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Steps toward the synthesis of a geodesic $C_{60}H_{12}$ end cap for a C_{3v} carbon [6,6]nanotube

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Dedicated to Professor Reginald H. Mitchell on the occasion of his 65th birthday

ABSTRACT

Several shape-persistent carbon-rich nanomolecules with diameters exceeding 1.7 nm have been prepared by the aldol trimerization of 20-carbon aromatic ketones bearing chlorine atoms at various sites. These $C_{60}H_{27}Cl_3$ and $C_{60}H_{24}Cl_6$ polycyclic aromatic compounds represent attractive intermediates for the synthesis of a geodesic $C_{60}H_{12}$ end cap of a C_{3v} carbon [6,6]nanotube.

1. Introduction

Carbon nanotubes have been widely touted for their potential to fulfill dreams in materials science and in the emerging realm of nanotechnology.[1–4] They also hold considerable intrinsic scientific interest owing to their unusual curved networks of trigonal carbon atoms. Despite intense scrutiny by scientists and engineers worldwide for nearly two decades, however, these fascinating carbon-rich materials are still being made today by poorly understood empirical methods.[5–8] We contend that such targets should be accessible by rational chemical synthesis and that the successful realization of the requisite synthetic methods will revolutionize the science of carbon-rich materials. Our 12-step laboratory synthesis of fullerene-C_{60} by chemical methods in 2002[9–11] represents one milestone in the journey toward that goal.

In recent years, we have begun to focus our research on the development of chemical methods for the rational, structure-specific synthesis of single-chirality, all-carbon, single walled nanotubes (SWNTs). The structural variety possible for carbon nanotubes is virtually limitless.[3,12,13] They come in all different diameters. The orientation of the benzene rings along the shaft can be chiral (helical) or achiral, and the chiral tubes vary according to the pitch of the helix. Achiral tubes are classified according to the appearance of their rims as either 'zig-zag' or 'armchair'. Both ends can be open, or both can be closed, or a single tube may have one end of each type. Superimposed on all of that, carbon nanotubes can be single walled, double walled, or multiwalled, with more than 10 coaxial tubes nested together.[3,12,13] Carbon nanotubes from all of these classes are already known, and their properties vary as a function of structure.[3,12,13] Unfortunately, empirical methods[5–8] do not produce homogeneous samples in which all the carbon nanotubes have the same predefined diameter and chirality (ring orientation). The problem is compounded by the fact that, unlike the fullerenes, carbon nanotubes made in this way cannot be separated and purified to homogeneity by chromatographic methods, because they are totally insoluble.[14,15] This problem represents a clear challenge to synthetic organic chemists!

Where should one begin? We have chosen the achiral, armchair, all-carbon, single walled nanotubes (e.g., [6,6]SWNTs) as our highest priority targets. Such nanotubes are expected to exhibit metal-like behavior, regardless of diameter.[1,3,12,13] Consequently, they all hold the potential to find use as ultra-thin, super-strong, electrically conducting nanowires in myriad nanoelectronic devices. Most zig-zag tubes and chiral tubes, by contrast, are expected not to exhibit metal-like behavior.[1,3,12,13] The choice of initial targets thus seems obvious to us. This paper describes one approach to the chemical synthesis of [6,6]SWNTs.

1.1. General strategy

The course we are pursuing builds on our previous experience with syntheses of open geodesic polyarenes.[11,16,17,18] Figure 1 illustrates the general strategy, as applied to a proposed synthesis of [6,6]SWNTs that are closed at one end and open at the other. As we see it, two major hurdles must be surmounted to produce SWNTs by this general strategy: (1) synthesis of a geodesic polyarene that has the initial armchair rim and six fully unsaturated five-membered rings, as required for a hemisphere by Euler's theorem[19] and

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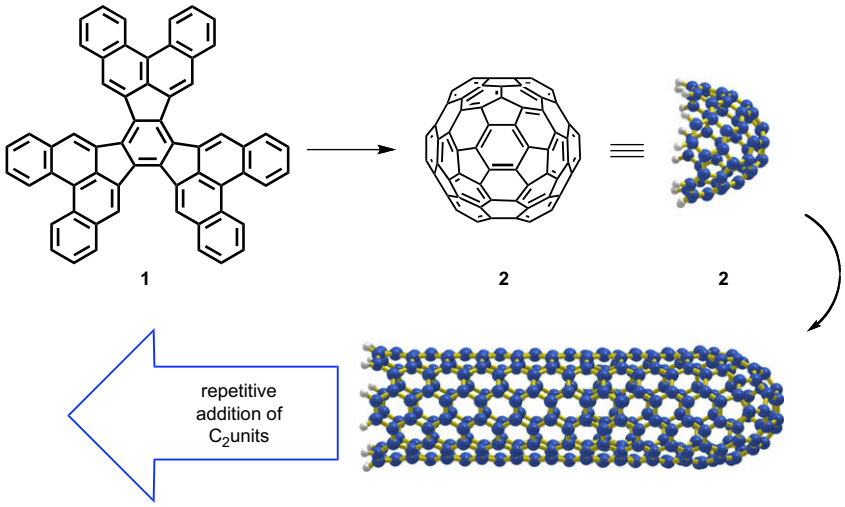

Figure 1. General plan for building a hemispherical end cap and extending it to produce an armchair SWNT.

(2) extension of the rim by adding C_2 units across the 'bay regions' to produce new six-membered rings.

For such a synthesis to be practical, the last step must be fully self-replicating, i.e., it must transform hydrocarbon bay regions into new, fully unsaturated, six-membered rings under a single set of conditions, without intervention by the chemist. Such a process would extend an armchair rim indefinitely, until the C_2 feedstock was consumed or the source shut off (not unlike a polymerization with 'living polymers'). In fact, catalytic methods for growing carbon nanotubes to lengths in excess of 1 mm, using acetylene as the C_2 feedstock, have already been reported,[20,21] so this aspect of the problem may already be solved, at least in principle. Conceivably, methods may even be found to extend such a nanotube template by uncatalyzed processes.

Herein lies the big payoff to the synthetic organic chemist. Only a few *micrograms* of the appropriate geodesic polyarene 'seed' need to be extended to a length of 1 mm or more in order to produce *gram quantities* of homogeneous SWNTs! The SWNTs derived in this manner will all necessarily have the same diameter and armchair rim structure, by virtue of the growth mechanism. The tremendous amplification in dimension (ca. 1 nm→1 mm=10^6 increase) will compensate for any low yields endured earlier in the synthesis.

What follows is a summary of our progress toward a synthesis of the C_{3v} nanotube end cap **2**, the geodesic $C_{60}H_{12}$ hydrocarbon that would result from 'stitching together' the arms of the $C_{60}H_{30}$ hydrocarbon **1**, a carbon-rich $C_{2n}H_n$ molecule of nanometer dimensions.

1.2. Retrosynthetic analysis

Figure 2 shows the loci of the nine new bonds that must be formed in stitching up **1** to give **2**.

Flash vacuum pyrolysis (FVP) has proven effective as a general method for transforming planar polycyclic aromatic hydrocarbons (PAHs) and halogenated derivatives thereof into their bowl-shaped counterparts by joining together carbon atoms that lie far apart in the planar conformations.[16–18] It has been our experience, however, that respectable yields of the desired geodesic polyarenes require the orchestrated generation of aryl radicals (or carbenes) at the sites where the new bonds must be formed.[22,23] Once curvature has been introduced, a 'cascade effect' seems to operate to close additional rings by thermal cyclodehydrogenations, without the need for additional radical generating groups.[18] Our FVP synthesis of C_{60} represents an extreme example of the cascade effect; in our $C_{60}H_{27}Cl_3$ synthetic intermediate, three chlorine atoms were incorporated at strategic sites, and FVP effected the closure of 15 new C–C bonds to produce isolable quantities of C_{60}, with an average yield of >60% per bond.[10,11]

We recognized at the outset of this project that the most difficult part of stitching together the arms of **1** by FVP would be formation of the first three bonds, those closest to the core, marked *a* in Figure 2. Closing these three new six-membered rings would introduce curvature comparable to that in C_{60}, and the cascade effect might then take over to form the remaining six bonds. Unfortunately, the incorporation of halogen atoms as radical precursors in the crowded fjord regions of molecules related to **1** has proven problematical, presumably for steric reasons.[24,25] In such

