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Synthesis of a $C_{56}H_{40}$ Hydrocarbon Bearing a 54-Carbon Framework of C_{60}[†]

Kung K. Wang,* Yu-Hsuan Wang, Hua Yang, Novruz G. Akhmedov, and Jeffrey L. Petersen

C. Eugene Bennett Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506-6045

kung.wang@mail.wvu.edu

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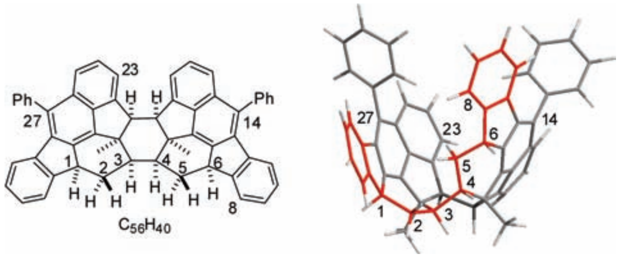
ABSTRACT



A $C_{56}H_{40}$ hydrocarbon possessing a 54-carbon framework represented on the surface of C_{60} was synthesized by solution-phase chemistry. The structure of this hydrocarbon has a 30-carbon core, which can be regarded as a partially hydrogenated [5,5]circulene, a $C_{30}H_{12}$ semibuckminsterfullerene, with only one of the carbon−carbon bonds remaining unconnected. The central 30-carbon core is fused with two indeno groups and bears two phenyl and two methyl substituents.

Construction of bowl-shaped polycyclic aromatic hydrocarbons (buckybowls) having carbon frameworks represented on the surface of C_{60} by solution-phase chemistry has enjoyed substantial progress in recent years.[1] The synthetic strategy of constructing a carbon framework containing multiple tetrahedral sp^3 carbons as a precursor prior to the final transformation to an aromatized adduct was employed by Barth and Lawton in the first synthesis of corannulene, a $C_{20}H_{10}$ buckybowl possessing significant curvature.[2] More recently, this approach was adopted in the synthesis of sumanene, a symmetric $C_{21}H_{12}$ subunit of C_{60}.[3] We recently reported the use of the cascade cyclization reactions of benzannulated enyne-allenes as key steps in the construction of three buckybowls[4] and a $C_{44}H_{26}$ fullerene fragment.[5] We have further extended this strategy to the synthesis of a $C_{56}H_{40}$ hydrocarbon possessing a 54-carbon fragment of C_{60}. There are 10 tetrahedral sp^3 carbons in this 54-carbon framework, causing the molecule to adopt an unsymmetrical, skewed structure with several parts of the molecule in close proximities to one another.

The synthetic sequence outlined in Scheme 1 produced the aromatic diketone **10** as a key intermediate leading to the $C_{56}H_{40}$ hydrocarbon **16**. Cyclopentadienone **1** was prepared in 70% yield from condensation between dimethyl acetonedicarboxylate and benzil followed by dehydration as reported previously.[6] Cycloaddition between **1** and 2,5-dihydrofuran (**2**) then gave the Diels−Alder adduct **3** as a mixture of the *endo*/*exo* (14:1) isomers. Treatment of **3** with water to induce decarbonylation then

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[†] Dedicated to Professor William R. Moore on the occasion of his 80th birthday.

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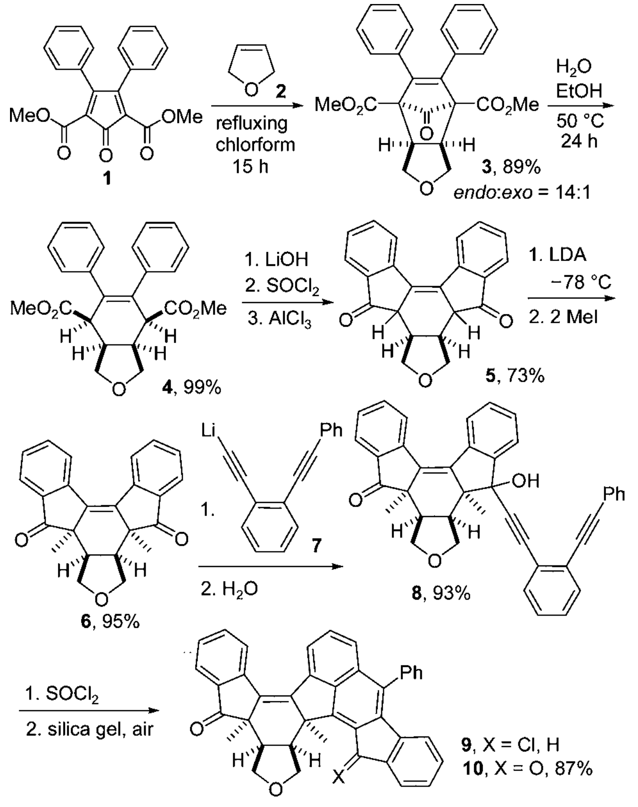
Scheme 1



