris(pentafluoroethyl) corannulene **13b** can be obtained in acceptable yield (Scheme 4) in a microwave reactor. In a typical experiment, we treated tetrabromocorannulene **2** with varying amounts of copper iodide and $Zn(C_2F_5)_2dmpu_2$. The ratio of desired fourfold substituted product to the trisubstituted side products could be influenced by varying the amount of copper iodide. Whereas the reduction from a molar 2:1 ratio of copper iodide to zinc reagent towards a 1:1 ratio significantly raised the yield of **12**, a further decrease of copper salt did not improve the outcome of the reaction. Investigation of different polar solvents showed, that dmpu is the best solvent for this type of reaction. Further we clearly could see, that the reactions run significantly better when performed under microwave irradiation instead of heating in an oil bath. The crude product mixture was analyzed by ^{19}F NMR spectroscopy to determine the product ratio. For full analysis, the mixture could be separated using reversed phase HPLC on silica with fluorinated tags.

Against our expectations we were unable to prepare 1,2,5,6-*tetrakis*(trifluoromethyl) corannulene **14** analogously by reacting tetrabromoarene **2** with copper iodide and the respective zinc reagent (Scheme 4). Surprisingly, we could not even observe the formation of any minor trifluoromethylated product. However, when we used Hartwig's reagent (phen)$CuCF_3$,[23] we could substitute all the bromo substituents by trifluoromethyl groups in 32% yield (Scheme 4). Compound **14** was purified by HPLC on unmodified silica using *n*-hexane as eluent. Due to the small differences in chemical shift values of the trifluoromethyl groups one can observe a high order ^{19}F NMR spectrum of product **14** which looks very complicated (Fig. 1, top). Additionally, scalar coupling ($J(F^A\text{-}F^B)$ = 17 Hz) between the fluorine nuclei of the CF_3 groups and additional splitting due to coupling to adjacent protons can be observed. By simulating the spectrum with gNMR, we were able to identify the chemical shifts as well as the respective coupling constants (Fig. 1, bottom).[24] The observation of scalar coupling between the different CF_3-groups is only explicable, when through space coupling is considered.

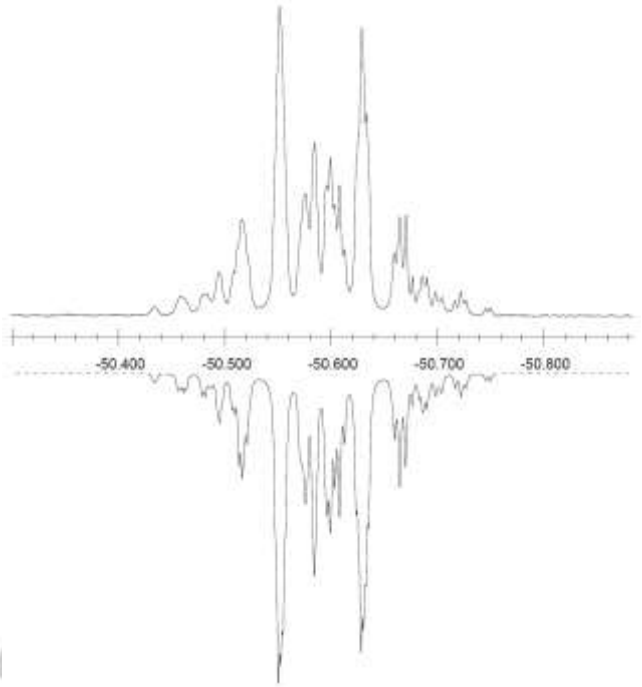
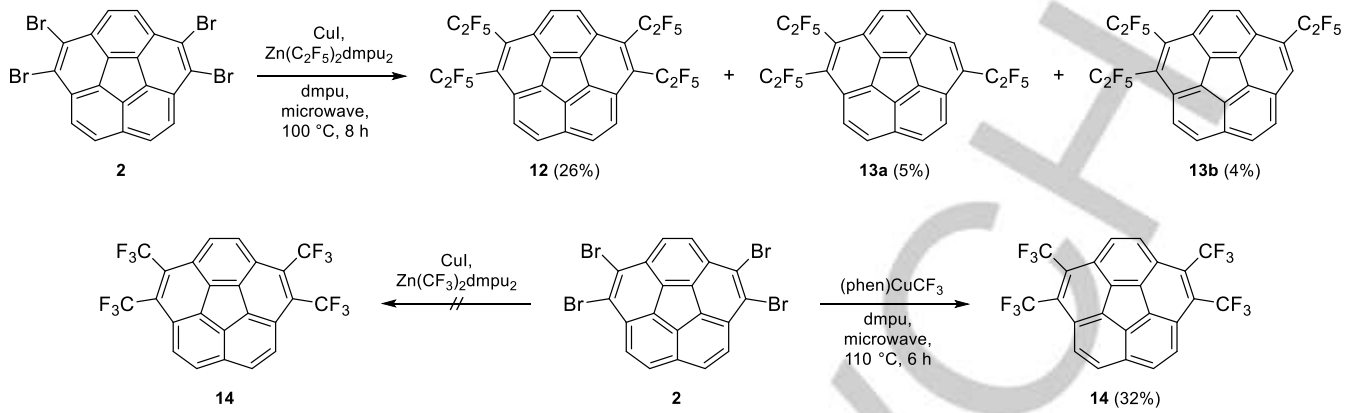


Figure 1. Recorded ^{19}F NMR spectrum of 1,2,5,6-*tetrakis*-(trifluoromethyl) corannulene **14** (top) and simulated resonances (mirrored, bottom). The obtained parameters are the following: $\delta(F^A)$ = -50.65 ppm, $\delta(F^B)$ = -50.54 ppm, $J(F^A\text{-}F^B)$ = 17 Hz, $J(F^A\text{-}H^A)$ = 2 Hz, $J(F^B\text{-}H^B)$ = 1 Hz.

