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Circumtrindene: A Geodesic Dome of Molecular Dimensions. Rational Synthesis of 60% of C_{60}[1]

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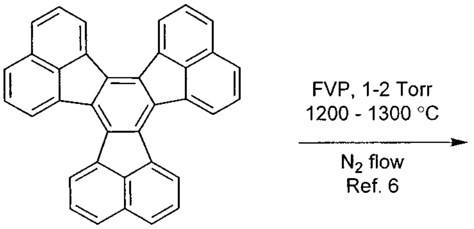
Abstract: The title compound (**1**), which had previously been available in only 0.2% yield by flash vacuum pyrolysis (FVP) of decacyclene (**2**) at 1200−1300 °C, has now been prepared in 25−27% yield by FVP of 3,9,15-trichlorodecacyclene (**5b**) at 1100 °C. The propeller-shape **5b** was synthesized by aldol cyclotrimerization of 8-chloro-1(2*H*)-acenaphthylenone (**8b**), which, in turn, was prepared by a simple four-step synthesis from 2-chloronaphthalene. The synthetic strategy demonstrated here, which has improved the yield of circumtrindene (**1**) by more than 2 orders of magnitude, should be applicable to the rational synthesis of larger geodesic polyarenes, both open (bowls, baskets, tubes, etc.) and closed (fullerenes).

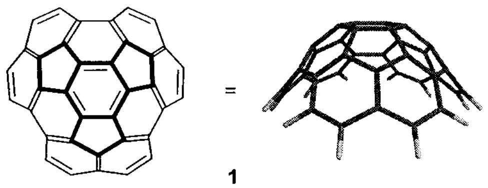
Introduction

Since the early 1990s,[2] much attention has been directed toward bowl-shaped hydrocarbons in which curved networks of trigonal carbon atoms map out the same patterns of 5- and 6-membered rings as those found on the surfaces of C_{60} and/or the higher fullerenes.[3] These "open geodesic polyarenes" constitute a novel family of carbon-rich compounds[4] that in many ways hold just as much fascination as their closed geodesic cousins, the fullerenes.[5]

The largest member of this family prepared to date is the $C_{36}H_{12}$ geodesic dome **1**, which represents 60% of C_{60}. We first synthesized **1** in 1996 by a brute force triple cyclodehydrogenation of decacyclene (**2**),[6] a transformation which could be effected in only 0.2% yield at that time. Herein we report the rational synthesis of a suitably functionalized decacyclene derivative that can be closed up by flash vacuum pyrolysis (FVP) to give **1** in yields of 25−27%.



2
"Decacyclene"



1
"Circumtrindene"

Because the IUPAC name for **1** is rather onerous (triacenaphtho[3,2,1,8-*c*,*d*,*e*,*f*,*g*; 3′,2′,1′,8′-*i*,*j*,*k*,*l*,*m*; 3″,2″,1″,8″-*o*,*p*,*q*,*r*,*a*]-triphenylene), we consider it appropriate to introduce a more convenient trivial name. As it happens, **1** belongs to a family of large polycyclic aromatic hydrocarbons (PAHs) in which a continuous ribbon of benzene rings encircles a recognizable core, and a well-entrenched system of colloquial nomenclature already exists to describe such compounds ("circulenes"). Names such as "circumanthracene" and "circobiphenyl" have been used for decades in both the chemical literature and *Chemical Abstracts* to describe such unwieldy PAHs as **3** and **4**.[7] Building on the

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(1) Aspects of this work have been reported previously in preliminary accounts: (a) Scott, L. T.; Bronstein, H. E.; Preda, D. V.; Ansems, R. B. M.; Bratcher, M. S.; Hagen, S. Presented at the Ninth International Symposium on Novel Aromatic Compounds, Hong Kong, August 1998 (Nozoe Memorial Lecture). (b) Scott, L. T.; Bronstein, H. E.; Preda, D. V.; Ansems, R. B. M.; Bratcher, M. S.; Hagen, S. Fourteenth International Conference on Physical Organic Chemistry, Florianópolis, Santa Catarina, Brazil, August 1998; Abstract IL5C. (c) Ansems, R. B. M.; Bratcher, M. S.; McComas, C. C.; Scott, L. T. *Abstracts of Papers*, 216th National Meeting of the American Chemical Society, Boston, MA; American Chemical Society: Washington, DC, 1998; Abstract ORGN 103. See also refs 3f and 3g.

(2) (a) Scott, L. T.; Hashemi, M. M.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 7082−7084. (b) Scott, L. T.; Hashemi, M. M.; Bratcher, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 1920−1921. (c) Borchardt, A.; Fuchicello, A.; Kilway, K. V.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 1921−1923.

(3) Several reviews have already been published: (a) Rabideau, P. W.; Sygula, A. In *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; JAI Press: Greenwich, 1995; Vol. 3, pp 1−36. (b) Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235−242. (c) Scott, L. T. *Pure Appl. Chem.* **1996**, *68*, 291−300. (d) Mehta, G.; Rao, H. S. P. *Adv. Strain Org. Chem.* **1997**, *6*, 139−187. (e) Mehta, G.; Rao, H. S. P. *Tetrahedron* **1998**, *54*, 13325−13370. (f) Scott, L. T.; Bronstein, H. E.; Preda, D. V.; Ansems, R. B. M.; Bratcher, M. S.; Hagen, S. *Atual. Fis.-Quim. Org.* **1999**, *11*, 138−150. (g) 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.

(4) Such compounds have sometimes been referred to as "fullerene fragments" or "buckybowls".

(5) 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.

(6) Scott, L. T.; Bratcher, M. S.; Hagen, S. *J. Am. Chem. Soc.* **1996**, *118*, 8743−8744.

(7) Clar, E. *Polycyclic Hydrocarbons*; Academic Press: New York, 1964; Vol. 1, pp 9−10.

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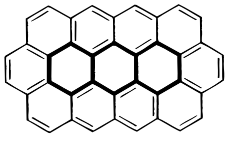

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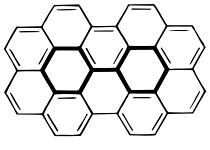
"Circumanthracene"



4

"Circobiphenyl"

name "trindene", which already appears in both the chemical literature and *Chemical Abstracts* to describe the 15-carbon core of our geodesic dome (**1**),[8] we propose the trivial name "circumtrindene" for everyday use in discussing this molecular geodesic dome, when circumstances do not demand the more formal IUPAC name.

