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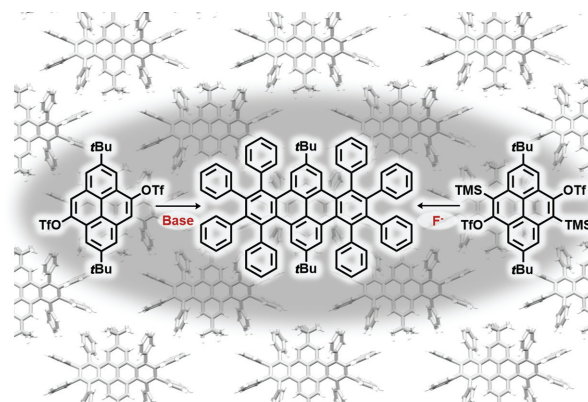
Pyrene-Based Diarynes as Precursors for Twisted Fused Polycyclic Aromatic Hydrocarbons: A Comparison of Two Routes

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Abstract Two bench-stable and readily accessible pyrene-based diaryne precursors based on triflate as well as TMS triflate motifs are introduced and compared in their [4+2]-Diels–Alder reactions with tetracyclone to give an oligophenyl-substituted dibenzo[e,l]pyrene in both cases. By single-crystal X-ray analysis, this twistacene showed helical chirality and an end-to-end contortion of 49.6° due to steric repulsion.
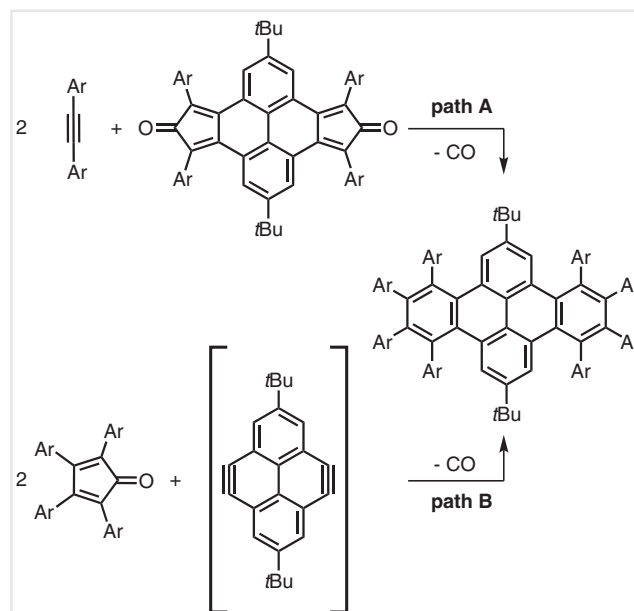
Key words polycyclic aromatic hydrocarbons, twistacene, Diels–Alder reaction, pyrenes, arynes

Introduction

Although a large portfolio of synthetic methods has already been developed for the synthesis of larger fused polyaromatic hydrocarbons (PAHs),[1] the [4+2] cycloaddition of (multifunctional) arynes with aryl-substituted cyclopentadienones under subsequent thermal CO extrusion is still one of the most frequently used and reliable methods to quickly provide PAH scaffolds in high yields.[2–4] Such structures can be further used, for example, for cyclodehydrogenative fusion of rings to synthesize larger 2D or 3D structures.[4,5]

In this respect, pyrene derivatives are excellent molecular precursors to build up larger PAHs.[3,5,6] For the above-mentioned approach (the [4+2] cycloaddition), pyrene derivatives can either act as precursors for arynes as dienophiles or as dienes. The latter was frequently used for the synthesis of PAHs, for example, dibenzo[e,l]pyrenes (path A in Scheme 1),[7] despite the fact that pyrene biscyclopentadienones are not very stable under ambient conditions and therefore difficult to purify and handle.[3,5,8] To the best of our knowledge, the approach with inverse electronic demand on the pyrene scaffold in the reaction with cyclopentadienones (path B in Scheme 1) has not been reported till date. There are a few examples where the in

Scheme 1 Comparison of two synthetic approaches involving pyrene biscyclopentadienones (path A) or pyrene diarynes (path B) exemplarily shown for the synthesis of dibenzo[e,l]pyrenes.

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situ generation of pyrene-based bis-arynes has been described in the cycloaddition to furans,[9,10] benzofurans,[11] or arylacetonitrils.[12] In all these cases, either pyrene dibromides[9,12] or tetrabromides[10,11,13] have been used as molecular precursors, which were transformed into the arynes with non-nucleophilic bases, or *n*-BuLi. Similar to aryl bromides, aryl triflates[14] can be transformed into arynes by non-nucleophilic bases, or, more elegant, *ortho*-TMS triflates[15] as bench stable precursors that are in situ transformed to arynes by fluoride anions.