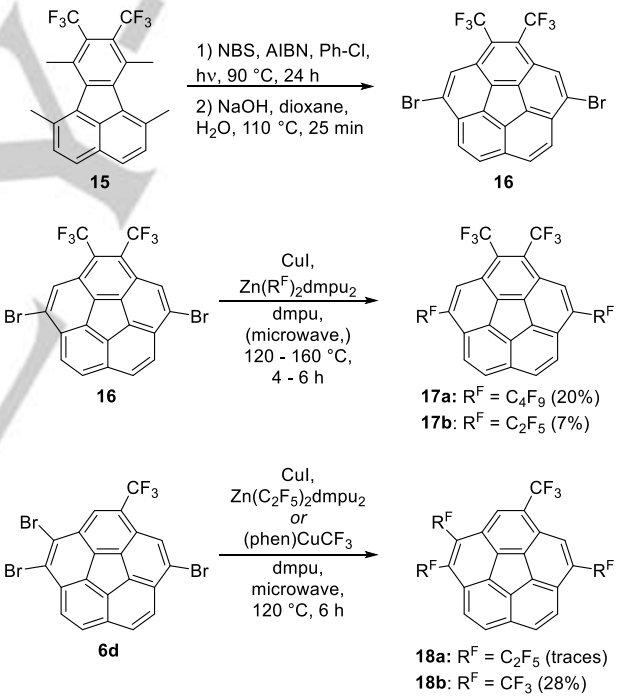
This phenomenon had been reported the first time on a protein with fluorinated tryptophan residues.[25] Further, it was possible to observe the same effect in smaller fluorinated molecules.[26] It could be shown previously, that the coupling constants strongly depend on the distance of the fluorine atoms.[27] If the nuclei are situated close together, they will interact more intensely, hence yielding larger coupling constants. The observed value for **14** of 17 Hz is in the lower range of the literature (~10 – 110 Hz). This is a consequece, as neighboring CF_3 groups are close enough



Scheme 4. Pentafluoroethylation and trifluoromethylation of 1,2,5,6-tetrabromocorannulene.

together to interact with each other, but they are too small to allow larger scalar coupling.

As mentioned above intermediates **16** and **6d** can be used to prepare selectively (mixed) fourfold perfluoroalkylated corannulenes with different substitution patterns. Radical bromination of the benzylic positions of the known *bis*(trifluoromethyl)fluoranthene **15** and cyclization of the intermediate compound furnishes **16**.[4c-e] The two bromo substituents in 1- and 6-position could be replaced by perfluoroalkyl groups applying the copper/zinc system again (Scheme 5). The products 1,6-*bis*(nonafluorobutyl)-3,4-*bis*(trifluoromethyl) corannulene **17a** and the pentafluoroethyl derivative **17b** were isolated and fully characterized. Another derivative with a 1,2,4,6 substitution pattern could be generated starting from known mono trifluoromethylated fluoranthene **5d**.[16] Upon radical bromination of the methyl groups and subsequent cyclization one obtains the unsymmetrical, tribrominated corannulene **6d** which then can be perfluoroalkylated. Surprisingly, the conditions that could be applied for substitution of compounds **2** and **16** were unsuccessful for the synthesis of compound **18a**. The target product could only be isolated in very poor yield. This changed, when we trifluoromethylated **6d** with Hartwig's reagent to get product **18b** in satisfying yield. In conclusion we could demonstrate, that in principle various substitution patterns and substituents are accessible in a systematic manner by choosing appropriate synthetic routes and starting materials.



Scheme 5. Preparation of fourfold perfluoroalkylated corannulenes with different substitution pattern.

X-ray crystal structure analysis.

The solid-state structures of the fluoranthene derivatives **10a-b** and the corannulenes **11b**, **12**, **13a** and **17b** were elucidated by X-ray diffraction. Analysis revealed very strained structures for the fluoranthene derivatives **10a** and **10b** (Figure 2). In the molecular structure of both compounds the perfluoroalkylated six-membered ring is twisted by 21° out of the naphthalene plane. Furthermore, in compounds **10** the C_4F_9 and C_2F_5 groups