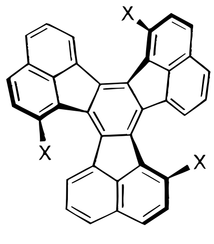
Our interest in circumtrindene (**1**) includes the exploration of its chemistry, and such an undertaking would obviously benefit from ready access to large amounts of the compound. For this reason, and because the crudeness and 0.2% yield of our first synthesis are somewhat embarrassing, we wanted to devise a better route to **1**.

Synthesis Plan

The strategy we chose is a simple one. Cyclodehydrogenations under FVP conditions rarely work well;[9] however, we have shown that dramatic improvements can be achieved by the incorporation of functional groups capable of generating radical centers at the sites of the desired ring closures[2b,3c,f,g,10,11] (or even just near the sites).[10c,12] Application of this strategy to the synthesis of **1** leads naturally to **5** (X = Cl or Br) as a potentially superior FVP precursor. The challenge, then, is reduced to finding an efficient way to prepare the C_3-symmetric isomer of a suitable trisubstituted decacyclene.[13]

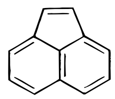
Unfortunately, most of the published syntheses of decacyclene (**2**), including the original preparation (1883!) by oxidative trimerization of acenaphthylene (**6**),[14] lack the elements of regiochemical control required to cyclotrimerize an unsymmetrically substituted acenaphthylene selectively to the C_3-symmetric decacyclene.[13b,15] Compounding the problem, simple statistics for the regiorandom trimerization of an unsymmetrically substituted acenaphthylene favor production of the C_1 isomer (**7**) over the C_3-symmetric isomer by a factor of 3:1.[16]

To control the regiochemistry, we planned to construct **5** by a head-to-tail aldol trimerization of a haloacenaphthenone, i.e., **8** or **9** (X = Cl or Br). This method for assembling substituted benzene rings with 3-fold symmetry works well for some ketones[17] but fails completely for others,[18] and the factors responsible for the success or failure of the reaction have never been firmly established. Only one report of the production of the parent decacyclene from unsubstituted acenaphthenone (**8a** → **2**) has appeared,[15a] but the reaction was not developed into a practical method for preparing the decacyclene ring system.[19]



5

a) X = H
b) X = Cl
c) X = Br



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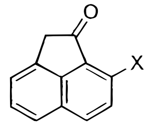

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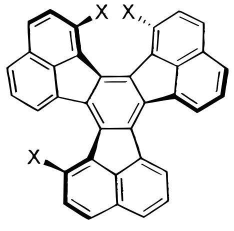

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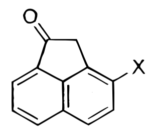

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Anticipating detrimental steric effects on the cyclotrimerization imparted by the halogen atoms,[20,21] we decided to use chlorine, rather than bromine, to serve as the X group. This choice was additionally influenced by our desire to maximize the volatility of the FVP precursor.

Results and Discussion

As predicted,[22] acetylation of 2-chloronaphthalene (**10**) gave almost exclusively the two products of monosubstitution at

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[8] (a) Katz, T. J.; Slusarek, W. *J. Am. Chem. Soc.* **1980**, *102*, 1058–1063. (b) Helvenston, M. C.; Lynch, T. J. *J. Organomet. Chem.* **1989**, *359*, C50–C52. See also *Chem. Abstr*. registry no. 73255-13-7.

[9] (a) Hagen, S.; Nuechter, U.; Nuechter, M.; Zimmermann, G. *Tetrahedron Lett.* **1994**, *35*, 7013–7014. (b) Hagen, S.; Nuechter, U.; Nuechter, M.; Zimmermann, G. *Polycyclic Aromat. Compd.* **1995**, *4*, 209–217. (c) Hagen, S.; Christoph, H.; Zimmermann, G. *Tetrahedron* **1995**, *51*, 6961–6970.

[10] (a) Bratcher, M. S.; Scott, L. T. *Abstracts of Papers*, 207th National Meeting of the American Chemical Society, San Diego, CA; American Chemical Society: Washington, DC, March 1994; Abstract ORGN 420. (b) Scott, L. T.; Bratcher, M. S. Eighth International Symposium on Novel Aromatic Compounds, Braunschweig, Germany, July 30 to Aug 4, 1995; Abstract 7. (c) Bratcher, M. S. Ph.D. Dissertation, Boston College, 1996. (d) Bronstein, H. E. Ph.D. Dissertation, Boston College, Chestnut Hill, 1999.

[11] See also: (a) Plater, M. J. *Tetrahedron Lett.* **1994**, *35*, 801–802. (b) Plater, M. J. *Tetrahedron Lett.* **1994**, *35*, 6147–6150.

[12] (a) Hagen, S.; Bratcher, M. S.; Erickson, M. S.; Zimmermann, G.; Scott, L. T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 406–408. (b) Brooks, M. A.; Scott, L. T. *J. Am. Chem.* Soc. **1999**, *121*, 5444–5449.

[13] For other recent attempts to prepare substituted decacyclenes as potential precursors to **1**, see: (a) Zimmermann, K.; Goddard, R.; Krueger, C.; Haenel, M. W. *Tetrahedron Lett.* **1996**, *37*, 8371–8374. (b) Zimmermann, K.; Haenel, M. W. *Synlett* **1997**, 609–611.

[14] (a) Rehländer, P. Ph.D. Dissertation, University of Berlin, Germany, 1883. (b) Rehländer, P. *Chem. Ber.* **1903**, *36*, 1583–1587.

