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Practical Synthesis of an Open Geodesic Polyarene with a Fullerene-type 6:6-Double Bond at the Center: Diindeno[1,2,3,4-*defg*;1′,2′,3′,4′-*mnop*]chrysene

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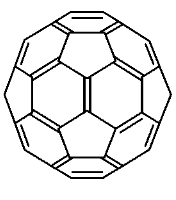
Abstract: Diindeno[1,2,3,4-*defg*;1′,2′,3′,4′-*mnop*]chrysene (**1**), the smallest possible alkene-centered C_{60} substructure with a curved π-system, is obtained in 25−35% yield by flash vacuum pyrolysis of the twisted 1,1′-dibromobifluorenylidene (**2**) on a 100 mg scale at 1050 °C. At 1200 °C, the bowl-shaped hydrocarbon **1** rearranges to the planar isomer diindeno[5,6,7,1-*defg*;5′,6′,7′,1′-*lmnop*]chrysene (**14**) by a double 5/6 ring-expansion/ring-contraction. X-ray crystallography establishes that the central carbon atoms of **1** are nearly 80% as pyramidalized as the carbon atoms of C_{60} (POAV angles = 9.0° and 11.6° for **1** and C_{60}, respectively). A four-step synthesis has been developed to prepare the pyrolysis precursor (**2**) as a mixture of (*E*)- and (*Z*)-isomers in 39% overall yield from commercially available 9-fluorenone-1-carboxylic acid (**10**).

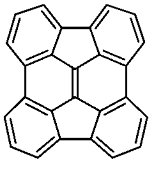
Introduction

For more than two decades, corannulene stood alone as the only known polycyclic aromatic hydrocarbon (PAH) with a curved π-surface.[1] The fortuitous discovery[2] that elemental carbon can exist as stable geodesic allotropes ("fullerenes"), however, stimulated the development of new synthetic methods that not only made corannulene suddenly more available[3] but also gave the chemical community access to numerous larger open geodesic polyarenes.[4] As the successes achieved by these methods continue to spread, it appears more and more likely that they will one day make possible the rational laboratory synthesis of closed geodesic polyarenes ("buckminsterfullerene" C_{60} and the higher fullerenes), carbon nanotubes, and related materials. Indeed, a 12-step, rational, chemical synthesis of C_{60} based on these methods was recently completed in our laboratory.[5]

Open geodesic polyarenes comprising networks of five- and six-membered rings that map onto the atomic framework of C_{60}, or onto that of a higher fullerene, have commonly been referred to as "fullerene fragments" or "buckybowls". Most of the compounds in this class that are known today contain a central five-membered ring, as in corannulene, or a central six-membered ring, as in circumtrindene,[6] and the great majority owe their curvature to the presence of one or more corannulene ring systems embedded within their structure. A notable exception to this paradigm is diindeno[1,2,3,4-*defg*;1′,2′,3′,4′-*mnop*]chrysene (**1**), a geodesic polyarene characterized by a central carbon−carbon double bond and by the conspicuous absence of corannulene moieties.[7]



C_{60}



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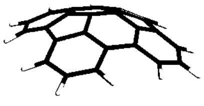

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A special appeal of hydrocarbon **1** derives from the close structural relationship between its central carbon−carbon double

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(1) (a) Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 380−381. (b) Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 1730−1745.

(2) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162−163.

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(4) Several reviews have been published: (a) Faust, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1429−1432. (b) Siegel, J. S.; Seiders, T. J. *Chem. Br.* **1995**, 313. (c) Rabideau, P. W.; Sygula, A. In *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; JAI Press: Greenwich, 1995; Vol. 3, pp 1−36. (d) Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235−242. (e) Scott, L. T. *Pure Appl. Chem.* **1996**, *68*, 291−300. (f) Mehta, G.; Rao, H. S. P. *Adv. Strain Org. Chem.* **1997**, *6*, 139−187. (g) Mehta, G.; Rao, H. S. P. *Tetrahedron* **1998**, *54*, 13325−13370. (h) 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.

(5) Scott, L. T.; Boorum, M. M.; McMahon, B. J.; Hagen, S.; Mack, J.; Blank, J.; Wegner, H.; de Meijere, A. *Science* **2002**, 1500−1502.

(6) (a) Scott, L. T.; Bratcher, M. S.; Hagen, S. *J. Am. Chem. Soc.* **1996**, *118*, 8743−8744. (b) Ansems, R. B. M.; Scott, L. T. *J. Am. Chem. Soc.* **2000**, *122*, 2719−2724.

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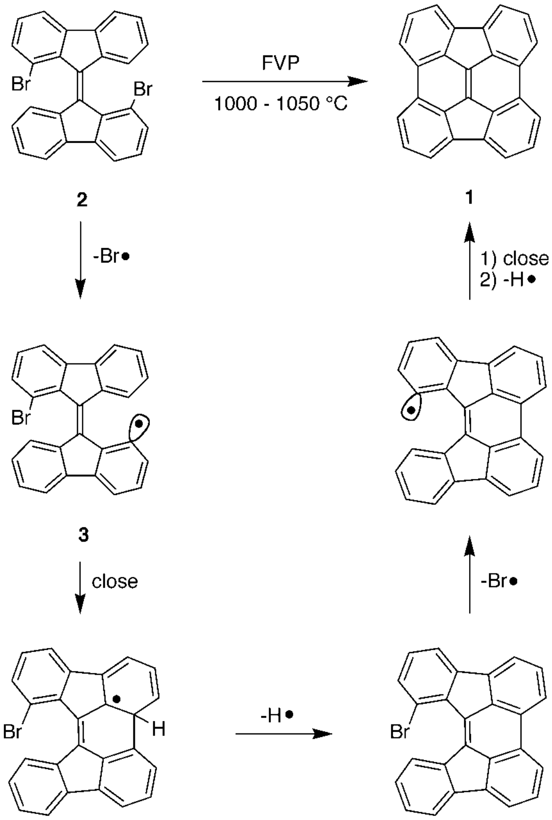
10.1021/ja0123148 CCC: $22.00

