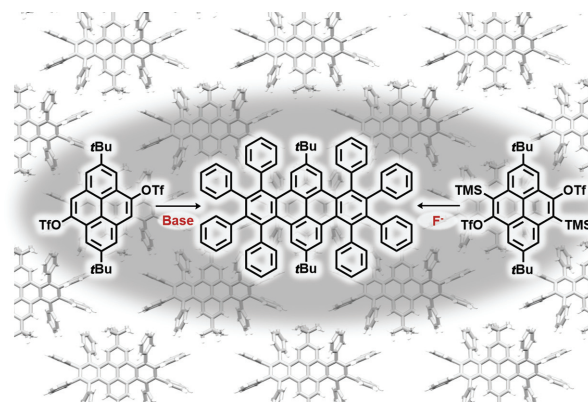


# Pyrene-Based Diarynes as Precursors for Twisted Fused Polycyclic Aromatic Hydrocarbons: A Comparison of Two Routes

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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.

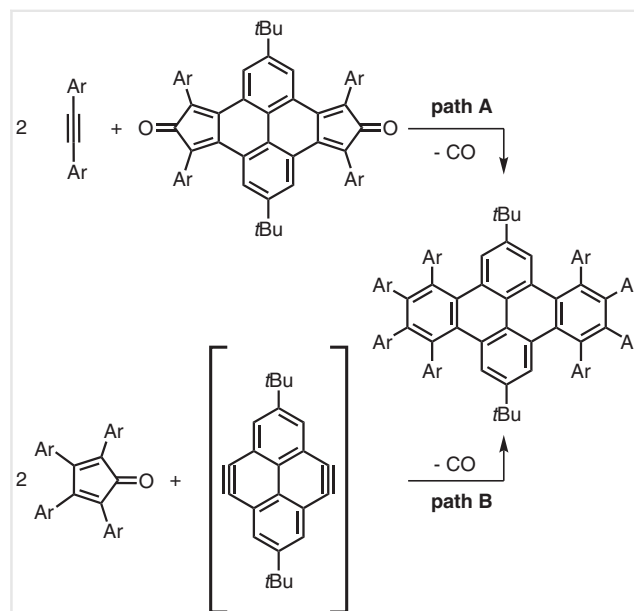
**Key words** polycyclic aromatic hydrocarbons, twistacene, Diels-Alder reaction, pyrenes, arynes

## Introduction

Although a large portfolio of synthetic methods has already been developed for the synthesis of larger fused polyaromatic hydrocarbons (PAHs),<sup>1</sup> 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.<sup>2–4</sup> Such structures can be further used, for example, for cyclodehydrogenative fusion of rings to synthesize larger 2D or 3D structures.<sup>4,5</sup>

In this respect, pyrene derivatives are excellent molecular precursors to build up larger PAHs.<sup>3,5,6</sup> 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),<sup>7</sup> despite the fact that pyrene biscyclopentadienones are not very stable under ambient conditions and therefore difficult to purify and handle.<sup>3,5,8</sup> 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.

situ generation of pyrene-based bis-arynes has been described in the cycloaddition to furans,<sup>9,10</sup> benzofurans,<sup>11</sup> or arylacetonitrils.<sup>12</sup> In all these cases, either pyrene dibromides<sup>9,12</sup> or tetrabromides<sup>10,11,13</sup> have been used as molecular precursors, which were transformed into the aryne with non-nucleophilic bases, or *n*-BuLi. Similar to aryl bromides, aryl triflates<sup>14</sup> can be transformed into aryne by non-nucleophilic bases, or, more elegant, *ortho*-TMS triflates<sup>15</sup> as bench stable precursors that are in situ transformed to aryne 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.<sup>16,17</sup>