Here we describe two routes to access pyrene-based diaryne precursors as bench-stable compounds for the synthesis of larger PAHs, such as twistarenes by [4+2] cycloadditions.[16,17]
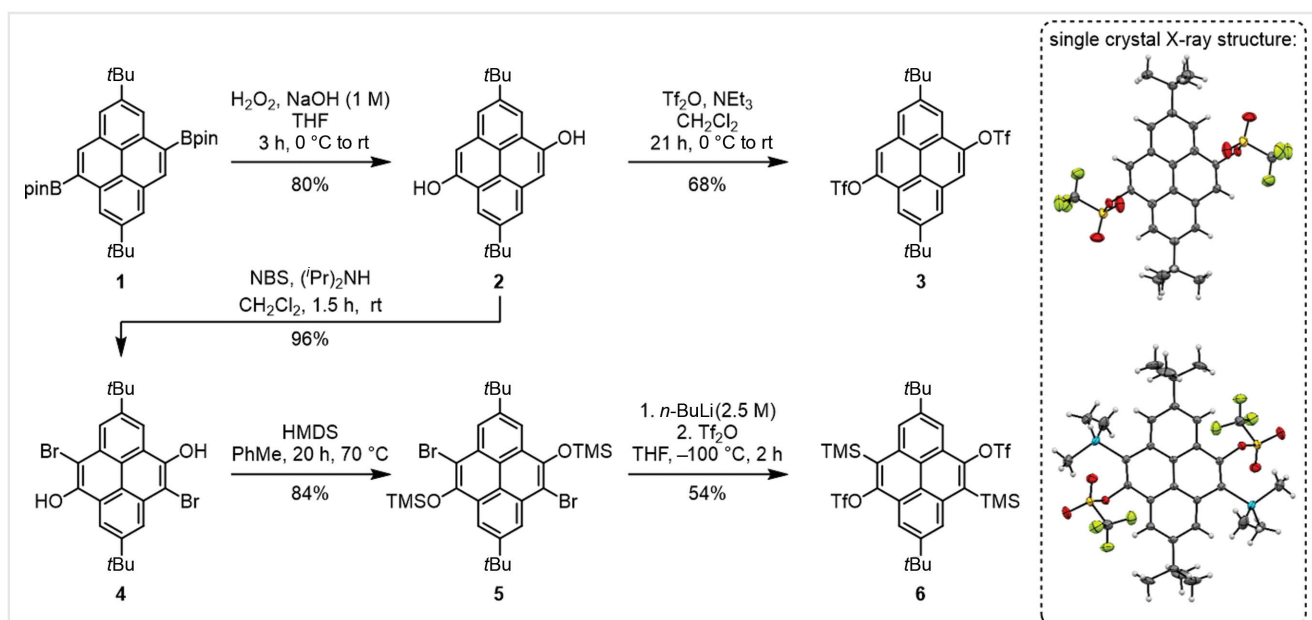
Results and Discussion

The synthesis of both aryne precursors **3** and **6** started from 4,9-diborylated pyrene **1**, which can be readily synthesized via literature-known procedures on gram scale.[18] Base-mediated ($NaOH_{aq}$) oxidation using H_2O_2 gave the corresponding pyrene diol **2** in 80% yield after recrystallization from a chloroform/*n*-heptane mixture (Scheme 2). The condensation with trifluoromethanesulfonic anhydride (Tf_2O; 2.4 equiv) under standard conditions [NEt_3 (4 equiv), CH_2Cl_2] gave pyrene bistriflate **3** in 68% yield (Scheme 2). Diol **2** and bistriflate **3** have been fully characterized by common analytical methods (see the
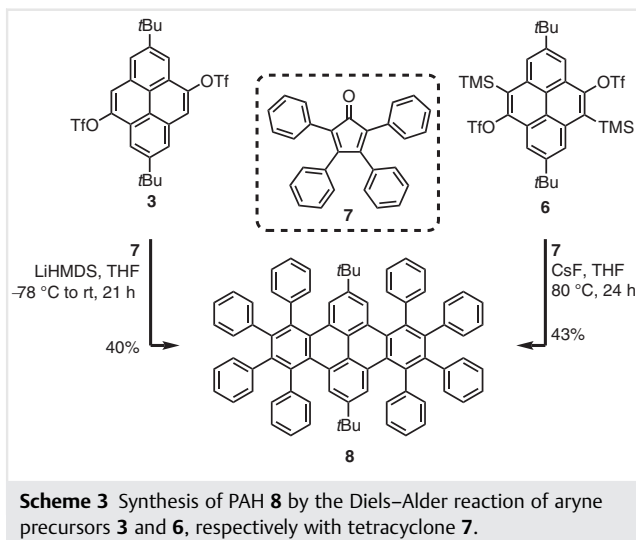
Supporting Information, SI). Additionally, the structure of bistriflate **3** was proven by single-crystal X-ray analysis (SCXRD; Scheme 2, top right).