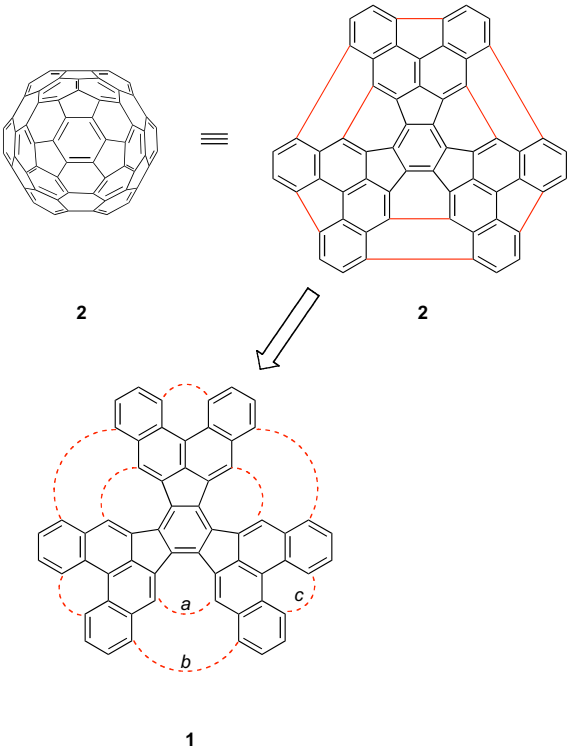

Figure 2. Nine new bonds must be formed in stitching up **1** to give **2**.

situations, a reliance on the 1,2-shift of hydrogen atoms in aryl radicals under FVP conditions[26] has allowed us to circumvent this problem by attaching the halogen to an adjacent carbon atom in the precursor (Fig. 3).[27]

Even this gambit is not possible with **1**, however, because all of the carbon atoms to be joined by *a* bonds are flanked on both sides by quaternary ring junctions. These constraints prompted us to consider whether aryl radicals might be capable of rearranging under FVP conditions by 1,3-shifts of hydrogen atoms between the *peri*-positions of a PAH (Fig. 4). If so, then a halogen atom incorporated in each fjord region, on a terminal ring, might promote the initial *a*-ring closures, following 1,3(*peri*)-shifts of interior hydrogens.

A preliminary examination of this process by B3LYP/6-31G* calculations revealed that the free energy of activation for 1,3(*peri*)-shift of a hydrogen atom is not higher than that for the known[26] 1,2-shift of hydrogen atoms in aryl radicals (64.6 kcal/mol and 66.0 kcal/mol, respectively).[28] We subsequently obtained experimental evidence for the feasibility of this unusual rearrangement,[29] and that emboldened us to incorporate three 1,3(*peri*)-shifts of hydrogen atoms into our plan. Our synthetic target was thus refined to include three chlorine atoms as depicted in **3a**. Chlorine atoms were chosen to serve as the radical precursors in preference to more weakly bonded bromine atoms so that the FVP precursor would be as volatile as possible and sufficiently robust to withstand the temperatures required to promote vacuum sublimation.

Before initiating a synthesis of **3a**, we recognized the opportunity to incorporate radical precursors also for the *c*-bond closures. A chlorine atom in each cove region (**3b**) would

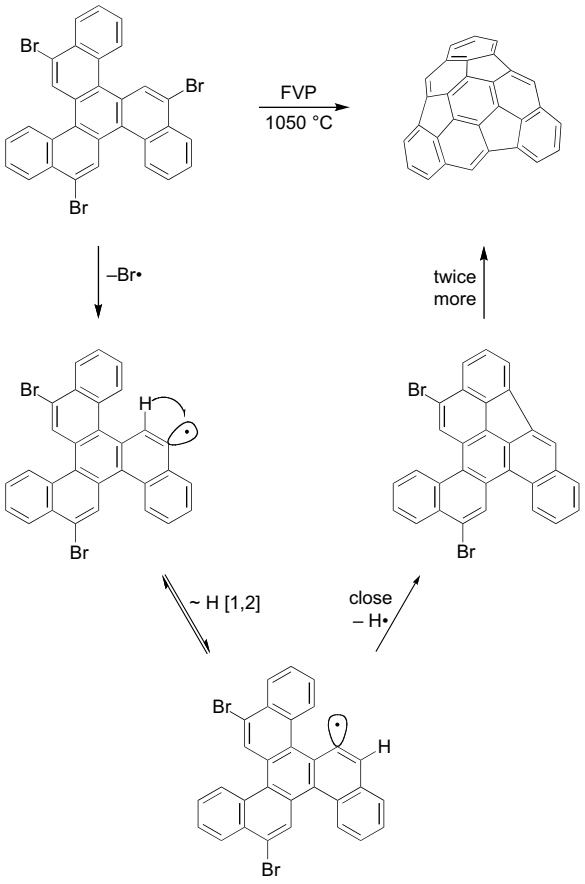

Figure 3. FVP synthesis of a $C_{30}H_{12}$ hemifullerene that capitalizes on 1,2-shifts of hydrogen atoms in the intermediate aryl radicals.[27]

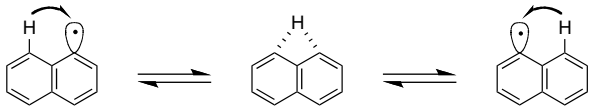

Figure 4. Proposed 1,3(*peri*)-shift of hydrogen in an aryl radical.

certainly favor those ring closures, but they might also present synthetic difficulties. Having the chlorine atoms moved over one position (**3c**) looked appealing from the synthesis perspective, and their attachment there might still achieve the desired effect, by exploiting the 1,2-shift of hydrogens, as in Figure 3. Accordingly, we chose **3c** as our initial target compound. Figure 5 summarizes our retrosynthetic analysis, which relies on an acid catalyzed aldol cyclotrimerization[24,25] to construct the triply fused benzene ring at the center.

2. Results and discussion

2.1. Synthesis of hexachlorinated trimer 3c

Bromination of the commercially available 1-(2-naphthyl)ethanol (**4**) was achieved using phosphorus tribromide in refluxing benzene to give 2-(1-bromoethyl)naphthalene (**5**) in 95% yield. Subsequent displacement of the benzylic bromide with triphenylphosphine gave the corresponding phosphonium salt (**6**) in 93% yield (Fig. 6).

We then carried out the Wittig reaction with phosphonium salt **6**, using 2,4-dichlorobenzaldehyde (**7**) as the coupling partner and *n*-butyl lithium to preform the ylide. A mixture of *E* and *Z* olefins (**8**) was obtained in 82% yield. There was no need to separate the *E* and *Z* isomers since they equilibrate under UV light in the next step. Photocyclization of **8** worked best in cyclohexane as the solvent, giving the substituted [4]helicene **9** in 68% yield by recrystallization, without any chromatography being necessary (Fig. 7).

With an efficient route to the [4]helicene intermediate **9** in hand, we turned to elaborating the methyl handle into the desired

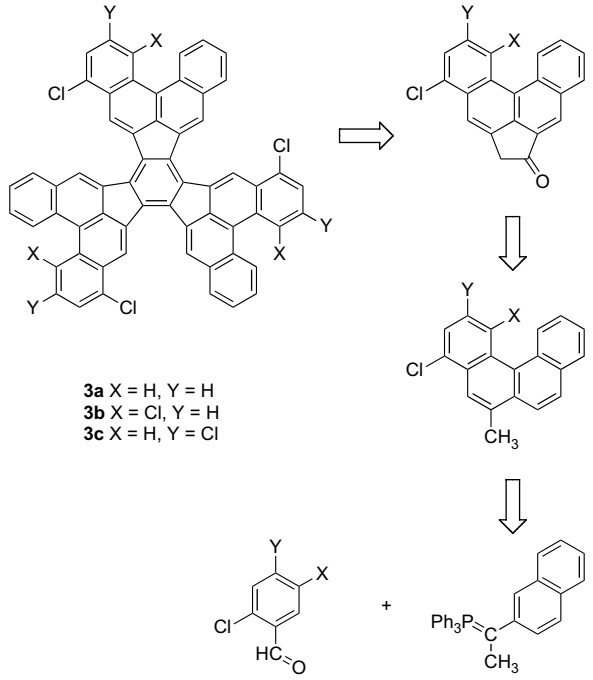

Figure 5. Retrosynthetic analysis of the FVP precursor **3**.