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point into opposite directions of the aromatic ring due to steric repulsion. Interestingly, the fluorine atoms of the CF_2 and the CF_3 groups of **10b** are in almost eclipsed position demonstrating the extreme congestion. All these structural properties underline the steric congestion in this type of compound. Looking at the intermolecular interactions reveals numerous F-F-contacts between the fluoroalkyl substituents which are about 0.25 Å shorter than the sum of their van der Waals radii. This results in a layered structure of fluorinated substituents and the nonfluorinated moieties of the fluoranthene molecules.[28] In addition, some H-F-contacts can be observed. Interestingly, there are no C-C-contacts for either of the derivatives **10**. This clearly shows, that the solid-state packing is dominated by the fluorinated substituents and not by the aromatic moieties. Another phenomenon can be found in the case of derivative **10a** which has a dichloromethane molecule incorporated in its solid-state structure. This structure shows contacts between fluorine atoms of the fluoranthene derivative and the chlorine atoms of the solvent that are about 0.1 to 0.2 Å shorter than their sum of van der Waals radii. One can consider this as some type of halogen bonding which is a quite recent topic.[29]

The disubstituted corannulene **11b** could be crystallized as two polymorphs that differ in packing of the bowls (Figure 3). In both phases, the packing is dominated by π–π-interactions resulting in one-dimensional columnar stacks along the crystallographic a-axis. However, the shortest contacts in the structures can be found between hydrogen and fluorine atoms as well as between fluorine and fluorine substituents of the fluoroalkyl groups. There exist a few C-C contacts that are a little shorter than the sum of their van der Waals radii. Of course, the latter strongly depends on the choice of the crystallographic or equilibrium radii, respectively.[30] In the asymmetric unit of the monoclinic structure one can find four molecules. In the stack two neighboring corannulenes are rotated by roughly 180° against each other

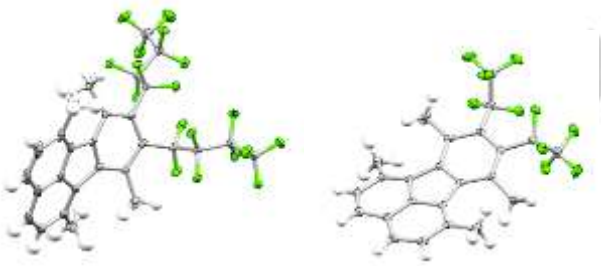

Figure 2. Molecular solid-state structures of perfluoroalkylated fluoranthene derivatives **10a** (left) and **10b** (right). Ellipsoids are at a probability level of 50%.

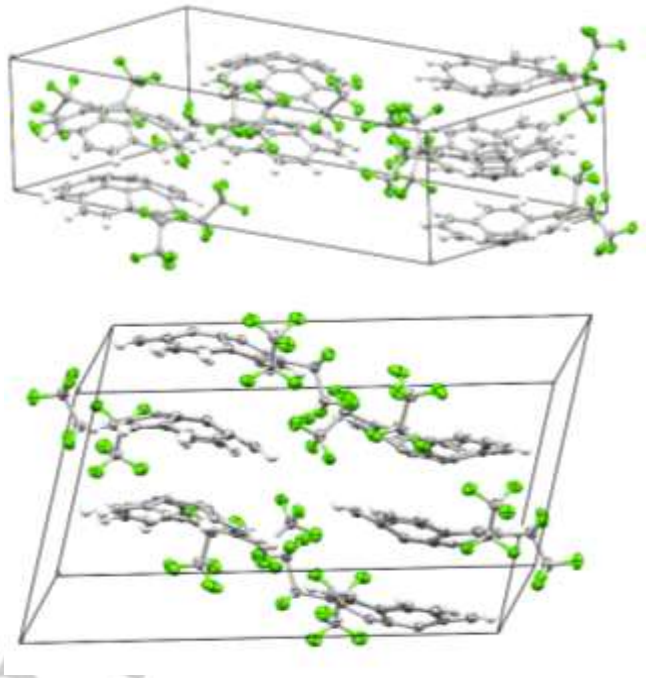

Figure 3. Solid-state cell packing of 1,2-*bis*(pentafluoroethyl) corannulene **11b** as monoclinic (top) and triclinic polymorph (bottom). Ellipsoids are at a probability level of 50%.

resulting in an ABAB stacking motif. In contrast, the asymmetric unit of the triclinic phase consists of three molecules. The twist angles of adjacent molecules in the ABCABC type stacks are roughly 90° between A and B as well as B and C, whereas the twist angle from C to A is about 180°. In both of the polymorphs the distance between two neighboring bowls is about 3.8 Å and the bowl depth of the molecules is comparable and ranges around 0.8 Å.

The trisubstituted side product **13a** could also be investigated by X-ray crystallography, revealing cell packing that is still dominated by π-π-interactions (Fig. 4). The analysis of the data set was achieved by refining it with disordered dichloromethane molecules that are incorporated in the crystals. Refinement by

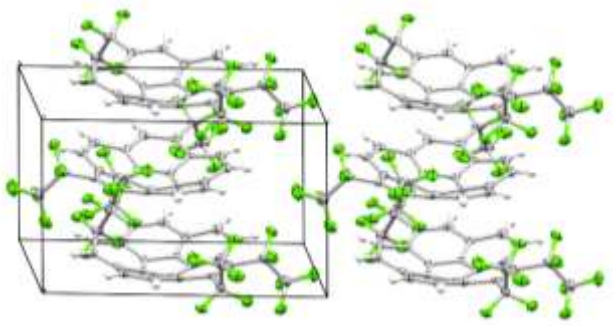

Figure 4. Solid-state cell packing of 1,2,6-*tris*-(pentafluoroethyl) corannulene **13a**. Solvent molecules (dichloromethane) are omitted for clarity. Ellipsoids are at a probability level of 50%.

squeezing the solvent out of the structure resulted in too faulty parameters of the final data set. In the structure, one can clearly observe one dimensional stacks along the crystallographic a-axis, which are slightly slipped. The stacking motif again follows an ABAB type, with a twist of 90° between A and B and 270° between B and A, respectively. The distance between two neighbouring bowls is already slightly elongated, compared to **11b**, being now very close to 4.0 Å. In contrast, the bowl depth is decreased to 0.7 Å.