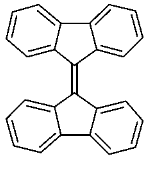
bond, which is shared by two fused six-membered rings at the point of greatest molecular curvature, and the so-called “6:6-bond” of C_{60}. Virtually all of the addition reactions on C_{60}, as well as those on the higher fullerenes, take place at 6:6-bonds,[8] so it seemed to us important to test for fullerene-like reactivity at the central 6:6-bond of **1**, the smallest possible alkene-centered fullerene fragment that is still curved. Because hydrocarbon **1** was unknown at the outset of this project, we began by developing the practical synthesis described here.

In our laboratory, the high temperatures attainable in flash vacuum pyrolysis (FVP) experiments have been used with considerable success to overcome the increase in strain energy associated with ring closure reactions that give bowl-shaped PAHs from less highly distorted molecular precursors.[3,4,6] Moreover, we have found that cyclizations initiated by aryl radicals generated thermally from homolytic dissociations of strategically placed halogen atoms[9] invariably proceed in higher yield, sometimes by as much as 2 orders of magnitude,[6] than cyclizations based on undirected cyclodehydrogenations of unfunctionalized hydrocarbons. An obvious application of this strategy to the synthesis of hydrocarbon **1** suggests 1,1′-dibromobifluorenylidene (**2**) as an attractive FVP precursor. Herein we report that FVP of **2** at 1000−1050 °C on a 100 mg scale does indeed produce **1** in 25−35% yield, presumably by the sequence of steps illustrated in Scheme 1.[10] An electrocyclic reaction followed by loss of HBr might be a reasonable alternative to the radical pathway for the first ring closure but seems improbable for the second cyclization.

Scheme 1



During the course of our work, several unsuccessful attempts by other groups to synthesize **1** or derivatives thereof were reported,[11−13] and the first marginally successful synthesis (0.3% overall yield) was achieved.[14] In the latter work, Hagen et al. managed to obtain tiny amounts of **1** through brute force cyclodehydrogenation of unfunctionalized bifluorenylidene (**4**), although the ring closures had to be conducted individually in two sequential pyrolyses. Initially, the pyrolysis of **4** gave no detectable **1** but only benz[*e*]indeno[1,2,3-*hi*]acephenanthrylene (**5**), the product of a single cyclodehydrogenation, in 51% yield, and dibenzo[*g*,*p*]chrysene (**6**, X = H), a rearrangement product,[15] in 11% yield. Relief of torsional strain at the central double bond of **4** presumably accounts for the uncharacteristically good yield in the first cyclodehydrogenation of **4** to **5**. By contrast, repyrolysis of purified **5** induced the second closure to give **1** in only 0.6% isolated yield. Pyrolysis of **6** (X = H) gave only benz[*g*]indeno[1,2,3,4-*mnop*]chrysene, the product of one closure, even when a Pt/SiO_2-catalyst was employed. Thus, Hagen and co-workers obtained just enough of the intriguing hydrocarbon **1** for characterization by ^{1}H NMR and mass spectrometry but had insufficient material to acquire a ^{13}C NMR spectrum or an X-ray crystal structure or to pursue any chemical investigations. The dramatic superiority of **2** over **4** as a FVP precursor to **1** serves as an excellent example of the advantages gained by the use of planned aryl radical cyclizations instead of undirected cyclodehydrogenations for the synthesis of strained geodesic polyarenes.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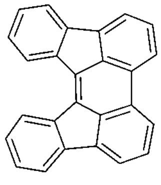
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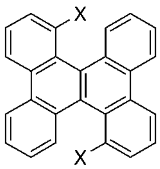

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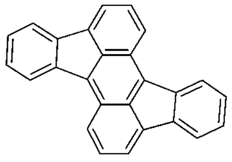
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As alternatives to **2**, we originally considered **6** (X = Br or Cl) and the 1,8-disubstituted isomers thereof as possible pyrolysis precursors to **1**. Compared to **2**, however, these crowded dibenzochrysenes appeared significantly more challenging to synthesize and were abandoned in favor of **2**. Nevertheless, we still believe that they would give **1** under FVP conditions.

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(8) For recent reviews of the fullerene field, see: (a) Hirsch, A. *Fullerenes and Related Structures*; Springer-Verlag: Berlin/Heidelberg, 1999. (b) Taylor, R. *Lecture Notes on Fullerene Chemistry: A Handbook for Chemists*; Imperial College Press: London, 1999.

(9) For the first application of this strategy, see: Bratcher, M. S.; Scott, L. T. *Abstracts of Papers*, 207th National Meeting of the American Chemical Society, San Diego, CA, March, 1994; abstr. no. ORGN 420. See also ref 4e and Plater, M. J. *Tetrahedron Lett.* **1994**, *35*, 6147−6150.