led to diester **4**. The structures of **3** and **4** were established by X-ray structure analyses. Saponification of **4** to produce the corresponding diacid followed by transformation to the diacid chloride with thionyl chloride for the $AlCl_3$-catalyzed intramolecular Friedel−Crafts acylation reactions then furnished diketone **5**. Dimethylation from the less hindered side opposite to tetrahydrofuran ring then furnished diketone **6**. Condensation of **6** with one equiv of lithium acetylide **7** produced propargylic alcohol **8**. Treatment of **8** with thionyl chloride promoted a cascade sequence of reactions leading to **9** as reported previously.[5] Air oxidation of **9** then furnished diketone **10** in 87% overall yield from **8**. The structure of **10** was established by X-ray structure analysis.

The cleavage of the tetrahydrofuran ring in **10** with Me_3SiI[7] produced diiodide **11** (Scheme 2). The structure of **11** was established by X-ray structure analysis. Condensation of **11** with one equiv of **7** was selective in producing propargylic alcohol **12**, which on exposure to $SOCl_2$ followed by oxidation with MnO_2 then furnished diketone **13**. In addition, chloride **14**, presumably derived from a [2 + 2] cycloaddition reaction of the in situ generated benzannulated enyne-allene,[8] was also isolated. The structures of **13** and **14** were established by X-ray structure analyses. Attempts to promote the intramolecular Barbier reactions of **13** with SmI_2 were unsuccessful.[9] However, treatment of **13** with diiododisilane in the presence of hydrogen iodide[10] to reduce the keto groups was successful with concomitant reduction of the central carbon−carbon double bond to give **15**. The newly formed C−H bonds on the central cyclohexyl ring in **15** are *cis* to the methyl groups as indicated by the NOE measurements. The methylene hydrogens on the five-membered rings of the benzofluorenyl substructures are relatively acidic, making the corresponding carbanions readily accessible. Treatment of **15** with sodium *t*-butoxide, prepared from sodium hydride in mineral oil and *t*-butyl alcohol, was successful in promoting the intramolecular alkylation reactions, giving rise to the $C_{56}H_{40}$ hydrocarbon **16**.

The final alkylation steps appeared to be sensitive to the reaction conditions. Removing the mineral oil from NaH by washing with hexanes prior to using it to prepare sodium *t*-butoxide for the intramolecular alkylation reactions produced a more complex mixture with several unidentified products. Attempts to remove mineral oil from **16** by silica gel column chromatography also resulted in the formation of a more complex mixture perhaps due in part to epimerization of the C1/C6 stereogenic centers. However, a rapid filtration through a silica gel column to give **16** along with the mineral oil appeared to produce the cleanest product. Because of the presence of mineral oil, the yield of **16** was determined by adding a known amount of methylene chloride as an internal standard to **16** and the proton NMR signal of methylene chloride at δ 5.30 and the signal of **16** at δ 6.34 were integrated.

The structure of **16** was elucidated by ^1H and ^{13}C NMR spectroscopy and high-resolution MS. A complete assignment of the ^1H NMR and ^{13}C signals of **16** was made on the basis of the applications of several two-dimensional experiments. The hydrogen connectivities were established from the COSY and 1D/2D TOCSY spectra. The *cis* relationship between the hydrogens on the five-membered rings and the hydrogens and the methyl groups on the central cyclohexyl ring was determined by NOE experiments. These NMR data are included in the Supporting Information.

The ^1H NMR spectrum of **16** indicates that it is unsymmetrical and adopts a skewed conformation. In addition to two distinct methyl signals, ten different aliphatic hydrogen signals could be discerned, indicating a slow rate of racemization on the NMR time scale. Furthermore, the signal of the aromatic hydrogen on C23 is shifted upfield to δ 3.98, and the *endo* and *exo* hydrogens on C5 are shifted upfield to δ −3.32 and 0.29, respectively. These observations could be attributed to the adoption of a twist-boat conformation by the central cyclohexyl ring with C4 and C21 holding the flagpole C−C bonds as shown in the structure optimized by MM2 calculations (Figure 1). The twist motion involves moving C38 and C39 up and C3 and C20 down, causing the two benzofluorenyl substructures to approach each other and providing significant magnetic shieldings for

