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 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.

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 triflates¹⁴ can be transformed into arynes by non-nucleophilic bases, or, more elegant, *ortho*-TMS triflates¹⁵ 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 $^i\text{Pr}_2\text{NH}$ 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-Fries²⁰ conditions (1. *n*-BuLi; 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^tBu in different solvents (THF, Et_2O , Ph_2O) 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 ^1H 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 ($\log \epsilon = 4.71$). 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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- (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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