(10) Portions of this work have been reported previously in preliminary accounts: Bronstein, H. E.; Scott, L. T. *Abstracts of Papers*, Fifth Chemical Congress of North America, Cancun, Mexico, November 11−15, 1997; abstr. no. 282. See also refs 4e and 4h.

(11) Kuo, C.-H.; Tsau, M.-H.; Weng, D. T.-C.; Lee, G. H.; Peng, S.-M.; Luh, T.-Y.; Biedermann, P. U.; Agranat, I. *J. Org. Chem.* **1995**, *60*, 7380−7381.

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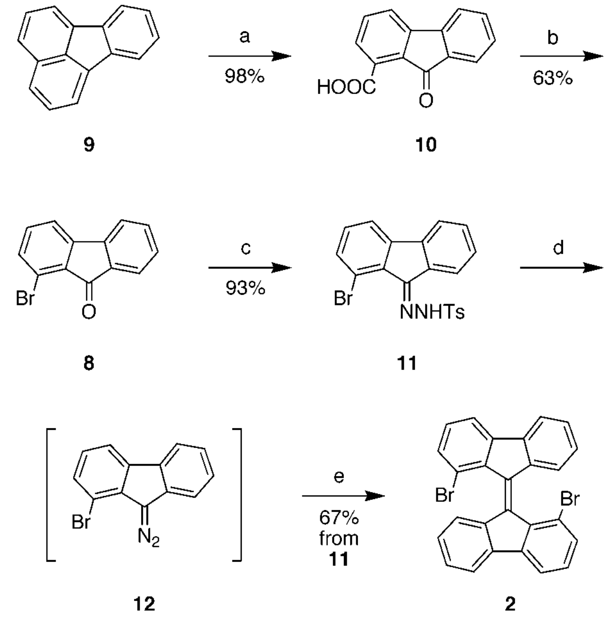
(14) Hagen, S.; Nuechter, U.; Nuechter, M.; Zimmermann, G. *Polycyclic Aromat. Compd.* **1995**, *4*, 209−217.

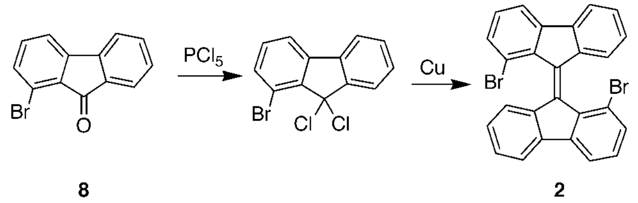
(15) Alder, R. W.; Whittaker, G. *J. Chem. Soc., Perkin Trans. 2* **1975**, 712−13.

Scheme 2 [a]



[a] (a) CrO_3, AcOH, H_2O; (b) HgO, Br_2, CCl_4, $h\nu$; (c) NH_2NHTs, HCl, $CH(OCH_3)_3$, CH_3OH; (d) $NaOCH_3$, pyridine; (e) CuBr, CH_2Cl_2.

Scheme 3



As a matter of historical perspective, it is interesting to note that the $C_{26}H_{12}$ structure (**1**) first appeared in the chemical literature in 1921 as the proposed molecular structure for "rubicene", a bright red hydrocarbon that had been known already at that time for nearly 50 years.[16] Later work, however, eventually established the correct molecular structure of rubicene to be **7**.[17]

Synthesis of 1,1′-Dibromobifluorenylidene (2). Scheme 2 summarizes our synthesis of 1,1′-dibromobifluorenylidene (**2**). The first intermediate on this route, 9-fluorenone-1-carboxylic acid (**10**), is commercially available but expensive. Fortunately, it can be synthesized easily and in large quantities by the oxidation of fluoranthene (**9**) with chromium oxide (98% yield on a 10 g scale).[18] Subsequent conversion to 1-bromo-9-fluorenone (**8**) was conveniently achieved in 63% yield by a Hunsdieker reaction.[19] We recommend this method over the multistep literature procedure for preparing **8** from **10** (24% overall yield),[20] which entails conversion of the acid to the corresponding amide, followed by a Hofmann rearrangement, diazotization of the resulting amino group, and decomposition of the diazonium salt with copper bromide.

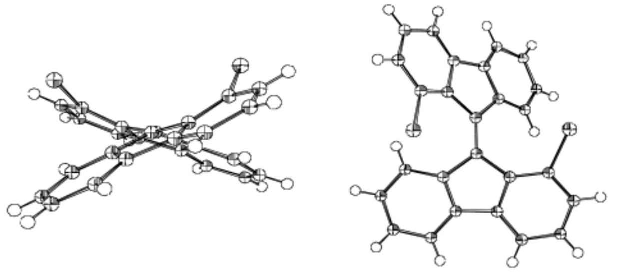


Figure 1. X-ray crystal structure of 1,1′-dibromobifluorenylidene (**2**).

The tosylhydrazone of 1-bromo-9-fluorenone (**11**) was prepared from **8** in 93% yield. Because this tosylhydrazone hydrolyzes back to the ketone very quickly in solution, trimethyl orthoformate was added to the reaction mixture to scavenge the H_2O formed. When the reaction is run in methanol, the starting ketone (**8**) dissolves, but the resulting tosylhydrazone (**11**) is insoluble and can easily be isolated by filtration. Treatment of the 1-bromo-9-fluorenone tosylhydrazone (**11**) with $NaOCH_3$ in dry pyridine[21] gave 1-bromo-9-diazofluorene (**12**), which was immediately decomposed with CuBr to give 1,1′-dibromobifluorenylidene (**2**) as a mixture of (*E*)- and (*Z*)-isomers in 39% overall yield from the commercially available **10**.