[15] (a) Moszew, J.; Zankowska-Jasinska, W. *Rocz. Chem.* **1958**, *32*, 225, 230 (*Chem. Abstr.* **1958**, *52*, 16316h). (b) Staab, H. A.; Ipaktschi, J.; Nissen, A. *Chem. Ber.* **1971**, *104*, 1182–1190. (c) Nakayama, J.; Segiri, T.; Oya, R.; Hoshino, M. *J. Chem. Soc., Chem. Commun.* **1980**, 791–2. (d) Chapman, O. L.; Gano, J.; West, P. R.; Regitz, M.; Maas, G. *J. Am. Chem. Soc.* **1981**, *103*, 7033–7036. (e) Nakayama, J.; Ohshima, E.; Ishii, A.; Hoshino, M. *J. Org. Chem.* **1983**, *48*, 60–65. (f) Do, Q. T.; Elothmani, D.; Simonet, J.; Le Guillanton, G. *Bull. Soc. Chim. Fr.* **1994**, *131*, 789–793.

[16] For recent examples of such regiorandom trimerizations, see: (a) Reference 13a. (b) Sarobe, M. Ph.D. Dissertation, University of Utrecht, The Netherlands, 1998; Chapter 8. (c) Sarobe, M.; Fokkens, R. H.; Cleij, T. J.; Jenneskens, L. W.; Nibbering, N. M. M.; Stas, W.; Versluis, C. *Chem. Phys. Lett.* **1999**, *313*, 31.

[17] (a) Elmorsy, S. S.; Pelter, A.; Smith, K. *Tetrahedron Lett.* **1991**, *32*, 4175–4176. (b) Pyrko, A. N. *Zh. Org. Khim.* **1992**, *28*, 215–216. (c) Plater, M. J. *Synlett* **1993**, 405–406. (d) Dehmlow, E. V.; Kelle, T. *Synth. Commun.* **1997**, *27*, 2021–2031.

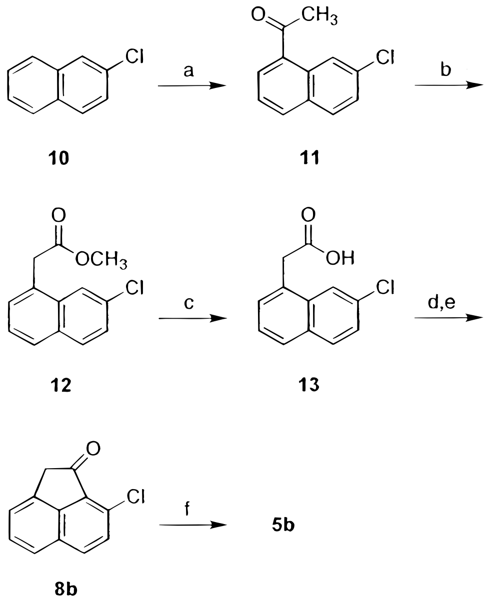
[18] (a) Elmorsy, S. S.; Pelter, A.; Smith, K.; Hursthouse, M. B.; Ando, D. *Tetrahedron Lett.* **1992**, *33*, 821–824. (b) Elmorsy, S. S.; Khalil, A. G. M.; Girges, M. M.; Salama, T. A. *Tetrahedron Lett.* **1997**, *38*, 1071–1074.

[19] After completing our work, we learned that Sarobe recently obtained decacyclene from the trimerization of acenaphthenone (**8a** → **2**) in 7% yield.[16b]

[20] The addition of three chlorine atoms (**5a** → **5b**) is calculated to increase the strain energy of the molecule by ca. 32 kcal/mol (from the heat of the isodesmic reaction: **5a** + $3C_6H_5Cl \rightarrow$ **5b** + $3C_6H_6$ calculated at the pBP/DN**//AM1 level of theory).

[21] Minimum energy molecular geometries were optimized at the AM1 level of theory, and single point energies were calculated at the pBP/DN** level of theory using the computational chemistry programs implemented in Spartan 5.0 (Wavefunction, Inc., Irvine, CA 92612).

Scheme 1

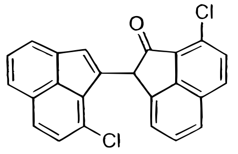


(a) CH_3COCl, $AlCl_3$, CH_2Cl_2, -78 °C (b) $Tl(NO_3)_3$•MeOH/K-10, $ClCH_2CH_2Cl$ (c) 5 *M* HCl, acetone (d) $SOCl_2$ (e) $AlCl_3$, CH_2Cl_2, 0 °C; then KF, H^+ (f) $TiCl_4$, o-$C_6H_4Cl_2$, 180 °C

positions 1 and 8. The known sensitivity of Friedel–Crafts acylations to steric effects[23] presumably accounts for the predominance of the latter isomer (**11**).[24,25] Low temperatures improved the isomer ratio to 13:1 in favor of **11**, and this solved our problem of regiochemistry.

Transposition of the carbonyl functionality to the end of the two-carbon chain with thallium(III) nitrate on K-10 clay[26] gave the acetic ester (**12**) in quantitative yield. Hydrolysis of **12** to the corresponding carboxylic acid (**13**), followed by Friedel–Crafts cyclization of the acid chloride, gave 8-chloroacenaphthenone (**8b**) on a multigram scale (Scheme 1).[27]

Cyclotrimerization of **8b** to the C_3-symmetric trichlorodecacyclene (**5b**) was achieved only after considerable experimentation. The best conditions found so far involve addition of the chloro ketone (**8b**) as a dilute solution in 1,2-dichlorobenzene (0.06–0.12 M) to an equal volume of boiling 1,2-dichlorobenzene (180 °C) that contains 6 molar equiv of $TiCl_4$. The rate of addition of the chloro ketone (**8b**) has little effect on the isolated yield of trichlorodecacyclene (**5b**), which never exceeds 25%.[28] In lower boiling solvents, such as 1,2-dichloroethane (bp = 83 °C), the trimerization proceeds only very slowly and gives numerous byproducts, including the β,γ-unsaturated dimer **14**.[29]



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An X-ray crystal structure of trichlorodecacyclene **5b** (Figure 1) reveals the three-bladed propeller shape of the molecule.[30] As expected from calculations, the chlorine atoms induce greater twists in the three blades than those seen in the unsubstituted hydrocarbon, decacyclene (**2**).[31] The somewhat greater solubility of trichlorodecacyclene **5b** in common organic solvents, relative to that of the parent hydrocarbon, probably derives from this increased deviation from planarity. Solutions of **5b** appear yellow with a strong green fluorescence. The amorphous solid is also yellow, but crystals of **5b** are red-brown in color. The UV–vis spectrum of trichlorodecacyclene **5b** (Figure 2) closely resembles that of the parent hydrocarbon, with a small bathochromic shift seen for all the peaks.

