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Fullerene-like Chemistry at the Interior Carbon Atoms of an Alkene-Centered $C_{26}H_{12}$ Geodesic Polyarene[1]

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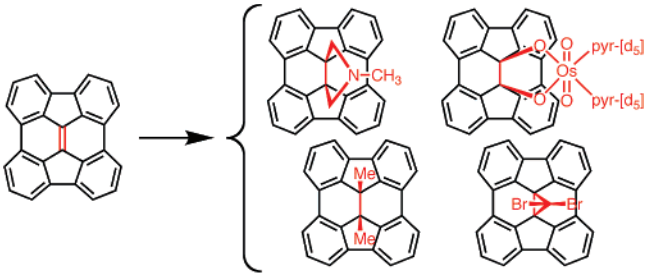

The title compound (**1**) undergoes 1,2-addition reactions of both electrophilic and nucleophilic reagents preferentially at the “interior” carbon atoms of the central 6:6-bond to give fullerene-type adducts **2**, **3**, **4**, and **5**. Such fullerene-like chemistry is unprecedented for a topologically 2-dimensional polycyclic aromatic hydrocarbon and qualifies this geodesic polyarene as a “bridge” between the old flat world of polycyclic aromatic hydrocarbons (PAHs) and the new round world of fullerenes. The relief of pyramidalization strain, as in the addition reactions of fullerenes, presumably contributes to the atypical mode of reactivity seen in **1**. Molecular orbital calculations, however, reveal features of the nonalternant π system in **1** that may also play an important role. Thus, the fullerene-like chemistry of **1** may be driven by two or more factors, the relative importances of which are difficult to discern.

Introduction

From the vast chemical literature on polycyclic aromatic hydrocarbons (PAHs), spanning more than 150 years,[2] there has emerged a paradigm that compounds of this class typically exhibit “edge chemistry”, i.e., their chemical reactions lead to the formation of new covalent bonds at carbon atoms located on the outer perimeter of the PAH and never at “interior” carbon atoms (trigonal carbon atoms shared by three rings).[3] Fullerenes such as C_{60}, on the other hand, have no edges, so any covalent attachment of appendages to the ball necessarily entail the formation of new bonds at interior carbon atoms, regardless of whether the reaction partner is an electrophile, a nucleophile, a radical, a carbene, a simple cycloaddition partner, or some other reagent.[4] With respect to chemical behavior, then, a marked distinction exists between topologically two-dimensional PAHs and the closed polyhedral fullerenes.

Intrigued by the apparent orthogonality of these two paradigms, we became interested some years ago in the $C_{26}H_{12}$ PAH **1** (diindeno[1,2,3,4-*defg*;1′,2′,3′,4′-*mnop*]chrysene), a fullerene subunit with a central 6:6-bond (Figure 1). This “open” geodesic polyarene shares structural features with both the topologically

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(1) Portions of these results have been reported previously in preliminary form: (a) Bronstein, H. E.; Scott, L. T. presented at the Fifth North American Chemical Congress, Cancun, Mexico, Nov 1997, abstract no. 282. (b) Baum, R. M. Science/Technology Highlights. *Chem. Eng. News* **1997**, *Dec 1*, 28. (c) Scott, L. T.; Bronstein, H. E.; Preda, D. V.; Ansems, R. B. M.; Bratcher, M. S.; Hagen, S. *Pure Appl. Chem.* **1999**, *71*, 209−219. (d) Bronstein, H. E. Ph.D. Dissertation, Boston College, 1999.

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(3) The carbon atoms of PAHs can be classified as either “interior” or “rim” carbon atoms. “Interior” carbon atoms are shared by three rings, whereas “rim” carbon atoms always belong to either one ring (methine) or two rings (quaternary) but not three.

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10.1021/jo7018224 CCC: $40.75

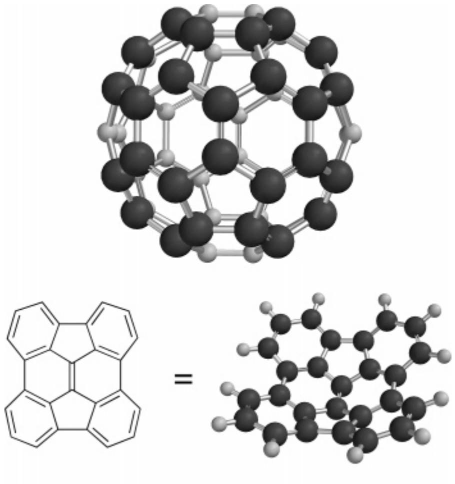

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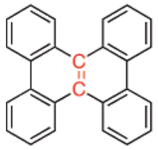
FIGURE 1. Top: Fullerene-C_{60}, showing a 6:6-bond in the center and all the rings attached to it darkened. Bottom: The alkene-centered $C_{26}H_{12}$ fullerene fragment **1** (diindeno[1,2,3,4-*defg*:1′,2′,3′,4′-*mnop*]-chrysene) derived by formal removal of all the unhighlighted atoms in the C_{60} model.