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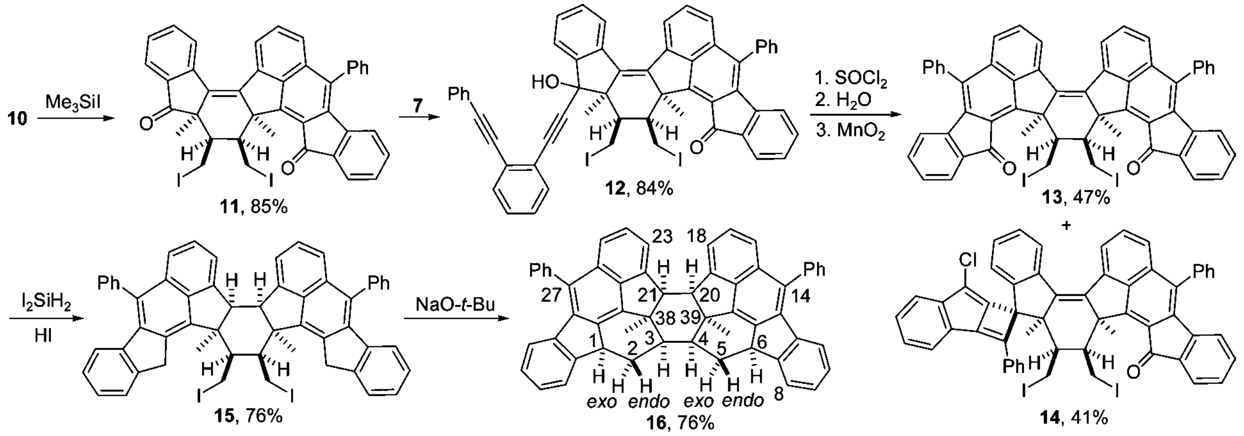
Scheme 2



the upfield-shifted hydrogens. The directions of the twist motion could also cause the C−H bond on C3 to become essentially orthogonal to the C−H bond of the *endo* hydrogen on C2, consistent with the observation that the vicinal coupling between them is negligible. Heating the sample in $CDCl_3$ at 50 °C did not appear to cause line broadening or coalescence of the signals, indicating the conformation is relatively stable on the NMR time scale.

Because of nonbonded steric interactions, the two phenyl substituents are orientated roughly perpendicular to the benzofluorenyl substructures, and the rate of rotation of the phenyl substituent on C27 is relatively slow on the NMR time scale as observed previously in a related structure.[11] The signal at δ 5.45 is attributable to the *ortho* hydrogen of the phenyl substituent on C27 pointing inward toward the endohedral side of the molecule. A significant NOE was observed between this *ortho* hydrogen and the aromatic hydrogen on C8, indicating that they are in close proximity to each other, although they are located on opposite sides of the structure. This observation further supports the twist-boat conformation of the central cyclohexyl ring, which could bring these two aromatic hydrogens in close proximity to each other.

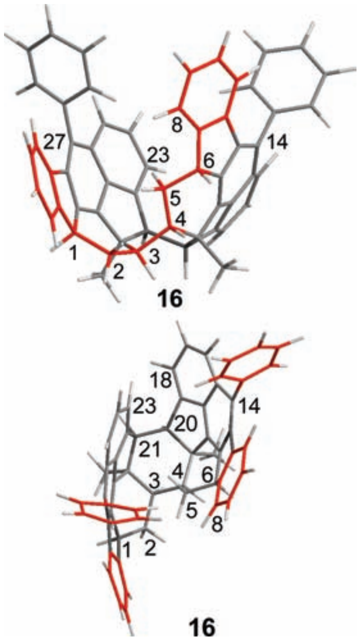


Figure 1. MM2-optimized structure of **16** viewing from two different perspectives.

The structure of **16** has a 54-carbon framework represented on the surface of C_{60}, missing only three two-carbon fragments. Diketone **5** provides 22 carbons of the 54-carbon framework, while the remaining 32 carbons come from two molecules of acetylene **7**. The presence of multiple sp^3 carbons in **15** makes it possible to move the iodo-bearing C2 and C5 close to C1 and C6 on the five-membered rings, respectively. As a result, the intramolecular alkylation reactions to connect C1 with C2 and C6 with C5 occurred readily, giving rise to **16** in good yield. The structure of **16** has a 30-carbon core, which can be regarded as a partially hydrogenated [5,5]circulene, a $C_{30}H_{12}$ semibuckminsterfullerene,[12] with only the carbon−carbon bond between C18 and C23 remaining unconnected. The presence of 10 sp^3 carbons in the 30-carbon core appears to relieve substantial strain of the fully aromatized [5,5]circulene.

The convergent nature of the synthetic sequence could allow placement of bromo substituents at various positions of the aromatic ring system of **16** by using brominated precursors. The Pd-catalyzed intramolecular arylation reaction for carbon−carbon bond formation could allow further connections of the carbon atoms in **16**.[4,13] The methyl groups on carbons 38 and 39 could also be replaced

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by other substituents to facilitate the final aromatization process.

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Supporting Information Available: All experimental procedures, NMR spectra, MS, and X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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