Expanded Tetrahedral Molecules from 1,3,5,7-Tetraphenyladamantane

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ABSTRACT: The goal of this and two succeeding papers was to investigate the effects of rigid tetrahedral cores (such as adamantane) on the properties of aramid and poly(phenylene) dendrimers as well as dendrimers that form single molecule micelles. This paper deals with model compound studies dealing with generating tetrasubstituted derivatives of adamantane. A previously reported procedure (for making tetraphenyladamantane) using *tert*-butyl bromide–$AlCl_3$ catalyzed arylation of 1-bromoadamantane was found not to be a general synthetic method for the preparation of other substituted adamantane derivatives. Adamantane derivatives with multiple phenyl substituents were isolated only when benzene and bromobenzene were used in the Friedel–Crafts reaction. Tetraphenyl-substituted adamantane derivatives were formed, however, by the traditional Friedel–Crafts arylation of 1,3,5,7-tetrabromoadamantane with bromobenzene and 1,3-dibromobenzene. A lack of regioselectivity for these reactions (isolated mixtures of the meta/para isomers or ortho/meta isomers) was observed. Large quantities (50–100 g) of 1,3,5,7-tetraphenyladamantane (**1**) were prepared from 1-bromoadamantane using a slightly modified literature procedure. This organic insoluble compound was iodinated with [bis(trifluoroacetoxy)iodo]benzene to give the all-para-substituted compound, **5**. Compound **5** was further reacted to give numerous derivatives and used as a core in the synthesis of first generation dendrimers.

Introduction

Highly branched, spherical structures or dendrimers have recently attracted much attention.[1] Numerous types of dendritic polymers have been reported using inorganic[2] or organic frameworks, sparking interest in both theoretical[3] and synthetic[4] studies of the relationship between molecular structure and physical properties.

Miller and Neenan have prepared a series of all-aromatic dendrimers based on poly(1,3,5-phenylene)s[5,6] by a repetitive convergent approach. Macromolecules containing up to 46 phenyl rings were found to be thermally stable, soluble in common organic solvents, and easily characterized. A simple, one-pot approach[7] gave similar, but structurally less-defined, hyperbranched poly(1,3,5-phenylene)s. These all-aromatic species were rendered water soluble by incorporation of terminal carboxylate groups and were found to complex small organic compounds in water. The dendritic polybenzamide analogs[5,8] were also synthesized and displayed good solubility in organic amide solvents in which they formed lyotropic liquid crystals.

The possibilities of designed unimolecular micelles for phase-transfer reactions, drug delivery, and small-molecule complexation and separation have prompted research in the area of hydrophobic/hydrophilic dendrimers.[9] In a study of hydrophilic aliphatic amide two-directional cascade polymers, core shape and size were found to effect their ability to gel in water.[10] Several four-directional cascades, including aliphatic amide cascades with a rigid tetrahedral core based on 1,3,5,7-adamantanetetracarboxylic acid, have also been prepared.[11]

We wished to further investigate the effects of rigid tetrahedral cores (such as adamantane) on the properties of aramid and poly(phenylene) dendrimers as well as dendrimers that form single-molecule micelles. Adamantane is an ideal nucleus for four-directional dendrimer systems due to its rigid T_d symmetry, all-hydrocarbon nature, and thermal stability and the fact that it can be selectively functionalized at the four tertiary positions.[12] This allows for controlled three-dimensional extension of adamantane's tetrahedral symmetry.

Several reports exist describing adamantane tetrahalogenation,[13] -oxygenation,[14] -nitration,[15] and -alkylation.[16] Problems encountered with these approaches stem from using multistep syntheses which give low yields and require demanding synthetic conditions which limit scaleup. One system that is free of these constraints is based on 1,3,5,7-tetraphenyladamantane (**1**). First synthesized by Setter and Krause,[17] **1** can easily be prepared in multigram quantities in high yields. Several derivatives of 1,3,5,7-tetraphenyladamantane[18] and 1,3,5-triphenyladamantane (Figure 1) would be ideal cores for dendrimers and/or star polymers. In these compounds, the phenyl groups act as rigid extenders of adamantane's tetrahedral symmetry, reducing steric and electronic problems encountered when trying to react groups attached directly to the adamantane nucleus.