Increasing the number of substituents to four, changes the stacking behavior. In both compounds **12** and **17b** the asymmetric unit is composed of two molecules forming a stacked pair. However, the pairs are in contact (3.5 Å) on the concave and convex side of both molecules, respectively, due to the crystallographic inversion centre (Figure 5). The shortest contact distance between two carbon atoms of the convex sides is around 3.1 Å, being about 0.3 Å shorter than the sum of their van der Waals radii. Interestingly the other molecule in the asymmetric unit of **12** does not exhibit C-C contacts at all. In total one can find only 20 contacts from which only five have a distance that is about 0.1 Å shorter than the sum of their van der Waals radii. The larger sterical congestion in comparison to mono- and disubstituted derivatives makes the bowls become even shallower with a depth of 0.6 to 0.7 Å. In all compounds with R^F groups larger than CF_3, the ortho substituents point into opposite directions of the bowl. In the case of derivative **12**, the molecule even adapts C_1 symmetry. This means, that molecular symmetry is lowered as much as possible in the solid state. Despite efforts to investigate various crystallization conditions and solvents, we were not able to crystallize a polymorph of **12** with higher molecular symmetry.

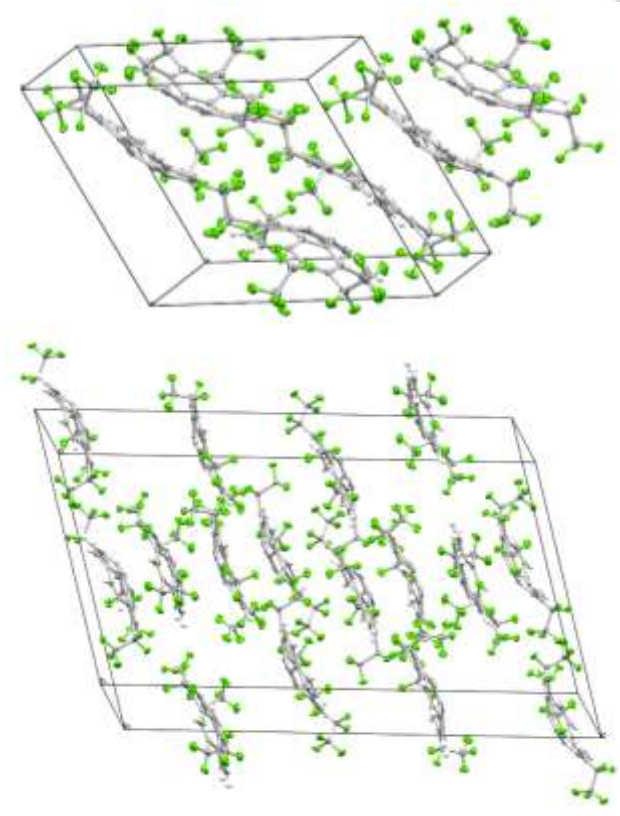

Figure 5. Solid-state cell packing of 1,2,5,6-*tetrakis*(pentafluoroethyl) corannulene **12** (top) and 1,6-*bis*(pentafluoroethyl)-3,4-*bis*(trifluoromethyl) corannulene **17b** (bottom). Ellipsoids are at a probability level of 50%.

Investigation of dynamic behavior by variable temperature ^{19}F NMR spectroscopy.

As Scott already could show more than 25 years ago, corannulene is a fluxional molecule.[12] The process of the bowl-to-bowl inversion can easily be investigated by measuring variable temperature NMR spectra of monosubstituted compounds bearing diastereotopic nuclei. Slowing down the fluxional behavior of the polyaromatic scaffold will give rise to an AB-type system instead of a singlet. This also holds for perfluoroalkylated derivatives **7**, out of which **7a** and **7c** were investigated by line shape analysis using gNMR. Due to limited simulation capacity of the software, the spin systems had to be simplified as only consisting of the relevant CF_2-groups directly attached to the polyaromatic moiety. Further, an automatic line shape analysis could not be run, so that the rate constants of the CF_2-exchange had to be iterated manually. The obtained rate constants *k* were plotted as *ln k* vs. *1/T* getting the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ from the slope and the intersection with the y-axis using the linearized Eyring equation.[31] Due to the error in *k*, the fitted lines might be tilted, which would especially result in faulty values for the activation entropy $\Delta S^{\ddagger}$. However, the graphical analysis of the Eyring plot yields at least a qualitative estimation for the observed energy barriers. For both monosubstituted derivatives **7a** and **7c** comparable results can be found (Tab. 1). The enthalpy of activation has a value of about 40 kJ/mol. In contrast, the contribution of the entropy of activation is only small. This is consistent with the consideration, that bowl-to-bowl inversion does not afford a highly ordered transition state. Hence, the free enthalpy of activation $\Delta G^{\ddagger}$ has only a small temperature dependence (Fig. 6). The values of the