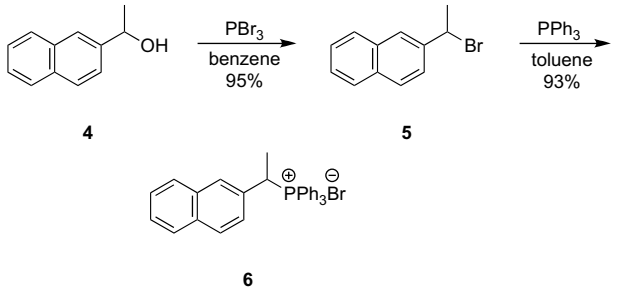

Figure 6. Synthesis of phosphonium salt **6.**

cyclic ketone **13**. This was accomplished in four steps (Fig. 8), beginning with benzylic bromination of **9**, which gave **10** very cleanly in 79% yield. The bromide was then displaced with cyanide ion under biphasic conditions in 96% yield to produce nitrile **11**, which was hydrolyzed under acidic conditions, using a 1:1:1 mixture of water, concentrated sulfuric acid, and acetic acid at reflux,[30,31] giving carboxylic acid **12** cleanly in 75% yield. The final cyclization was accomplished by a two step, one pot procedure in which carboxylic acid **12** was first transformed into the corresponding acid chloride with thionyl chloride, and that product was subjected to Friedel–Crafts acylation conditions to generate cyclic ketone **13** in 63% yield.

To access the 60-carbon target **3c**, we planned to rely on the aldol trimerization of ketone **13**. Our laboratory has enjoyed good success in the past using titanium tetrachloride as the Lewis acid catalyst in hot *o*-dichlorobenzene to promote aldol trimerizations of other aromatic ketones,[9,10,22,24,25] so we treated ketone **13** with this catalyst system at 115 °C. MALDI-TOF MS analysis of the product mixture (see Section 4) revealed that the desired cyclic trimer **3c** was indeed formed, but we also saw evidence for significant amounts of the α,β-unsaturated dimer **14** and cyclic tetramer **15** (Fig. 9).

This aldol trimerization reaction was repeated many times, varying the concentrations, the rate of addition, the amount of catalyst, the reaction time, the Lewis acid, the solvent, and the temperature (up to 180 °C); however, no significant improvement in the ratio of **3c** to other products could ever be achieved. Separation of the very insoluble **3c** from other products was attempted using Soxhlet extraction with several different solvents but to no

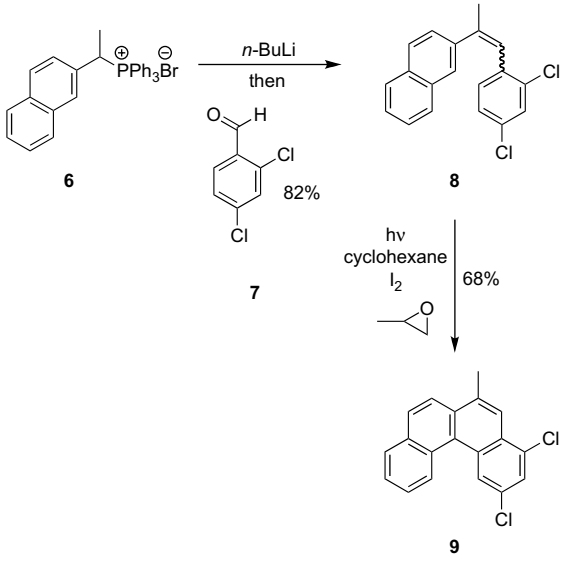

Figure 7. Synthesis of the substituted [4]helicene **9**.

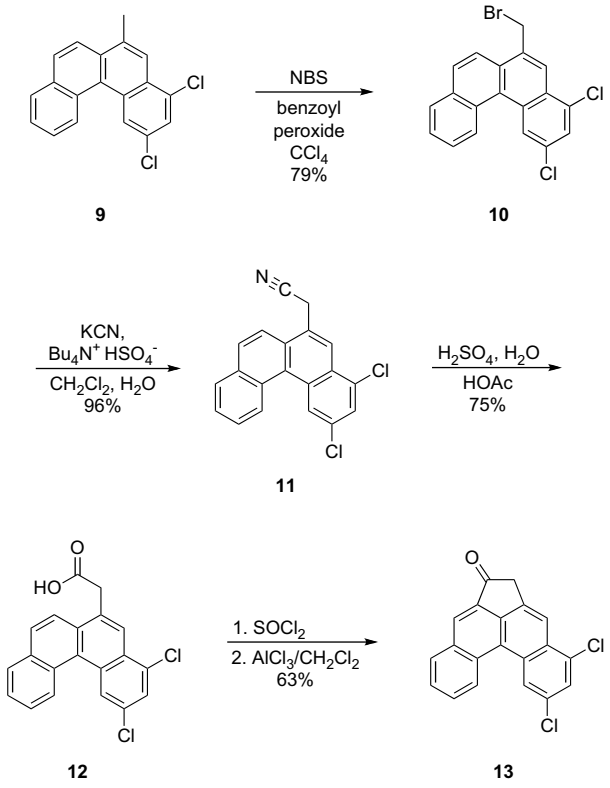

Figure 8. Elaboration of [4]helicene **9** into ketone **13**.

avail. Likewise, all attempts to separate and purify cyclic trimer **3c** by recrystallization proved fruitless.

We believe that the poor behavior of ketone **13** in the aldol trimerization reaction is a direct consequence of the very poor solubility of the α,β-unsaturated dimer **14**, which lies on the pathway to cyclic trimer **3c**. Ketone **13** itself is only sparingly soluble in *o*-dichlorobenzene, and planar α,β-unsaturated aldol dimers of aromatic ketones generally exhibit even lower solubility than the corresponding monomeric ketones. Previous studies from our laboratories[24,25] have shown that aldol trimerization reactions can be easily derailed by the poor solubility of any intermediates along the pathway to a cyclic trimer. Consequently, we elected to modify our plan to address this solubility problem.

As a general rule, the presence of multiple chlorine atoms around the rim of a polycyclic aromatic hydrocarbon diminishes its solubility, relative to the hydrocarbon. We therefore decided to reduce the number of chlorine atoms in our target and aim for the synthesis of trimer **3a**. Although this would result in a 60-carbon pyrolysis precursor having only three radical generators, we anticipated that they would still promote the three initial C–C bond closures, each following a 1,3-shift of hydrogen. Formation of the first three new rings should then impose enough curvature on the molecule to set up the cascade closure of the remaining six bonds by thermal cyclodehydrogenations. Remembering that our synthesis of C_{60} had only three chlorine atoms attached to the pyrolysis precursor,[10] we viewed **3a** as still constituting a reasonable target.