two-dimensional PAHs and the closed polyhedral fullerenes, which led us to speculate that it might exhibit fullerene-like chemistry at the pyramidalized interior carbon atoms of its central 6:6-bond. To pursue this prospect, we found it necessary first to develop a practical synthesis of **1**, the details of which have been published.[5,6] With usable quantities of material available, we then systematically examined the chemistry of **1** and were rewarded with evidence that our hypothesis was correct. Herein we report details on four distinct fullerene-like addition reactions at the interior carbon atoms of **1** (Figure 2).

We are unaware of any instances that predate these findings,[1] other than with fullerenes, in which external reagents permanently destroy the cyclic conjugation in one or more benzene rings by forming new covalent bonds to interior carbon atoms of a polycyclic aromatic hydrocarbon. The closest examples we can find involve chemistry at the highlighted bonds in hydrocarbons **6**, **7**, and **8**. The twisted central double bond of dibenzo-[*g*,*p*]chrysene (**6**) undergoes addition reactions (e.g., *cis*-dihydroxylation with osmium tetroxide);[7] however, the quaternary carbon atoms at which the new covalent bonds are formed (highlighted) lie on the rim of the polycyclic π system, not at interior positions.[3] In the two $C_{16}H_{10}$ hydrocarbons **7** and **8**, the central double bonds also react with external reagents,[8,9] and these atoms (highlighted) do occupy interior positions. Reactions that saturate the central double bonds in these molecules, however, do not destroy the cyclic conjugation of any benzene rings, and they leave the aromaticity of the [14]-annulene perimeters intact. The $C_{26}H_{12}$ geodesic polyarene **1**, therefore, represents the first topologically two-dimensional PAH to exhibit genuine fullerene-like chemical reactivity. Subsequent to our initial observations of these addition reactions of **1**, fullerene-like chemistry was also observed in our laboratory at the interior carbon atoms (highlighted below) of corannulene (**9**)[1c,10] and circumtrindene (**10**).[1c,11]



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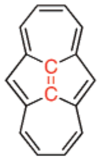

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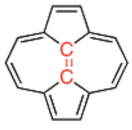

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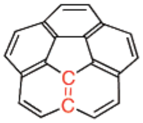

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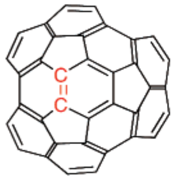

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Results

[3+2] Cycloaddition to 1. The [3+2] cycloaddition of azomethine ylides has gained favor over the years as one of the most reliable and versatile methods available for the irreversible functionalization of fullerenes.[4,12] Under essentially neutral reaction conditions, highly reactive azomethine ylides can be generated and trapped by fullerenes to give stable adducts in high yield. In keeping with other 1,2-additions to fullerenes,[4] these cycloadditions invariably occur at 6:6-bonds.

In a completely analogous manner, the azomethine ylide generated in situ by the reaction of *N*-methylglycine with paraformaldehyde adds to the pyramidalized interior carbon atoms of the $C_{26}H_{12}$ geodesic polyarene **1** to give the corresponding cycloadduct (**2**) in 79% isolated yield. As with fullerenes, the reaction occurs preferentially at the most pyramidalized 6:6-bond.[13] It is interesting to note that this reaction requires only 1 h at 80 °C, whereas the corresponding reactions with C_{60} and higher fullerenes are generally run for longer periods of time and at higher temperatures.

As expected, the formation of pyrrolidine **2** from **1** causes an upfield shift in the ^{1}H NMR signals for all the hydrogen atoms around the perimeter of the ring system: δ 8.26 (d), 7.86 (d), 7.62 (dd) $\rightarrow$ δ 7.25 (d), 7.24 (d), 7.16 (dd). The simplicity of the ^{1}H NMR spectrum for **2** further indicates that pyramidal inversion of the nitrogen atom must be rapid at room temperature. Predictably, saturation of the interior carbon atoms of **1** as a result of the conversion to **2** also causes a sizable hypsochromic shift of the long wavelength maximum in the UV−vis absorption spectrum: 402 → 372 nm (yellow **1** → colorless **2**). In the mass spectrometer (70 eV electron impact ionization), the molecular ion of **2** fragments by a [3+2] cycloreversion to give back **1** (*m*/*z* 324) as the base peak.