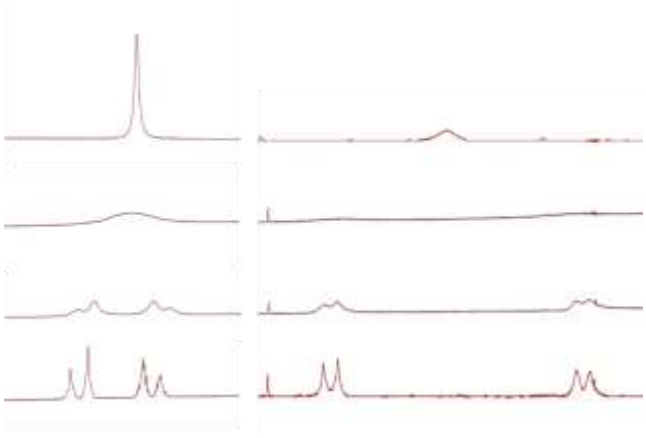

Figure 6. Cutout of CF_2-resonances in variable temperature ^{19}F NMR spectra of *bis*(pentafluoroethyl) compounds **10b** (δ ~ -90 ppm, left) and **11b** (δ = -85 - -100 ppm, right). The measurements were performed at -50, -20, 10 and 60 °C (**10b**, from bottom to top) and -30, 0, 30 and 100 °C (**11b**) in toluene-d8.

Table 1. Activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ obtained by graphical analysis. Errors are based on standard deviations of slope and intersection of the fitted lines.

	7a	**7c**	**10a**
$\Delta H^{\ddagger}$ [kJ/mol]	40.2 ± 0.5	37.8 ± 1.1	46.3 ± 0.8
$\Delta S^{\ddagger}$ [J/(mol*K)]	-1.3 ± 2.5	-11.3 ± 5.0	-37.1 ± 2.6
	10b	**11b**	**13a**
$\Delta H^{\ddagger}$ [kJ/mol]	32.6 ± 0.6	38.7 ± 1.8	26.0 ± 1.6
$\Delta S^{\ddagger}$ [J/(mol*K)]	-61.2 ± 2.6	-48.7 ± 5.9	-90.3 ± 5.9

free enthalpy of activation of **7a** and **7c** are in line with the result obtained by Scott of about 10 kcal/mol.[12]

Interestingly, one can also observe dynamic behavior in the case of *ortho*-disubstituted perfluoroalkyl fluoranthenes **10** and -corannulenes **11** (Fig. 6). This is consistent with the molecular solid-state structures shown in Fig. 2 and 3. Due to steric congestion conformations resulting in C_S-symmetric molecules are energetically disfavored. Thus, the fluoranthenes **10** and corannulenes **11** both are C_1-symmetric as has been investigated by single crystal X-ray diffraction (Fig. 2 and 3). For the explanation of the fluxional behavior, one has to consider two different processes. A twisting motion of the fluoranthene framework and a bowl-to-bowl inversion of the corannulene moiety result in C_2-symmetric transition states and interconversion of the R^F-groups into each other. Nevertheless, no higher symmetry than C_2 can be found, keeping the fluorine nuclei of the CF_2-groups diastereotopic. However, concerted rotation of the neighbored perfluoroalkyl substituents makes them chemically equivalent. Further, it helps to think about possible stereoisomers in order to understand the NMR-spectra. Keeping the conformers with the lowest energy in mind, one can neglect the C_S-symmetric molecules. This yields only two possible ways to arrange the R^F-groups. The resulting isomers form a pair of enantiomers. When the system is cooled below -50 °C, further broadening of the signals is observed. This can be explained by deceleration of the bowl-inversion process that makes the perfluoroalkyl substituents inequivalent. However, we were not able to observe the low temperature limiting spectrum of this phenomenon. Thus, we could only analyze the synchronous rotation of the neighbored R^F-groups for compounds **10a**, **10b,** and **11b** (Tab. 1). For this process, the enthalpy of activation is comparable to the bowl-to-bowl inversion. In contrast, the entropic contribution is much larger in this case as the transition state geometry for the concerted rotation has to be highly ordered. Hence, the free enthalpy of activation for this transformation is quite temperature dependent (Fig. 7).

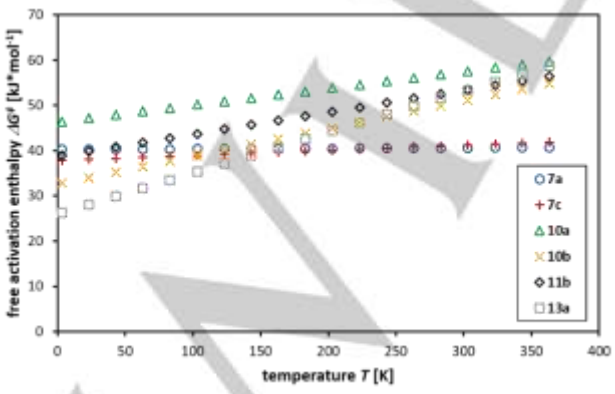

Figure 7. Free activation enthalpies $\Delta G^{\ddagger}$ in dependence of the temperature *T*, based on the parameters from Tab.1.