Results and Discussion

Direct Substitution of Adamantanes. 1,3,5,7-Tetraphenyladamantane has been prepared by the Friedel–Crafts reaction of 1,3,5,7-tetrabromoadamantane with benzene.[17] Newman[19] reported an alternative synthesis of **1** which involved the Friedel–Crafts reaction of the commercially available 1-bromoadamantane with benzene in the presence of *tert*-butyl bromide (Figure 2; R = H). Multiple substitution during Lewis acid catalyzed arylations of adamantane by benzene with $FeCl_3$ similarly was reported to give 1-phenyladamantane and 1,3-diphenyladamantane;[20] to avoid multiple arylation, weak Lewis acids and low reaction temperatures have been employed.[21] A highly reactive system based on $AlCl_3$ catalyst and reagent amounts of *tert*-butyl bromide has also been used in rearrangement reactions of tricyclic hydrocarbons to give adamantane through pathways involving carbocation formation.[22] With a modification of the reaction temperature, we have optimized the formation of **1** (R = H, n = 4 in Figure 2) to 50–70%. 1-Phenyladamantane (n = 1), 1,3-diphenyladamantane (n = 2), and 1,3,5-triphenyladamantane (n = 3) are also formed during the reaction

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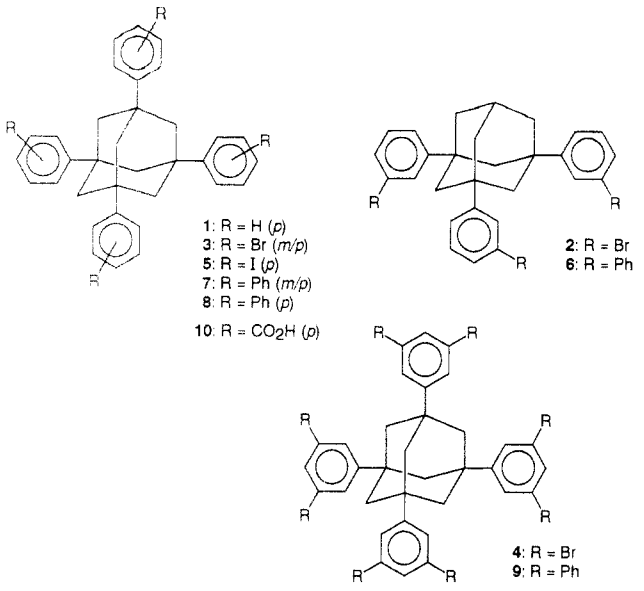

Figure 1. Target derivatives of 1,3,5-triphenyladamantane and 1,3,5,7-tetraphenyladamantane.

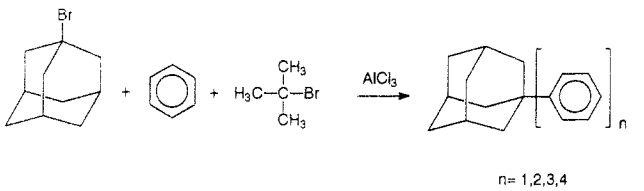

Figure 2. Friedel–Crafts reaction of 1-bromoadamantane with benzene in the presence of *tert*-butyl bromide.

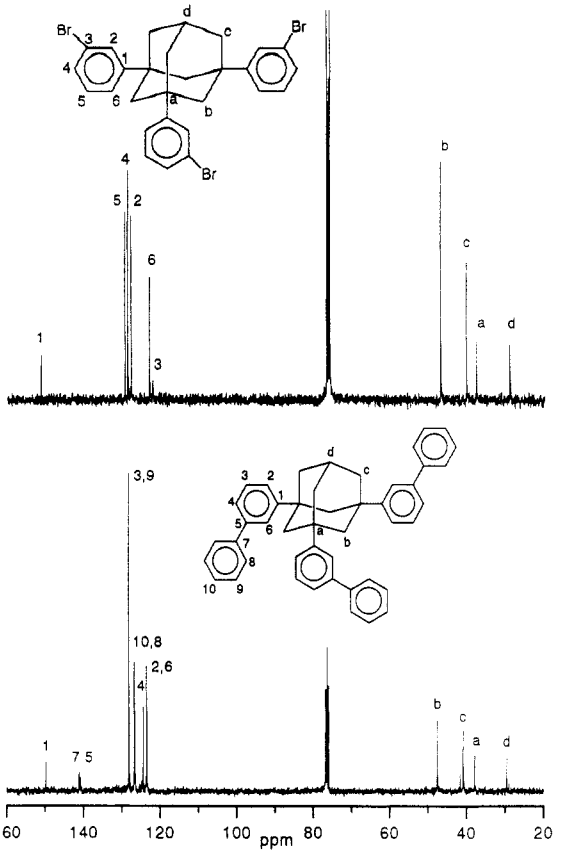

Figure 3. ^{13}C NMR spectra (in $CDCl_3$) of **2** (top) and **6** (bottom).

with the amount of each formed dependent on the ratio of reactants used. Of these four products, only the target compound, 1,3,5,7-tetraphenyladamantane, is insoluble in most organic solvents. This simplifies purification but limits further functionalization of this key intermediate.

