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Synthesis and Structure of a Helical Diindenophenanthrene with Four Congested Phenyl Substituents as a Molecular Spiral Staircase[†]

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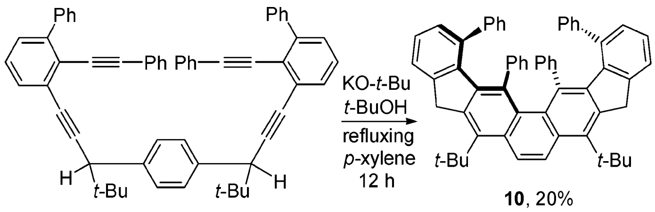
ABSTRACT

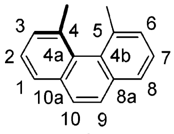


9

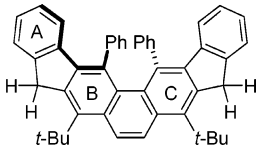
10, 20%

Treatment of 9 with potassium *tert*-butoxide produced 10 having a helical twist in a single operation. The X-ray structure of 10 shows that the four phenyl substituents are essentially parallel to one another but are virtually perpendicular to the helical axis of the diindenophenanthrene ring system. Viewing from the direction perpendicular to the helical axis, the structure of 10 resembles that of a segment of a spiral staircase having four parallel steps.

The distorted structure of 4,5-disubstituted phenanthrenes[1] and related compounds[2] has long been a subject of interest. The nonbonded steric interactions between the two substituents at the C4 and C5 positions cause them to bend away from the mean plane of the aromatic system and exert a torsional force that produces a helical twist of the aromatic framework. The X-ray crystallographic structure of 4,5-dimethylphenanthrene (**1**) shows a 27.9° twist between the mean planes of the two outer aromatic rings (planes 1−2−3−4−4a−10a and 4b−5−6−7−8−8a).[1b] The twist of the corresponding aromatic rings of **2** (rings B and C), a diindeno-fused 4,5-diphenylphenanthrene, was more pronounced at 46.1°.[1c] In addition, the two phenyl substituents are oriented essentially parallel to each other (within 1.3°), but are at a 53.1° angle from the diindenophenanthrene system as indicated by X-ray structure analysis. The presence of a helical twist in **2** could also be discerned from its ^{1}H NMR spectrum with a set of AB quartet signals (J = 21.0 Hz) from the diastereotopic methylene hydrogens on the five-membered rings.



1



2

Our continued interest in nonplanar polycyclic aromatic compounds led us to apply the synthetic sequence developed for **2** to the construction of **10** having two additional phenyl

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[†] Dedicated to Professor Denis W. H. MacDowell on the occasion of his 80th birthday.

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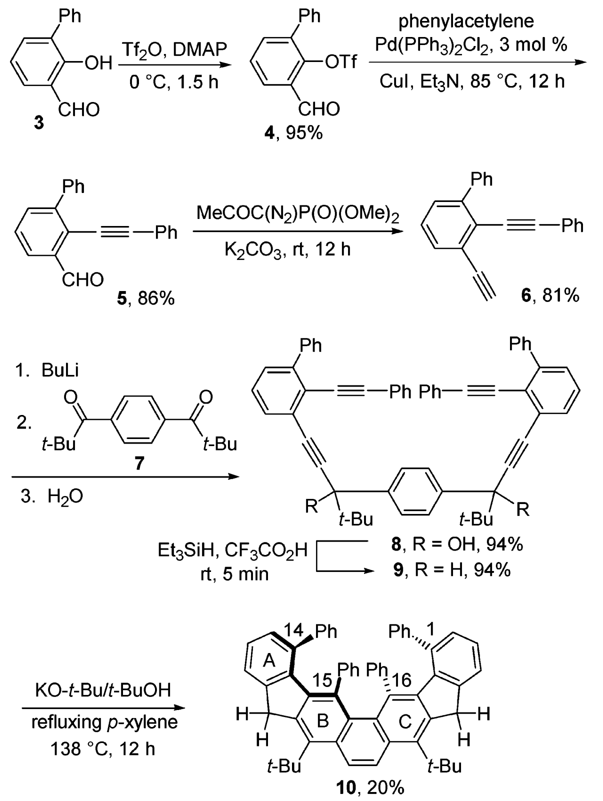
10.1021/ol0481434 CCC: $27.50

