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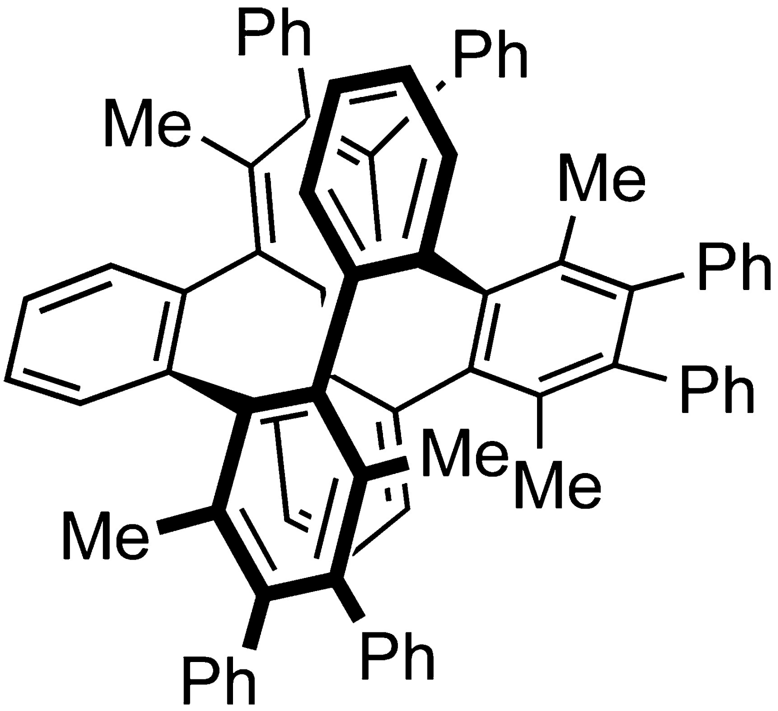

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Polyphenyl Macrocyclic Oligophenylenes

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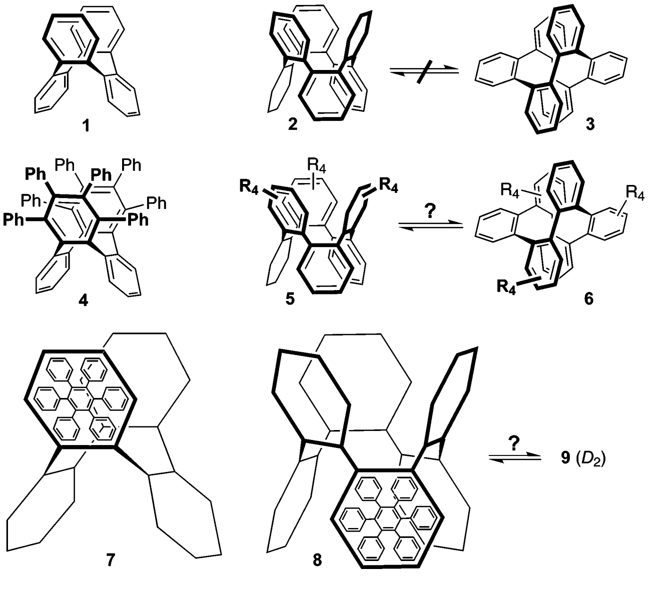
Abstract: The Diels–Alder reaction of tribenzohexadehydro[12]annulene (**12**) and 3,4-diphenyl-2,5-dimethylcyclopentadienone (**13**) at 300 °C gave the triple adduct 2,3,10,11,18,19-hexaphenyl-1,4,9,12,-17,20-hexamethylhexa-*o*-phenylene (**6b**) in 13% yield. NMR and X-ray analysis indicated that **6b** adopts a screw conformation (C_2) rather than a crown conformation (C_3), and computational studies seem to rule out any interconversion of the two. Palladium-catalyzed coupling of 1,2-bis(4-bromophenyl)-3,4,5,6-tetraphenylbenzene (**17**) and the corresponding bis(boronic acid) **18** gave a mixture of linear and cyclic oligomers of hexaphenylbenzene containing two to six hexaphenylbenzene subunits. A macrocyclic tetramer was isolated from this mixture in 5% yield, and X-ray analysis showed it to be the “supertetraphenylene” **7** ($C_{168}H_{112}$) that contains a large central cavity and packs to form highly solvated, porous crystals. The difficulties encountered in the purification of **7** led to the development of alternative, more highly selective syntheses that give the pure macrocycle more easily but in essentially the same overall yield.

Introduction

“Polyphenylene nanostructures” are of great current interest, but the term embraces an enormous variety of molecules differing greatly in their structures, properties, and representation in the literature. Judging from recent reviews,[1,2] large linear or dendrimeric polyphenylenes are the most common forms, followed by large “graphenes” (planar, highly condensed, polycyclic aromatic hydrocarbons) that are themselves prepared by dehydrogenation of dendrimeric polyphenylenes. Much less common are cyclic oligophenylenes: medium or large rings constructed entirely from benzene subunits connected by single bonds.