2.2. Synthesis of trichlorinated trimer 3a

The synthesis of monochloroketone **21** is completely analogous to our synthesis of ketone **13**. The same phosphonium salt (**6**) was used for the Wittig reaction, and *n*-butyl lithium was again used as the base. The ylide was combined this time with 2-chlorobenzaldehyde to give the new stilbene derivative **16** as

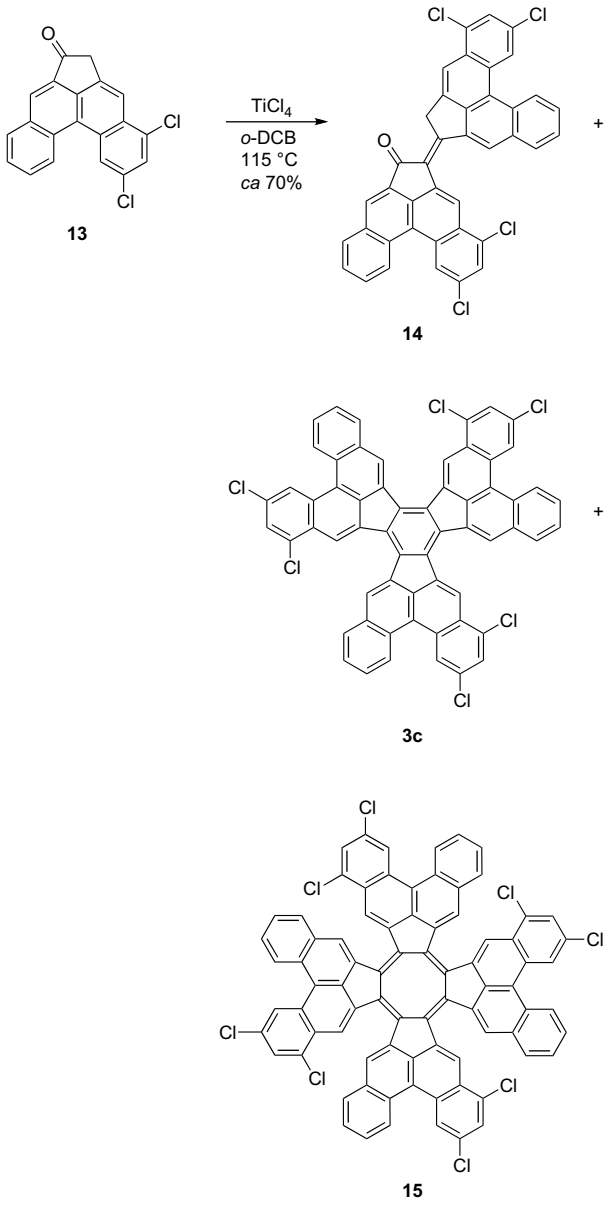

Figure 9. Mixture of products obtained from the attempted aldol trimerization of ketone **13** using $TiCl_4$ in *o*-dichlorobenzene at 115 °C.

a mixture of *E* and *Z* olefins in 87% yield. Photocyclization of the stereoisomeric mixture was carried out as before in cyclohexane in the presence of iodine and propylene oxide to give the substituted [4]helicene **17** in 57% yield. Subsequent benzylic bromination proceeded cleanly, giving **18** in 90% yield, and displacement of the bromide with cyanide ion provided nitrile **19** in 92% yield. Acid catalyzed hydrolysis of the nitrile group gave an 89% yield of carboxylic acid **20**, which was converted to the acid chloride as before, followed by addition of aluminum chloride to produce the desired monochloroketone **21** in 57% yield (Fig. 10). It was gratifying to find that our prediction about improved solubility was correct.

With the new, more soluble substrate, we began working on conditions to effect the aldol trimerization. Treatment of ketone **21** with titanium tetrachloride in hot *o*-dichlorobenzene was carried out as before and the product was precipitated with methanol. Figure 11 shows the MALDI-TOF mass spectrum of the material obtained by filtration.

As can clearly be seen from the mass spectrum, we were again producing mixtures of α,β-unsaturated dimer **22** (*m*/*z* 586/588), the desired trimer **3a** (*m*/*z* 854/856), and cyclic tetramer **23** (*m*/*z* 1136/1138), under conditions that consumed 100% of the starting material. This time, however, we also observed a dione of the acyclic tetramer (**24**, *m*/*z* 1168/1170), which could be separated as a red band by preparative TLC.[32]

This aldol trimerization reaction was repeated many times, varying the conditions as in the attempted synthesis of **3c**, but no improvement could ever be achieved, and the challenge of isolating pure **3a** from these product mixtures proved to be insurmountable. We again ascribe the poor results of the aldol trimerization reaction to poor solubility of the intermediate α,β-unsaturated dimer (**22**, in this case). Reducing the number of chlorine atoms from six to three did not solve the problem.

Faced with this setback, we devised a new plan to address the frustrating solubility problem. In our experience, large polycyclic aromatic compounds that are nonplanar exhibit significantly greater solubility than their planar counterparts, presumably because they are less able to achieve strong intermolecular attractions through π–π stacking. Accordingly, we began to reconsider the chlorinated derivative of **3** that bears a chlorine atom in the cove region of each arm (**3b**). We reasoned that such a large substituent protruding into such a tight space ought to enforce a severe helical twist in each arm, thereby enhancing the solubility of the trimer significantly. Molecular modeling[28] confirms that **3b** deviates from planarity substantially more than either **3a** or **3c**. Moreover, as noted earlier, the cove region chlorine atoms in trimer **3b** are positioned to generate aryl radicals precisely where they are needed to promote the *c*-bond closures. As an added benefit, the extra twist might even improve the volatility of the trimer (**3b**), thereby facilitating sublimation in the pyrolysis. As it turned out, synthesizing the required ketone proved less troublesome than we had originally feared.

2.3. Synthesis of hexachlorinated trimer 3b

Using the same phosphonium salt **6** as before, the Wittig reaction with 2,5-dichlorobenzaldehyde (**25**)[33,34] gave a mixture of *E* and *Z* isomers of **26** in 85% yield. Photocyclization of this stilbene derivative proceeded in yields comparable to the prior cases, giving the dichloro[4]helicene **27** in 62% yield, despite the steric problems, and bromination of the methyl group was accomplished with *N*-bromosuccinimide to give benzylic bromide **28** in 96% yield.

The 400 MHz ^{1}H NMR spectrum of **28**, unlike those of the previous benzylic bromides (**10** and **18**), shows an AB-quartet for the two benzylic hydrogens (J_{gem}=10.5 Hz). This indicates that [4]helicene **28** is not interconverting between *P* and *M* atropisomers on the NMR timescale. A barrier of 19.8 kcal/mol was calculated for this interconversion in the parent 1-chlorobenzo[*c*]phenanthrene at the B3LYP/6-31G* level of theory (no thermodynamic corrections).[28] The carboxylic acid (**30**) derived from **28** likewise shows diastereotopic hydrogens on the methylene group in its ^{1}H NMR spectrum.

Displacement of the bromide with cyanide ion gives the benzylic nitrile **29** in 90% yield, and acid catalyzed nitrile hydrolysis proceeds cleanly to give a 93% yield of the carboxylic acid **30**. The synthesis of ketone **31** is completed by in situ generation of the acid chloride of **30**, followed by intramolecular Friedel–Crafts acylation in 83% yield (Fig. 12).

As predicted, dichloroketone **31** is indeed more soluble than either of the other ketones described above (**13** and **21**). Much to our disappointment, however, treatment of ketone **31** with titanium tetrachloride in hot *o*-dichlorobenzene produced an inseparable mixture of the α,β-unsaturated dimer, the cyclic

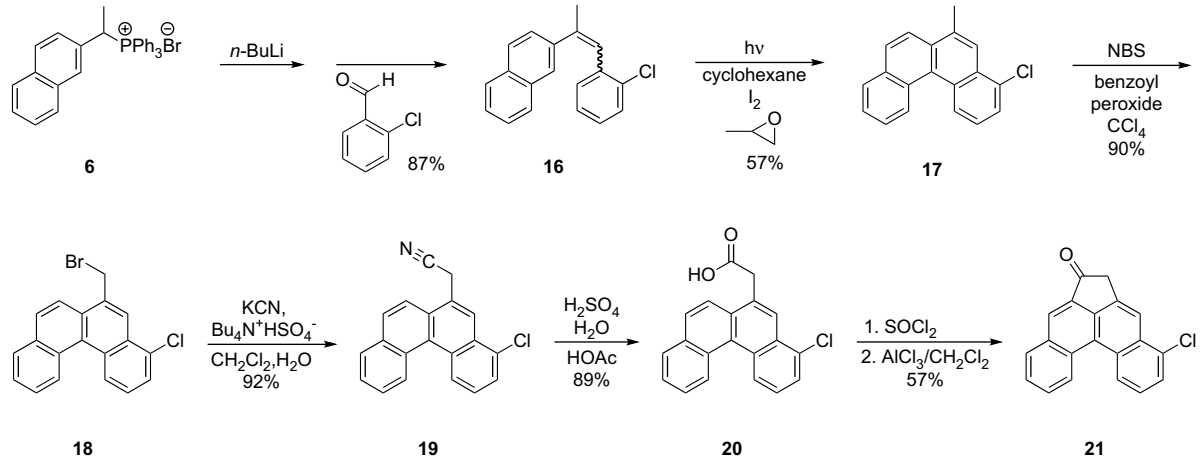

Figure 10. Synthesis of monochloroketone **21**.

trimer, and the cyclic tetramer, very similar to those we had seen before. The Lewis acid catalyzed aldol trimerizations of these ketones (**13**, **21**, and **31**) simply were not clean enough to be useful.