The low volatility of trichlorodecacyclene **5b** made its flash vacuum pyrolysis (FVP) something of a challenge, and our hope that the compound would be sufficiently robust to withstand the high heat necessary to promote its sublimation at reduced pressure was only partially realized. We found it necessary to introduce nitrogen as a carrier gas through a tiny inlet at the head of the sample chamber to push the vaporized trichlorodecacyclene through the hot tube (final pressure ca. 1.0 mmHg, see Experimental Section). In the end, approximately 70% of the trichlorodecacyclene sublimed and passed through the pyrolysis tube, while the remaining material decomposed in the sample chamber.

With the oven set at 1100 °C, FVP of trichlorodecacyclene gives 25–27% isolated yields of purified circumtrindene (**1**), based on the total amount of starting material used. The actual yield for the triple cyclization, based on the amount of trichlorodecacyclene that made it into the pyrolysis tube, is 35–40% after purification. Either method of calculating indicates an improvement in yield of more than 100-fold over the first synthesis of **1** (0.2% yield) by cyclodehydrogenation of decacyclene (**2**). The latter process fails completely at 1100 °C and requires temperatures of 1200–1300 °C to go at all.

After three years of tinkering with the cyclodehydrogenation of decacyclene (**2**), we have increased the yield of circumtrin-

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[22] Both AM1 calculations and simple resonance theory predict preferential attack at positions 1 and 8. The partial rate factors for protiodetritiation of 2-chloronaphthalene (experimental values) are also greatest at positions 1 and 8 (ref 23, p 106).

[23] Taylor, R. *Electrophilic Aromatic Substitution*; Wiley: New York, 1990; Section 6.7.3.

[24] Chloromethylation of **10** likewise gave almost exclusively the two products of monosubstitution at positions 1 and 8; however, the isomer ratio was closer to 1:1, and the two products could not be separated easily. Treatment of the mixture of chloromethyl compounds with KCN and cyclization of the corresponding carboxylic acids gave a mixture of the two acenaphthenones **8b** and **9b** in good overall yield, but no separation of isomers could be achieved at any intermediate stage in the synthesis. By tedious chromatography, it is possible to effect the separation of **8b** and **9b** on a small scale; however, this route was never developed into a practical synthesis.

[25] Friedel–Crafts acetylation of 2-bromonaphthalene likewise gave almost exclusively the two products of monosubstitution at positions 1 and 8; however, the site selectivitiy was lower than with 2-chloronaphthalene.

[26] Taylor, E. C.; Chiang, C.-S.; McKillop, A.; White, J. F. *J. Am. Chem. Soc.* **1976**, *98*, 6750–6752.

[27] The only prior preparation of 8-chloro-1(2*H*)-acenaphthylenone (**8b**) also entailed cyclization of (7-chloronaphthalen-1-yl)acetic acid (**13**); however, the published synthesis of **13** was considered too impractical for our purposes: (a) Price, C. C.; Voong, S. T. *J. Org. Chem.* **1949**, *14*, 111–115. (b) Karishin, A. P.; Mikhailenko, P. I.; Magda, V. I.; Lykho, V. P. *Vestn. Khar'k. Politekh. Inst.* **1975**, *104*, 52–56 (From: *Ref. Zh., Khim.* **1975**, Abstr. No. 17ZH219; *Chem. Abstr.* **1976**, *84*, 121534).

[28] Mass spectroscopic analysis of the byproducts formed in the trimerizations carried out at 180 °C in 1,2-dichlorobenzene reveals the presence of what appears to be a cyclic tetramer, the next higher homologue of trichlorodecacyclene **5** (X = Cl).

[29] ^1H NMR for **14** (400 MHz, $CDCl_3$): δ 8.38 (d, J = 6.8 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 8.8 Hz, 1H), 7.72 (dd, J = 8.0, 7.2 Hz, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.35 (dd, J = 8.4, 7.2 Hz, 1H), 7.20 (d, J = 8.8 Hz, 1H), 7.15 (d, J = 7.6 Hz, 1H), 5.65 (s, 1H), 2.75 (s, 1H).

[30] For a recent discussion of overcrowded "D_{3h}" polycyclic aromatic compounds, see: Barnett, L.; Ho, D. M.; Baldridge, K. K.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **1999**, *121*, 727–733.

[31] X-ray structure of **2**: Ho, D. M.; Pascal, R. A., Jr. *Chem. Mater.* **1993**, *5*, 1358–1361. The experimentally determined dihedral angles in the bottoms of the fjord regions (C3a–C3b–C3c–C3d) for decacyclene (**2**) and 3,9,15-trichlorodecacyclene (**5b**) are 9.10° and 13.34°, respectively. AM1 geometry optimizations predict 8.50° and 13.14°, respectively.