We are particularly interested in molecules with the topology of the cyclic *o*-phenylenes, tetra-*o*-phenylene (**1**, Chart 1), and hexa-o-phenylene (**2**).[3] These molecules are substructures of the hypothetical carbon allotrope “cubic graphite”,[4] and their conical cavities suggest that they might be used as hosts in molecular association or as building blocks for porous solids. Indeed, compound **1** forms a variety of crystalline solvates,[5] and Müller et al. have prepared the octaphenyl derivative **4** that also encapsulates solvent in the crystal.[6] However, larger cavities, able to accommodate more complex or numerous guests, would be more interesting, and in this work we explore the chemistry of larger, macrocyclic oligophenylenes. We report the synthesis and structure of a highly substituted derivative of hexaphenylene (**6**), computational studies of the conformational preferences and interconversion of the hexaphenylenes, and several syntheses and the structure of “supertetraphenylene” **7**,[7] in which each benzene ring of **1** is replaced by a hexaphenylbenzene.

Chart 1



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[1] Berresheim, A. J.; Müller, M.; Müllen, K. *Chem. Rev.* **1999**, *99*, 1747–1785.

[2] Watson, M. D.; Fechtenkötter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267–1300.

[3] Inasmuch as this paper deals only with the ortho isomers, henceforth, tetra-*o*-phenylene and hexa-*o*-phenylene will be named simply “tetraphenylene” and “hexaphenylene”.

[4] Gibson, J.; Holohan, M.; Riley, H. L. *J. Chem. Soc.* **1946**, 456–461.

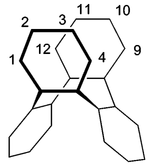
[5] (a) Huang, N. Z.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1982**, 543–544. (b) Wong, H. N. C.; Man, Y.-M.; Mak, T. C. W. *Tetrahedron Lett.* **1987**, *28*, 6359–6362.

[6] Müller, M.; Iyer, V. S.; Kübel, C.; Enkelmann, V.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1607–1610.

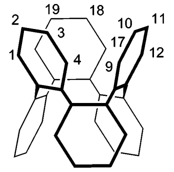
[7] One synthesis and the structure of **7** has been reported in a preliminary communication: Shen, X.; Ho, D. M.; Pascal, R. A., Jr. *Org. Lett.* **2003**, *5*, 369–371.

10.1021/ja0541985 CCC: $30.25

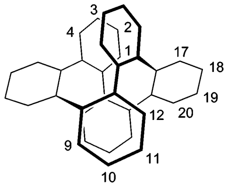
Table 1. Computational Data for Macrocyclic Oligophenylenes



1 hexagons = benzene
4 hexagons = benzene, 1,2,3,4,9,10,11,12-Ph_8
7 hexagons = Ph_6benzene



2 hexagons = benzene
5a hexagons = benzene, 1,2,3,4,9,10,11,12,-17,18,19,20-Ph_{12}
5b 2,3,10,11,18,19-Ph_6-1,4,9,12,17,20-Me_6
8 hexagons = Ph_6benzene



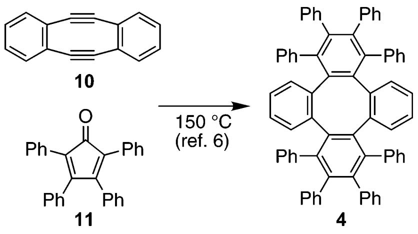
3 hexagons = benzene
6a hexagons = benzene, 1,2,3,4,9,10,11,12,-17,18,19,20-Ph_{12}
6b 2,3,10,11,18,19-Ph_6-1,4,9,12,17,20-Me_6
9 hexagons = Ph_6benzene

compd[a]	symm	*E* (MMFF) (kcal/mol)	*E* (AM1) (kcal/mol)	*E* (HF/3-21G) (au)[b]	*E* (B3LYP/6-31G(d)) (au)[b]
1	D_{2d}	114.65	111.64		
4	C_2	350.11	357.82		
7	D_2	757.93 (0.0)[c]	810.78 (3.0)[c]		
	C_2 (∼D_2)	758.52 (0.6)	807.75 (0.0)		
2	D_{3d}	181.35 (0.0)	176.67 (0.0)	−1369.571478 (0.0)[c]	−1386.293677 (0.0)[c]
3	D_2	203.45 (22.1)	195.67 (19.0)	−1369.552311 (12.0)	−1386.284023 (6.1)
16	C_2		267.62 (91.0)[d]	−1369.397073 (109.4)[e]	
5a	C_3	626.60 (40.5)	611.68 (22.0)	−4108.579855 (35.0)	
6a	C_2	586.08 (0.0)	589.68 (0.0)	−4108.635638 (0.0)	
5b	C_3	409.02 (0.0)	344.40 (0.0)	−2972.008288 (4.3)	−3008.433571 (5.2)
6b	C_2	410.06 (1.0)	351.12 (6.7)	−2972.015212 (0.0)	−3008.441843 (0.0)
8	D_3	1136.80 (20.7)			
	C_i	1121.05 (15.8)			
9	C_2 (∼D_2)	1116.09 (0.0)			

