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# Ring-Expanding Rearrangement of Benzo-Fused Tris-Cycloheptenylenes towards Nonplanar Polycyclic Aromatic Hydrocarbons

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**Abstract:** A strongly twisted benzo-fused tris-cycloheptylene, containing three dibenzosuberone units fused to a common benzene ring, was subjected to Ramirez olefination and subsequent palladium-catalyzed Suzuki-Miyaura cross-coupling with 4-substituted phenylboronic acids. The high steric demand within the overcrowded, benzene-rich benzo-fused tris-cycloheptenylenes enforced an unprecedented 1,2-rearrangement upon  $\pi$ -extension during the Suzuki coupling

reaction. According to crystal structure analysis, the resulting negatively curved polycyclic aromatic hydrocarbons consist of two heptagons and one octagon surrounding a central benzene ring as a result of strain release. In the solid state, the materials exhibit a blue to blue-green fluorescence with increased quantum yields and a hypsochromic shift of the emission maxima compared to their respective solutions.

## Introduction

A great challenge within the science of carbon nanostructures is the synthesis of nonplanar carbon allotropes with negative curvature, as they are predicted to exhibit fascinating properties in terms of optoelectronics, chirality, aromaticity and energy storage<sup>[1]</sup> with potential applications.<sup>[1d,e,2]</sup> These attractive, but not yet synthesized materials can be described as an array of polycyclic aromatic hydrocarbons (PAHs)<sup>[3]</sup> containing densely packed benzenes in combination with non-hexagonal rings. The most studied nonplanar PAHs are those incorporating pentagonal rings inducing bowl-shaped structures.<sup>[2f]</sup> In contrast, seven- and eight-membered rings distort the ideal hexagonal lattice into negatively curved structures with saddle-shaped geometries.<sup>[2f]</sup> PAHs containing heptagons and octagons

cannot only be regarded as small segments of negatively curved carbon nanostructures, such as Mackay crystals,<sup>[2b]</sup> but can also serve as starting compounds for subsequent  $\pi$ -expansion. Although non-hexagonal rings are widely found in natural graphitic materials,<sup>[4]</sup> PAHs bearing more than one heptagon are rare due to the difficult synthetic access, mainly related to the accompanying considerable strain. The first heptagon-embedded PAH, [7]circulene, was made in 1983<sup>[5]</sup> by Yamamoto. Since then, several synthetic approaches toward heptagon-containing hydrocarbons have been developed. They include intramolecular cyclizations,<sup>[6]</sup>  $\pi$ -extension<sup>[7]</sup> or ring expansions or cyclotrimerization reactions.<sup>[8]</sup> Seven-membered rings can also be formed by ring-expanding<sup>[9]</sup> or ring-contracting<sup>[10]</sup> rearrangements under strongly acidic or Friedel-Crafts conditions,<sup>[11]</sup> or in the presence of oxidants.<sup>[12]</sup> The rearrangements are thought to occur via cationic spiro-structured intermediates involving an internal 1,2-bond shift or an 1,2-aryl migration. The 1,2-aryl migration accompanied by ring expansion is driven by ring strain, while contraction of eight-membered ring to seven-membered and, further on, to six-membered rings seems to be induced by strain-release and aromaticity.<sup>[10b,12-13]</sup> Strain-induced rearrangements, so-called Stone-Wales rearrangement, have been also observed as a typical reaction of carbon allotropes yielding defects consisting of heptagons and pentagons.<sup>[14]</sup>

In recent years, several negatively curved PAHs containing heptagons have been reported.<sup>[1a,b,e,6a,b,e,g,7a,b,15]</sup> They exhibited improved solubility and enhanced fluorescence in the solid state resulting from nonplanarity of their polycyclic backbones.<sup>[7c,16]</sup> The number of embedded seven-membered rings affects the shape and geometry as well as the properties of negatively curved PAHs. While a grossly warped nanographene reported by Itami et al.<sup>[6f]</sup> contains five heptagons surrounding a corannulene unit and while an aromatic saddle