We attempted to extend Newman's methodology to the preparation of other multi-phenyl-substituted adamantane derivatives. Using the same reaction conditions as for the tetraphenyl derivative, 1-bromoadamantane was allowed to react with toluene, anisole, phenol, iodobenzene, and bromobenzene. Friedel–Crafts reaction with anisole and phenol gave the respective monosubstituted products (para isomers in both cases) in yields of 40–60%. These were characterized by NMR, IR, and melting points in comparison with literature data to confirm structures.[12] With toluene and iodobenzene, the monosubstituted products were also isolated (50–65% yield) but as a mixture of the meta and para isomers as determined by ^1H NMR and comparison with literature reports.[23,24] Most promising was the reaction of 1-bromoadamantane with bromobenzene which gave 1,3,5-tris(3-bromophenyl)adamantane (**2**) as a white crystalline solid from a viscous mixture of the mono- and disubstituted derivatives. The ^{13}C NMR spectrum of **2** is shown in Figure 3. However, there was no evidence for the formation of the tetrasubstituted adamantane derivative.

The formation of the sterically and electronically favored para isomer as well as the less favored meta isomer has precedent.[23] Laszlo and co-workers[19] have shown that, while adamantane can be directly arylated with benzene to give 1-phenyladamantane and 1,3-diphenyladamantane, a mixture of products was obtained with toluene, chlorobenzene, or bromobenzene. For example, arylation with toluene resulted in five products, *m*- and *p*-1-tolyladamantane, the disubstituted (1,3-ditolyl) meta and para isomers, and the disubstituted meta/para mixed isomers. Similar results were reported for chlorobenzene and bromobenzene. As in our case, no ortho substitution was observed, probably due to large steric inhibition in the intermediate. However, Inamoto and co-workers have reported that the reaction of 1-chloroadamantane with phenol gave an ortho/para isomer mixture of 1-adamantylphenol.[25] The ortho isomer was successfully converted to the para isomer by heating with excess phenol in the presence of hydrogen chloride. These observations suggest that the adamantyl cation is very reactive but that substitution is reversible (at least in some cases), and this can allow gradual buildup of mixtures of isomers.

To force tetrasubstitution, we also investigated the Friedel–Crafts reactions of 1,3,5,7-tetrabromoadamantane, which was prepared by the bromination of adamantane with refluxing bromine.[26] 1,3,5,7-Tetrakis(3/4-bromophenyl)adamantane (**3**) was isolated from the $AlBr_3$-catalyzed reaction of the tetrabromide with bromobenzene. The organic soluble mixture contained 50–70% of *m*-bromophenyl groups based on proton integration. The ^1H and ^{13}C NMR spectra of **3** are shown in Figure 4. The predominance of the meta isomer prompted us to attempt the arylation of 1,3,5,7-tetrabromoadamantane with 1,3-dibromobenzene which might give a symmetrical product if reaction at the 5-position predominates (meta to both bromines). 1,3,5,7-Tetrakis(1,3-dibromophenyl)adamantane (**4**) was isolated in good yields. Surprisingly, the slightly-chloroform-soluble product showed evidence of "ortho" as well as "meta" isomer formation by ^{13}C NMR. A model reaction of 1-bromoadamantane with 1,3-dibromobenzene gave a 1:4 ratio of ortho to meta isomers of 1,3-dibromo-4/5-(1-adamantyl)benzene (see Figure 5 for structures and the ^{13}C NMR spectrum), consistent with the formation of isomer mixtures in the tetrasubstituted case.

Extension of 1,3,5,7-Tetraphenyladamantane. Formation of well-defined dendrimers and other chain-

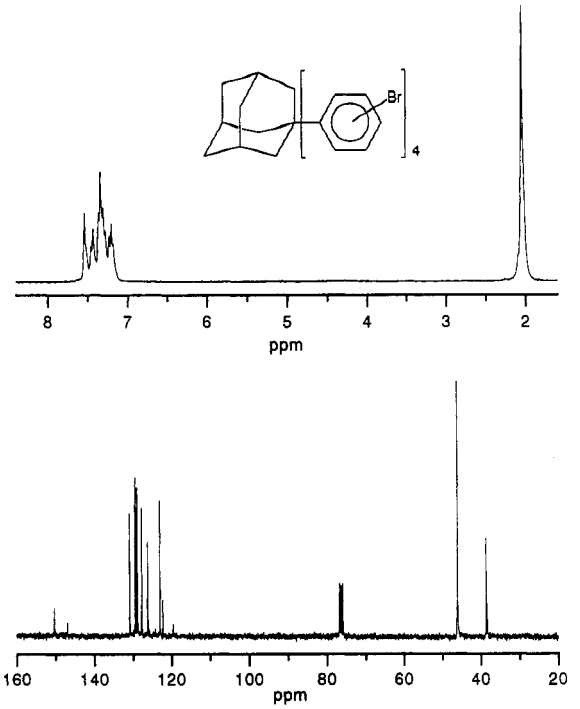

Figure 4. ^1H NMR spectrum (top) and ^{13}C NMR spectrum of **3** ($CDCl_3$).