Scheme 1



substituents at the two outermost aromatic rings (Scheme 1). Conversion of **3**,[3] prepared from 1,1′-biphenyl-2-ol, to triflate **4** followed by coupling with phenylacetylene produced **5**, which was then treated with dimethyl (1-diazo-2-oxopropyl)phosphonate and K_2CO_3[4] to afford diyne **6**. The transformations from **6** to **10** are similar to what were reported previously for **2**. Condensation between 2 equiv of **6** and **7** produced **8**, which was then reduced to furnish **9**. Treatment of **9** with potassium *tert*-butoxide under refluxing *p*-xylene then produced **10** in a single operation. The transformation from **9** to **10** presumably involved two prototropic acetylene to allene rearrangements of the two internal acetylenic moieties followed by two formal intramolecular Diels−Alder reactions and subsequent prototropic rearrangements of the resulting Diels−Alder adduct as described previously for **2**.

The X-ray structure of **10** (Figure 1) shows that the four phenyl substituents are essentially parallel to one another but are virtually perpendicular to the helical axis of the diindenophenanthrene system. Because the perpendicular distances of ca. 3.1 Å between the neighboring phenyl substituents are shorter than the optimal π-system van der Waals contact distance of ca. 3.4 Å,[5] the phenyl substituents are not directly on top of one another but are in a skewed conformation. Sighting along the line joining C1 and C16, the dihedral angle between the bonds attaching the two phenyl substituents to C1 and C16 is 53.6°, whereas viewing along the C15−C16 line the dihedral angle between the bonds connecting the two inner phenyl groups to C15 and C16 is even more pronounced at 63.5°. As a result, the two outer phenyl substituents are pointed essentially in opposite directions. Viewing along the C1−C14 line and following the direction of rotation of the helical twist, the bond connecting a phenyl substituent to C14 is rotated 184.3° from the bond connecting a phenyl substituent to C1. The diindenophenanthrene system is also severely distorted with a 29.3° twist angle between the mean planes of rings A and B and a more pronounced 59.2° twist angle between the mean planes of rings B and C, which is substantially larger than that of **2** at 46.1°. Viewing from the direction perpendicular to the helical axis of the diindenophenanthrene ring system, the structure of **10** resembles that of a segment of a spiral staircase having four parallel steps or that of a portion of one strand of DNA containing four bases.[6]

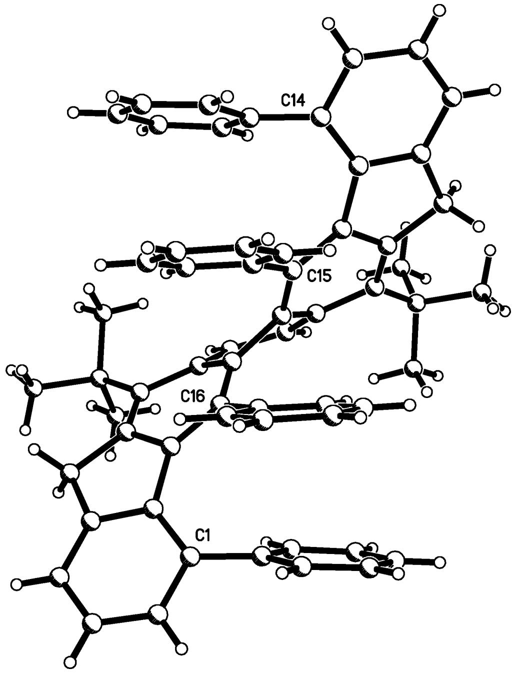


Figure 1. Molecular structure of **10**. Its solid structure is constrained by a crystallographic 2-fold rotation axis.

Due to additional buttressing effect, the rate of racemization of **10** could be expected to be even slower than that of **2**, which is most likely to be conformationally stable at 25 °C.[1c] The ^{1}H NMR spectrum (600 MHz) of **10** in $CDCl_3$ also exhibited a set of AB quartet at δ 4.34 and 4.39 (J = 21.0 Hz) from the diastereotopic methylene hydrogens, manifesting the presence of a helical twist.