The obvious route to **2** by a McMurry coupling of **8**, unfortunately, was foiled by the intervention of reductive debromination as a serious side reaction. Wittig reactions and other coupling methods also failed.[22] We attempted to repeat the synthesis of **2** published in 1962 by Suzuki and Kajigaeshi (Scheme 3);[23] however, mass spectrometric analysis of the dimer we isolated revealed that a significant degree of Br/Cl exchange had occurred and that some molecules had suffered undesirable chlorination on the edge (presumably by the $CuCl_2$ formed during the coupling). Others have likewise reported difficulties in repeating this tricky synthesis.[24] We did have some success preparing **2** by coupling 1,9-dibromofluorene with KOH in DMSO, but the most practical route overall is the one summarized in Scheme 2.

Although the ^1H NMR spectrum of 1,1′-dibromobifluorenylidene (**2**) prepared as in Scheme 2 shows signals for both the cis and the trans isomer in solution, only the trans isomer is seen in the crystal used for X-ray structural analysis (Figure 1). The central double bond obviously suffers from considerable strain as a result of the twisting required to avoid steric hindrance of the bromine atoms. The average dihedral angle at the central double bond is 40°. An energy barrier of only 19−21 kcal/mol has been reported for cis/trans-isomerization in the structurally related 1,1′-dimethylbifluorenylidene,[25] so cis/trans-isomerization of **2** is probably fast on the time scale for its crystallization.

Preparation of the $C_{26}H_{12}$ Bowl (1) by FVP of 1,1′-Dibromobifluorenylidene (2). Scheme 1 shows the mechanism by which we believe 1,1′-dibromobifluorenylidene (**2**) goes to diindeno[1,2,3,4-*defg*;1′,2′,3′,4′-*mnop*]chrysene (**1**) under FVP conditions. The complete picture, however, is actually somewhat more complicated than that. The relatively free rotation around

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[16] (a) Dziewonski, K.; Suszko, J. *Rocz. Chem. I* **1921**, 347. (b) Dziewonski, K.; Suszko, J. *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* ⟨*A*⟩ **1921**, 72. (c) Fittig, R.; Ostermayer, E. *Justus Liebigs Ann. Chem.* **1873**, *166*, 373.

[17] Schlenk, W.; Karplus, M. *Chem. Ber.* **1928**, *61*, 1675.

[18] Modification of Fieser, L. F.; Seligman, A. M. *J. Am. Chem. Soc.* **1935**, *57*, 2174.

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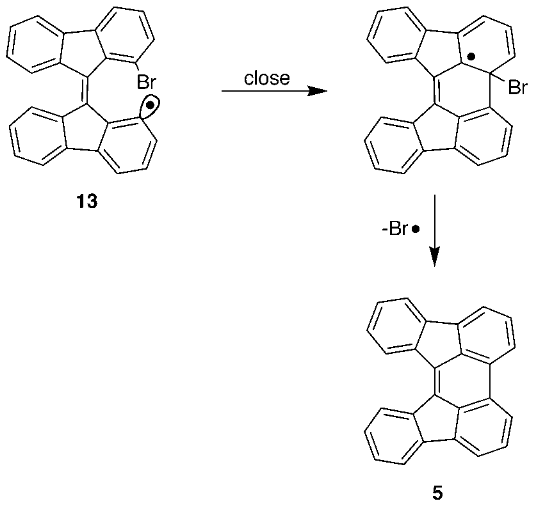
[23] Suzuki, K.; Kajigaeshi, S. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 408.

[24] Gosnay, I.; Bergmann, E. D.; Rabinovitz, M.; Agranat, I. *Isr. J. Chem.* **1972**, *10*, 423.

[25] Agranat, I.; Rabinovitz, M.; Weitzen-Dagan, A.; Gosnay, I. *J. Chem. Soc., Chem. Commun.* **1972**, 732.

Scheme 4



Scheme 5

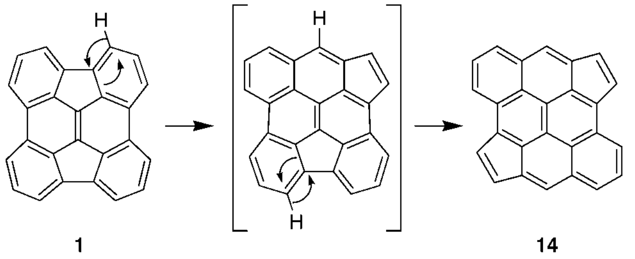


Table 1. Ratio of Products from the Pyrolysis of **2**

temperature (°C)	relative amounts^a		
	1	**5**	**14**
900	1	2	0
1000	3	2	0
1050	3	2	0
1075	2	3	0
1100	1	2	0
1200	1	2	3
1250	0	2	3

[a] Determined by integration of the ^{1}H NMR spectra of crude pyrolysate.

the central double bond in these bifluorenylidene derivatives at elevated temperatures allows rapid equilibration of radical **3** with its geometric isomer (**13**) during the pyrolysis. Radical **13** can then cyclize and subsequently re-aromatize by loss of the second bromine atom to give **5** as a byproduct (Scheme 4). Because PAH **5** does not undergo another closure readily, as Hagen and co-workers discovered,[14] it is not surprising that we also obtain **5** in 20−25% yield.