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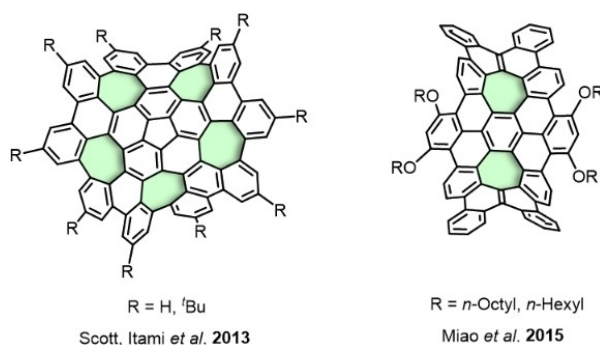
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**Figure 1.** Reported negatively curved PAHs with embedded heptagons (highlighted in green).<sup>[6f,7c]</sup>

achieved by Miao *et al.*<sup>[7c]</sup> consists of two heptagons connected by a benzene ring (Figure 1), we pursued a  $\pi$ -extended PAH consisting of *three* heptagons separated by a central benzene ring.<sup>[17]</sup>

## Results and Discussion

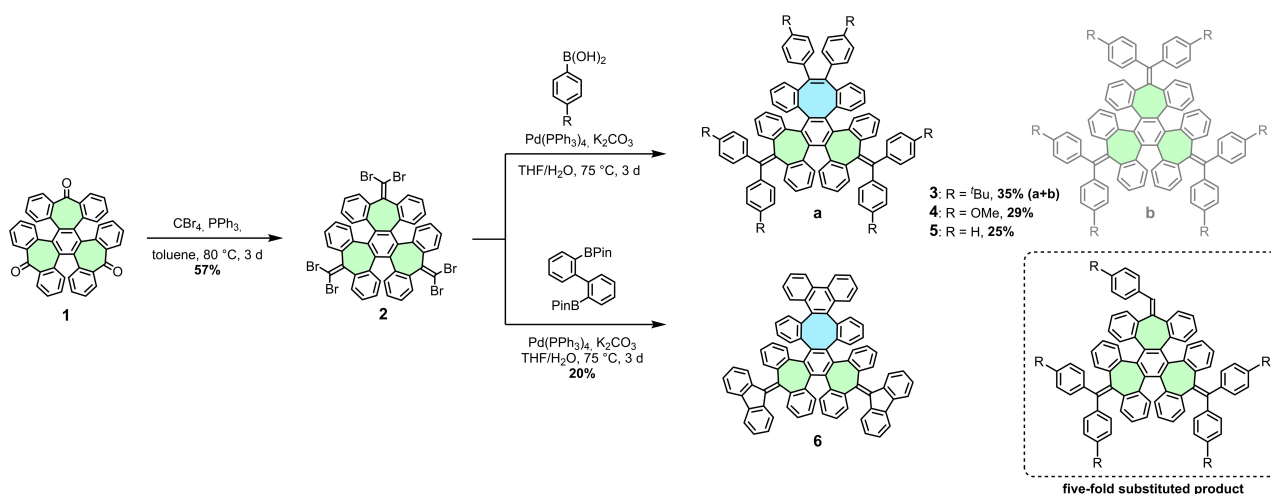
In this work, we explored the limit of steric encumbrment within  $\pi$ -extended benzo-fused tris-cycloheptenylenes. To this end, we derivatized the benzannulated tris-tropone **1**,<sup>[18]</sup> accessible on the gram scale, to obtain benzene-rich, sterically congested saddle-shaped PAHs (Scheme 1). **1** was transformed into the tris(1,1-dibromomethylidene) derivative **2** by Ramirez olefination<sup>[19]</sup> utilizing triphenylphosphine and tetrabromomethane in toluene. Reaction at 80 °C over 3 days afforded **2** in 57% yield.

Compound **2** was then subjected to Suzuki coupling reactions under basic conditions in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> as catalyst with phenyl boronic acids or 4-substituted phenylboronic acids. The Suzuki reaction was carried out with 4-*tert*-butylphenylboronic acid to ensure the solubility of the target