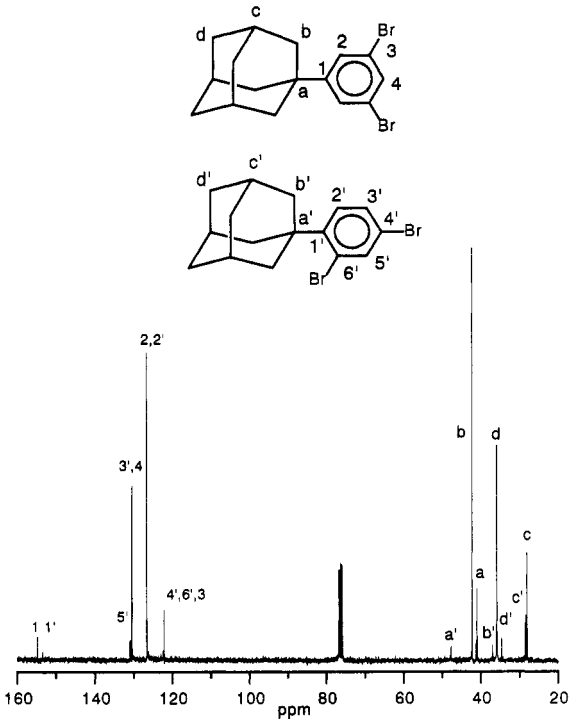

Figure 5. ^{13}C NMR spectrum ($CDCl_3$) of 1,3-dibromo-4/5-(1-adamantyl)benzene.

extended materials requires structurally well-defined cores. The lack of regioselection during arylation discouraged us from attempting further Friedel–Crafts reactions on adamantane and led to further study of the derivatization of the easily formed 1,3,5,7-tetraphenyladamantane (**1**). This compound's insolubility hampered traditional approaches, although use of [bis(trifluoroacetoxy)iodo]-benzene (BFIB) as an iodinating reagent[27] was successful. Thus, 1,3,5,7-tetrakis(4-iodophenyl)adamantane (**5**) was formed in 50–70% in the two-phase reaction of 1,3,5,7-tetraphenyladamantane with BFIB and iodine in CCl_4 or $CHCl_3$. The ^1H and ^{13}C NMR spectra of **5** are shown in Figure 6. The yield can be increased by grinding the reactants together before adding the solvent. Placing the

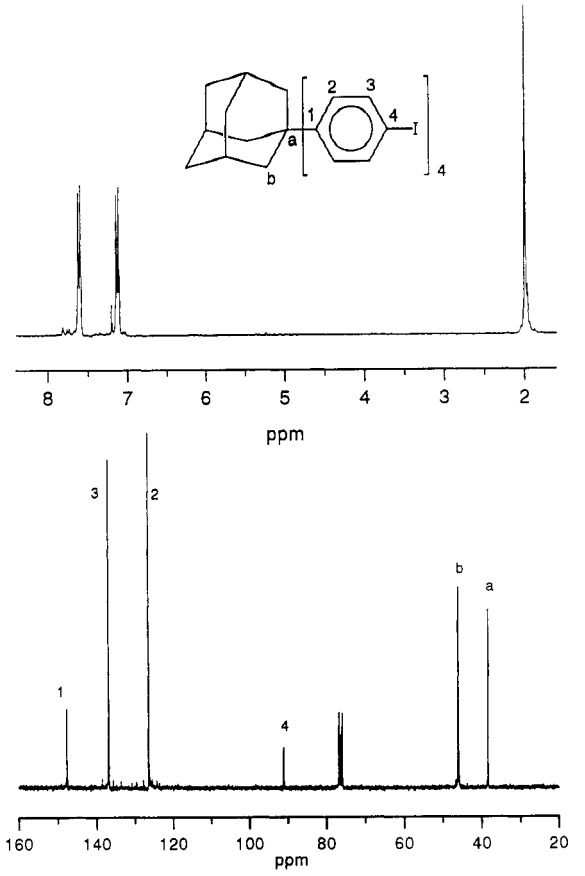

Figure 6. ^1H and ^{13}C NMR spectra of **5** ($CDCl_3$).

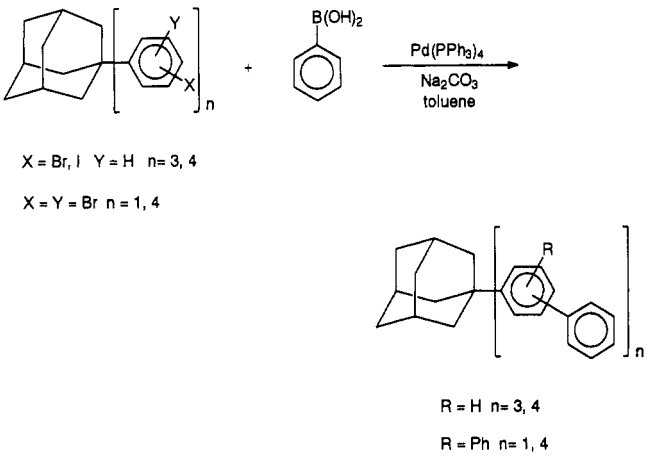

Figure 7. General phenylboronic acid coupling synthetic scheme.

reaction vessel in a sonication bath served only to increase the yield of the side product, 1,4-diiodobenzene. 1,3,5,7-Tetrakis(4-iodophenyl)adamantane (**5**) is soluble and easily isolated from the insoluble starting material. The side product (1,4-diiodobenzene) was eliminated by recrystallization from $CHCl_3$/MeOH which gave a white crystalline product. The pure, all-para-substituted compound **5** has been prepared in up to 10-g quantities with this simple two-step route from the commercially available 1-bromoadamantane. This makes possible a number of synthetic pathways to chain-extended tetrahedral compounds using a variety of aryl halide coupling reactions.