As summarized in Table 1, pyrolysis of **2** between 900 and 1100 °C produces varying ratios of **1**:**5**. The best yields of the bowl (**1**) are obtained in the temperature range 1000−1050 °C. Above 1100 °C, the material balance worsens, and diindeno-[5,6,7,1-*defg*;5′,6′,7′,1′-*lmnop*]chrysene (**14**), a secondary product from the rearrangement of **1**, begins to appear. The previously unknown **14** comes from a double 5/6 ring-expansion/ring-contraction of **1** (Scheme 5). Such rearrangements have been known for many years,[26] and all of the evidence points to a stepwise mechanism in which the H-shift precedes the C-bond shift.[27] This process allows the five-membered rings formally to “migrate” to the outer edges, thereby alleviating strain. High temperatures overcome the large energy barrier for formation of the strained target (**1**), but too much energy promotes the unwanted rearrangement.

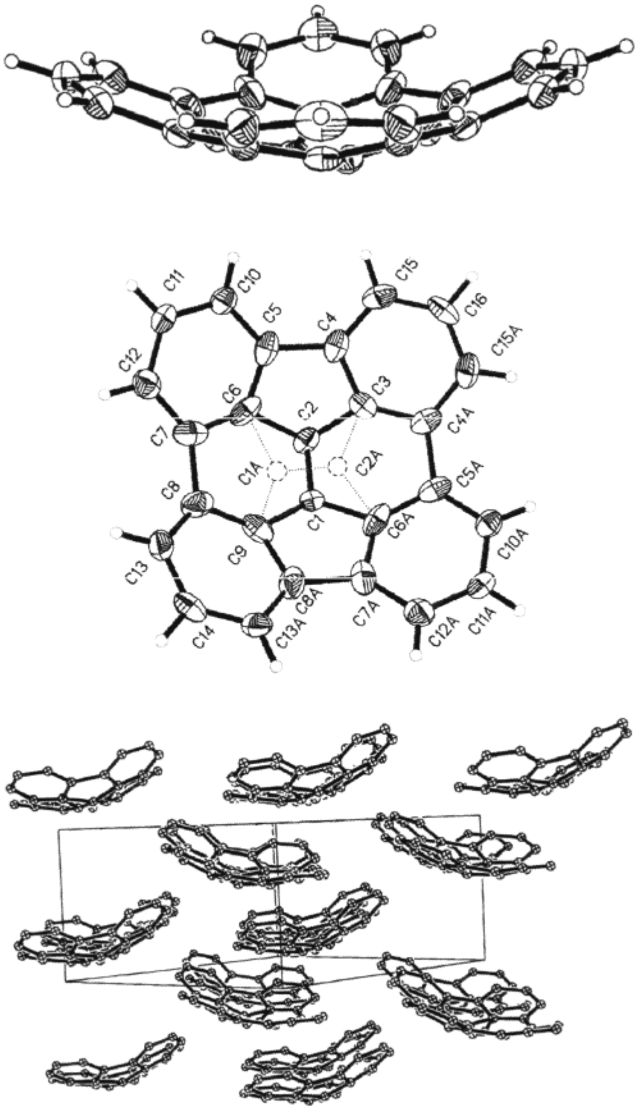


Figure 2. X-ray crystal structure of diindeno[1,2,3,4-*defg*;1′,2′,3′,4′-*mnop*]-chrysene (**1**).

Purification of **1** is made difficult by the similar and very limited solubilities of all of the pyrolysis products. The compounds exhibit strange chromatographic behavior and cannot be separated by fractional sublimation. The only successful separation of **1** from **5** that we have found takes advantage of the fact that the bowl-shaped hydrocarbon **1**, once removed from it neighbors, adheres to Al_2O_3 less strongly than does the planar **5**. In practice, the pyrolysate is adsorbed onto Al_2O_3 and placed at the top of a short Al_2O_3 chromatography column. The column is then eluted exhaustively with cyclohexane, a solvent in which neither solid **1** nor solid **5** seems at all soluble. Flushing the column with cyclohexane continuously over a period of several days gradually elutes **1** from the column, leaving **5** behind. More

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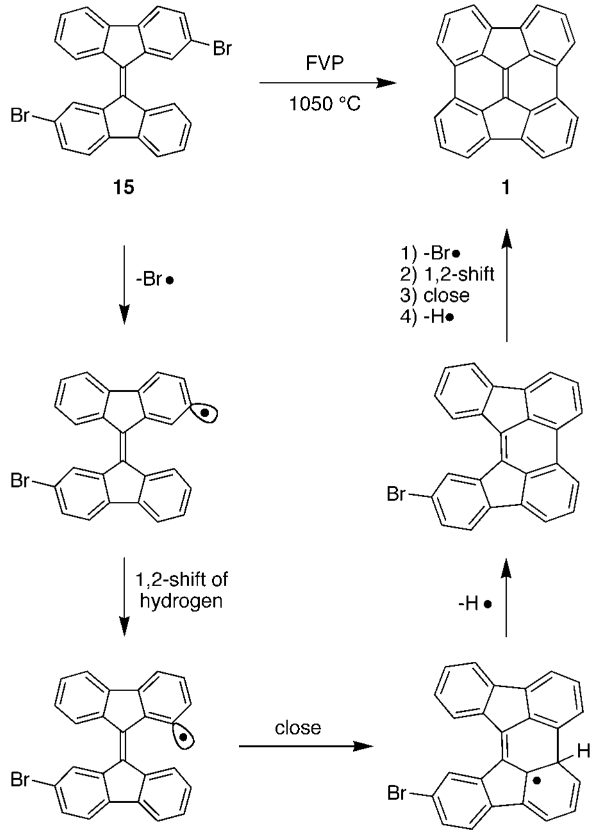
(26) (a) Scott, L. T.; Roelofs, N. H. *J. Am. Chem. Soc.* **1987**, *109*, 5461. (b) Scott, L. T.; Roelofs, N. H. *Tetrahedron Lett.* **1988**, *29*, 6857−6860. See also: Necula, A.; Scott, L. T. *J. Anal. Appl. Pyrolysis* **2000**, *54*, 65−87.