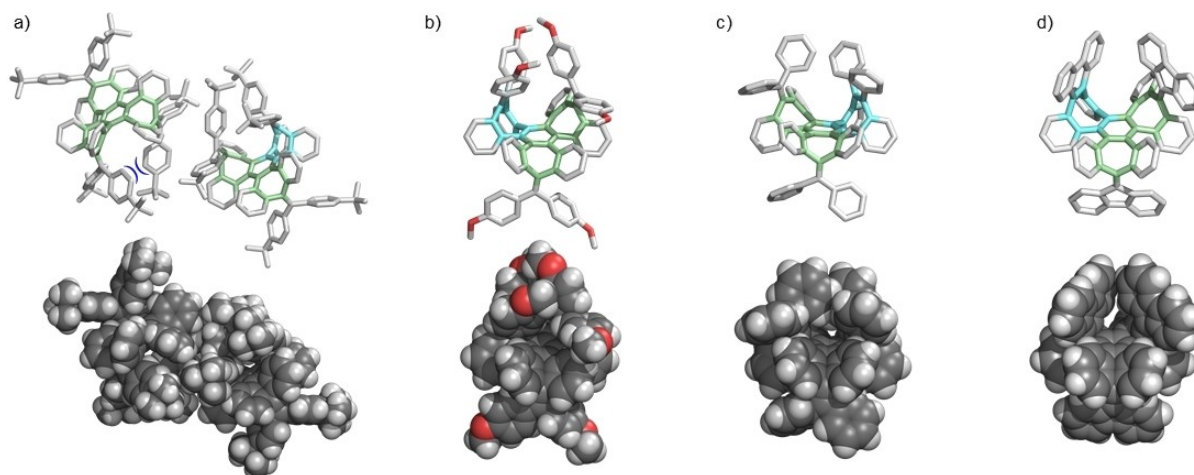
compound. The crude product was first identified by mass spectrometry, which also showed the presence of the hard-to-separate fivefold coupling product, observed for all Suzuki coupling products.

However, after purification single-crystal analysis of the resulting product revealed a co-crystallization of the unexpected (778) isomer **3a** consisting of two heptagons and one octagon connected via a central benzene ring and of the expected  $\pi$ -extended tris-cyclohepta-fused benzene **3b** ((777) isomer, isomer ratio 3:1). This indicated that a 1,2-rearrangement with concomitant *E/Z*-isomerization occurred during the Suzuki coupling reactions. Reaction of **2** with 4-methoxyphenylboronic acid furnished only the corresponding (778) isomer **4**, which was identified by mass spectrometry, NMR and single-crystal analysis (see the Supporting Information). Furthermore, the unsubstituted phenylboronic acid was tested in order to minimize the spatial proximity of the phenyl groups (Figure 2, top). However, the single-crystal structure analysis proved the sole existence of the (778) isomer **5** consisting of two heptagons and one octagon.<sup>[20]</sup> In an attempt at suppressing the 1,2-rearrangement of the phenyl groups and the concomitant ring expansion, **2** was coupled with biphenylene-bis(pinacolate), to yield a poorly soluble yellow solid after two days. Here again, however, single-crystal analysis confirmed the formation of the corresponding (778) isomer **6**.

Single crystals of **3**, **4** and **5** were obtained after slow evaporation of overlaid CH<sub>2</sub>Cl<sub>2</sub>/MeOH solutions. The rigid and poorly soluble derivative **6** afforded suitable crystals only by slow evaporation of a CS<sub>2</sub> solution. All compounds exhibit an  $\alpha,\alpha,\beta$ -conformation (Figure 2), whereby the boat-shaped COT-ring and one of the heptagons face the opposite molecular hemisphere ( $\alpha$ -position) with respect to the central benzene ring compared to the other heptagon ( $\beta$ -position). The position ( $\alpha$ -position) of the COT-unit indicates that the rearrangement occurs only during the sixth Suzuki coupling due to the high steric demand. The spatial proximity of the functionalized phenyl rings, evident from the crystal structure of all-seven-membered **3b** (Figure 2a, highlighted in deep blue) exerts



**Scheme 1.** Synthetic approaches towards heptagon-containing PAHs **3–6**.



**Figure 2.** Top: Solid-state structures of the heptagon-embedded PAHs a) **3a** (right) and **b** (left), b) **4**, c) **5** and d) **6**. Eight-membered rings are highlighted in blue and seven-membered rings are highlighted in green. Steric repulsion between the respective phenyl rings in **3b** is highlighted in deep blue. Bottom: space-filling models.