Adding a third perfluoroalkyl substituent makes the situation more complicated. Again, it is convenient to think about possible conformers first. Ignoring the ones with neighbored R^F-groups on the same side of the bowl yields four pairs of enantiomers (Fig. 8). There are three different processes to interconvert these conformers into each other. The easiest transformation is the rotation of the single C_2F_5-group (red arrows) which can be considered as barrierless under the measurement conditions. Further, the two processes described before for mono- and disubstituted corannulenes hold. Bowl-to-bowl inversion (grey arrows) isomerizes the neighboring pentafluoroethyl substituents whereas concerted rotation (blue arrows) is liable for the exchange of diastereotopic ^{19}F-nuclei again. The analysis of the low temperature NMR-spectra of compounds **13a** and **13b** did not allow any insight into the energetics of the dynamic processes of these compounds. The reason is, that both transformations seem to be significantly decelerated below room temperature. Furthermore, we could not obtain the low temperature limiting spectra of **13a** and **13b**.[32] Thus, it was not possible to assign any set of signals to one of the probable conformers. Due to this, we could only gain qualitative insight into the activation barrier of the concerted rotation of compound **13a** (Tab. 1). In this case, the enthalpy of activation is quite low with about 26 kJ/mol, which is reasonable as for this compound the bowl depth is decreased, too (Fig. 4). As expectable, the entropy of activation has a large contribution to the free activation enthalpy. In total, the barrier has a $\Delta G^{\ddagger}$ value comparable to the aforementioned compounds, being around 10 kcal/mol. But in this case, the temperature dependence is quite large (Fig. 7). Again, this is reasonable due to highly ordered transition state structures which are likely to be present. The situation gets even more complicated for compound **12**. Keeping in mind that the preferred orientation of neighbouring C_2F_5 groups is on opposite sides of the bowls and that only synchronous movement of those is possible, three conformers can be described (Figure 9b). As can be seen from Figure 9a, the molecule is not rigid at higher temperatures. At room temperature, the ^{19}F NMR spectrum of 1,2,5,6-*tetrakis*(perfluoroethyl) corannulene **12** shows four signals. Two different CF_3 groups can be observed at -79.0 and -79.5 ppm, further, different types of fluorine atoms of the CF_2 groups can be found at -87.4 and -100.2 ppm. Upon heating to 100 °C, the fluorine atoms of the difluoromethylene units become equivalent, still showing a very broad signal. When the compound is cooled to -70 °C, additional splitting is observed. Interestingly, both of the fluorine atoms of the CF_2 units exhibit a different fine structure. Further, the number and integrals of the signals clearly

point to the presence of different conformers at low temperature. For example, the C_1 symmetric compound has four inequivalent C_2F_5 groups. Those can be identified in the region from -98 to -103 ppm where different doublet of quartet resonances are found. The doublets ($^2J_{FF}$ ~ 280 Hz) result from geminal coupling to the other CF_2 fluorine atom, whereas the quartets ($^{\geq 4}J_{FF}$ ~ 30 Hz) rise from through space coupling with the CF_3 group of the neighbouring pentafluoroethyl substituent, which could be proven by low temperature ^{19}F COSY NMR.[33] In contrast, the other CF_2 fluorine atom has to point away from the CF_3 groups and exhibits only geminal doublet splitting, which underlines, that quartet splitting can only result from coupling through space. The integrals of the aforementioned species are clearly underlining, that the C_1 symmetric molecule is the conformer of lowest energy. This is also in line with the conformation of the obtained solid-state crystal structure (Fig. 5). As mentioned above, scalar coupling through space had been described several times in literature before. The observed through space coupling constant for **12** of about 30 Hz is in the medium range of literature (~10 – 110 Hz). This is consequent, as neighboring C_2F_5 groups are in proximity and can interact with each other, but rotation of CF_3 groups is still possible. Otherwise, the situation in the low temperature ^{19}F NMR spectrum would be even more complicated.

For comparison, we also investigated the dynamic behavior of non-fluorinated tetraethyl corannulene **19**, which could be prepared following a procedure described for methylation of tetrabromocorannulene.[7b] As expected, in variable temperature