(27) Scott, L. T.; Hashemi, M. M.; Schultz, T. H.; Wallace, M. B. *J. Am. Chem. Soc.* **1991**, *113*, 9692−9693 and references therein.

Scheme 6



polar solvents cause **5** to coelute with **1**. Applying N_2 pressure does speed up the process, but not significantly. Despite the tedious chromatography, we have been able to isolate sufficient quantities of this unique, geodesic polyarene to begin studying its chemistry.[4h]

As expected, **1** is bowl-shaped (Figure 2). Interestingly, X-ray crystallography is not able to differentiate between the two bay regions. Stated another way, it is not possible to tell in which direction the central double bond is oriented.

A POAV analysis[28] of the X-ray data reveals that the two carbon atoms of the central "6:6-bond" of **1** (C1 and C2 in Figure 2) are pyramidalized to an extent of 9.0°. The curvature of the π-system at the center of **1** therefore corresponds to 77% of that found for C_{60}, the carbon atoms of which all have POAV angles of 11.64°. By comparison, the five carbon atoms at the hub of corannulene have an average POAV angle of 8.2° (70% of that found for C_{60}). Thus, in terms of curvature at the center, diindeno[1,2,3,4-*defg*;1′,2′,3′,4′-*mnop*]chrysene (**1**) represents a better model for C_{60} than does corannulene.

As with all bowl-shaped PAHs, the steepness of the curvature diminishes at carbon atoms located away from the center. For the four carbon atoms attached to the central double bond of **1**, an average POAV angle of 6.7° is found.

Preparation of 1 by FVP of 2,2′-Dibromobifluorenylidene (15). Unlike 1-bromo-9-fluorenone (**8**), the commercially available 2-bromo-9-fluorenone undergoes smooth McMurry coupling to the corresponding dimer (**15**).[29] Consequently, this compound was also examined as a potential precursor to **1**. In principle, pyrolysis should generate a radical through homolysis of the carbon−bromine bond, and then a 1,2-shift of hydrogen[30] could move the radical to the position required for cyclization (Scheme 6). We have previously exploited this strategy in other systems.[30,31] FVP of **15**, however, gave the desired PAH **1** in only 2−3% yield; the major product of this pyrolysis is the singly closed PAH **5**.

Conclusion

We have devised a short, practical synthesis of the $C_{26}H_{12}$ bowl-shaped fullerene fragment diindenochrysene (**1**). Flash vacuum pyrolysis of the twisted bifluorenylidene **2**, with bromine atoms strategically placed at the sites of the desired closures, gives **1** in 25−35% yield. The dramatic superiority of **2** over the unfunctionalized bifluorenylidene (**4**) as a FVP precursor to **1** serves as a prime example of the advantages gained by the use of planned aryl radical cyclizations instead of undirected cyclodehydrogenations for the synthesis of strained geodesic polyarenes. Typically, pyrolyses of **2** were run on a 100 mg scale to give 15−25 mg of the purified $C_{26}H_{12}$ bowl. Finding a route to **1** in such quantities was a prerequisite for the exploration of its chemistry.

Experimental Section

General. Sodium methoxide was freshly prepared as needed from anhydrous methanol and sodium metal. All other solvents and chemicals were of the best commercial grade or were purified and dried as described in the literature.[32] For column chromatographies, Silica Gel 60-200 mesh or aluminum oxide (activated, neutral, Brockman I, ~150 mesh) was used. Proton NMR chemical shifts are reported in ppm downfield from tetramethylsilane with tetramethylsilane ($\delta = 0.00$ 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). High-resolution mass spectrometry (HRMS) and some low-resolution mass spectrometry (MS) were performed by the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois. All other low-resolution mass spectrometry was performed on a Hewlett-Packard 5890 GC/5970 MS Series, with a HP 25 m × 0.2 mm × 0.11 μm capillary column. Elemental analyses were performed by Robertson Microlit Laboratories, Madison, New Jersey. Melting points were obtained using a Mel-Temp II or a Fisher-Johns melting point apparatus and are uncorrected. UV spectrometry was performed on a Hewlett-Packard 8452A diode array spectrophotometer unless otherwise stated. Infrared (IR) spectrometry was performed neat on NaCl plates on a Perkin-Elmer 781 spectrophotometer.