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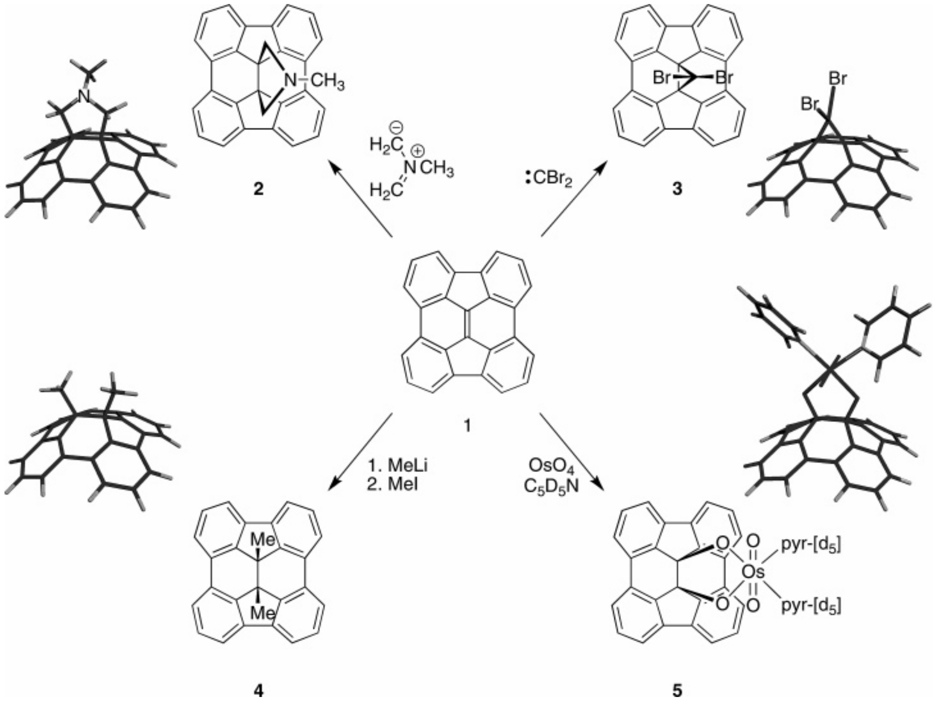


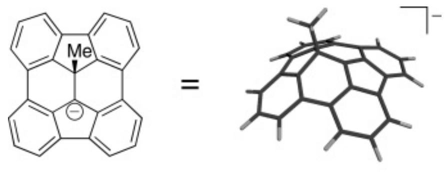
FIGURE 2. Fullerene-like chemistry at the pyramidalized interior carbon atoms of the alkene-centered $C_{26}H_{12}$ geodesic polyarene **1**.

Cyclopropanation of 1 with Dibromocarbene. Dihalocarbenes are also known to add to fullerenes at their 6:6-bonds[4,14] and have even been reported to add to the sidewalls of carbon nanotubes.[15] Hydrocarbon **1** likewise reacts with dibromocarbene at its central 6:6-bond to give the analogous cyclopropanated derivative (**3**). A two-phase system of bromoform in methylene chloride with concentrated aqueous sodium hydroxide and a phase transfer catalyst was used to generate the dibromocarbene in situ.[16]

Unlike the [3+2] cycloaddition above, this reaction proceeds very slowly. It could not be pushed to completion at room temperature even after many days with a large excess of bromoform, although yields in the range of 75−80% could eventually be achieved under these conditions. Like fullerenes,[4] hydrocarbon **1** appears to react more readily with electron-rich partners than with electrophilic reagents. The spectroscopic properties of **3** mirror those reported above for **2**.

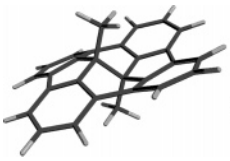
Nucleophilic Addition of Methyl Lithium to 1. The rapid additions of organolithium and Grignard reagents to fullerenes were discovered shortly after C_{60} and C_{70} first became available[17] and have been studied quite extensively since then.[4] Unless special precautions are exercised, C_{60} takes on multiple alkyl groups, and alkylation of the resulting polyanions with methyl iodide yields $C_{60}R_nMe_n$ ($n = 1−10$). Quenching of the monoanion obtained by the careful attachment of a single alkyl group to C_{60} gives the 1,2-addition product at a 6:6-bond.[4,17,18]

With the fullerene fragment **1**, overalkylation presents no problem. The green color of anion **11** appears almost immediately when **1** is stirred with an excess of methyllithium in benzene, and quenching with methyl iodide gives the 1,2-addition product **4**.



11 **11**

In this reaction, stereochemistry becomes an issue, because the atoms being attached to the interior carbon atoms of **1** come from independent sources. If methyl iodide were to approach the anion from the side opposite that to which the first methyl group is attached, the trans isomer **12** could be formed. In fact, calculations at the B3LYP/6-31G(d) level of theory[19] actually predict a 1.9 kcal/mol lower heat of formation for the trans isomer (**12**) than for the cis (**4**).