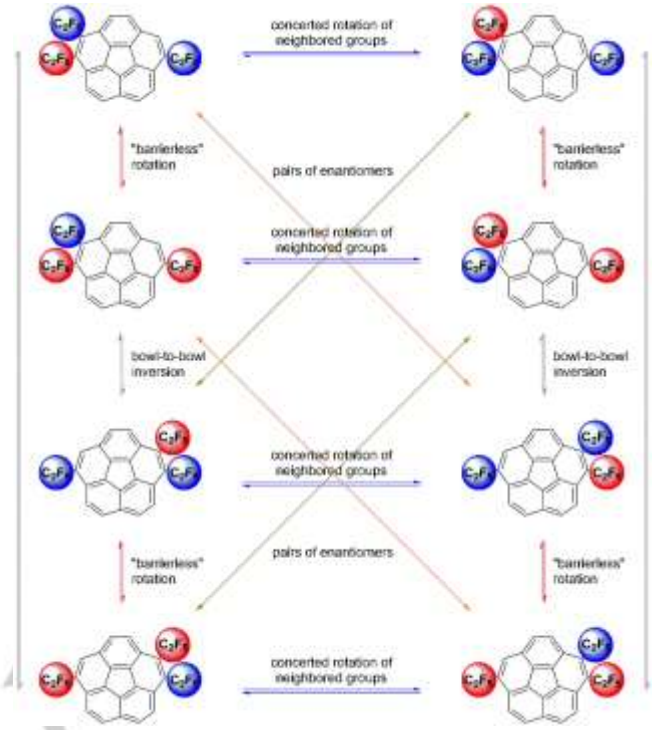

Figure 8. Possible conformers of **13a**. Molecules with neighboring substituents on the same side are neglected. The blue and red spheres represent C_2F_5 groups pointing to the convex and concave side of the bowl, respectively.

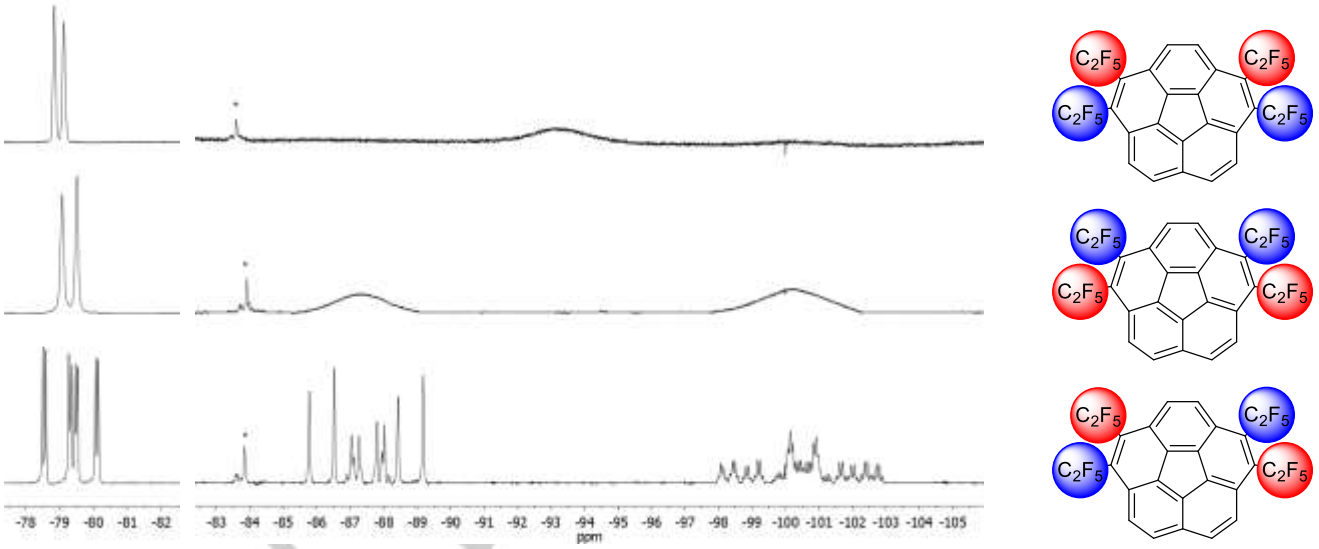

Figure 9. Figure 9. a) Variable temperature ^{19}F NMR of 1,2,5,6-*tetrakis*(pentafluoroethyl) corannulene **12** in toluene-d8 at 100 °C (top), 20 °C (middle) and -70 °C (bottom). The intensity of the right part of the spectrum is enlarged by factor four for clarification. The asterisk marks an unknown impurity. b) Schematic drawing of different C_S-symmetric (top, middle) and C_1-symmetric (bottom) conformers of **12**. The blue and red spheres represent C_2F_5 groups pointing to the convex and concave side of the bowl, respectively.

^{1}H NMR, no dynamic processes can be observed. This is reasonable, as the van der Waals radius of a hydrogen atom is considerably smaller than that of a fluorine atom (110 vs. 146 pm).[34] Thus, two ortho substituted ethyl groups can freely rotate at -70 °C, whereas rotation is strongly hindered in case of the fluorinated derivative. To observe the same effect for the ethyl derivative, NMR measurements at temperatures close to or even below -100 °C would be necessary, which is then a

problem in terms of appropriate NMR solvents. For a better comparison, one would have to investigate the respective isopropyl compound, or derivatives with even larger branched alkyl substituents as Mislow and coworkers have studied earlier for benzene derivatives.[14] The problem of these derivatives is their synthetic accessibility. The introduction of these alkyl groups with a Ni(dppp)Cl_2 catalyst and alkyl alanes does not satisfyingly afford the alkylated corannulenes maybe due to competitive β-hydride elimination.