9-Fluorenone-1-carboxylic Acid (10). A solution of 34.5 g of CrO_3 (345 mmol) in 20 mL of acetic acid and 30 mL of water was added dropwise to a solution of 10.0 g of fluoranthene (49.4 mmol) in 250 mL of acetic acid at 85 °C. The solution was heated to just below reflux for 2 h and then poured into 1.5 L of water. The solid precipitate was filtered out and dissolved in 1.5 L of 2 M NaOH solution. Concentrated HCl was added, and the yellow solid obtained was filtered and dried in the oven at 100 °C to give 10.9 g (98% yield) of pure 9-fluorenone-1-carboxylic acid: mp 186−188 °C (lit.[18] 48% yield, 191−193 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (d, 1H, $J = 7.8$ Hz), 7.77−7.51 (m, 5H), 7.37 (t, 1H, $J = 7.4$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.9, 164.6, 145.7, 144.2, 137.4, 136.5, 134.3, 132.3, 131.4, 131.0, 130.4, 126.5, 124.9, 121.1. IR (neat): 2750, 2660, 1741, 1674, 1411 cm^{-1}.

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1-Bromo-9-fluorenone (8). A solution of 5.0 g (22 mmol) of **10** and 7.75 g (33.4 mmol) of red mercuric oxide in 100 mL of carbon tetrachloride was heated to reflux for 30 min. Bromine (1.8 mL, 34 mmol) was then added slowly, and the solution was irradiated with a 250 W tungsten lamp for 3.5 h. After the solution was allowed to cool to room temperature, the mercury salts were filtered out and washed with dichloromethane. The filtrate was washed with 10% sodium bisulfite solution, saturated sodium bicarbonate solution, and water (2 × 75 mL portions of each) and dried over $MgSO_4$. Evaporation of the solvent under reduced pressure followed by chromatography of the crude product on silica gel, using 10% ethyl acetate/hexane as eluant, gave 3.65 g (63% yield) of **8**. Fractional recrystallization from ethyl acetate gives pure, thick, yellow needles: mp 136−138 °C (lit.[20] 134.5−135.0 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, 1H, $J = 7.4$ Hz), 7.53−7.48 (m, 3H), 7.42 (d, 1H, $J = 8.0$ Hz), 7.36−7.30 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.29, 147.13, 142.52, 135.40, 134.99, 134.27, 134.07, 131.36, 129.88, 124.73, 120.63, 120.49, 119.46. IR (neat): 1722 cm^{-1}. MS (EI, 70 eV) *m/z* (rel intensity): 260 (100, M$^+$, ^{81}Br), 258 (100, M$^+$, ^{79}Br), 232 (10, [M − CO]$^+$, ^{81}Br), 230 (10, [M − CO]$^+$, ^{79}Br), 179 (5, [M − Br]$^+$).

1-Bromo-9-fluorenone Tosylhydrazone (11). A solution of 2.5 g (9.7 mmol) of **8**, a few drops of concentrated HCl, and 2.5 mL (23 mmol) of trimethyl orthoformate in 60 mL of dry methanol was heated to reflux. Tosylhydrazide (1.7 g, 9.1 mmol) was added, and the solution was heated to reflux for another 16 h. After the reaction mixture was cooled to room temperature, the yellow precipitate was isolated by filtration to give 3.8 g (93% yield) of pure **11**. Recrystallization from ethyl acetate gives shiny yellow plates: mp 185−190 °C (dec). Unchanged **8** can be recovered from the filtrate by chromatography on silica gel with 10% ethyl acetate/hexane as the eluant. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (s, 1H), 8.07 (d, 2H, $J = 8.4$ Hz), 7.94 (d, 1H, $J = 7.2$ Hz), 7.68 (d, 1H, $J = 7.2$ Hz), 7.55 (d, 1H, $J = 7.2$ Hz), 7.48 (t, 1H, $J = 7.6$ Hz), 7.47 (d, 1H, $J = 8.4$ Hz), 7.38 (t, 1H, $J = 7.6$ Hz), 7.33 (d, 2H, $J = 8.0$ Hz), 7.19 (t, 1H, $J = 7.6$ Hz), 2.24 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 150.93, 143.81, 142.58, 139.23, 134.94, 133.57, 132.28, 131.77, 131.60, 129.21, 128.93, 128.87, 128.80, 127.93, 120.74, 119.72, 116.90, 21.10. IR (neat): 3425, 1642, 1166 cm^{-1}. UV ($CHCl_3$) λ_{max} (log ϵ): 338 (3.96), 324 (3.99), 266 (4.58), 258 (4.56), 246 nm sh (4.44). HRMS (EI, 70 eV): calcd for $C_{20}H_{15}BrN_2O_2S$ (M$^+$) 426.0037, found 426.0035. Anal. Calcd for $C_{20}H_{15}BrN_2O_2S$: C, 56.22; H, 3.54; N, 6.56. Found: C, 56.04; H, 3.49; N, 6.58.