To synthesize bis-TMS triflate **6**, pyrene diol **2** was selectively *ortho*-brominated using NBS and $^iPr_2NH_2$ to give dibromo dihydroxy pyrene **4** in 96% yield.[19] Using hexamethyldisilazane, **4** was transformed in 84% yield to the double TMS ether **5** (Scheme 2). Subsequently, **5** was converted under Sila-Fries[20] conditions (1. nBuLi; 2. Tf_2O) under careful control of the reaction temperature (−100 °C to −80 °C) to the TMS triflate **6** and isolated in 54% yield. Pyrenes **4**, **5**, and **6** have been fully characterized (see SI) and the structures of **5** (see SI) and **6** (Scheme 2, right, bottom) were additionally proven by SCXRD analyses.

The in situ generation of pyrene diarynes from **3** and **6** was investigated in the Diels–Alder reaction with tetracyclone **7** to obtain PAH **8** (Scheme 3), whose dibenzo[*e,l*] pyrene core structure was till now only accessible via path A with dodecyl chains as discussed in Scheme 1.[7] Different bases for the deprotonation of bistriflate **3** were tested to generate the aryne in situ and react with tetracyclone **7** to give **8**. Neither KO*t*Bu in different solvents (THF, Et₂O, Ph₂O) in a wide temperature range (0 °C to 180 °C) nor *n*-BuLi gave the twisted PAH **8**. Treatment of **3** with lithium hexamethyldisilazane as a strong non-nucleophilic base for 21 h at −78 °C to rt followed by thermal treatment at 150 °C for 3 h (for details, see SI) resulted in **8**, which was isolated in 40% yield after column chromatography (Scheme 3). Besides characterization by ^{1}H and ^{13}C NMR spectroscopy, a
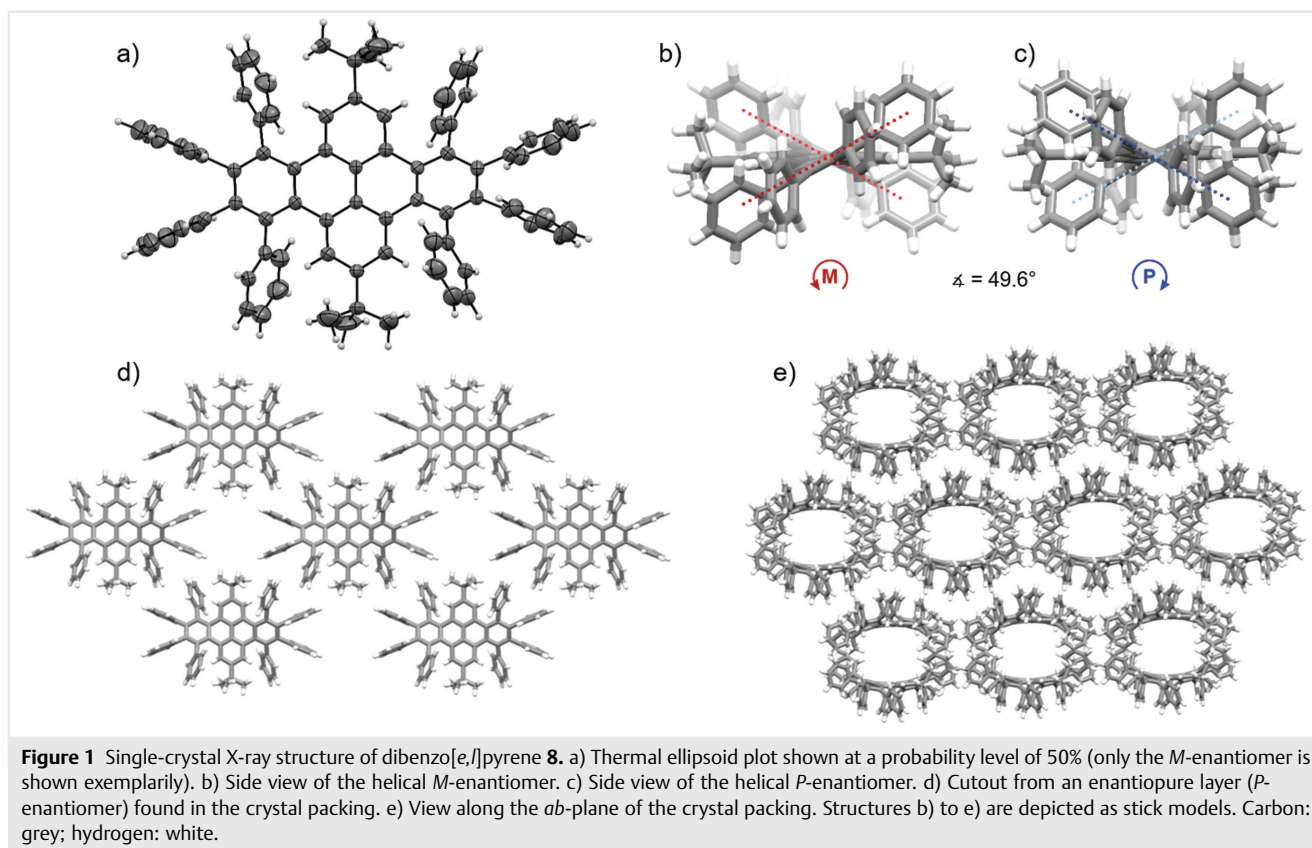