Electrochemical investigations by cyclic voltammetry.
It has already been shown before, that the introduction of a single trifluoromethyl group into corannulene shifts its reduction potential by roughly 0.2 V to more anodic potential. The effect of several of these substituents depends on their substitution pattern, but in general can be considered as being almost linear in respect to the number of electron-withdrawing substituents. The same trend can be observed for the derivatives that we synthesized and investigated electrochemically by cyclic voltammetry. Whereas the single substituted derivatives **7** show only irreversible reductions at strong negative potentials, as was also observed by Siegel recently, the higher substituted corannulenes can be reduced easier (Fig. 10).[5] This can clearly be observed, when the disubstituted compound **11b** is investigated. In this case, the reduction potential is shifted by about 0.5 V, compared to unsubstituted corannulene. This is in line with earlier results for *bis*-(trifluoromethyl) corannulene.[4e] Adding one more substituent yields a shift in reduction potentials of about 0.8 V for derivatives **13a** and **13b**. Compared to an earlier synthesized, analogous compound of **13a**, but with trifluoromethyl substituents these values are again the same.[4e] Moving to fourfold substituted perfluoroalkyl corannulenes further increases the shifts of reduction potentials to about 0.9 to 1.0 V. As already shown in earlier studies, the substitution pattern has an influence. Here, the double *ortho*-disubstituted compounds **12** and **14** are shifted by about 0.1 V towards anodic potentials compared to the other symmetrically fourfold perfluoroalkylated compounds **17a** and **17b** which only bear one ortho-disubstitution. The unsymmetrically trifluoromethylated derivative **18b** ranges between the symmetrically substituted compounds, but still the differences are very small. Compared to pentasubstituted compound **1**, which was first investigated in CH_3CN by Boltalina and coworkers and recently remeasured by Siegel in THF for better comparability, the reduction potentials of **12** and **14** can be considered being equal.[4a, 4b, 5] The small difference in potentials which is caused due to the effect of chain length of the perfluoro substituents can rather be neglected. The electron-withdrawing abilities of longer perfluoroalkyl chains might be slightly larger, however, the reduction potentials for fourfold trifluoromethylated and pentafluoroethylated derivatives **14** and **12** are identical within the error of the measurement.

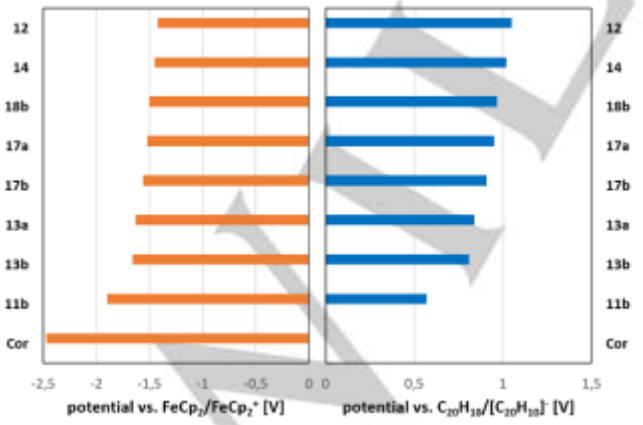

Figure 10. Relative reduction potentials of synthesized corannulene derivatives **x**. Shift values are referenced to ferrocene/ferrocenium (left part, orange bars) and the first reduction of corannulene to its monoanion (right part, blue bars). Corannulene (Cor) is also shown for comparison.

Conclusions

In conclusion, we demonstrated that corannulenes with a well-defined substitution pattern are accessible by introduction of perfluoroalkyl groups into different substrates. The intermolecular packing is strongly influenced by the number of substituents and their size. Dynamic behavior of the substituted compounds and the corresponding activation parameters could be investigated by line shape analysis of variable temperature ^{19}F-NMR spectra. Graphical evaluation revealed a free energy barrier for the bowl-to-bowl inversion of about 10 kcal/mol, which is in line with the literature. Further, for ortho-disubstituted compounds another dynamic process could be discovered. Concerted rotation has a comparable activation barrier but is much more temperature dependent due to larger contribution of the entropy of activation. Finally, the dynamic processes of a tetrasubstituted derivative could be investigated by ^{19}F NMR spectroscopy, revealing through space coupling. The resulting coupling constants of about 30 Hz underline the rather strong steric congestion of ortho-disubstituted perfluoroalkyl corannulenes. Electrochemical investigation of the perfluoroalkyl derivatives is in line with the prediction and demonstrates that the reduction potential is not only influenced by the number of functional groups but also the substitution pattern. As expected, the fourfold perfluoroalkylated compounds have the least negative reduction potentials. To our delight, their substitution pattern results in a shift in reduction potentials which is almost as large as for symmetrical pentakis-trifluoromethyl corannulene.

Acknowledgements

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Keywords: perfluoroalkylation • X-ray crystallography • variable temperature NMR • cyclic voltammetry • corannulene

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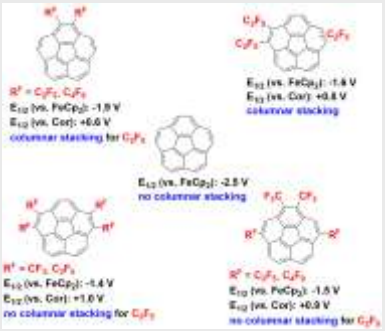

*Axel Haupt, Lisa-Marie Keller, Maximilian Kutter, Dieter Lentz**

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