[a] Formulas: $C_{24}H_{16}$ (**1**); $C_{36}H_{24}$ (**2**,**3**); $C_{72}H_{48}$ (**4**); $C_{108}H_{72}$ (**5a**,**6a**); $C_{78}H_{60}$ (**5b**,**6b**); $C_{168}H_{112}$ (**7**); $C_{252}H_{168}$ (**8**,**9**). [b] 1 au = 627.503 kcal/mol. [c] The relative energy of the isomeric compounds (in kcal/mol) is given in parentheses. [d] Zero-point energy corrections give a ΔE of 90.1 kcal/mol. [e] Zero-point energy corrections give a ΔE of 107.9 kcal/mol.

Results and Discussion

Synthesis of Substituted Hexaphenylenes. Müller et al. prepared the octaphenyl-tetraphenylene **4** by Diels−Alder reaction of bisalkyne **10** with tetracyclone **11**, and because of the strain in **10**, this reaction required a temperature of only 150 °C.[6]

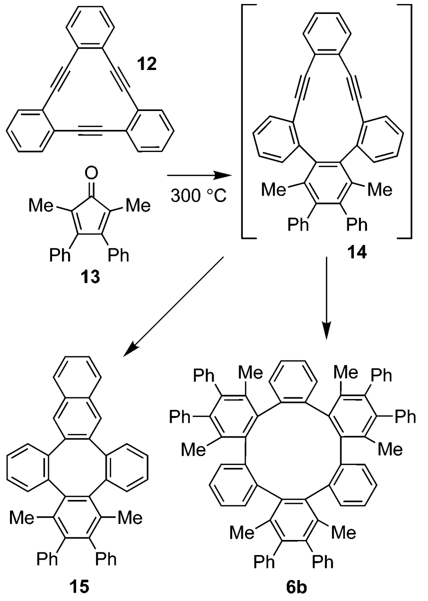


10

11

4

A similar reaction of tetracyclone with tribenzohexadehydro-[12]annulene (**12**) might produce a dodecaphenylhexaphenylene (**5a** or **6a**, see Table 1), but higher temperatures would be required. When compounds **11** and **12** were heated overnight in refluxing nitrobenzene (210 °C), no addition products were observed. However, when **11** and **12** were heated in phenyl ether at 300 °C (sealed tube), a mixture of monoadducts was observed. The ^{1}H NMR spectrum of this material was extremely complex, but mass spectrometry (MS) analysis showed prominent ions at *m*/*z* 656 and 658. The former corresponds to the simple Diels−Alder adduct of **11** and **12**, and the latter might arise by Bergman cyclization of the initial adduct followed by hydrogen abstraction. Although these products were not well characterized, the proposed structures are consistent with the products observed in subsequent reactions with the less sterically encumbered cyclopentadienone **13**.



12

13

14

15

6b

When 3,4-diphenyl-2,5-dimethylcyclopentadienone[8] (**13**) and **12** were heated for 5 h at 300 °C in diphenyl ether, monoadducts

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(8) Cyclopentadienone **13** is a dimer at room temperature but dissociates to the monomer upon heating.