12 (*trans* isomer of **4**)

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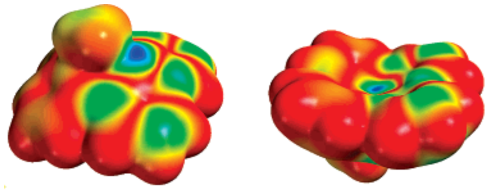
(19) Density functional calculations were performed with Spartan '02 for Linux software (Wavefunction, Inc.: Irvine, CA 92612).


11
convex

11
concave

FIGURE 3. Anion **11** derived from MeLi addition to the $C_{26}H_{12}$ geodesic polyarene **1** (global energy minimum at the B3LYP/6-31G* level of theory). The HOMO mapped onto the van der Waals surface of **11** exhibits a larger coefficient on the convex surface than on the concave surface (blue = largest coefficient; red = smallest).

Product stability, however, would not dictate the stereochemical course of a kinetically controlled reaction such as this one, which is almost certainly irreversible under the reaction conditions. The greater congestion on the concave face undoubtedly impedes alkylation of the anionic center from that direction to some extent. Furthermore, molecular orbital calculations on anion **11**[19] show a significantly larger coefficient for the highest occupied molecular orbital (HOMO) on the convex face than on the concave face (Figure 3). Thus, steric and electronic factors *both* favor the approach of methyl iodide from the convex face and preferential formation of the cis isomer (**4**).

The spectroscopic data also point to a cis disposition of methyl groups, as depicted in **4**. Most notably, the long wavelength maximum in the UV−vis absorption spectrum of the dimethyl compound matches perfectly that of the *syn* [3+2] cycloadduct **2** (both 372 nm). The ^1H NMR chemical shifts of the hydrogen atoms around the perimeters of these two compounds also all match very closely (average difference = 0.08 ppm, see the Experimental Section). Finally, the ^1H NMR chemical shifts measured experimentally for the hydrogen atoms around the perimeter of the dimethyl compound match very closely the values calculated by the GIAO method (B3LYP/6-31G**)[19] for the cis isomer (average absolute difference = 0.18 ppm), whereas the values calculated for the trans isomer differ from the experimental values by 1.14 ppm (average absolute difference). Consequently, although not rigorously proven, the cis stereochemical assignment for **4** seems reasonably secure.

Addition of Osmium Tetroxide to 1. The X-ray crystal structure that first confirmed the soccer ball connectivity of C_{60} was obtained on an osmate ester of C_{60}, stabilized by two *tert*-butylpyridine ligands.[20] Osmium tetroxide additions were also used to demonstrate that the relative reactivity of nonequivalent 6:6-bonds on higher fullerenes depends on the degrees of pyramidalization at the two carbon atoms of the 6:6-bond and not on relative π bond orders or bond lengths.[21] Treatment of the geodesic polyarene **1** with OsO_4 at room temperature in pyridine likewise gives the osmate ester formed by addition to the 6:6-bond between the two most pyramidalized carbon atoms (**5**).

Unlike the other addition products of **1**, this one proved to be rather labile. Coordination of the osmium by pyridine seems to be beneficial, so the addition reaction was conducted in pyridine. A clean ^1H NMR spectrum and a FAB mass spectrum provide convincing evidence for the structural assignment of **5**, but the instability of the compound precluded acquisition of a ^{13}C NMR spectrum and a precise mass measurement.

Discussion

Why does this geodesic polyarene (**1**) exhibit fullerene-like addition reactions at interior carbon atoms whereas planar PAHs do not? We believe that two distinct features of this unusual, topologically 2-dimensional π-system contribute to its unprecedented mode of reactivity. One is the relief of pyramidalization strain, a feature that all four addition reactions share in common with those of their 3-dimensional counterparts, the fullerenes. Superimposed on that, however, the intrinsic electronic properties of the nonalternant polycyclic π-system in **1** probably also play an important role.

Relief of Pyramidalization Strain. The conversion of two strongly pyramidalized tricoordinated carbon atoms to tetracoordinated carbon atoms (nominally, $sp^2 \rightarrow sp^3$) by 1,2-addition to a 6:6-bond on C_{60} has been estimated to relieve approximately 16 kcal/mol of "local" strain energy.[22] Such a relief of strain attends all addition reactions to 6:6-bonds on fullerenes but would be absent in addition reactions to the interior C═C bonds of planar π-systems. Furthermore, addition reactions such as osmylation of C_{60} (cf **5**) are estimated to relieve *an additional* 23 kcal/mol of "global" strain energy in the remaining 58 carbon atoms.[22a] This tremendous overall relief of pyramidalization strain was recognized quite early as the primary reason why fullerenes exhibit addition chemistry at interior C═C bonds whereas planar PAHs do not.[22a]

In hydrocarbon **1**, the pyramidalization of the central carbon atoms (POAV angle 8.1°)[23] approaches 70% of that of the carbon atoms of C_{60} (POAV angle 11.6°).[24] Consequently, a significant relief of "local" pyramidalization strain would be expected for all of the addition reactions we observed (Figure 1). A relief of pyramidalization strain at the four carbon atoms attached to the central 6:6-bond in **1** would also be expected, although the magnitude of this effect is undoubtedly smaller than that resulting from the relief of "global" strain energy in C_{60}.