Derivatization was first investigated by coupling of phenylboronic acid[29] with the aryl halide derivatives under Suzuki conditions to give the corresponding biphenyl compounds. Figure 7 shows the general phenylboronic acid coupling synthetic scheme. Coupling of phenylboronic acid with **3**, 1,3,5-tris(3-bromophenyl)adamantane,

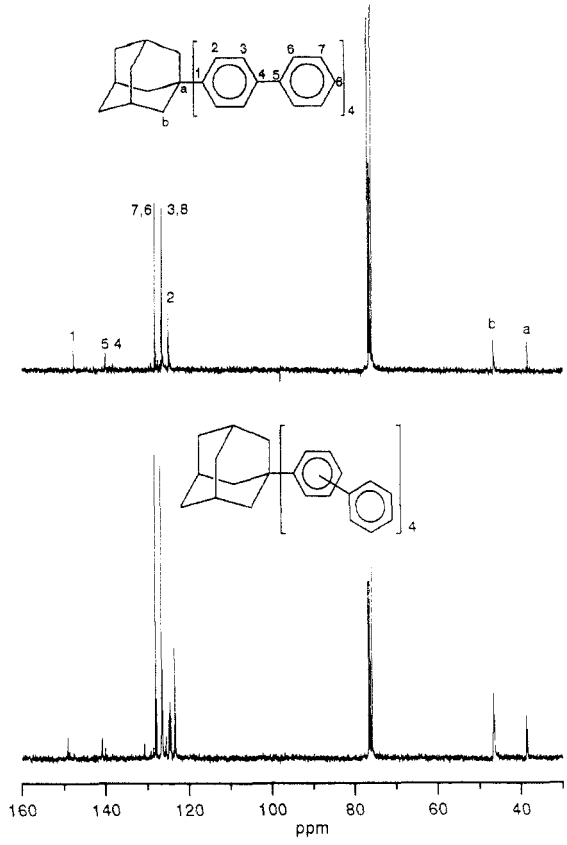

Figure 8. ^{13}C NMR spectra ($CDCl_3$) of **7** (bottom) and **8** (top).

gave **6**, in yields of 40–70%. The ^{13}C NMR of **6** is shown in Figure 3 along with that of the starting material **2**. The same reaction was performed on 1,3,5,7-tetrakis(3/4-bromophenyl)adamantane and 1,3,5,7-tetrakis(4-iodophenyl)adamantane. The expected meta/para isomer product mixture, **7**, was isolated from the former, while reaction with **5** gave the pure *p*-biphenyl derivative, **8**. Isomer contents are apparent from the ^{13}C NMR spectra shown in Figure 8. All of the biphenyl compounds obtained were very soluble in $CHCl_3$ and were characterized by NMR and IR (see the Experimental Section). One problem encountered in these boronic acid coupling reactions was the purity and age of the catalyst. If fresh catalyst was used, the product was isolated in 50–75% yields, while if a catalyst was used that had been stored under an inert atmosphere in the freezer, little or no product was isolated.

Incorporation of multiply-substituted phenyl rings onto adamantane was examined next. The model compound, 1,3-dibromo-4/5-(1-adamantyl)benzene, was reacted with phenylboronic acid to give the expected isomer mix of 1,3-diphenyl-4/5-(1-adamantyl)benzene in moderate yields. The tetrakis(*o*/*m*-terphenylyl)adamantane (**9**) was then obtained from 1,3,5,7-tetrakis(1,3-dibromophenyl)adamantane (**4**). The coupling reaction was performed in THF due to the insolubility of **4** in toluene. The resulting tetrakis(terphenyl) derivative (12 phenyl rings) was insoluble in $CHCl_3$ but soluble in THF. Solution NMR was obtained in THF with a DMSO-d_6 insert. Solid-state ^{13}C NMR and FTIR were also used to confirm product identity. The white microcrystalline material showed no thermal transitions up to 450 °C. Miller and Neenan[5] reported that dendrimers of poly(1,3,5-phenylene) containing 10 and 22 phenyl rings were quite soluble in common organic solvents, including chloroform. Similar results were reported by Kim and Webster[7] on the solubility of hyperbranched poly(phenylene)s in THF and *o*-dichlorobenzene.