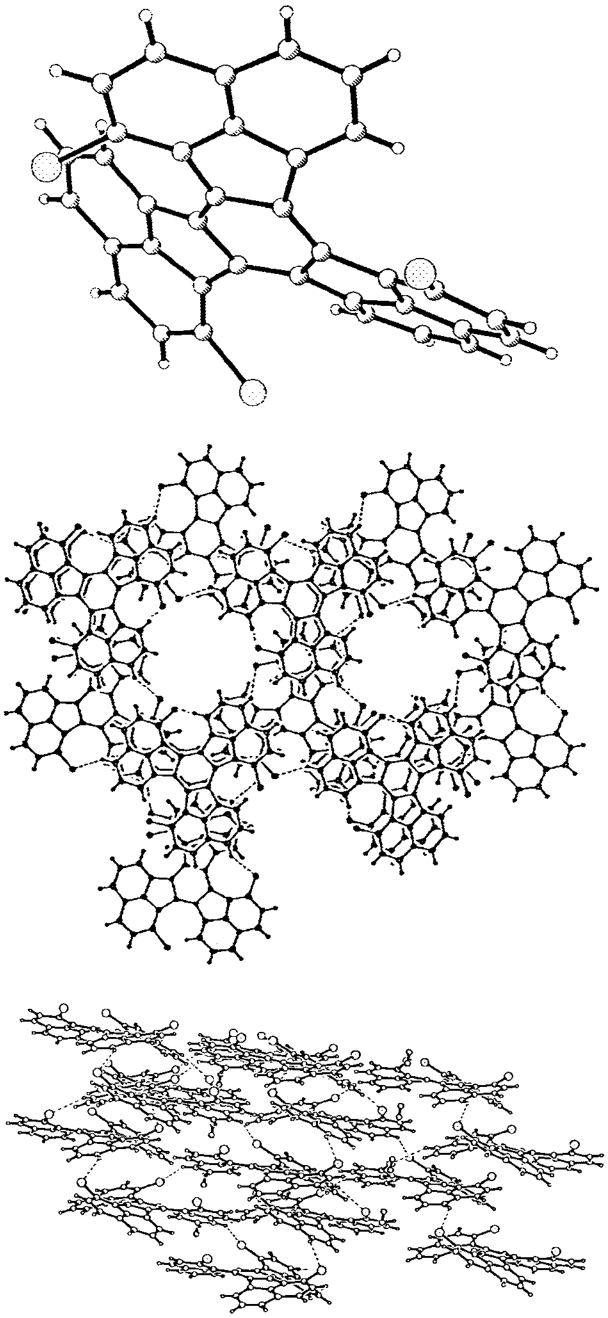

Figure 1. X-ray crystal structure of 3,9,15-trichlorodecacyclene (**5b**).

dene (**1**) by that route to 0.6%; however, further improvements seem unlikely. The striking superiority of trichlorodecacyclene **5b** over the unsubstituted hydrocarbon as a precursor to circumtrindene (**1**) dramatically underscores the value of incorporating functionality capable of generating radical centers at the sites where one wishes to close rings by carbon−carbon bond formation under FVP conditions.

Properties of Circumtrindene (1)

In agreement with AM1 calculations, an X-ray crystal structure of **1**[32] has confirmed that the carbon atoms comprising the top of the dome are distorted as much from planarity as are the carbon atoms in C$_{60}$ (in fact, slightly more!).[33,34] The UV−vis spectrum of **1** also resembles that of C$_{60}$,[6] and this open geodesic molecule even undergoes fullerene-like cycloaddition reactions at the 6:6-bonds closest to the top of the dome.[1,3f,g] The NMR signals for the hydrogen atoms in **1** fall in the "aromatic" region of the spectrum (7.58 and 7.20 ppm); however, the ring currents within the molecule provide substantially less deshielding than one sees in large, planar or less strongly curved PAHs.[35] High level molecular orbital calculations successfully reproduce the ^{1}H NMR chemical shifts for **1**,[36] but they provide no explanation for the relatively feeble deshielding power of the 13-ring π-system.

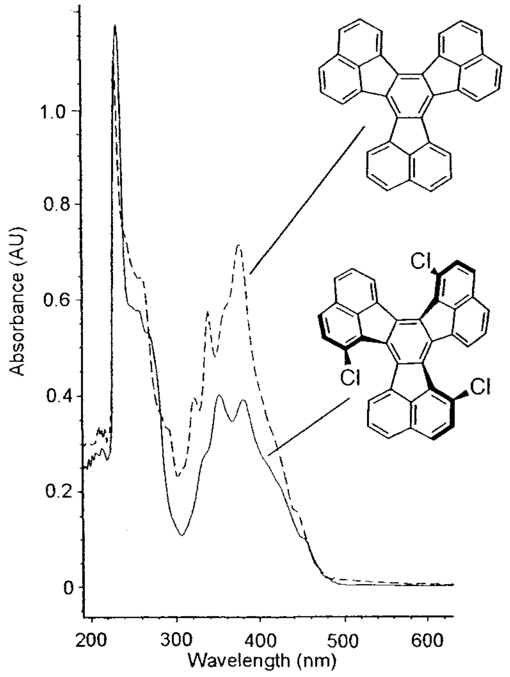

Figure 2. UV−vis spectra of 3,9,15-trichlorodecacyclene (**5b**) and unsubstituted decacyclene (**2**).

Future Directions

The synthesis described above was developed not only to provide a more rational route to circumtrindene (**1**) but, more importantly, to serve as a prototype for rational syntheses of still larger open geodesic polyarenes. Aldol trimerization of the next higher benzolog of **5b** (i.e., **15b**) should give the C_3-symmetric isomer of trichlorotribenzodecacyclene (**16b**), and FVP of this trimer should give the tribenzo derivative of circumtrindene (**17**). In our experience, once curvature has been introduced into a polycyclic aromatic π-system, further ring closures by cyclodehydrogenations sometimes occur without the need for additional radical-generating groups.[37] A 3-fold cyclodehydrogenation of **17** would give the molecular basket **18**, a C$_{48}$H$_{12}$ open geodesic polyarene that represents 80% of C$_{60}$. We have already succeeded in preparing the C_3-symmetric tribenzodecacyclene derivatives **16a**[37,38] and **16b**[39] and are currently examining their suitability as synthetic precursors to the 48-carbon polyarenes **17** and **18**.

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[32] Forkey, D. M.; Attar, S.; Noll, B. C.; Koerner, R.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1997**, *119*, 5766−5767.

[33] In C$_{60}$, the angle between the p-orbital axis vector and the adjacent σ-bonds (i.e., the "POAV angle")[34] is 101.6°, whereas the POAV angles at the carbon atoms comprising the top of the dome in **1** average 102.15°.[32]

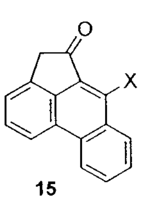
[34] (a) Haddon, R. C.; Scott, L. T. *Pure Appl. Chem.* **1986**, *58*, 137−142. (b) Haddon, R. C. *J. Am. Chem. Soc.* **1990**, *112*, 3385−3389. (c) Haddon, R. C. *J. Am. Chem. Soc.* **1997**, *119*, 1797−1798.

[35] Compare, for example, corannulene (C$_{20}$H$_{10}$) at 7.8 ppm and coronene (C$_{24}$H$_{12}$) at 8.9 ppm.

[36] Schulman, J. M.; Disch, R. L. *J. Comput. Chem.* **1998**, *19*, 189−194.