Addition reactions to 6:6-bonds on fullerenes permanently destroy the cyclic conjugation of electrons around two 6-membered rings. This change would be expected to reduce the overall "aromaticity" of the molecule, thereby imposing an energetic penalty that diminishes to some extent the benefits of pyramidalization strain relief. For π-systems as large as that of C_{60}, however, the energetic consequences of losing two imbedded benzene rings is relatively small. For the π-system of **1**, the energetic price of sacrificing the aromaticity of the two central benzene rings should be somewhat larger, but it apparently does not outweigh the overall energy benefits of the addition

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[20] Hawkins, J. M.; Meyer, A.; Lewis, T. A.; Loren, S.; Hollander, F. J. *Science* **1991**, *252*, 312−313.

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[23] The X-ray crystal structure of **1** has been reported in ref 5a. Unfortunately, disorder in the crystal resulting from the nearly square geometry of **1** precludes an experimental determination of the exact POAV angles in **1**. The value quoted here for the POAV angle in **1**, therefore, was taken from a geometry optimization calculated at the B3LYP/6-31G* level of theory.[19] Calculations at this level of theory have been shown to faithfully reproduce the geometric parameters derived from X-ray structure determinations on other geodesic polyarenes: Petrukhina, M. A.; Andreini, K. W.; Mack, J.; Scott, L. T. *J. Org. Chem.* **2005**, *70*, 5713−5716.

[24] For a discussion of the POAV angle as a measure of carbon atom pyramidalization, see: (a) Haddon, R. C.; Scott, L. T. *Pure Appl. Chem.* **1986**, *58*, 137−142. (b) Haddon, R. C. *J. Am. Chem. Soc.* **1987**, *109*, 1676−1685. (c) Haddon, R. C. *J. Am. Chem. Soc.* **1990**, *112*, 3385−3389 [Erratum: *J. Am. Chem. Soc.* **1990**, *112*, 8217].

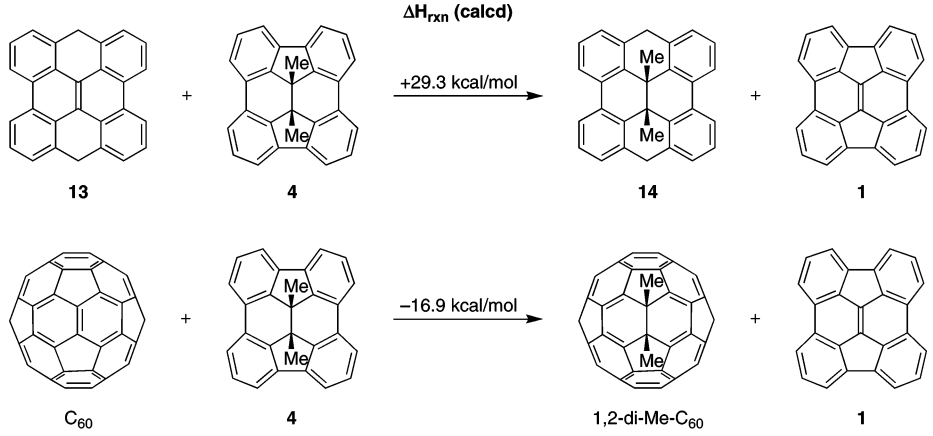

FIGURE 4. Homodesmic reaction energies calculated at the B3LYP/6-31G* level of theory.

reactions. Mestres et al. have analyzed the chemistry of polyarene **1** computationally and have reached the same conclusion.[25]

To obtain an estimate for the relative energetic consequences of 1,2-additions at the 6:6-bond of **1** and the corresponding additions to an unstrained, planar counterpart, we carried out DFT calculations (B3LYP/6-31G*)[19] for the homodesmic reaction pictured on the top line in Figure 4. As the reference compound, hydrocarbon **13** was chosen instead of **6** in order to eliminate all steric destabilization of the reference starting material. At this level of theory, 1,2-addition to the central 6:6-bond of **1** is favored relative to that of **13** by 29.3 kcal/mol. Thus, the relief of strain associated with 1,2-addition to the central 6:6-bond of **1** is quite substantial, on the order of 30 kcal/mol. Some fraction of this relief of strain energy presumably shows up even in the transition states for these additions and contributes to a lowering of the activation energies.