(*E*)- and (*Z*)-1,1′-Dibromobifluorenylidene (2). A solution of 2.00 g (4.68 mmol) of **11** and 350 mg (6.48 mmol) of freshly prepared, dry sodium methoxide in 55 mL of dry pyridine was heated at 110 °C for 45 min (until the reaction mixture bubbles vigorously and turns brown). The mixture was diluted with 100 mL of water and extracted quickly with 3 × 50 mL of dichloromethane. The organic layer was dried over $MgSO_4$ and evaporated quickly under reduced pressure with minimal heating. The crude 1-bromo-9-diazofluorene (**12**) [^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89 (d, 1H, $J = 7.8$ Hz), 7.84 (d, 1H, $J = 7.8$ Hz), 7.43−7.28 (m, 4H), 7.13 (t, 1H, $J = 7.6$ Hz). IR (neat): 2062 cm^{-1}] was then dissolved quickly in 50 mL of dichloromethane, and approximately 20 mg of copper (I) bromide was added. The solution was heated to reflux for 15 min. Evaporation of the solvent under reduced pressure followed by chromatography on silica gel with 5% ethyl acetate/hexane as the eluant gave 763 mg of **2** (67% yield). Recrystallization from acetone gave red crystals: mp of the isomer mixture 224−226 °C (lit.[23] 230−231 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ major isomer, 7.73 (dd, 2H, $J = 7.6$ and 0.8 Hz), 7.66 (dd, 2H, $J = 7.6$ and 0.8 Hz), 7.52 (dd, 2H, $J = 8.0$ and 0.8 Hz), 7.41 (d, 2H, $J = 7.6$ Hz), 7.31−7.17 (m, 6H); characteristic of minor isomer, 8.37 (d, 2H, $J = 7.6$ Hz). UV ($CHCl_3$) λ_{max} (log ϵ): 476 (4.3), 388 (3.8), 284 sh (4.6), 266 (4.7), 254 (4.7), 244 nm sh (4.7). MS (EI, 70 eV) *m/z* (rel intensity): 488 (13, M$^+$, ^{81}Br$_2$), 486 (23, M$^+$, ^{81}Br^{79}Br), 484 (14, M$^+$, ^{79}Br$_2$), 406 (2, [M − Br]$^+$, ^{81}Br), 404 (2, [M − Br]$^+$, ^{79}Br), 326 (100, [M − 2Br]$^+$), 162 (22). HRMS (EI, 70 eV): calcd for $C_{26}H_{12}Br_2$ (M$^+$) 483.9462, found 483.9459.

Diindeno[1,2,3,4-*defg*;1′,2′,3′,4′-*mnop*]chrysene (1). A 100 mg (0.206 mmol) sample of **2** was pyrolyzed under reduced pressure from a bed of quartz chips with a nitrogen bleed as described previously in detail.[6a] With the oven at 1050 °C and a pressure of 0.8−1.0 mmHg, the pyrolysis took 20 min. The crude pyrolysate (65% mass recovery) was suspended in dichloromethane and filtered through a plug of silica gel, flushing with dichloromethane. The $C_{26}H_{12}$ bowl was isolated by chromatography on aluminum oxide with cyclohexane as the eluant (see text). The product thus obtained was washed with acetone, giving 24.8 mg (37% yield) of **1** as a yellow powder:[33] mp > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, 4H, $J = 8.0$ Hz), 7.86 (d, 4H, $J = 6.8$ Hz), 7.62 (dd, 4H, $J = 8.0$ Hz and $J = 7.2$ Hz). ^{1}H NMR (400 MHz, 423 K, $C_6D_5NO_2$): δ 8.30 (d, 4H, $J = 8.1$ Hz), 7.98 (d, 4H, $J = 7.1$ Hz), 7.69 (t, 4H, $J = 7.6$ Hz). ^{13}C NMR (100 MHz, 423 K, $C_6D_5NO_2$): δ 142.38, 139.32, 137.31, 134.15, 129.62, 125.21, 123.16. UV (CH_2Cl_2, from diode array detector of the HPLC) λ_{max} (A_{rel}): 402 sh (1.0), 360 (4.3), 342 (3.5), 323 sh (6.6), 288 (10.3), 280 (17.9), 260 (18.6), 252 (14.6), 226 nm (16.0). MS (EI, 70 eV) *m/z* (rel intensity): 324 (100, M$^+$), 322 (18), 162 (10, M^{2+}). HRMS (EI, 70 eV): calcd for $C_{26}H_{12}$ 324.0937, found 324.0939.

Diindeno[5,6,7,1-*defg*;5′,6′,7′,1′-*lmnop*]chrysene (14). A 50 mg (0.10 mmol) sample of **2** was pyrolyzed as above at 1200 °C. After purification as above, approximately 1 mg (ca. 3% yield) of **14** was isolated as a yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.02 (d, 2H, $J = 7.6$ Hz), 8.44 (d, 2H, $J = 7.6$ Hz), 8.43 (s, 2H), 8.08 (t, 2H, $J = 7.6$ Hz), 7.73 (d, 2H, $J = 5.2$ Hz), 7.56 (d, 2H, $J = 5.2$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 104.4, 89.6 (other signals too weak to observe). UV (CH_2Cl_2, from diode array detector of the HPLC) λ_{max} (A_{rel}): 510 (30), 484 (40), 448 (41), 414 sh (80), 384 (230), 370 (290), 350 (210), 348 sh (310), 338 (330), 322 (500), 310 (310), 298 (180), 288 (160), 284 sh (140), 248 nm (440). MS (EI, 70 eV) *m/z* (rel intensity): 324 (100, M$^+$), 322 (16), 162 (10, M^{2+}). HRMS (EI, 70 eV): calcd for $C_{26}H_{12}$ 324.0937, found 324.0942.

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Supporting Information Available: NMR and UV spectra of compounds **1** and **14**. Tables of data and several views of the X-ray crystal structures of **1** and **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(33) Crystals were obtained for X-ray crystal analysis by first heating a solution of **1** in DMF at reflux in an oil bath. The bath was then turned off but not removed, and the solution was allowed to cool slowly overnight, giving **1** as fine needles.