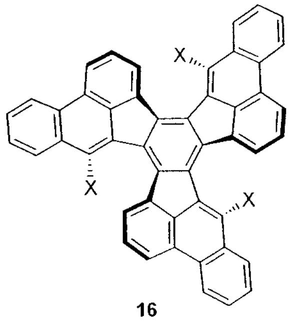
[37] (a) McMahon, B. J. B.S. Thesis, Boston College, 1996. (b) Scott, L. T.; Hagen, S. Unpublished observations.

Aldol trimers of the 20-carbon halo ketones **19** and **20** (or their keto-transposed isomers) represent attractive intermediates for the rational synthesis of C_{60}, and we are pursuing these enchanting prospects as well.[40]

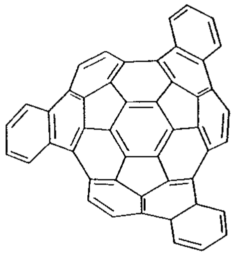


15

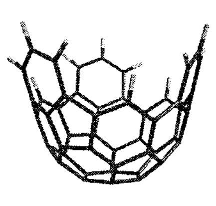
a) X = H
b) X = Cl
c) X = Br



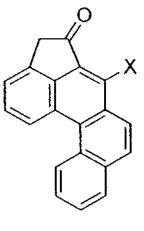
16



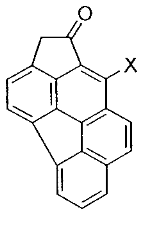
17



18



19



20

Experimental Section

General. All 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 the residual solvent peak of deuteriochloroform ($\delta = 7.26$) as the reference standard, unless otherwise specified. Carbon NMR shifts are reported in parts per million downfield of tetramethylsilane with deuteriochloroform ($\delta = 77.2$) as the reference standard. For column chromatographies, aluminum oxide, activated, neutral, Brockmann I, ~150 mesh, was used. High-resolution mass spectrometry (HRMS) was performed by the Mass Spectroscopy Laboratory, School of Chemical Sciences, University of Illinois. Elemental analysis was performed by Robertson Microlit Laboratories. Melting points are uncorrected.

1-(7-Chloro-1-naphthalenyl)ethanone (11). In a flame-dried 250 mL round-bottomed flask, fitted with a nitrogen inlet, was dissolved 10.0 g (61.5 mmol) of 2-chloronaphthalene (**10**) in 100 mL of methylene chloride. The resulting clear solution was cooled to −10 °C, and 25 g (190 mmol) of aluminum chloride was added. The reaction mixture was stirred at −10 °C until it became dark green; it was then cooled to −78 °C, and 10.0 g (127 mmol) of acetyl chloride was added with stirring. The resulting suspension was maintained at a temperature between −78 and −65 °C with stirring, and the progress of the reaction was monitored by GC−MS. After 5 h the peak for **10** had disappeared. The product mixture consisted roughly of 93% 1-(7-chloro-1-naphthalenyl)ethanone (**11**) along with 6−7% of the unwanted isomer 1-(2-chloro-1-naphthalenyl)ethanone. The reaction was quenched with a dilute HCl solution, and the products were extracted with methylene chloride. Removal of the solvent under reduced pressure gave an off-white solid. After repeated recrystallization of the crude product from methanol, 10.1 g (80% yield) of the desired isomer **11** was obtained as white crystals that were free of isomeric impurities (GC−MS): mp 63−64 °C (lit.[27a] mp 65−66 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, $J = 2.0$ Hz, 1H), 7.99 (dd, $J = 7.2, 1.0$ Hz, 1H), 7.96 (d, $J = 8.4$ Hz, 1H) 7.78 (d, $J = 8.8$ Hz, 1H), 7.49 (dd, $J = 8.0, 7.2$ Hz, 1H), 7.47 (dd, $J = 8.4, 2.4$ Hz, 1H), 2.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.17, 134.62, 134.17, 133.18, 132.34, 130.87, 130.15, 129.93, 127.59, 125.46, 124.74, 29.86; IR ($CHCl_3$) 1683 cm^{-1} (C═O); UV−vis (CH_2Cl_2) λ_{max} (ϵ, cm^{-1} M^{-1}) 232 (43 800), 304 (7500); MS (EI, 70 eV) *m/z* (relative intensity) 206 (M$^+$, ^{37}Cl, 20), 204 (M$^+$, ^{35}Cl, 51), 191 (39), 189 (100), 163 (21), 161 (55), 126 (37); HRMS (EI, 70 eV) calcd for $C_{12}H_9ClO$ (M$^+$) 204.0342, found 204.0347. Anal. Calcd for $C_{12}H_9ClO$: C, 70.43; H, 4.43; Cl, 17.32; O, 7.82. Found: C, 70.59; H, 4.39; Cl, 17.24; O, 7.57.

(7-Chloro-1-naphthalenyl)acetic Acid Methyl Ester (12). In a 500 mL round-bottomed flask, 10.0 g (48.9 mmol) of 1-(7-chloro-1-naphthalenyl)ethanone (**11**) was dissolved in 200 mL of 1,2-dichloroethane. To this solution was added 87.0 g (58.7 mmol) of thallium(III) nitrate (TTN) on a K-10 clay support.[26] The resulting suspension was stirred vigorously and heated to reflux. The reaction progress was monitored by GC−MS. Almost immediately after the reaction mixture was heated to reflux, no more **11** could be detected; only a single peak for the (7-chloro-1-naphthalenyl)acetic acid methyl ester (**12**) was observed. The reaction mixture was cooled to room temperature, and the K-10 clay was filtered off. Removal of the solvent under reduced pressure gave 11.4 g (99% yield) of a brown yellow oil that slowly crystallized: mp 40−42 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, $J = 1.6$ Hz, 1H), 7.80 (d, $J = 8.8$, 1H), 7.77 (X portion of ABX pattern, 1H), 7.46−7.41 (AB portion of ABX pattern, 2H), 7.44 (dd, $J = 8.4, 1.6$, 1H), 4.03 (s, 2H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.75, 132.92, 132.49, 132.16, 130.42, 129.95, 129.13, 128.03, 126.84, 125.87 123.06, 52.38, 38.86; IR ($CHCl_3$) 1736 cm^{-1} (C═O); UV−vis (CH_2Cl_2) λ_{max} (ϵ, cm^{-1} M^{-1}) 232 (76 700), 284 (6500); MS (EI, 70 eV) *m/z* (relative intensity) 236 (M$^+$, ^{37}Cl, 18), 234 (M$^+$, ^{35}Cl, 46), 177 (34), 175 (86), 139 (26); HRMS (EI, 70 eV) calcd for $C_{12}H_9ClO$ (M$^+$) 234.0448, found 234.0452. Anal. Calcd for $C_{13}H_{11}ClO_2$: C, 66.53; H, 4.72; Cl, 15.11; O, 13.64. Found: C, 66.22; H, 4.71; Cl, 15.08; O, 13.40.