Fortunately, at the time when these results were obtained, other work in our laboratory had just uncovered a new protocol for effecting the aldol trimerization of cyclic ketones using a Brønsted acid system. To our great relief, these new conditions worked beautifully, not only for the aldol trimerization of dichloroketone **31** but also for the monochloroketone **21**, as described below.

2.4. A superior aldol trimerization method

The new Brønsted acid conditions developed by Amick and Scott[25] for the aldol trimerization call for a combination of *p*-toluenesulfonic acid and propanoic acid in hot *o*-dichlorobenzene. The role of the propanoic acid remains uncertain, but its presence was found to raise the yields in other aldol trimerizations tested by as much as 10–15%. We began by heating a solution of ketone **31**, *p*-toluenesulfonic acid, and propanoic acid in *o*-dichlorobenzene overnight at 110 °C. MALDI-TOF analysis of the crude product

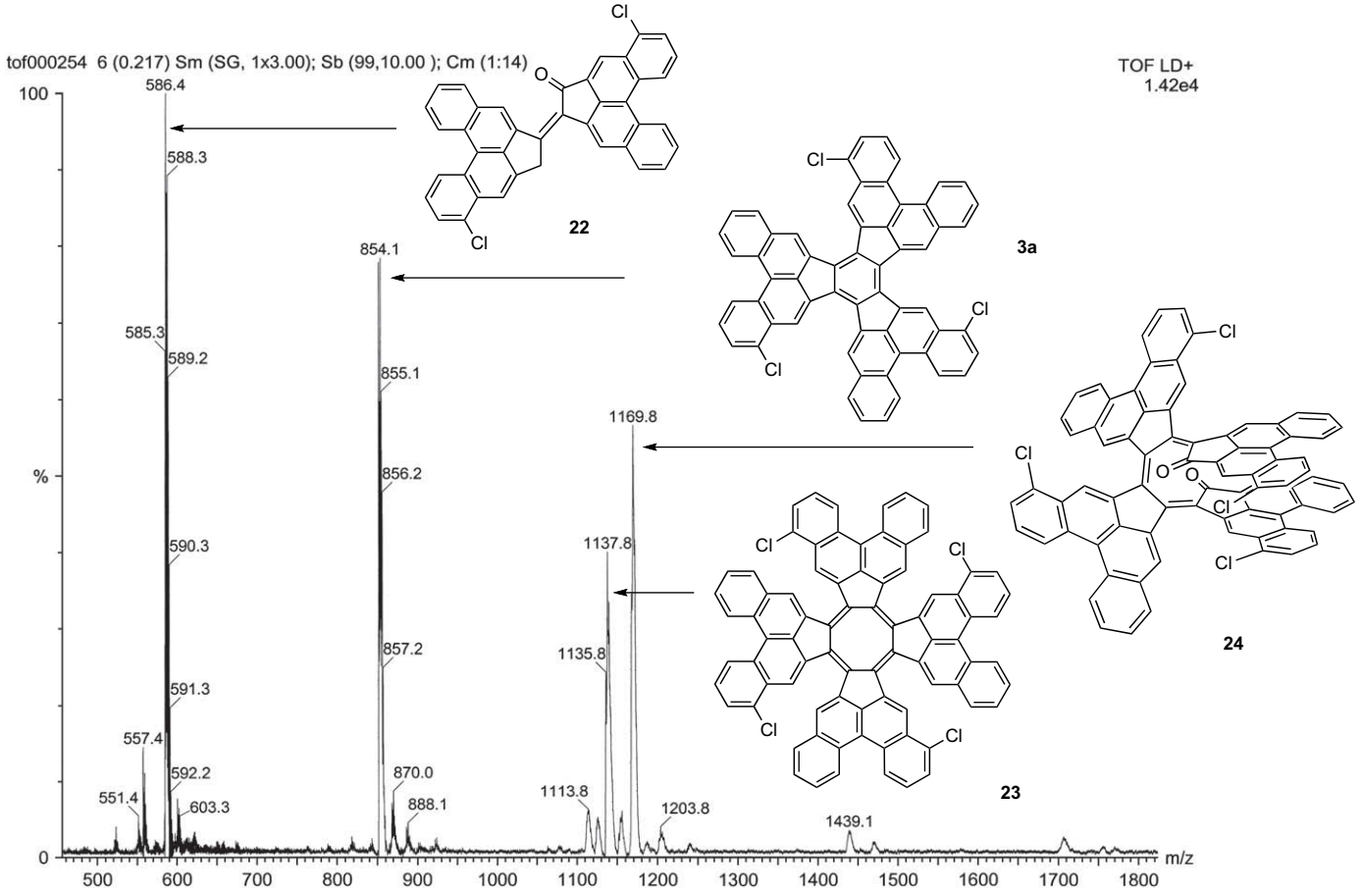

Figure 11. MALDI-TOF mass spectrum of the product mixture from attempted aldol trimerization of **21** with titanium tetrachloride in hot *o*-dichlorobenzene.

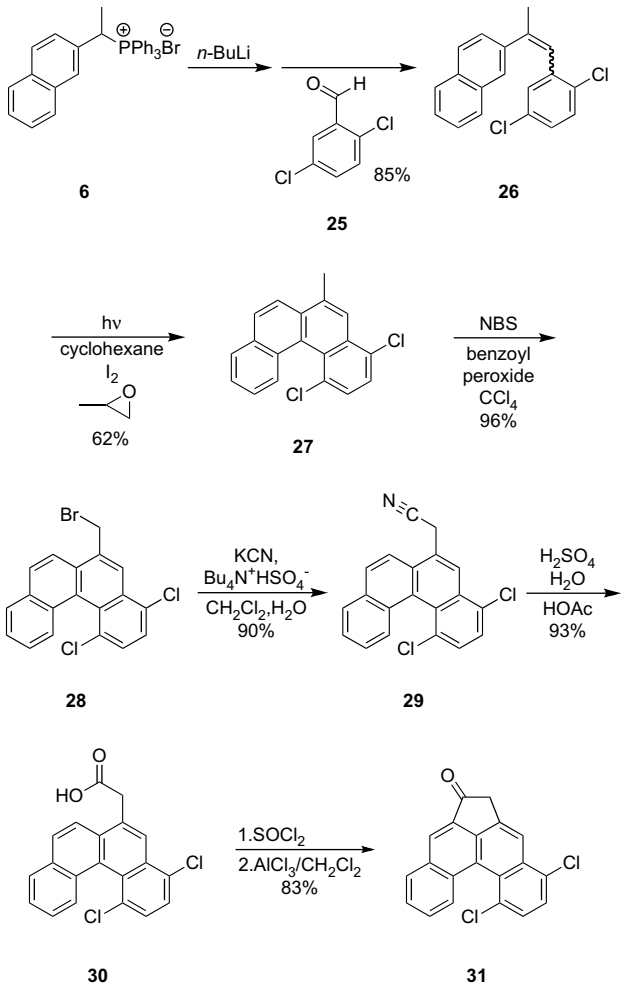

Figure 12. Synthesis of dichloroketone **31**.

revealed the desired trimer **3b** and substantial quantities of the α,β-unsaturated ketone dimer; however, for the first time, no peaks were seen for the cyclic tetramer or for other compounds larger than the trimer. By varying the temperature, we soon found that this catalyst system gives the desired cyclic trimer **3b** almost exclusively at 180 °C in *o*-dichlorobenzene (Fig. 13).

Furthermore, the isolation of cyclic trimer **3b** also turned out to be trivial. At the end of the reaction, the product mixture is cooled back to room temperature, and methanol is added to precipitate the clean trimer in 79% yield. Despite the nonplanarity induced by chlorine atoms in the three cove regions, **3b** proved to be too insoluble for ^{1}H NMR analysis in a variety of solvents, even at elevated temperatures.