The same level of theory reveals that the relief of strain associated with 1,2-addition to the central 6:6-bond of **1**, though substantial, is not as great as that for addition to C_{60} (Figure 4, bottom). The combined relief of "local" and "global" strain energy resulting from 1,2-addition to C_{60} exceeds that resulting from 1,2-addition to **1** by another 16.9 kcal/mol.

Overall, theory predicts that the 6:6-bond of **1** should resemble the 6:6-bond of C_{60} more closely than it does the π-system of a planar PAH, and our experiments confirm that conclusion.

Additional Electronic Factors. Mapping the coefficients of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of **1** onto the van der Waals surface of the molecule reveals that both frontier orbitals are concentrated on the central 6:6-bond (Figure 5, top).[26] Interestingly, these frontier orbital patterns persist even when the molecule is constrained to adopt a planar geometry (Figure 5, bottom). Thus, the intrinsic electronic characteristics of the nonalternant π-system of **1** predict that the central 6:6-bond would be the kinetically preferred site for attack by both electrophilic and nucleophilic reagents, *even in the absence of carbon atom pyramidalization!*

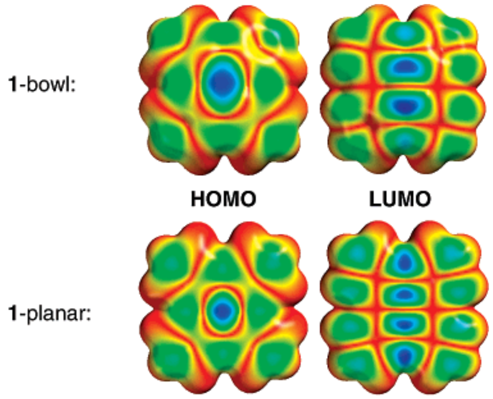

FIGURE 5. Frontier molecular orbital maps on the van der Waals surface of the title compound **1**, calculated at the B3LYP/6-31G* level of theory (blue = largest coefficient; red = node). Top: Natural bowl-shaped geometry. Bottom: Artificially enforced planar geometry.

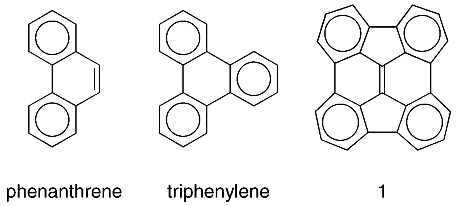

FIGURE 6. Clar representations of phenanthrene, triphenylene, and the title compound **1**, showing the closed aromatic sextets.

Application of the Clar model[2c] to hydrocarbon **1** leads to the same conclusion. In the Clar model, the reactivities of PAHs are predicted by focusing on the valence bond representations that maximize the numbers of closed aromatic sextets. Any double bonds left out of the closed aromatic sextets constitute sites of greater reactivity. The Clar representations of phenanthrene and triphenylene shown in Figure 6, for example, successfully predict the "olefinic reactivity" of the 9,10-bond in phenanthrene and the benzene-like character of triphenylene.[27] The Clar representation of C_{60} ascribes closed aromatic sextets to a maximum of eight benzene rings, leaving six double bonds as localized olefins, and this valence bond picture has been cited as an explanation for the "olefinic reactivity" of C_{60}.[28] In the Clar representations of **1** (Figure 6), the central 6:6-bond stands

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[25] (a) Sola, M.; Mestres, J.; Duran, M. *J. Phys. Chem.* **1995**, *99*, 10752−10758. (b) Mestres, J.; Sola, M. *J. Org. Chem.* **1998**, *63*, 7556−7558.

[26] The HOMOs and LUMOs in Figure 4 were calculated at the B3LYP/6-31G(d) level of theory.[19]

[27] For a more detailed discussion of the Clar model and its application to the reactivity patterns of carbon nanotubes, see the following very recent paper: Ormsby, J. L.; King, B. T. *J. Org. Chem.* **2007**, *72*, 4035−4038.

[28] El-Basil, S. *THEOCHEM* **2000**, *531*, 9−21.

out as the only segment of the overall π-system that is not tied up in a closed aromatic sextet. Accordingly, the Clar model predicts greatest reactivity at the central 6:6-bond in **1**, just as we observe.

This inherent reactivity pattern of the nonalternant π-system reinforces the tendency of **1** to relieve pyramidalization strain by adding external reagents in a 1,2-manner at the central 6:6-bond. The relative importance of the two factors, however, is not easy to resolve. It would be interesting to examine the behavior of planar PAHs that have HOMO and LUMO coefficients concentrated at their interior carbon atoms to see if they might also exhibit "fullerene-like chemistry".