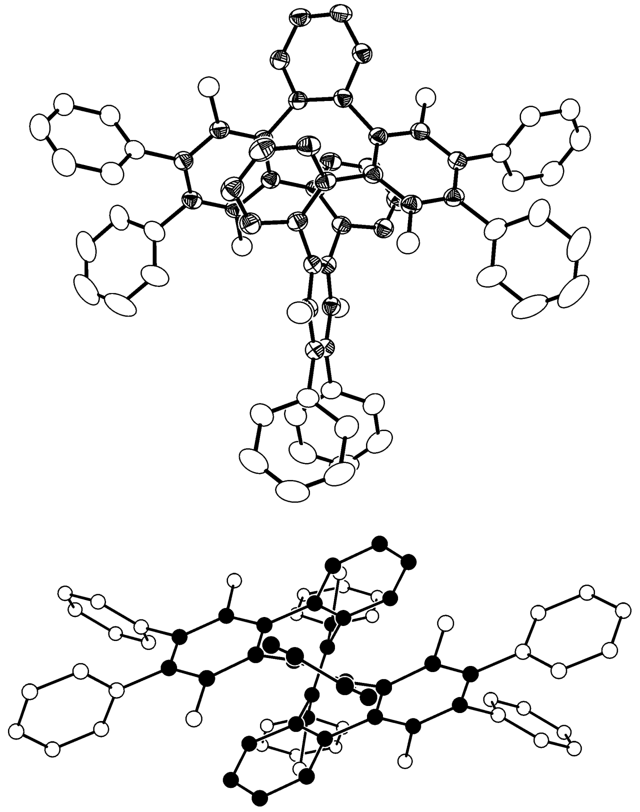

Figure 1. Two views of the molecular structure of compound **6b**. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms have been omitted for clarity.

and the desired triple Diels–Alder adduct were observed. The mass spectrum of the monoadduct fraction exhibited a prominent molecular ion at m/z 534, corresponding to the Bergman cyclization product **15**. An exact mass measurement confirmed the formula as $C_{42}H_{30}$. However, this same material had very complex ^1H and ^{13}C NMR spectra; the 19 strong peaks in the ^{13}C NMR spectrum are consistent with the C_s-symmetric structure **15**, but a more complex, less intense subspectrum indicated that a less symmetric isomer is also present.

The triple adduct from the reaction of **12** and **13** showed a fast-atom bombardment (FAB) MS molecular ion at m/z 997 ($^{12}C_{77}{}^{13}CH_{60}$), as expected for a hexaphenylhexamethylhexaphenylene. However, hexaphenylenes may exist in either a “crown” conformation (**2** and **5**, Chart 1) or a “screw” conformation (**3** and **6**), which do not interconvert under normal conditions.[9] The ^1H NMR spectrum of the triple adduct showed three methyl resonances, the number expected for the C_2-symmetric screw isomer **6b** (see Table 1), and the X-ray structure (Figure 1) confirms that assignment. Indeed, the molecule lies on a special position in the X-ray structure and possesses crystallographic C_2 symmetry.

For hexaphenylene itself, the crown isomer **2** is thought to be more stable than the screw isomer **3**, but both are formed in each of the two literature syntheses of hexaphenylene.[9,10] However, MMFF calculations[11,12] suggest that the immediate precursor of **6b**, a double adduct of **13** to **12**, strongly prefers a C_2 conformation that would lead directly to **6b** upon the third Diels–Alder addition, which may explain the observation of only this conformation. The 12 substituents on **6b** largely project away from the hexaphenylene core, which differs little from the X-ray structure of the parent hydrocarbon **3**,[13] but the substitution pattern gives rise to an unusual twisted, T-shaped morphology with no large molecular cavity.

Computational Studies of Cyclic Oligophenylenes. We were somewhat disappointed to obtain the screw isomer **6b**, for it is the crown isomer **5b** that contains a large cavity formed by the “crowning” phenyls. Might **6b** be converted to **5b**? Aromatic hydrocarbons are relatively stable compounds, and high temperatures could be employed for the isomerization. For this reason, we used computational methods to examine the interconversion of hexaphenylene atropisomers, a process that seems not to have been considered previously by theorists.

Two questions must be asked. First, which of the isomers in each pair is more stable, and second, what is the barrier to interconversion? We examined the isomeric pairs **2** and **3** and **5b** and **6b** at four levels of theory (Table 1).[11] At all levels, the crown isomer **2** is more stable than **3**, but the difference drops from an estimated 22.1 kcal/mol by molecular mechanics (MMFF) to 6.1 kcal/mol by density functional theory (B3LYP/6-31G(d)[14]). In contrast, the results for **5b** and **6b** are scattered, but the higher level calculations favor **6b** by 4–5 kcal/mol. No doubt the steric strain from colliding substituents at carbons 1, 4, 9, 12, 17, and 20 (the “equatorial” sites) in **5b** nearly balances the face-to-face repulsion of the benzene rings in **6b**, and even relatively high levels of theory can have difficulties assessing nonbonded interactions accurately.[15] Notably, in the case of the dodecaphenylhexaphenylenes **5a** and **6a**, the screw isomer is strongly favored: the “equatorial” phenyls are simply too crowded in the crown isomer.

The question of interconversion is more difficult. In Wittig’s original work,[9] compound **2** was heated at 480 °C for 24 h without detectable conversion to **3**, and **3** was heated at 470 °C for 8 h without conversion to **2**! (Some decomposition was observed in both cases, of course.) We examined the interconversion at both the AM1[16] and HF/3-21G[17] levels of theory. Extensive searches for any intermediates in the interconversion were unsuccessful. Instead, only a single bona fide transition state (**16**) was located at each level of theory,[11] and small perturbations to these structures cause them to evolve smoothly to either **2** or **3** upon optimization. At the AM1 level, the transition state is more than 90 kcal/mol above the ground state **2** and 71 kcal/mol above **3**; at HF/3-21G, these values increase to a daunting 109 and 97 kcal/mol! The two calculated transition states are similar; both have C_2 symmetry, and they result from pulling two adjacent phenylene groups past each other. The HF/

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[9] Wittig, G.; Rümpler, K.-D. *Liebigs Ann. Chem.* **1971**, *751*, 1–16.