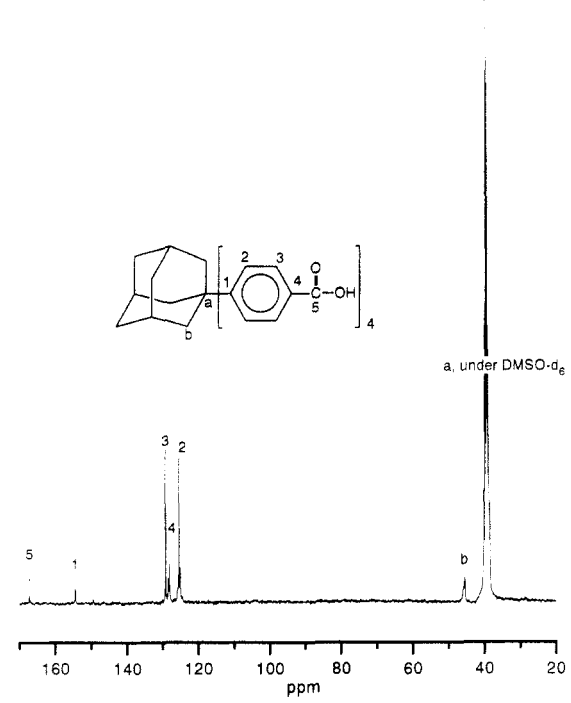

Figure 9. ^{13}C NMR spectrum (DMSO-d_6) of **10**.

We next investigated the formation of extended aromatic amide derivatives of **5** through metallation reactions. 1,3,5,7-Tetrakis(carboxylatophenyl)adamantane[28] (**10**) was prepared in yields of 55–70% by formation of the tetraanion with *sec*-butyllithium followed by reaction with carbon dioxide and acid; the product was soluble in DMSO and hot acetic acid. Compound **10** is an expanded, or laterally extended, tetrahedral analog of 1,3,5,7-adamantanetetracarboxylic acid. Possible side reactions are aryl coupling and quenching of one of the anions by adventitious water; we believe the later explains the presence of the small peaks at 125.1 and 128.2 ppm in the ^{13}C NMR spectrum shown in Figure 9. The FTIR and NMR spectra, after one recrystallization, indicated that only one type of carbonyl was present, and **10** was used in further reactions despite having ca. 5% nonreactive phenyl substituents.

Direct condensation of **10** with 1-aminoadamantane in the presence of triphenylphosphine and hexachloroethane[30] gave the tetraadamantylamide derivative, **11**. The light yellow solid obtained was readily soluble in $CHCl_3$, unlike the starting acid. The impurities present in the starting acid were also evident in the amide. While such unreactive impurities are a drawback in the synthesis of well-defined chain-extended structures and dendrimers from **10**, more careful control of reaction conditions should allow complete carboxylation.

Amides can also be directly prepared from aryl halides and amines through palladium-catalyzed carbonylation reactions. Aryliodo compounds undergo these reactions quite readily and even give high polymer from difunctional monomers.[31] For example, **5** was reacted with aminoadamantane under 1 atm of carbon monoxide in the presence of $Pd(PPh_3)_2Cl_2$, triphenylphosphine, and DBU (Figure 10). The resulting tetraadamantylamide, **11a**, can be directly compared with **11**. Both **11** and **11a** are very soluble in $CHCl_3$, sublime (with decomposition) at ca. 250 °C, and show similar NMR and FTIR spectra (though the ^{13}C NMR spectrum of **11a** shows resonances for both the *cis* and *trans* amide isomers). The FTIR spectra of **11** and **11a** are shown in Figure 11. The spectra are similar in that both show the characteristic adamantane absorbances as well as the peaks associated with amide groups.

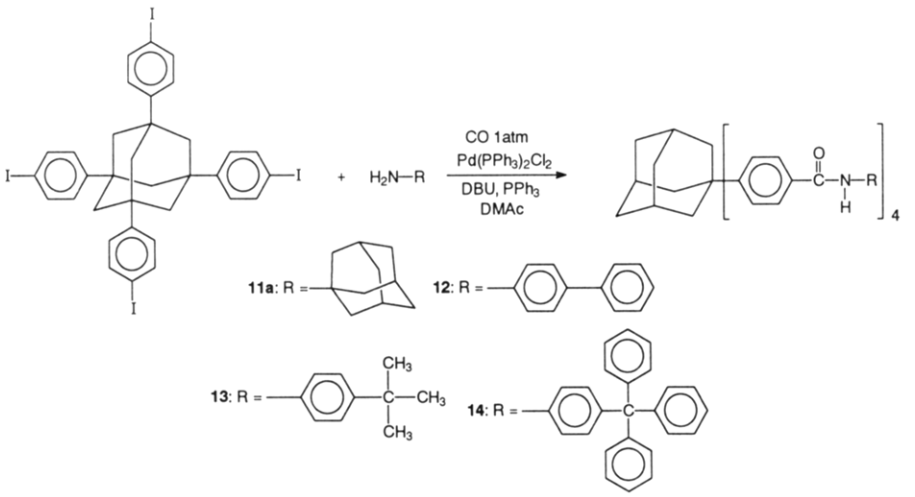

Figure 10. Synthetic scheme for the Pd-catalyzed carbonylation of **5** with various amines.