Scheme 2 Left: synthesis of the pyrene-based diaryne precursors **3** and **6** from bisborylated pyrene **1**. Right: single-crystal X-ray structures of **3** (top) and **6** (bottom) as thermal ellipsoids at the 50% probability level. Carbon: grey; hydrogen: white; oxygen: red; sulfur: yellow; fluorine: lime, silicon: light blue. HMDS: hexamethyldisilazane.

Scheme 3 Synthesis of PAH **8** by the Diels–Alder reaction of aryne precursors **3** and **6**, respectively with tetracyclone **7**.

molecular ion peak at $m/z = 1022.575$ (calcd. for $C_{80}H_{62}$: 1022.485) for $[8]^+$ was clearly detected by MALDI-TOF MS (see SI). As mentioned above, TMS triflate **6** was also used as an aryne precursor, which was generated by CsF in THF at 80 °C to give nearly the same yield of **8** (43%), again after thermal treatment.

By slow evaporation of an n-hexane/CHCl$_3$ solution of **8**, crystals of suitable quality for single-crystal X-ray diffraction have been obtained (Figure 1).

PAH **8** crystallizes in the orthorhombic space group *Fddd* with $Z = 8$ and approximately 24 molecules of disordered chloroform within the one-dimensional channels along the ab-plane formed by PAH **8**, which had to be removed by the SQUEEZE routine function of Platon.[21] Because of the eight phenyl groups of the aromatic backbone of **8**, the dibenzo[e, l]pyrene core structure is contorted by 49.6° (considering the outer edges, see Figure 1b, c), creating a helical chirality. This twist is noticeably smaller than that for the structurally related dodecaphenyltetracene (97°)[17] due to the stiffening of the tetracene backbone by the annulated benzene rings. Within the racemic crystal structure of **8**, enantiopure sheets can be found (Figure 1d) with dispersion interactions between the peripheral phenyl group and the *tert*-butyl groups as main interactions (Figure 1e). Dibenzo[e,l]pyrene **8** was furthermore investigated using UV-vis spectroscopy and the colorless compound shows an absorption maximum at $\lambda_{abs} = 309$ nm (log $\varepsilon = 4.71$). Upon excitation ($\lambda_{ex} = 309$ nm), a blue fluorescence with $\lambda_{em} = 412$ nm and a resulting considerably large Stokes shift of $\tilde{v} = 8090$ cm^{-1} were observed (see SI).

Figure 1 Single-crystal X-ray structure of dibenzo[e,l]pyrene **8.** a) Thermal ellipsoid plot shown at a probability level of 50% (only the *M*-enantiomer is shown exemplarily). b) Side view of the helical *M*-enantiomer. c) Side view of the helical *P*-enantiomer. d) Cutout from an enantiopure layer (*P*-enantiomer) found in the crystal packing. e) View along the ab-plane of the crystal packing. Structures b) to e) are depicted as stick models. Carbon: grey; hydrogen: white.

Conclusions

Two routes to twisted PAH **8** via different pyrene-based aryne precursors were compared. While for the bistriflate **3** low temperatures and a strong non-nucleophilic base (LHDMS) were necessary to generate the desired diaryne, the bis-TMS triflate **6** was transferred to the bis-aryne using CsF as a fluoride ion source at 80 °C. In both cases, the Diels–Alder reaction with tetracyclone gave twisted phenyl-substituted dibenzo[*e,l*]pyrene **8** in comparable yields of 40% and 43%. Since bistriflate **3** is synthesized with two steps less than **6**, this route is preferred to generate a valuable pyrene-based aryne in situ. Currently we are exploiting both precursors in the broader sense for PAH synthesis.

Funding Information

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0040-1721851.

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(19) Compound **4** can be isolated in 96% yield in sufficient purity to be used in further synthetic steps. To obtain an analytical pure sample, purification by column chromatography has to be taken into account, accompanied by a material loss and an isolated yield of 31% (see the SI).

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