[10] Simhai, N.; Iverson, C. N.; Edelbach, B. L.; Jones, W. D. *Organometallics* **2001**, *20*, 2759–2766.

[11] Molecular mechanics (MMFF) and semiempirical molecular orbital (AM1) calculations were performed by using SPARTAN 5.0, and ab initio (HF/3-21G) and density functional (B3LYP/6-31G(d)) calculations were performed by using GAUSSIAN 98. In both programs, the default thresholds for wave function and gradient convergence were employed. Transition states were located by using the QST3 option in GAUSSIAN 98, and they were verified by analytical frequency calculations.

[12] Halgren, T. A. *J. Comput. Chem.* **1996**, *17*, 490–519.

[13] Irngartinger, H. *Acta Crystallogr., Sect. B* **1973**, *29*, 894–902.

[14] (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789. (c) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200–206.

[15] (a) Pascal, R. A., Jr. *J. Phys. Chem. A* **2001**, *105*, 9040–9048. (b) Pascal, R. A., Jr.; Hayashi, N.; Ho, D. M. *Tetrahedron* **2001**, *57*, 3549–3555.

[16] Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909.

[17] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986; pp 63–100.

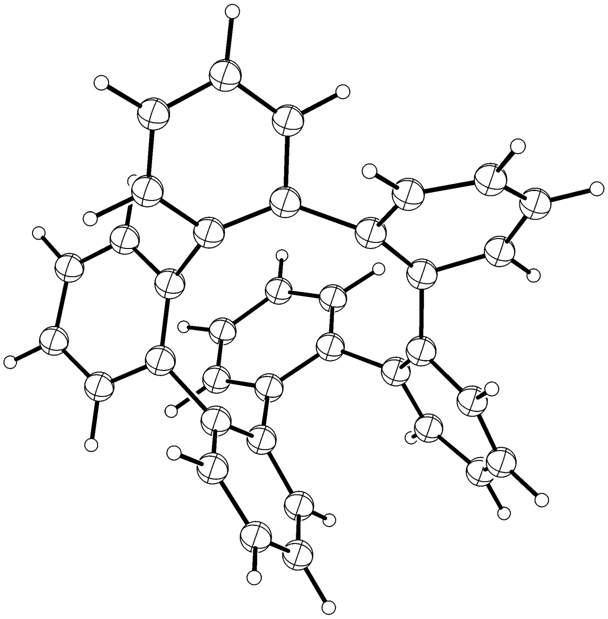


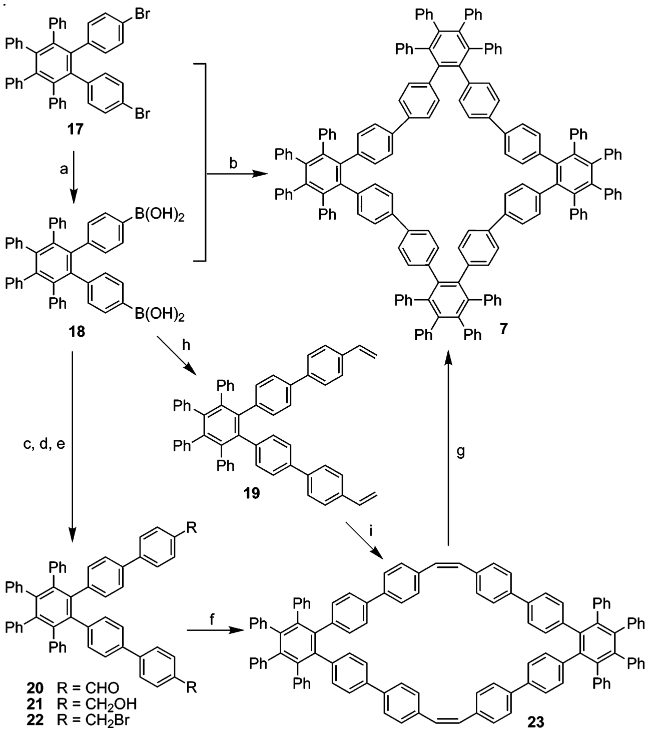
Figure 2. Calculated (HF/3-21G) transition state (**16**) for the interconversion of **2** and **3**.