(7-Chloro-1-naphthalenyl)acetic Acid (13). In a round-bottomed flask, equipped with a reflux condenser, 11.4 g (48.6 mmol) of (7-chloro-1-naphthalenyl)acetic acid methyl ester (**12**) was dissolved in a 1:1 mixture of 5 M HCl and acetone (total 850−900 mL). The solution was stirred and heated to reflux. After 2.5 h at reflux, the reaction mixture was cooled to room temperature, and the acetone and methanol were removed under reduced pressure. The (7-chloro-1-naphthalenyl)acetic acid (**13**) was extracted from the aqueous residue with methylene chloride. After removal of the methylene chloride, **13** was dissolved in a very dilute NaOH solution, which was then washed with benzene. Slow addition of 5 M HCl to the basic solution, with cooling, until a pH of 1 was reached caused **13** to precipitate out. The precipitate was collected by filtration and dried to give 9.8 g (91% yield) of an off-white solid: mp 163.5−164.5 °C (lit.[27a] mp 162−163 °C); ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.51 (s, 1H), 8.01 (d, $J = 2.4$ Hz, 1H), 8.00 (d, $J = 8.8$ Hz, 1H), 7.90 (X portion of ABX pattern, 1H), 7.55 (dd, $J = 8.8, 2.2$ Hz, 1H), 7.05 (AB portion of ABX pattern, 2H), 4.06 (s, 2H); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, $J = 1.6$ Hz, 1H), 7.80 (d, $J = 8.8$ Hz, 1H), 7.78 (X portion of ABX pattern, 1H), 7.45−7.41 (AB portion of ABX pattern, 2H), 7.44 (dd, $J = 8.8, 2.2$ Hz, 1H), 4.04 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.46, 132.92, 132.72, 132.22,

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[38] For an alternative approach to **16a**, see: De Frutos, O.; Gomez-Lor, B.; Granier, T.; Monge, M. A.; Gutierrez-Puebla, E.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 204−207.

[39] Scott, L. T.; Boorum, M. M. Unpublished results.

[40] Other research groups have independently recognized the attractiveness of the C_3-symmetric trimer of **19** (X = H) and related hydrocarbons as potential precursors to C_{60}: (a) Chang, T. M.; Naim, A.; Ahmed, S. N.; Goodloe, G.; Shevlin, P. B. *J. Am. Chem. Soc.* **1992**, *114*, 7603−7604. (b) Wang, L.; Shevlin, P. B. *Abstracts of Papers*, 212th National Meeting of the American Chemical Society, Orlando, FL; American Chemical Society: Washington, DC, 1996; Abstract ORGN-345. (c) One regiorandom synthesis of $C_{60}H_{30}$ hydrocarbon trimers has been reported, but the authors were not able to effect conversion to C_{60}.[16b,c] (d) Gomez-Lor, B.; de Frutos, O.; Echavarren, A. M. *Chem. Commun.* **1999**, 2431−2432.

130.53, 129.40, 129.22, 128.38, 127.03, 125.93 123.02, 38.69; IR ($CHCl_3$) 1713 cm^{-1} (C=O); UV−vis (CH_2Cl_2) λ_{max} (ϵ, cm^{-1} M^{-1}) 232 (74 700), 284 (6200); MS (EI, 70 eV) *m*/*z* (relative intensity) 222 (M$^+$, ^{37}Cl, 18), 220 (M$^+$, ^{35}Cl, 50), 177 (39), 175 (100), 139 (26); HRMS (EI, 70 eV) calcd for $C_{12}H_9ClO$ (M$^+$) 220.0291, found 220.0293. Anal. Calcd for $C_{12}H_9ClO_2$: C, 65.32; H, 4.11; Cl, 16.07; O, 14.50. Found: C, 65.26; H, 4.06; Cl, 16.01; O, 14.19.

8-Chloro-1(2*H*)-acenaphthylenone (8b). Into a flame-dried 1 L three-necked round-bottomed flask, fitted with a condenser and nitrogen inlet, was placed 3.00 g (13.6 mmol) of (7-chloro-1-naphthalenyl)-acetic acid (**13**). To this was added 50 mL of thionyl chloride. The resulting brown solution was stirred and heated to reflux under nitrogen for 1 h. The excess thionyl chloride was removed under reduced pressure by replacing the nitrogen inlet with a vacuum adapter and trapping the thionyl chloride in a dry ice/acetone bath. After the vacuum had been released, the nitrogen inlet was reattached, 750 mL of methylene chloride was added, and the solution was cooled to 0 °C in an ice bath. Then 3.7 g (28 mmol) of aluminum chloride was added, and the resulting dark green solution was stirred at 0 °C for 1 h. The solution was heated to reflux for 15 min and cooled to room temperature, and 2.5 g (43 mmol) of potassium fluoride in 10% hydrochloric acid was added. The dark orange/red solution was extracted with methylene chloride and washed with 10% hydrochloric acid, saturated sodium bicarbonate, and saturated sodium chloride. A small amount of activated charcoal was added, and the solution was dried over magnesium sulfate. Filtration through a short pad of Florisil and removal of the solvent under reduced pressure gave 2.30 g (83% yield) of 8-chloro-1(2H)-acenaphthylenone (**8b**) as a white/yellow solid: mp 141−143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.61 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.50 (dd, *J* = 7.2, 0.8 Hz, 1H), 3.86 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.97, 143.82, 133.93, 132.77, 130.32, 130.01, 129.52, 129.25, 128.62, 124.20, 122.06, 42.52; IR ($CDCl_3$) 1710 cm^{-1} (C=O); UV−vis (CH_2Cl_2) λ_{max} (ϵ, cm^{-1} M^{-1}) 232 (15 700), 262 (25 100), 326 (5 600), 340 (5 700); MS (EI, 70 eV) *m*/*z* (relative intensity) 204 (M$^+$, ^{37}Cl, 15), 202 (M$^+$, ^{35}Cl, 46), 176 (5), 174 (16), 167 (6), 139 (100). Anal. Calcd for $C_{12}H_7ClO$: C, 71.13; H, 3.48; O, 7.90. Found: C, 70.99; H, 3.56; O, 7.53;