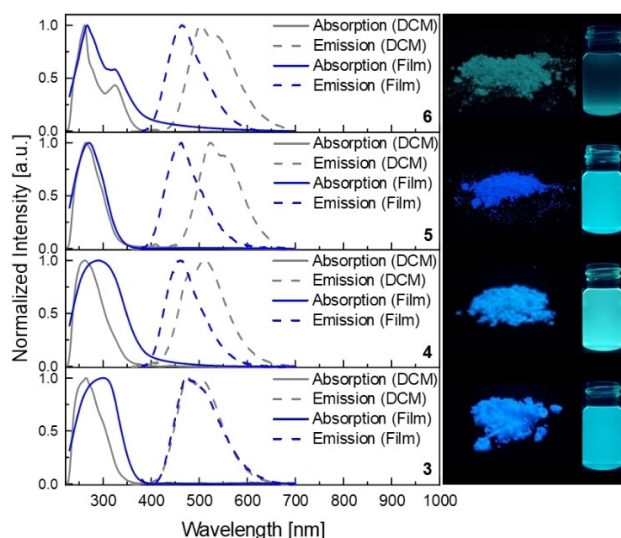
sufficient steric pressure to induce ring expansion and the 1,2-rearrangement of the phenyl groups. Consequently, the resulting sterically more relaxed structure (778 isomer) allows their spatial separation and reduces the steric demand. This conclusion was supported by density functional calculations (DFT, B3LYP/6-311G\*\*) according to which the corresponding 778 isomers are energetically more favorable than the 777 isomers (see the Supporting Information). The larger the functional groups of the phenyl substituents, the larger is the energy difference between the two isomers. The experimental and theoretical results suggest that the 1,2-rearrangement occurs due to the sterically overcrowded three-dimensional structures.

The high steric hindrance distorts the heptagons and octagons in all compounds (Figure 2) in order to minimize the still remaining spatial proximity of the phenyl rings. Even the central benzene rings deviate ( $1.4\text{--}16.3^\circ$ ) from planarity.

The crystal packings of **3**, **4** and **5** exhibit no  $\pi$ -interactions, while the packing of **6** shows intermolecular contacts of the fluorene units (plane distance:  $3.7\text{ \AA}$ ) and the phenanthrene units (plane distance:  $3.5\text{ \AA}$ , see the Supporting Information).

Compounds **3–6** fluoresce both in solution (DCM) and in the film (spin-coated from DCM,  $c=6\text{ mg mL}^{-1}$ ) with blue to blue-green emission (Figure 3). The emission maxima of thin films show a drastic hypsochromic shift compared to those in solutions.

The compounds exhibit approximately a doubling of the quantum yields (Table 1) in thin films (11–68%) compared to the respective solutions (4–30%). The flexibility of their

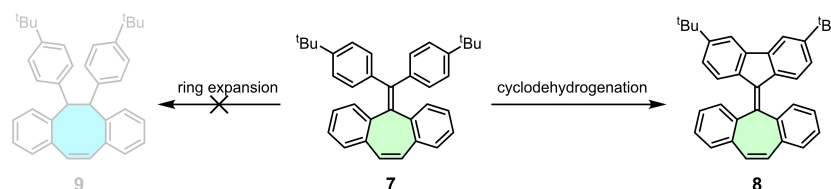


**Figure 3.** Left: absorption and emission spectra of **3–6**. Right: photographs of solids (left) and solutions in DCM (right) of **3–6** under 365 nm. Note that the inseparable mixture of **3a,b** was employed for characterization.

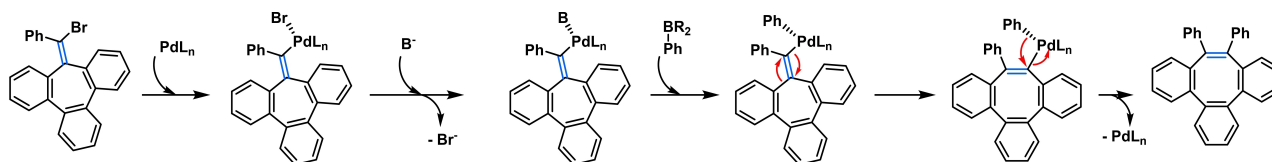
polycyclic backbones in solution leads to rotational freedom of phenyl groups or intramolecular motion allowing radiationless deactivation of the excited state. The enhanced fluorescence in the solid state is attributed to aggregation-induced emission enhancement (AIEE)<sup>[21]</sup> due to suppression of intramolecular

**Table 1.** Experimental and calculated (gas phase) properties of the heptagon-embedded PAHs **3–6** in solution (DCM) and films (spin-coated from DCM).