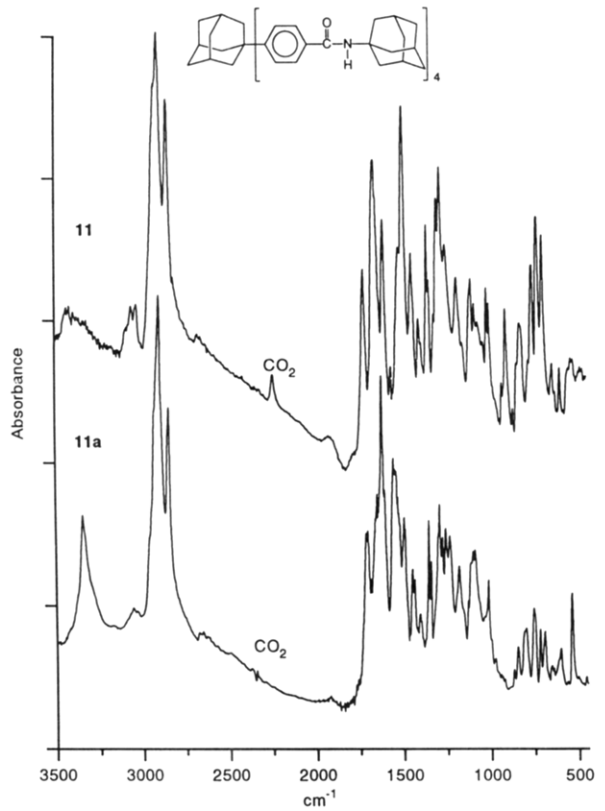

Figure 11. FTIR (KBr) spectra of **11** (top) and **11a** (bottom).

The N–H stretch at ca. 3300 cm^{-1} is much sharper and more intense in **11a** than in **11**. The fingerprint region also differs in the number and intensity of the peaks. Again, this is probably due to the marked difference in *trans* isomer content as well as compositional purity of the two compounds.

The efficiency of this reaction encouraged us to use it to prepare more highly branched systems. We were specifically interested in preparing highly symmetrical branched molecules. We first reacted **5** with 4-biphenylylamine to give the biphenyl-extended compound **12** in high yield and purity though (even after extensive drying in the presence of P_2O_5) elemental analysis indicated the presence of two water molecules per four amide groups. A conformationally minimized structure of **12** is shown in Figure 12; the open nature of this molecule would inhibit close packing in the solid state, leaving free volume to accommodate solvent and water of crystallization.

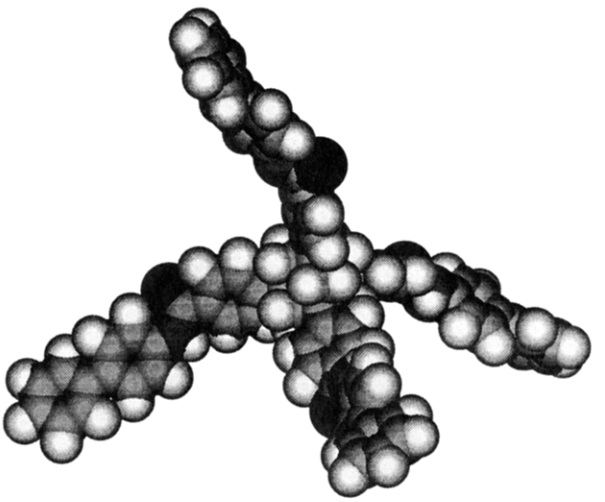

Figure 12. Conformationally minimized molecular model of **12**.

Compound **12** also showed some interesting thermal transitions. Figure 13 shows the DSC thermograms obtained upon heating of **12**. The first run to 400 °C showed what appear to be overlapping endotherms and exotherms at 230–260 °C followed by an endothermic transition at 368–371 °C. A second run of the material gave only a T_g-like transition at 215 °C. Optical microscopy showed no changes in the crystalline material up to 300 °C (i.e., the material did not melt or shrink under cross-polarizers). The compound was synthesized again and this behavior confirmed. Our only explanation is that the nonreversible transitions at 230–260 °C may be associated with a crystal–crystal transition or reordering of less-perfect crystals to more perfect ones that melt at 368 °C. Cooling from the melt may not allow recrystallization since subsequent DSC analysis of the same sample showed only a glass to amorphous transition and no higher temperature melt; many polymers behave similarly.

Intermediate **5** was then reacted with *tert*-butyl aniline under palladium-catalyzed carbonylation conditions to give **13**. This first-generation dendrimer has an expanded tetrahedral core based on 1,3,5,7-tetraphenyladamantane and 12 surface methyl groups. A conformationally minimized structure of **13** is shown in Figure 14. The relatively open star structure obtained suggests that steric inhibition around the ball-like tetraphenyladamantane core should not limit extension and dendrimer formation.