3-21G transition state is illustrated in Figure 2. It is amusing to note that the π system of the interior macrocycle adopts a Möbius topology. Given that a barrier of even 71 kcal/mol corresponds to a half-life of 6 h at 600 °C, the successful interconversion of hexaphenylene atropisomers is highly unlikely, and the methyl substituents in **5b** and **6b** will only make the barrier higher!

Synthesis of "Supertetraphenylene" 7. The substitution of tetraphenylene and hexaphenylene with many phenyl groups gives reasonably large molecules, but a more ambitious approach is to replace each benzene ring in **1** and **2** with a larger, 6-fold symmetric substructure such as hexaphenylbenzene. The resulting molecules, **7** and **8** (or perhaps **9**, Chart 1), have very large internal cavities, and might be expected to stack in crystals to form highly porous solids.[18,19] There are three synthetic approaches to such molecules, and they are illustrated for **7** in Scheme 1.

In the most direct approach, dibromohexaphenylbenzene **17** was converted to the bis(boronic acid) **18**, and equimolar quantities of the two were subjected to a Suzuki coupling reaction.[20] Such a procedure might yield both compounds **7** and **8** or even larger macrocycles composed of an even number of hexaphenylbenzene subunits. In the event, a 35% yield of nonpolar oligomers of hexaphenylbenzene, as well as a considerable amount of polar material (possibly unreacted boronic acids), was obtained. The nonpolar material was fractionated into five components, and FABMS analysis indicated that these five fractions contained two, three, four, five, and six hexaphenylbenzene units, respectively. However, the structures of these compounds could not be assigned with complete confidence on the basis of their MS, ^{1}H NMR, and ^{13}C NMR spectra, so we focused our attention on crystallization of the tetramer **7** and hexamer **8**.

Scheme 1 [a]



[a] (a) (*i*) *n*-BuLi, ether, (*ii*) B(OMe)$_3$, (*iii*) H$_3$O$^+$; (b) (Ph$_3$P)$_4$Pd, toluene, EtOH, K$_2$CO$_3$; (c) 4-bromobenzaldehyde, (Ph$_3$P)$_4$Pd, toluene, aq. NaHCO$_3$; (d) NaBH$_4$, EtOH; (e) Ph$_3$PBr$_2$, MeCN; (f) (*i*) Ph$_3$P, xylenes, (*ii*) *n*-BuLi, THF, (*iii*) **20**; (g) **11**, Ph$_2$O, 300 °C; (h) 4-bromostyrene, (Ph$_3$P)$_4$Pd, toluene, aq. NaHCO$_3$; (i) Grubbs 2, CH$_2$Cl$_2$.

Both **7** and (the presumed) **8** are freely soluble in common organic solvents, but after many trials only compound **7** gave satisfactory crystals. Its hepta(nitrobenzene) solvate was obtained from nitrobenzene−ethylene glycol, an unusual solvent combination (subsequently, nitrobenzene-2-methoxyethanol was also found to give the same crystal form). The molecular structure of **7** is illustrated in Figure 3. It is one of only four crystal structures of very large (>150 carbons) hydrocarbon macrocycles.[21] In the crystal, **7** lies on a general position and thus possesses C_1 symmetry, but its conformation is nearly C_2 or (less closely) D_2 symmetric. Both MMFF and AM1 calculations find C_2 and D_2 symmetric structures that differ only slightly in energy (Table 1), and optimization of the X-ray geometry leads rapidly to the C_2 structure. The molecule contains two large, V-shaped clefts and a central channel between them. The width of the channel is approximately 6 Å, and from it the clefts open to a width of 15 Å. These spaces are occupied by disordered nitrobenzene molecules in the crystal. In addition, the molecules of **7** are stacked in a manner that forms large, infinite channels in the crystal (Figure 4), a common feature in our structures of large polyphenyl molecules.[18,22]

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(18) Pascal, R. A., Jr.; Barnett, L.; Qiao, X.; Ho, D. M. *J. Org. Chem.* **2000**, *65*, 7711−7717.

(19) For a concise review of ordered porous materials, see: Davis, M. E. *Nature* **2002**, *417*, 813−821.

(20) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457−2483.

(21) For the others, see: (a) Müller, P.; Uson, I.; Hensel, V.; Schlüter, A. D.; Sheldrick, G. M. *Helv. Chim. Acta* **2001**, *84*, 778−785. (b) Nielsen, M. B.; Schreiber, M.; Baek, Y. G.; Seiler, P.; Lecomte, S.; Boudon, C.; Tykwinski, R. R.; Gisselbrecht, J.-P.; Gramlich, V.; Skinner, P. J.; Bosshard, C.; Günter, P.; Gross, M.; Diederich, F. *Chem.−Eur. J.* **2001**, *7*, 3263−3280. (c) Ipaktschi, J.; Hosseinzadeh, R.; Schlaf, P.; Dreiseidler, E.; Goddard, R. *Helv. Chim. Acta* **1998**, *81*, 1821−1834.