Comp.	$\lambda_{(\text{DCM})\text{max,abs}}$ [nm]	$\lambda_{(\text{DCM})\text{onset,abs}}$ [nm]	$\lambda_{(\text{DCM})\text{max,em}}$ [nm]	$\lambda_{(\text{film})\text{max,abs}}$ [nm]	$\lambda_{(\text{film})\text{onset,abs}}$ [nm]	$\lambda_{(\text{film})\text{max,em}}$ [nm]	$E_{\text{bandgap}}$ [eV]	$\phi_{\text{solution}}$ [%]	$\phi_{\text{film}}$ [%]
<b>3</b>	265	356	476	301	360	473	4.51	30	68
<b>4</b>	262	352	480	289	411	460	4.29	18	34
<b>5</b>	264	346	523	270	344	463	4.50	4	11
<b>6</b>	325(262)	373	504	325(267)	389	464	3.86	24	55



**Scheme 2.** Synthetic approaches towards the ring expansion of monomer 7. The eight-membered ring is highlighted in blue and seven-membered rings are highlighted in green.



**Scheme 3.** Rearrangement pathway as a Pd-catalysed mechanism.

vibration/rotation, similar to tetraphenylethene and its bridged/conformationally locked derivatives.<sup>[22]</sup>

In order to investigate whether the ring expansion to eight-membered rings can also be observed in sterically less hindered systems, we prepared monomer 7 as model compound (Scheme 2). Coupling of 5-(dibromomethylene)-5*H*-dibenzo[*a,d*][7]-annulene (S1) with 4-*tert*-butylphenylboronic acid under the identical Suzuki-conditions furnished 7<sup>[23]</sup> in 65% yield so that formation of the eight-membered ring was not observed. This is a clear hint at the influence of the steric constraint induced by the tris-cycloheptenylene scaffold. With 7 in hand, different reaction conditions were tested in order to achieve its selective ring expansion (Table S1 in the Supporting Information) but neither oxidative reaction conditions nor the aforementioned Suzuki-conditions afforded the expected ring expansion to 9. Treating monomer 7 with TfOH and DDQ led to an intramolecular cyclization furnishing 8.<sup>[24]</sup>

In a further control experiment, the mixture of the isomers 3a and 3b was resubjected to the Suzuki-conditions. NMR-spectroscopy failed to indicate any further rearrangement, which would have been detectable in a change of the isomer ratio.

These findings confirmed that the rearrangement and resulting ring expansion occurring during the Suzuki reaction are enforced by the high steric demand of the overcrowded, benzene-rich structures of the target compounds.

Note, that in previous work<sup>[18a]</sup> we demonstrated that three benzannulated eight-membered rings could be fused around a benzene ring by cyclotrimerization of a cyclooctatrienylene. However, the steric encumbrance is markedly enhanced upon going to benzo-fused tris-cycloheptenylenes.

The rearrangement described herein is structurally similar to that of 9,9'-bifluorenylidene furnishing dibenzo[*g,p*]chrysene under thermal conditions (400 °C).<sup>[25]</sup> However, the mechanism in the present work should be different from that of 9,9'-bifluorenylidene, as that of the latter can be described as being via radical species or via carbene intermediates.<sup>[14a,b]</sup> A possible

mechanistic pathway for the Pd-catalyzed rearrangement after oxidative addition is illustrated in Scheme 3.

## Conclusions

In conclusion, we have prepared an intriguing precursor 2 with three embedded heptagons as a building block for negatively curved hydrocarbons containing densely packed benzenes. The subsequent  $\pi$ -expansion upon Suzuki coupling led to novel, distorted and overcrowded PAHs 3–6 with attractive optical properties. We demonstrated the limit of steric encumbrance within  $\pi$ -expanded benzo-fused tris-cycloheptenylenes, which enforced a 1,2-rearrangement of the phenyl groups and, thus, a ring expansion during the Suzuki reactions. The driving force for the ring expanding rearrangement is the steric overcrowding of benzene rings in a negatively curved, nonplanar hydrocarbon. The target compounds 3–6, containing two heptagons and one octagon surrounding a central benzene ring, exhibit a blue to blue-green fluorescence and increased emission intensity as well as a hypsochromic band shift in the solid state as a consequence of nonplanarity and “frozen” intramolecular motions.

## Experimental Section

Deposition Numbers 2219878 (for 2), 2219879 (for 3), 2219880 (for 4), 2219881 (for 5), 2219882 (for 6) 2116878 (for 7) and 2116879 (for 8) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** Fluorescence · negative curvature · overcrowded structures · polycyclic aromatic hydrocarbons · rearrangements

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