Conclusion

The title compound (**1**) exhibits fullerene-like chemistry (Figure 2) that is unprecedented for a topologically 2-dimensional polycyclic aromatic hydrocarbon. Additions of both electrophilic and nucleophilic reagents occur preferentially at the "interior" carbon atoms of the central 6:6-bond to give fullerene-type adducts **2**, **3**, **4**, and **5**. As in the addition reactions of fullerenes, a relief of pyramidalization strain presumably accounts, at least in part, for this atypical mode of reactivity. Molecular orbital calculations reveal, however, that the specific network of 5- and 6-membered rings in **1** leads to a concentration of the HOMO and LUMO at the central 6:6-bond, even in the hypothetical planar conformation of **1** that totally lacks carbon atom pyramidalization. The electronic preference for 1,2-addition at the central 6:6-bond is independently predicted by the Clar "aromatic sextet" model. Thus, at least two factors drive **1** to behave chemically like a fullerene, and the relative importance of each is difficult to discern.

Experimental Section

General. Proton NMR chemical shifts are reported in ppm downfield from tetramethylsilane with tetramethylsilane (δ 0.00 ppm) as the reference standard. Carbon NMR shifts are reported in ppm downfield from tetramethylsilane with the NMR solvent as the reference standard (77.23 for $CDCl_3$, 39.51 for DMSO-d_6, and 29.92 for acetone-d_6).

12d,12e-(*N*-Methyl-3′,4′-pyrrolo)diindeno[1,2,3,4-*defg*:1′,2′,3′,4′-*mnop*]chrysene (2). To a suspension of 4.5 mg (14 μmol) of **1** in 5 mL of benzene were added 30 mg (0.34 mmol) of sarcosine (*N*-methylglycine) and 48 mg (1.6 mmol) of paraformaldehyde. The reaction mixture was brought to reflux for 2.5 h and was then diluted with 20 mL of benzene. The solution was washed with water (3 × 10 mL), dried over $MgSO_4$, and evaporated under reduced pressure. Preparative chromatography on silica gel with 5% ethyl acetate/hexanes as the eluant gave 4.2 mg (79%) of **2** as a white solid: mp >300 °C (begins to discolor at 210 °C); ^{1}H NMR (400 MHz, [d_6]-acetone) δ 7.38 (d, 4H, $J = 8.0$ Hz), 7.37 (d, 4H, $J = 7.2$ Hz), 7.20 (t, 4H, $J = 7.6$ Hz), 3.31 (s, 4H), 2.33 (s, 3H); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.25 (d, 4H, $J = 8.0$ Hz), 7.24 (d, 4H, $J = 7.2$ Hz), 7.16 (t, 4H, $J = 7.4$ Hz), 3.31 (s, 4 H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.9, 141.8, 130.3, 128.8, 121.0, 120.7, 77.4, 75.4, 41.5; UV ($CHCl_3$) λ_{max} (nm) (log ϵ) 372 (2.7), 338 (3.2), 322 (3.2), 292 sh (3.5), 268 (3.8), 246 (3.5), 242 sh (3.5); MS (EI, 70 eV) *m/z* (rel intensity) 381 (20, M^+), 324 (100, $[M - C_3H_7N]^+$); MS (CI, methane) *m/z* (rel intensity) 382 (100, $[M + H]^+$), 367 (3, $[M + H - CH_3]^+$), 353 (16, $[M + H - C_2H_5]^+$), 325 (70, $[M + H - C_3H_7N]^+$); HRMS (EI, 70 eV) calcd for $C_{29}H_{19}N$ (M^+) 381.1517, found 381.1516.

12d,12e-(Dibromomethano)-12d,12e-dihydrodiindeno[1,2,3,4-*defg*:1′,2′,3′,4′-*mnop*]chrysene (3). A suspension of 6.0 mg (19 μmol) of **1**, 80 μL (920 μmol) of bromoform, and a small amount (~10 mg) of tetrabutylammonium hydrogen sulfate in 3 mL of dichloromethane and 2 mL of 50% NaOH solution was stirred at room temperature for 11 days. The mixture was then diluted with dichloromethane, and the organic layer was washed successively with 10% HCl solution and water (2 × 15 mL each), dried over $MgSO_4$, and evaporated to dryness under reduced pressure. Analysis of the product thus obtained by ^{1}H NMR spectroscopy, using pyrene as an internal standard, revealed only **3** (79% yield) and unconsumed starting material (**1**). Repeated chromatography on silica gel and alumina failed to separate the product from the residual starting material. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, 4H, $J = 8.0$ Hz), 7.51 (d, 4H, $J = 7.2$ Hz), 7.37 (t, 4H, $J = 7.8$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 142.8, 133.4, 129.6, 124.7, 122.7, 122.1, 121.6, 94.6, 20.4 (extra aromatic signals from **1**); UV (CH_2Cl_2, from diode array detector of the HPLC) λ_{max} (nm) (A_{rel}) 398 sh (8.2), 364 (31), 290 sh (170), 278 (280), 262 (310), 254 (270); MS (EI, 70 eV) *m/z* (rel intensity) 498 (3, M^+, $2Br^{81}$), 496 (4, M^+, $Br^{79}Br^{81}$), 494 (3, M^+, $2Br^{79}$), 417 (10, $[M - Br]^+$, Br^{81}), 415 (10, $[M - Br]^+$, Br^{79}), 337 (23, $[M - Br_2]^+$), 324 (100, $[M - CBr_2]^+$); HRMS (EI, 70 eV) calcd for $C_{27}H_{12}Br_2$ (M^+) 493.9306, found 493.9298.