(22) (a) Qiao, X.; Padula, M. A.; Ho, D. M.; Vogelaar, N. J.; Schutt, C. E.; Pascal, R. A., Jr. *J. Am. Chem.* Soc. **1996**, *118*, 741−745. (b) Lu, J.; Zhang, J.; Shen, X.; Ho, D. M.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **2002**, *124*, 8035−8041. (c) Shen, X.; Ho, D. M.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **2004**, *126*, 5798−5805.

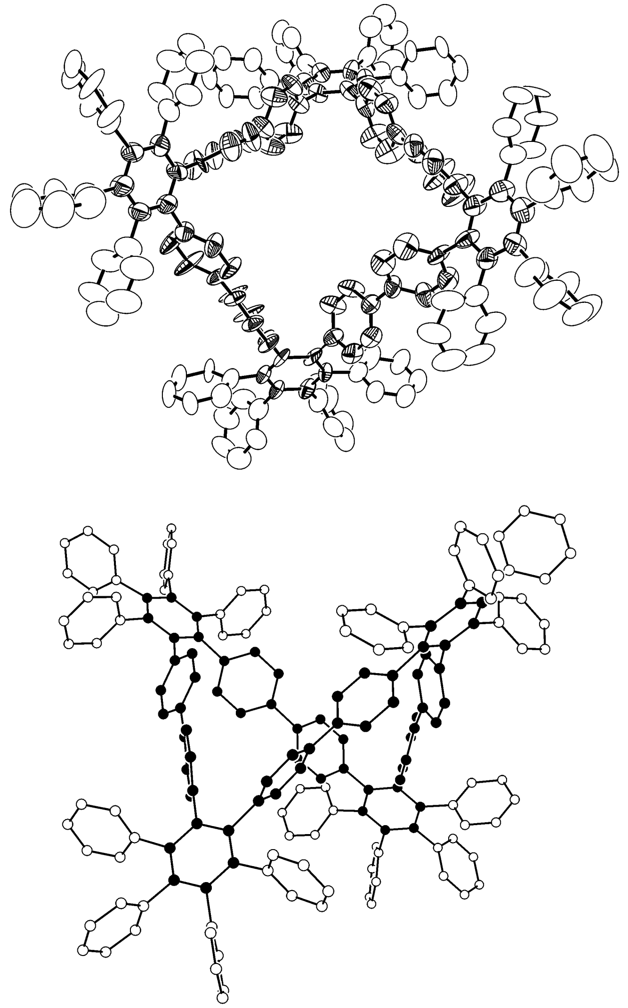

Figure 3. Two views of the molecular structure of compound **7**. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms have been omitted for clarity.

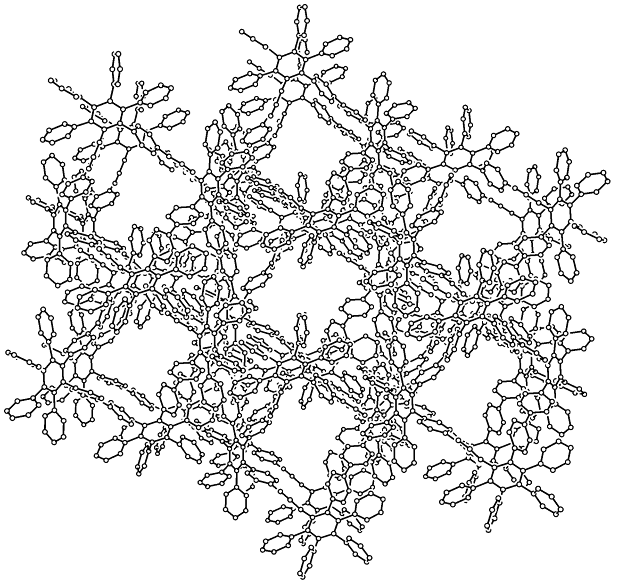

Figure 4. Crystal packing of compound **7** viewed along the *b* axis.

The purification and crystallization of **7** from the Suzuki reaction mixture is both tedious and inefficient, and although the “superhexaphenylene” **8** was almost certainly present based on FABMS analysis, it was never obtained in pure form. We therefore sought alternative methods for the synthesis of **7** and **8**. If the macrocyclic diene **23** could be prepared, a double Diels−Alder reaction with **11**, at a high enough temperature to promote decarbonylation and dehydrogenation of the adduct, should yield **7**, and similar treatment of an analogous macrocyclic triene might give **8**.