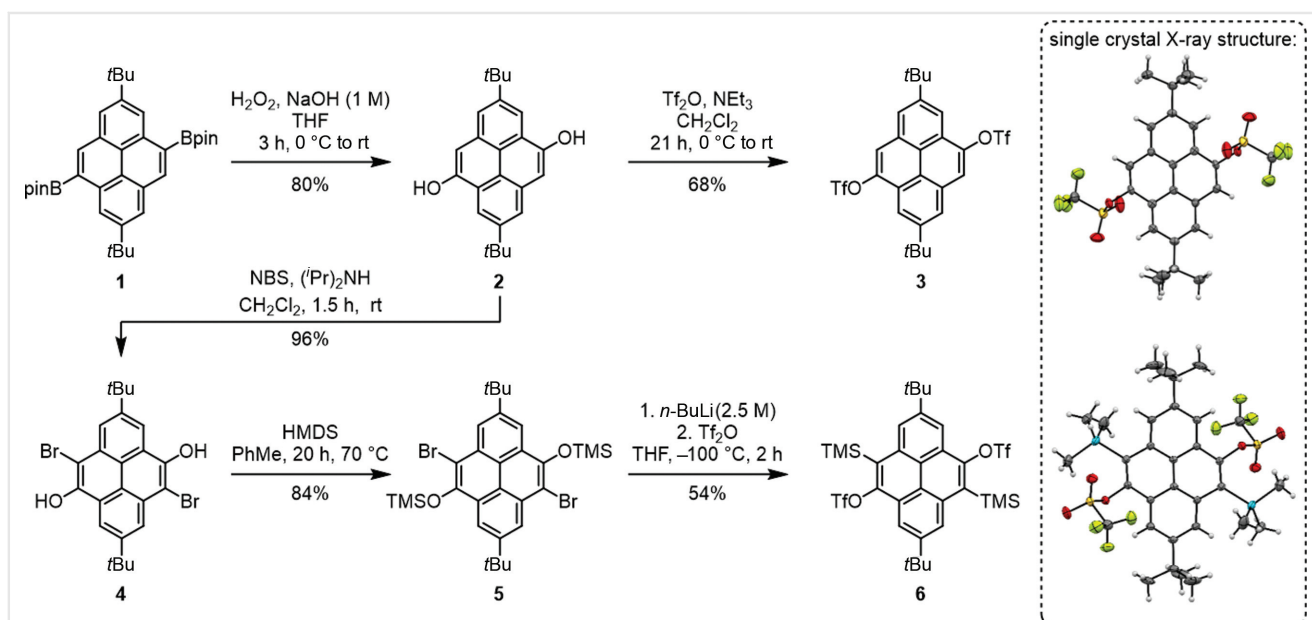
## Results and Discussion

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.<sup>18</sup> Base-mediated (NaOH<sub>aq</sub>) oxidation using H<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O; 2.4 equiv) under standard conditions [NEt<sub>3</sub> (4 equiv), CH<sub>2</sub>Cl<sub>2</sub>] gave pyrene bistriflate **3** in 68% yield (Scheme 2). Diol **2** and bistriflate **3** have been fully characterized by common analytical methods (see the

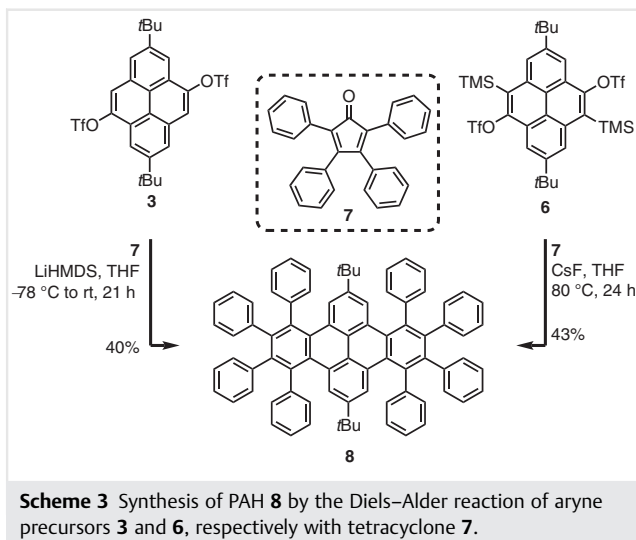
Supporting Information, SI). Additionally, the structure of bistriflate **3** was proven by single-crystal X-ray analysis (SCXRD; Scheme 2, top right).