Exposure of the monochloroketone **21** to these same reaction conditions gave cyclic trimer **3a** cleanly in 74% isolated yield. We did not go back to try these new Brønsted acid trimerization conditions with ketone **13**, because access to ample supplies of the superior nanotube end cap precursor **3b** quickly curtailed our interest in trimer **3c**.

3. Concluding remarks

Figure 14 shows a space filling model of the parent $C_{60}H_{30}$ hydrocarbon **1** to which all of the trimers reported here are structurally related. By conventional criteria, this is a large molecule. The diameter across the widest part measures somewhat more than 1.7 nm. Clearly, the aldol trimerization of aromatic ketones offers a powerful method for the rapid construction of carbon-rich nanomolecules that have well-defined, relatively rigid shapes.

We are pursuing the proposed conversion of cyclic trimer **3b** to the C_{3v} nanotube end cap **2** but have no results to report at this time.

4. Experimental section

4.1. General

Tetrahydrofuran, dichloromethane, and *o*-dichlorobenzene were obtained anhydrous and air-free from a solvent purification system from Glass Contour Solvent Systems, Inc. All other solvents and commercial chemicals were of the best available grade and were used without further purification. Proton NMR chemical shifts are reported in parts per million downfield from tetramethylsilane with deuteriochloroform (δ=7.26 ppm) as the reference standard, unless otherwise specified. Carbon NMR chemical shifts are reported in parts per million downfield from tetramethylsilane with deuteriochloroform (δ=77.0 ppm) as the reference standard. Preparative thin layer chromatographies were performed on 20 cm×20 cm Analtech Uniplate Taper plates, Silica GF. For column chromatographies, silica gel 32–63 μm was used. High-performance liquid chromatographies (HPLC) were performed on a Waters Delta 600 with a Supelcosil LC-PAH (21.2×250 mm) reversed-phase column. Gas Chromatograph–Mass Spectrometer (GC–MS) analysis was performed on a Thermo Finnigan Trace DSQ with electron impact ionization with a Thermo TR-5MS (15 m×0.25 mm×0.25 μm film) column. MALDI-TOF MS analyses were performed in the Boston College Mass Spectrometry Center using a solvent-free sample preparation with TCNQ as the matrix.[35] High-resolution mass spectrometry (HRMS) was performed in the Boston College Mass Spectrometry Center, or by the Mass Spectrometry Laboratory at the University of Illinois. Elemental analysis was performed by Robertson Microlit Laboratories. Melting points are uncorrected.

4.2. 2-(1-Bromoethyl)naphthalene (5)

This compound has previously been synthesized by benzylic bromination of 2-ethylnaphthalene.[36] To a flame-dried 500 mL three-necked round-bottom flask equipped with a reflux condenser were added 1-(2-naphthyl)ethanol (20.90 g, 121.4 mmol) and 250 mL of benzene. The solution was brought to reflux and stirred vigorously while phosphorus tribromide (7.00 mL, 74.5 mmol) was added dropwise. After 20 min, the solution was allowed to cool to room temperature and was then quenched with 1 M NaOH. The organic layer was washed with water (3×100 mL) until the yellow color no longer remained and then with a solution of saturated aqueous sodium chloride (100 mL). Drying over magnesium sulfate, filtration, and removal of the solvent under reduced pressure gave 27.16 g (95%) of the title compound as an oil, which solidified upon standing. The spectroscopic properties matched with those of the commercially available material.

4.3. 1-(2-Naphthyl)ethyltriphenylphosphonium bromide (6)

2-(1-Bromoethyl)naphthalene (27.16 g, 115.5 mmol) and triphenylphosphine (33.33 g, 127.1 mmol) were dissolved in 70 mL of toluene, and the mixture was heated to reflux (110 °C) with vigorous stirring for 12 h, during which time a white solid precipitated from solution. The reaction mixture was placed in the freezer at −10 °C for 4 h and then filtered to collect the solid. Any large crystals were pulverized using a mortar and pestle. The solid was washed again, collected by filtration, and washed with cold hexanes to give a total of 49.37 g (93%) of the phosphonium salt as a white powder, mp 207 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (dd,

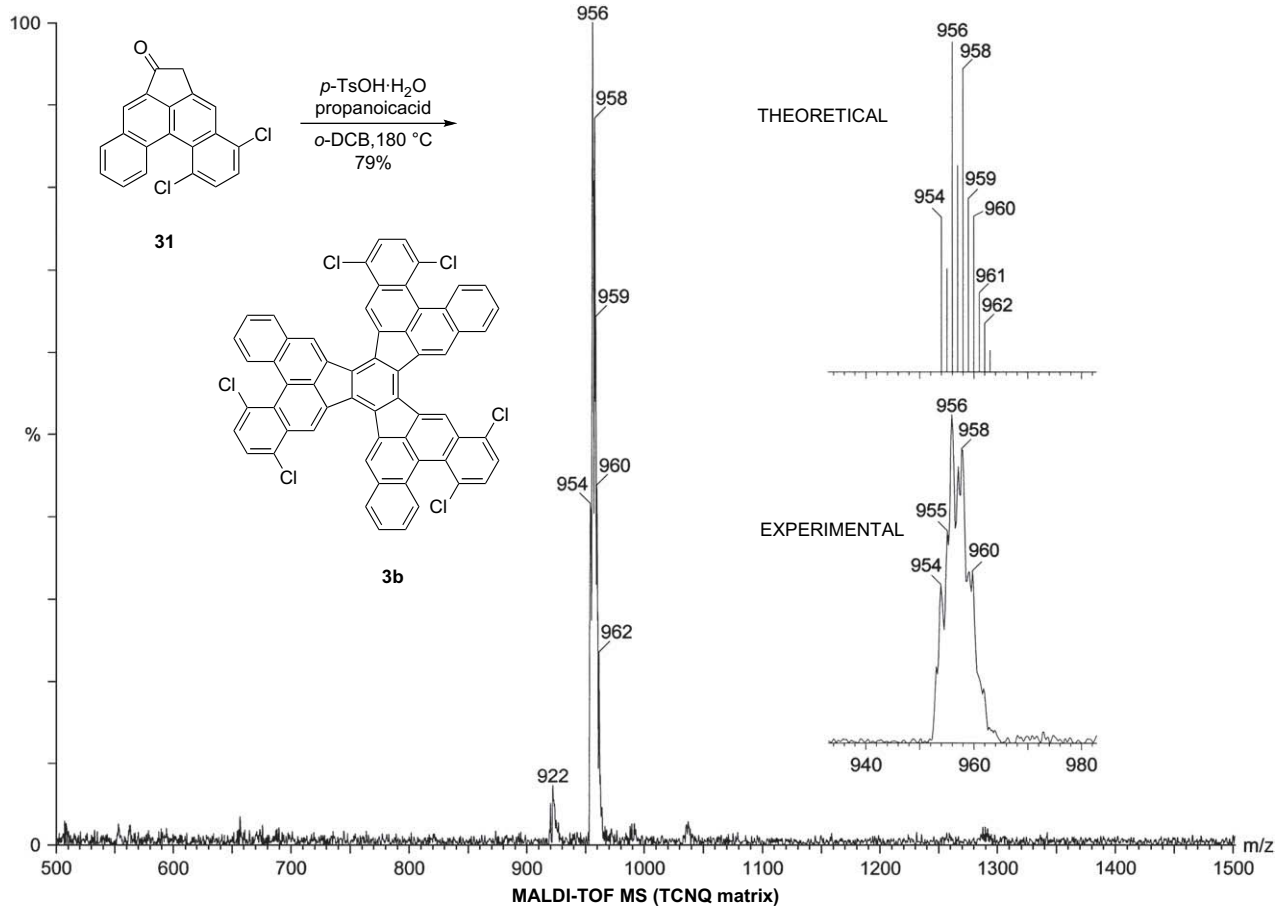

Figure 13. Clean cyclic trimer **3b** is the only product seen by MALDI-TOF analysis of the material isolated from aldol trimerization of **31** using the new Brønsted acid conditions.