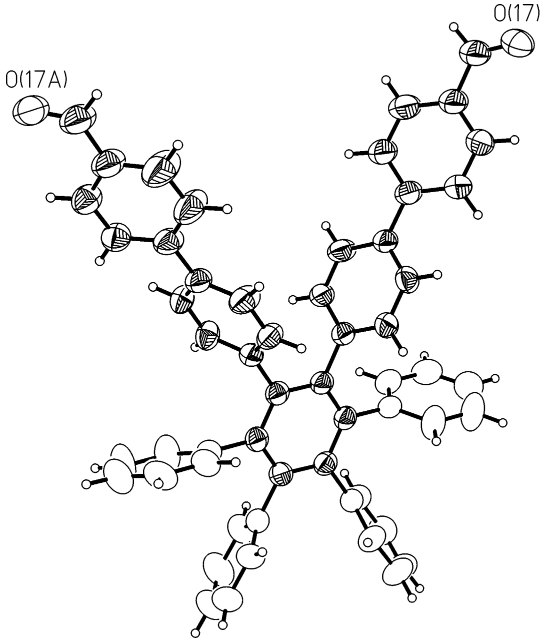

Figure 5. Molecular structure of compound **20**. Thermal ellipsoids are drawn at the 50% probability level.

Three methods were used to prepare **23**. In the first, a Suzuki coupling of bis(boronic acid) **18** with 4-bromostyrene gave the divinyl compound **19** in 97% yield. This material was subjected to reactions with Grubbs' first and second generation olefin metathesis catalysts[23] in attempts to generate macrocyclic olefins containing two or three hexaphenylbenzene subunits. The first generation catalyst gave no macrocyclic products, but the second did form compound **23**, though in only 9% yield.

In the second method, a Suzuki coupling of compound **18** with *p*-bromobenzaldehyde gave the dialdehyde **20** in 90% yield. The molecular structure of this highly crystalline compound is shown in Figure 5. The aldehyde groups are on the top of a broad hydrocarbon cleft, and they should be unencumbered for further reaction. A McMurry coupling reaction[24] was performed with **20** as the sole carbonyl substrate, but in the best of several trials, diene **23** was obtained in only 4% yield, and no macrocyclic triene was ever detected.

The third method was the longest, but it gave the best, if still mediocre, results. Dialdehyde **20** was reduced to the diol **21** in 86% yield, and this material was converted to the dibromide **22** (91%). A double Wittig reagent was generated from **22**, and the reaction of the ylid with dialdehyde **20** gave macrocycle **23** in 32% yield. In this case, because of the use of two distinct precursors, it is not possible to generate a macrocyclic triene.

Compound **23** was then heated with tetracyclone (**11**) in refluxing diphenyl ether for 24 h to give the desired polyphen-

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ylene **7** in 19% yield. The product was of good quality, but the yield was low for such a reaction. The ^{1}H and ^{13}C NMR spectra of diene **23** are relatively simple, and there seems to be only one double bond isomer present, presumably the *Z* isomer. One might expect such a molecule to react smoothly in a Diels–Alder reaction, but this was not the case. With two inefficient late steps, the overall yield of the multistep synthesis of **7** from bis(boronic acid) **18** is only 4%. However, it is easier to obtain pure material in this way than by the one-step Suzuki coupling of **17** and **18**, because of the straightforward purifications in the multistep synthesis. Still, compound **7** is not yet a readily available material!

Conclusion

We have described the synthesis and crystal structures of the two new, large, polyphenyl macrocyclic oligophenylenes **6b** and **7**. Compound **6b** is a polysubstituted derivative of the "screw" conformer of hexaphenylene, and contains no significant internal cavities (unlike its "crown" conformation **5b**), but compound **7**, a "phenylog" of tetraphenylene, contains a large internal cavity. In the crystal structure of **7**, this cavity contains seven molecules of nitrobenzene, and the molecules of **7** stack in the crystal to form infinite channels made up of the roughly tubular molecules. Computational studies indicate that both **6b** and **7** adopt their most stable conformations in the crystal and that the thermal isomerization of "screw" hexaphenylenes to "crown" hexaphenylenes is essentially precluded.

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Supporting Information Available: The Experimental Section (containing the full procedures for the syntheses of compounds **6b**, **15**, **18**, **19**, **20**, **21**, **22**, **23**, and **7** and a summary of crystallographic methods and data), the ^{1}H NMR spectrum of compound **6b**, ^{13}C NMR spectra for compounds **7**, **15**, **19**, **20**, **21**, **22**, and **23**, crystallographic information files (CIF) containing the X-ray structural information for compounds **6b**, **7**, and **20**, and an ASCII text file containing the coordinates of the calculated structures of **2**, **3**, **5b**, and **6b** at the B3LYP/6-31G(d) level and **5a**, **6a**, and the transition state **16** at the HF/3-21G level. This material is available free of charge via the Internet at http://pubs.acs.org.

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