3,9,15-Trichlorodecacyclene (5b). Into a flame-dried 100 mL three-necked round-bottomed flask, fitted with a condenser and a nitrogen inlet, was placed 4 mL of *o*-dichlorobenzene. To this was added 0.170 mL (1.55 mmol) of titanium tetrachloride by syringe, and the resulting yellow solution was heated to reflux. A solution of 50 mg (0.25 mmol) of 8-chloro-1(2*H*)-acenaphthylenone (**8b**) in 4 mL of *o*-dichlorobenzene was then added dropwise over ca. 45 min. Immediately after the addition of **8b** began, the solution turned dark. After the last drop of the 8-chloro-1(2*H*)-acenaphthylenone solution had been added, the reaction mixture was maintained at reflux for an additional 45−60 min. The resulting black solution was allowed to cool to room temperature and was then poured over concentrated hydrochloric acid/ice to quench the reaction. Dilution with 200−300 mL of methylene chloride gave a dark red organic layer. The organic layer was separated, washed with an additional portion of 10% hydrochloric acid, saturated sodium bicarbonate, and saturated sodium chloride, and dried over calcium carbonate. Evaporation of the solvents under reduced pressure gave a dark red/brown solid. Flash column chromatography on activated alumina with 4% ethyl acetate in hexane gave 11.2 mg (25%) of 3,9,15-trichlorodecacyclene (**5b**) as a yellow solid: mp 319−322 °C. Slow evaporation of a solution of **5b** in methylene chloride resulted in crystals suitable for X-ray structure determination: mp >410 °C, starts to slowly decompose at 375 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.2 Hz, 3H), 7.90 (d, *J* = 8.8 Hz, 3H), 7.89 (d, *J* = 7.6 Hz, 3H), 7.74 (dd, *J* = 8.0, 7.2 Hz, 3H), 7.67 (d, *J* = 8.8 Hz, 3H); ^{13}C NMR[41] (100 MHz, $CDCl_3$) δ 135.70, 130.70, 128.56, 127.53, 127.39, 126.49; UV−vis (CH_2Cl_2) λ_{max} (ϵ, cm^{-1} M^{-1}) 234 (81 800), 258 (41 700), 270 (38 400), 352 (31 000), 382 (29 800); MS (EI, 70 eV) *m*/*z* (relative intensity) 556 (M$^+$, ^{35}Cl^{37}Cl$_2$, 1), 554 (M$^+$, ^{35}Cl$_2$^{37}Cl, 3), 552 (M$^+$, ^{35}Cl$_3$, 3), 446 (18), 203 (42), 189 (100), 161 (50), 126 (34), 84 (45); HRMS (EI, 70 eV) calcd for $C_{36}H_{15}Cl_3$ (M$^+$) 552.0239, found 552.0232.

Circumtrindene (1) from Flash Vacuum Pyrolysis of 3,9,15-Trichlorodecacyclene (5b). The apparatus used for this flash vacuum pyrolysis (FVP) has been described previously.[6] In a typical run, 49.8 mg of 3,9,15-trichlorodecacyclene (**5b**) was placed in a preweighed sample boat. As soon as the oven reached the desired temperature of 1100 °C, the sample boat was inserted into the front end of the quartz furnace tube so that it was positioned at a distance of about 2 cm from the entrance to the furnace. During this operation, this external section of the pyrolysis tube was cooled with a hair dryer set on cold. The system was then closed up by attaching to the pyrolysis tube a head chamber, which was connected to a 1.0 atm reservoir of nitrogen gas through a capillary inlet tube made out of a section of GC capillary. On the other side of the oven, the pyrolysis tube was connected to a high-capacity vacuum pump through a cold trap filled with liquid nitrogen. As soon as the pressure in the pyrolysis apparatus got down to 1−2 mm of mercury, the hair dryer was removed, and the section of the furnace tube housing the sample boat inside was slowly heated with a heating tape. The variable AC controller was slowly turned up from about 25% to 40% over a period of about 5 h. At the end of this period, some of the trichlorodecacyclene (**5b**) could still be seen at the rear of the boat, but the material closest to the hot zone had decomposed into a black insoluble solid. The pyrolysis was stopped, and the oven was allowed to cool. The total residue left in the boat was 16.5 mg. The pyrolysate collected from the elbow of the tube and the trap gave 20.3 mg of crude product. After column chromatography with hexane/methylene chloride (8:1) on aluminum oxide, 10.5 mg of circumtrindene (**1**) was obtained. The yield was 26.3% based on the total amount of 3,9,15-trichlorodecacyclene used for the pyrolysis. Based on the amount of starting material that actually went through the pyrolysis tube, the yield was 39.3%: mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 9.2 Hz, 6H), 7.20 (d, *J* = 9.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 139.4, 136.8, 135.1, 127.2, 126.8, 125.4; UV−vis (CH_3CN) λ_{max} (ϵ, cm^{-1} M^{-1}) 232.5 (37 000), 290.5 (25 000), 322 (sh, 16 000), 368 (sh, 4 000); MS (EI, 70 eV) *m*/*z* (relative intensity) 445 (37, M + 1), 444 (100, M$^+$), 443 (10), 442 (15), 222.5 (10), 222 (28, M^{2+}), 221 (15); HRMS (EI, 70 eV) calcd for $C_{36}H_{12}$ (M$^+$) 444.0939, found 444.0938.

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Supporting Information Available: NMR spectra of compounds **1**, **5b**, **8b**, **11**, **12**, and **13**. Tables of data and several views of the X-ray crystal structure of 3,9,15-trichlorodecacyclene (**5b**) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(41) Poor solubility precluded observation of the remaining ^{13}C NMR signals.