J_{PH}=11.0 Hz, J_{HH}=7.4 Hz, 6H), 7.80–7.71 (m, 4H), 7.63 (td, J=8.0, 3.4 Hz, 7H), 7.51 (d, J=8.1 Hz, 1H), 7.47–7.33 (m, 4H), 6.83 (qd, J=14.3, 7.3 Hz, 1H), 1.89 (dd, J=19.0, 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.6, 134.4 (d, J=9.2 Hz), 132.7, 132.5, 130.6 (d, J=5.6 Hz), 130.0, 129.9, 129.8, 128.2, 127.7, 127.3, 126.5, 126.3, 117.5 (d, J=82.5 Hz), 34.7 (d, J=42.3 Hz), 17.1. Elemental analysis calcd for $C_{30}H_{26}BrP$: C, 72.44; H, 5.27. Found: C, 72.42; H, 5.21.

4.4. (*E*) and (*Z*)-1-(2,5-Dichlorophenyl)-2-(2-naphthyl)-propene (26)

Into a flame-dried round-bottom flask under nitrogen were added 1-(2-naphthyl)ethyltriphenylphosphonium bromide (17.05 g, 34.28 mmol) and 100 mL of anhydrous THF. The mixture was cooled to −78 °C and stirred while *n*-butyl lithium (15.1 mL of a 2.5 M solution in hexanes, 38 mmol) was added dropwise. The solution turned orange/red while stirring for 45 min, at which point it was allowed to come to room temperature and stirred for an additional 45 min. At this point, the solution was deep red. The 2,5-dichlorobenzaldehyde (6.00 g, 34.3 mmol) was added as a solution in THF (5 mL). The reaction mixture turned light yellow in color after being stirred for 14 h. THF was removed and the resulting material was deposited onto silica gel by evaporation of the solvent under reduced pressure. The compound was then passed through a short silica gel plug using hexanes as the eluent. Concentration of the hexanes gave 9.09 g (85%) of the title compound as a white solid. The *E* and *Z* isomers were obtained in a ratio of 5.3 to 1, respectively, as judged by ^{1}H NMR spectroscopic analysis, but they were not separated. The major isomer had its methyl hydrogens chemical shift at 2.30 ppm (d, J=1.3 Hz), and those of the minor isomer appeared at 2.36 ppm (d, J=1.5 Hz). The corresponding ^{13}C chemical shifts were 17.69 ppm and 26.53 ppm, respectively. HRMS DART (m/z): $[M+H]^+$calcd for $C_{19}H_{15}Cl_2$ 313.0551; found 313.0563.

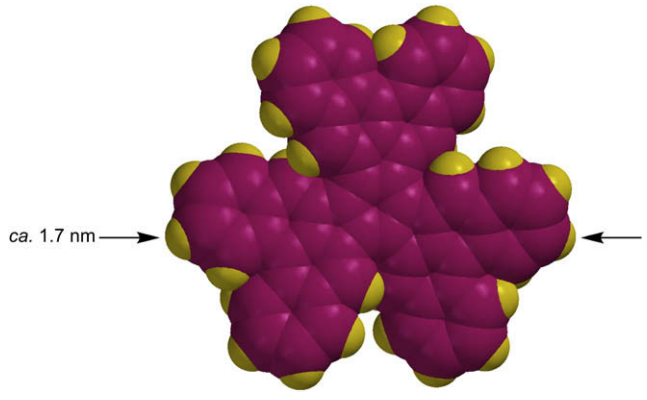

Figure 14. Space filling model of the parent $C_{60}H_{30}$ hydrocarbon **1**.

4.5. 1,4-Dichloro-6-methylbenzo[*c*]phenanthrene (27)

A solution of (*E*)- and (*Z*)-1-(2,5-dichlorophenyl)-2-(2-naphthyl)propene (3.980 g, 12.02 mmol), iodine (3.200 g, 12.62 mmol), and propylene oxide (80.0 mL, 1.14 mol) in 4 L of cyclohexane was photolyzed in a quartz vessel for 35 h in a Rayonet photochemical apparatus equipped with 15 mercury lamps of 254 nm and 35 W. The solvent was removed by rotary evaporation to give an orange solid. Recrystallization of the crude mixture from ethanol yielded

2.15 g of 1,4-dichloro-6-methylbenzo[*c*]phenanthrene as a yellow crystalline solid, mp 131 °C. A second crop of crystals was obtained from the mother liquor to give an additional 0.30 g of product (combined yield 62%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (d, J=1.1 Hz, 1H), 8.11 (dd, J=8.2, 1.2 Hz, 1H), 8.05 (d, J=8.8 Hz, 1H), 8.02 (d, J=8.8 Hz, 1H), 7.98 (dd, J=7.9, 1.4 Hz, 1H), 7.62 (d, J=8.1 Hz, 1H), 7.59 (ddd, J=8.4, 7.0, 1.5 Hz, 1H), 7.56 (ddd, J=8.2, 6.9, 1.6 Hz, 1H), 7.53 (d, J=8.1 Hz, 1H), 2.82 (d, J=1.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 134.7, 132.2, 132.0, 131.8, 131.4 130.9, 130.0, 129.0, 128.9, 127.8, 127.7, 127.1, 126.6, 126.3, 126.1, 124.8, 122.8, 121.3 20.1. HRMS DART (m/z): $[M+H]^+$calcd for $C_{19}H_{13}Cl_2$ 311.0394; found 311.0397.

4.6. 6-Bromomethyl-1,4-dichlorobenzo[*c*]phenanthrene (28)

Into a 250 mL round-bottom flask equipped with a reflux condenser were added 1,4-dichloro-6-methylbenzo[*c*]phenanthrene (1.53 g, 4.92 mmol), *N*-bromosuccinimide (0.962 g, 5.41 mmol), and a pinch (approximately 10 mg) of dibenzoylperoxide. Carbon tetrachloride (75 mL) was added, and the mixture was heated to reflux (approximately 80 °C) and monitored by NMR spectroscopy; all starting material was consumed typically within 24 h, but some larger scale reactions required 3 days.[37] After being allowed to cool to room temperature, the mixture was filtered through filter paper to remove solid succinimide, which was then rinsed with hexane. The filtrate was deposited onto silica gel by evaporation of the solvent under reduced pressure and passed through a short plug of silica using dichloromethane as the eluent. The solvent was concentrated to give 1.84 g (96%) of the title compound as a tan solid, mp 150 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (s, 1H), 8.19 (d, J=8.9 Hz, 1H), 8.13 (d, J=8.9 Hz, 1H), 8.10 (dd, J=8.1, 0.8 Hz, 1H), 8.03 (dd, J=7.7, 1.6 Hz, 1H), 7.68 (d, J=8.2 Hz, 1H), 7.64 (td, J=7.3, 1.5 Hz, 1H), 7.62 (d, J=8.1 Hz, 1H), 7.59 (td, J=6.9, 1.5 Hz, 1H), 5.10 (d, J=10.5 Hz, 1H) 5.03 (d, J=10.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.5, 131.9, 131.4, 131.2, 131.1, 130.8, 130.0, 129.4, 129.2, 129.0, 128.9, 127.21, 127.19, 126.9, 126.6, 124.9, 124.2, 120.7, 31.4. HRMS DART (m/z): $[M+H]^+$calcd for $C_{19}H_{12}BrCl_2$ 388.9499; found 388.9480.