12d,12e-Dimethyl-12d,12e-dihydrodiindeno[1,2,3,4-*defg*:1′,2′,3′,4′-*mnop*]chrysene (4). Over a 5 min period at room temperature, 4.5 mL (3.2 mmol) of methyl lithium (0.7 M in diethyl ether) was added to a suspension of 10 mg (31 μmol) of **1** in 3 mL of benzene. The resulting green solution was stirred at room temperature for 1 h and then quenched slowly with approximately 1 mL of methyl iodide. After dilution with benzene the solution was washed with water (2 × 10 mL), dried over $MgSO_4$, and concentrated to dryness under reduced pressure. The product was purified by preparative chromatography on silica gel with hexanes as the eluant, to give 2.9 mg (27% yield) of **4** as a yellow solid: mp >300 °C (begins to discolor at 245 °C); ^{1}H NMR (400 MHz, [d_6]-acetone) δ 7.31 (d, 4H, $J = 7.6$ Hz), 7.26 (d, 4H, $J = 8.0$ Hz), 7.14 (dd, 4H, $J = 8.0$ and 7.2 Hz), 2.11 (s, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 161.9, 141.7, 130.4, 128.7, 121.5, 120.1, 95.0, 36.7; UV ($CHCl_3$) λ_{max} (nm) (log ϵ) 372 sh (2.86), 338 (3.78), 326 (3.73), 296 sh (4.05), 266 (4.32), 246 (4.13); MS (EI, 70 eV) *m/z* (rel intensity) 354 (28, M^+), 339 (100, $[M - CH_3]^+$), 324 (82, $[M - 2CH_3]^+$), 322 (25), 168 (41), 162 (39), 161 (36); HRMS (EI, 70 eV) calcd for $C_{28}H_{18}$ (M^+) 354.1409, found 354.1408.

Osmate Ester of 12d,12e-Dihydroxy-12d,12e-dihydrodiindeno[1,2,3,4-*defg*:1′,2′,3′,4′-*mnop*]chrysene (5). To a suspension of 6.0 mg (19 μmol) of **1** in 3 mL of [d_5]-pyridine was added 312 μL (24.9 μmol) of a 2.5% solution of OsO_4 in *tert*-butyl alcohol. The reaction mixture was stirred for approximately 18 h in the dark, diluted with ethyl ether, and then filtered to give 8.0 mg (59% yield) of relatively pure **5** as a brown solid. The instability of the product when dissolved in DMSO precluded the recording of a ^{13}C NMR spectrum. ^{1}H NMR (400 MHz, [d_6]-DMSO) δ 7.30 (d, 4H, $J = 7.6$ Hz), 7.25 (d, 4H, $J = 7.2$ Hz), 7.17 (dd, 4H, $J = 8.0$ and 7.2 Hz); MS (FAB+, BpV: 14.2 V in 3NBA) *m/z* (rel intensity) 750 (10, $[M + 1]^+$), 749 (14, $[M + 1]^+$), 748 (9, $[M + 1]^+$), 747 (12, $[M + 1]^+$), 746 (10, $[M + 1]^+$), 745 (8, $[M + 1]^+$), 666 (27, $[M - C_5D_5N + 1]^+$), 665 (100, $[M - C_5D_5N + 1]^+$), 664 (24, $[M - C_5D_5N + 1]^+$), 663 (44, $[M - C_5D_5N + 1]^+$), 662 (36, $[M - C_5D_5N + 1]^+$), 661 (27, $[M - C_5D_5N + 1]^+$).

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Supporting Information Available: NMR spectra of compounds **2**, **3**, **4**, and **5**, UV−vis spectra of compounds **2**, **3**, and **4**, and calculated DFT energies and *X*,*Y*,*Z*-coordinates for **1**, **4**, **11**, **12**, **13**, **14**, C_{60}, and 1,2-dimethyl-C_{60}. This material is available free of charge via the Internet at http://pubs.acs.org.

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