To synthesize bis-TMS triflate **6**, pyrene diol **2** was selectively *ortho*-brominated using NBS and <sup>1</sup>Pr<sub>2</sub>NH<sub>2</sub> to give dibromo dihydroxy pyrene **4** in 96% yield.<sup>19</sup> Using hexamethyldisilazane, **4** was transformed in 84% yield to the double TMS ether **5** (Scheme 2). Subsequently, **5** was converted under Sila-Fries<sup>20</sup> conditions (1. *n*-BuLi; 2. Tf<sub>2</sub>O) 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.<sup>7</sup> 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<sup>t</sup>Bu in different solvents (THF, Et<sub>2</sub>O, Ph<sub>2</sub>O) 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 <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, a



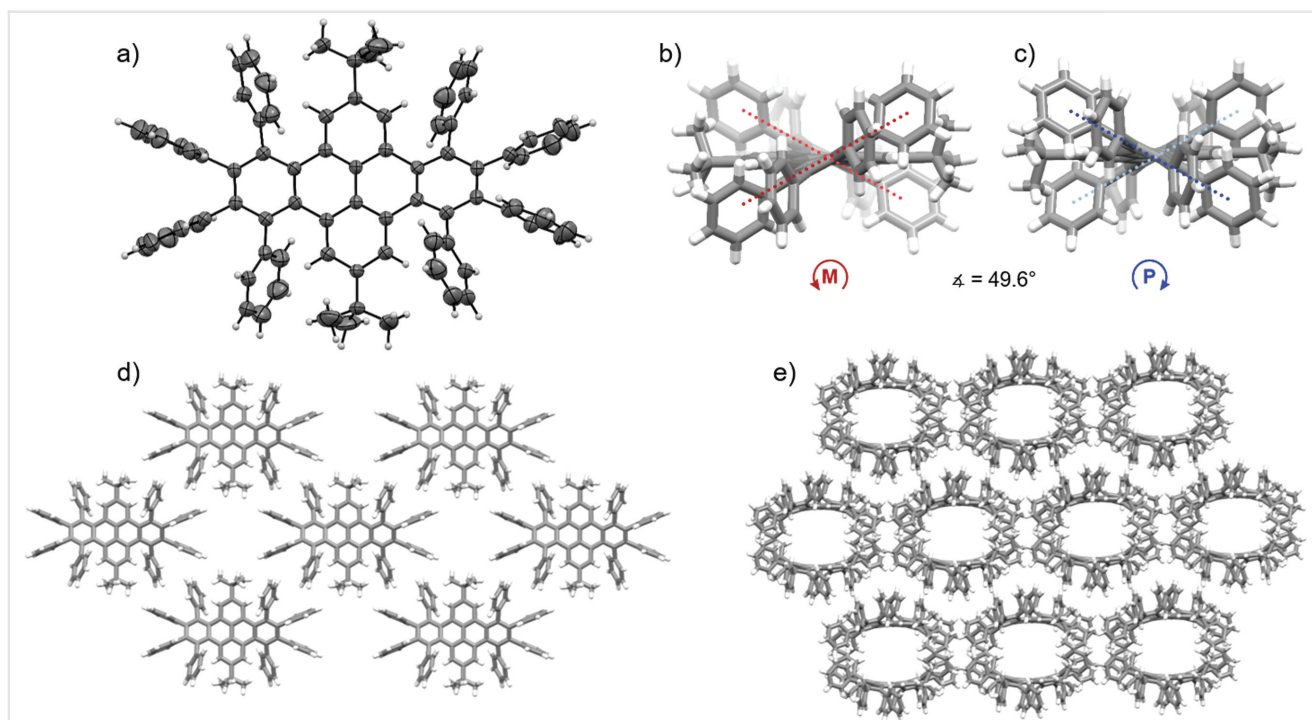
**Scheme 2** Left: synthesis of the pyrene-based diaryne precursors **3** and **6** from bisborylated pyrene **1**. Right: single-crystal X-ray structures of **3** (top) and **6** (bottom) as thermal ellipsoids at the 50% probability level. Carbon: grey; hydrogen: white; oxygen: red; sulfur: yellow;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



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.<sup>21</sup> 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°)<sup>17</sup> 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 ( $\log \epsilon = 4.71$ ). Upon excitation ( $\lambda_{ex} = 309$  nm), a blue fluorescence with  $\lambda_{em} = 412$  nm and a resulting considerably large Stokes shift of  $\tilde{\nu} = 8090$   $cm^{-1}$  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.

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## Supporting Information

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

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