4.7. (1,4-Dichlorobenzo[*c*]phenanthren-6-yl)acetonitrile (29)

6-Bromomethyl-1,4-dichlorobenzo[*c*]phenanthrene (5.280 g, 13.52 mmol), potassium cyanide (3.520 g, 54.09 mmol), and tetrabutylammonium hydrogensulfate (4.590 g, 13.52 mmol) were placed in a round-bottom flask. To this were added 250 mL of dichloromethane and 125 mL of water. The reaction mixture was stirred vigorously for 10 h at room temperature to ensure that the two layers were mixing. The layers were then allowed to separate, and the organic layer was washed with water (2×150 mL) and finally with saturated aqueous sodium chloride (150 mL). After the organic layer was dried over magnesium sulfate, it was filtered, deposited onto silica gel by evaporation of the solvent under reduced pressure and passed through a short plug of silica using dichloromethane as the eluent. The product was concentrated to dryness and yielded 4.12 g (90%) of the title compound as a pale yellow solid, mp 158 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H), 8.14 (d, J=8.8 Hz, 1H), 8.12 (d, J=8.1 Hz, 1H), 8.03 (dd, J=7.8, 1.4 Hz, 1H), 7.91 (d, J=8.8 Hz, 1H), 7.71 (d, J=8.2 Hz, 1H), 7.66 (td, J=7.2, 1.3 Hz, 1H), 7.65 (d, J=8.3 Hz, 1H), 7.61 (ddd, J=8.4, 7.0, 1.6 Hz, 1H), 4.27 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.8, 131.2 (2C?), 130.9, 130.7, 129.9, 129.6 129.1, 128.6, 128.5, 127.2, 127.1, 126.9, 126.7, 126.3, 125.3, 123.3, 119.2, 117.0, 22.3 (one overlapping peak). IR (KBr) $\nu_{(C\equiv N)}$: 2248 cm^{-1}. HRMS APPI (m/z): $[M]^+$calcd for $C_{20}H_{10}Cl_2N$ 334.0190; found 334.0195.

4.8. (1,4-Dichlorobenzo[*c*]phenanthren-6-yl)acetic acid (30)

A 500 mL round-bottom flask was charged with (1,4-dichlorobenzo[*c*]phenanthren-6-yl)acetonitrile (4.120 g, 12.24 mmol) and 80 mL each of glacial acetic acid, concd sulfuric acid, and water. The mixture was heated to reflux (approximately 110 °C) with stirring for 16 h. The reaction mixture was then cooled to room temperature and diluted with water. The precipitate was collected by vacuum filtration and washed with water. Any large solids were broken up with a mortar and pestle, washed again with water, and filtered. The gray powder was dried thoroughly under vacuum to yield 4.05 g (93%) of the title compound, mp 209–211 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (s, 1H), 8.01 (d, J=8.0 Hz, 1H), 7.95 (d, J=8.8 Hz, 1H), 7.89 (d, J=7.8 Hz, 1H), 7.86 (d, J=8.8 Hz, 1H), 7.56 (d, J=8.1 Hz, 1H), 7.54–7.46 (m, 3H), 4.19 (d, J=16.2 Hz, 1H), 4.09 (d, J=16.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.3, 131.7, 131.5, 131.3, 131.1, 130.9, 130.5, 130.2, 129.4 128.9, 128.6, 128.4, 127.1, 126.8, 126.7, 126.4, 124.93, 124.91, 120.7, 39.1. IR (KBr) $\nu_{(O-H)}$: 3046 cm^{-1}, $\nu_{(C=O)}$: 1708 cm^{-1}. HRMS DART (m/z): $[M+H]^+$calcd for $C_{20}H_{13}Cl_2O_2$ 355.0293; found 355.0299.

4.9. 1,4-Dichloro-6*H*-benzo[*a*]acephenanthrylen-7-one (31)

(1,4-Dichlorobenzo[*c*]phenanthren-6-yl)acetic acid (1.01 g, 2.84 mmol) was added to a flame-dried 1 L three-necked round-bottom flask equipped with a reflux condenser under nitrogen. To this was added thionyl chloride (40 mL, 548 mmol) and the resulting solution was heated to reflux (approximately 80 °C). After 1 h, the excess thionyl chloride was removed by vacuum distillation to leave a yellow-brown oil in the flask. The system was refilled with nitrogen, and the oil was dissolved in 650 mL of anhydrous dichloromethane, which was then cooled to 0 °C with an ice bath. The yellow solution turned dark red upon addition of aluminum chloride (1.14 g, 8.53 mmol). The solution was stirred at 0 °C for 1 h, at which point it was heated to reflux (approximately 40 °C) for 15 min. After being cooled to room temperature, the reaction was quenched by addition of 1 N aqueous hydrochloric acid (50 mL). The yellow solution was washed first with water (2×250 mL), then with saturated sodium chloride solution (250 mL), and finally dried over magnesium sulfate and filtered. The solvent was removed by rotary evaporation, and the crude material was passed through a short plug of silica with dichloromethane as the eluent. Removal of the solvent gave 0.96 g (83%) of 1,4-dichlorobenzo[*a*]acephenanthrylen-7-one as a yellow solid, mp 190 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1H), 8.39 (s, 1H), 8.35 (d, J=8.4 Hz, 1H), 8.24 (d, J=8.4 Hz, 1H), 7.81–7.68 (m, 4H), 3.99 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.9, 140.2, 134.6, 133.6, 133.5, 131.5, 131.31, 131.28, 131.2, 130.9, 130.4, 128.6, 127.7, 127.2, 127.1, 126.8, 126.4, 123.3, 118.5, 41.8. IR (KBr) $\nu_{(C=O)}$: 1719 cm^{-1}. HRMS DART (m/z): $[M+H]^+$calcd for $C_{20}H_{11}Cl_2O$ 337.0187; found 337.0188.

4.10. Trimerization of 1,4-dichloro-6*H*-benzo[*a*]-acephenanthrylen-7-one (3b)

Into a flame-dried 50 mL sealable tube were added 1,4-dichloro-6*H*-benzo[*a*]acephenanthrylen-7-one (0.500 g, 1.48 mmol) and *p*-toluenesulfonic acid monohydrate (0.987 g, 5.19 mmol). The tube was flushed with nitrogen, and then 10 mL of *o*-dichlorobenzene and 0.04 mL of propanoic acid were added via syringe. The tube was sealed and immersed in an oil bath at 180 °C for 16 h. After the reaction mixture had cooled to room temperature, it was diluted with sufficient methanol to precipitate the crude product (200 mL). From vacuum filtration, 0.374 g (79%) of a brown solid was obtained. The product was too insoluble for NMR characterization. MALDI-TOF MS analysis matched with the calculated isotope pattern and showed no other major peaks: (m/z) $[M]^+$ 954/956/958/960/962. HRMS DART negative ion mode (m/z): $[M^+]$ calcd for $C_{60}H_{24}Cl_6$ 954.0009; found 953.9963. HRMS DART positive ion mode (m/z): $[M+1]^+$ calcd for $C_{60}H_{25}Cl_6$ 955.0082; found 955.0069.

4.11. Trimerization of 4-chloro-6*H*-benzo[*a*]-acephenanthrylen-7-one using *p*-TsOH (3a)

Into a flame-dried 10 mL sealable tube were added 4-chloro-6*H*-benzo[*a*]acephenanthrylen-7-one (0.050 g, 0.17 mmol) and *p*-toluenesulfonic acid monohydrate (0.110 g, 0.578 mmol). The tube was flushed with nitrogen, and then 1 mL of *o*-dichlorobenzene and 0.04 mL of propanoic acid were added via syringe. The tube was sealed and immersed in an oil bath at 180 °C for 16 h. After the reaction mixture had cooled to room temperature, it was diluted with sufficient methanol to precipitate the crude product (approximately 50 mL). From vacuum filtration, 0.035 mg (74%) of a dark brown solid was obtained. The product was too insoluble for NMR characterization. MALDI-TOF MS showed no other major peaks: (*m*/*z*) $[M]^+$ 852/854.

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Supplementary data

The supplementary data contains experimental procedures for all the reactions depicted in Figures 7–11, as well as ^{1}H NMR and ^{13}C NMR spectra for compounds **6**, **8**–**13**, **16**–**21**, and **26**–**31** and mass spectra for compounds **3a**, **3c**, **14**, and **15**. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.09.087.

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31. Hydrolysis of nitrile **11** was first attempted under basic conditions using KOH in ethylene glycol; however, the reaction did not proceed cleanly, giving decomposition products that were difficult to separate.
32. Chromatography of the mixture gave a slow moving red band that was tentatively identified as the tetramerdione **24** on the basis of its mobility and its ^{1}H NMR spectrum; the most characteristic signals appeared far downfield at δ 9.80 (singlet), 9.21 (doublet), and 9.09 (triplet).
33. We have found that 2,5-dichlorobenzaldehyde (**25**) can be easily prepared in 67% yield by *ortho*-lithiation of *p*-dichlorobenzene with 1 equiv of *n*-butyl lithium,[34] followed by 1 equiv of *N*,*N*-dimethyl formamide and aqueous hydrolysis.
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