The two most upfield signals (doublet) of the aromatic hydrogens at δ 5.34 and 5.68 are attributable to the *ortho*

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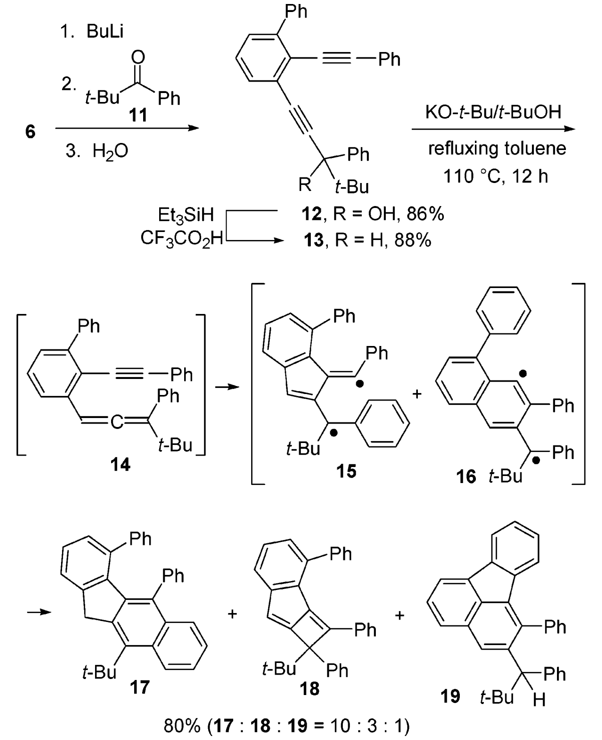
hydrogens of the two inner phenyl substituents connected to C15 and C16. The fact that two distinct signals were observed for these *ortho* hydrogens suggests that the rate of rotation of the two inner phenyl groups is relatively slow on the NMR time scale at 25 °C. Two distinct signals attributable to the *meta* hydrogens were also observed at δ 6.03 and 6.24. This is in sharp contrast to the ^{1}H NMR spectrum (600 MHz) of **2** at 25 °C, which showed only one signal (doublet) at δ 6.52 for the *ortho* hydrogens and one signal (triplet) at δ 7.00 for the *meta* hydrogens. However, temperature-dependent NMR study of **2** showed that at −40 °C two doublets at δ 6.46 and 6.51 for the *ortho* hydrogens and two triplets at δ 6.93 and 7.05 for the *meta* hydrogens appeared, and the coalescence temperatures were determined to be −22 and −10 °C, respectively, corresponding to rotational barriers of 12.5 and 12.6 kcal/mol at these two temperatures.

Interestingly, signals from the *ortho* and *meta* hydrogens of the two outer phenyl substituents connected to C1 and C14 of **10** were conspicuously missing. Instead, broad humps could be discerned on the baseline due to restricted rotation of the phenyl groups. On lowering the temperature from +25 to −20 °C, additional peaks started to appear, and at −20 °C two doublets at δ 6.21 and 6.36 attributable to the *ortho* hydrogens and two triplets at δ 6.46 and 6.73 attributable to the *meta* hydrogens could be identified. The coalescence temperatures for the *ortho* and *meta* hydrogens are 25 and 30 °C, respectively, corresponding to rotational barriers of 14.3 and 14.2 kcal/mol at these two temperatures. At 55 °C on a 270 MHz NMR spectrometer, a single doublet at δ 6.29 for the *ortho* hydrogens and a single triplet at δ 6.58 for the *meta* hydrogens could be clearly discerned.

Compared to the synthesis of **2**, the use of diyne **6** bearing a phenyl substituent on the central benzene ring resulted in a lower yield for **10**. A model study with **13** revealed that the expected benzo[*b*]fluorene **17** was produced via a sequence of reactions involving a prototropic rearrangement to form the benzannulated enyne−allene **14** followed by a Schmittel cyclization reaction[7] to form biradical **15**, which in turn underwent an intramolecular radical−radical coupling and a prototropic rearrangement (Scheme 2). However, two additional adducts, **18** and **19**, were also produced. A competing intramolecular [2 + 2] cycloaddition reaction of **14** could account for **18**. The generation of biradical **16** from the Myers−Saito cyclization reaction[8] of **14** followed by trapping the aryl radical center with the phenyl substituent and a prototropic rearrangement could furnish **19**. Presumably, the emergence of nonbonded steric interactions between the two phenyl substituents along the pathway toward **17** could be responsible for an increase of its activation energy, allowing a minor portion of **14** to undergo the Myers−Saito cyclization reaction.[9] On the other hand, the use of the diyne without a phenyl substituent on the central benzene ring produced the corresponding benzo[*b*]fluorene exclusively in 90% yield.[10]

Scheme 2



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Supporting Information Available: Experimental procedures, spectroscopic data, and ^{1}H and ^{13}C NMR spectra of **4−6**, **8−10**, **12**, **13**, and **17−19**; ORTEP drawings of the crystal structures of **10** and **19**; and X-ray crystallographic data of **10** and **19** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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