A first-generation dendrimer with 20 phenyl rings (12 on the exterior) was prepared by reaction of **5** with

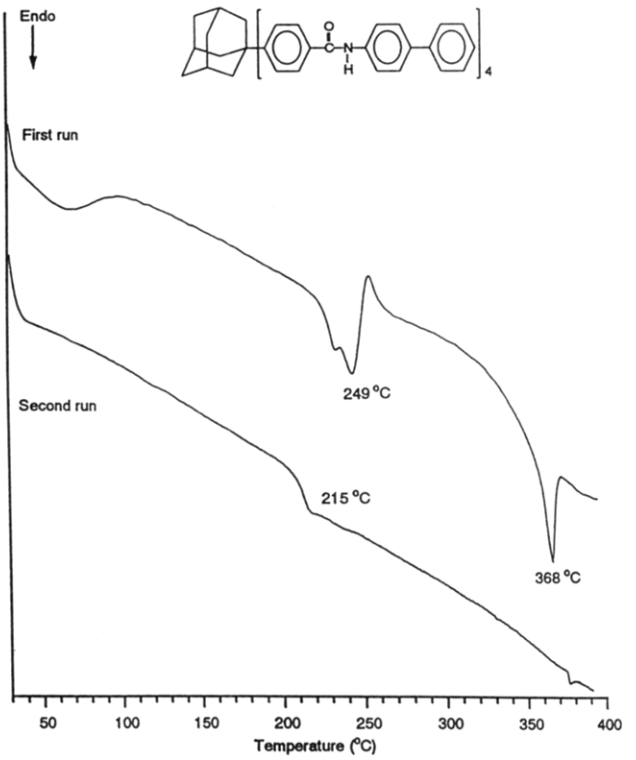

Figure 13. DSC thermograms of **12** (scan rate of 20 °C/min).

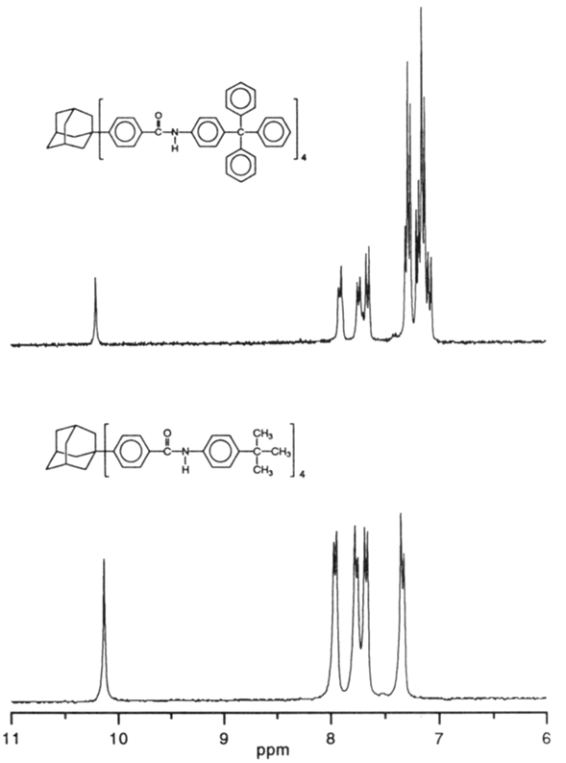

Figure 15. ^{1}H NMR spectra (DMSO-d_6) of **14** (top) and **13** (bottom); aromatic region only.

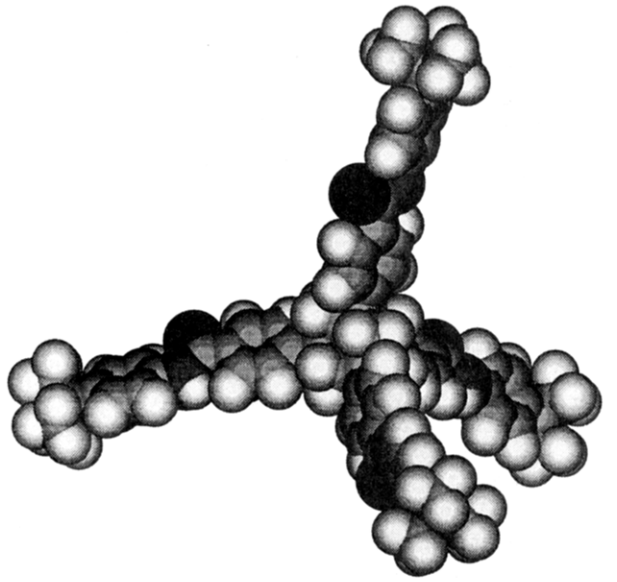

Figure 14. Conformationally minimized molecular model of **13**.

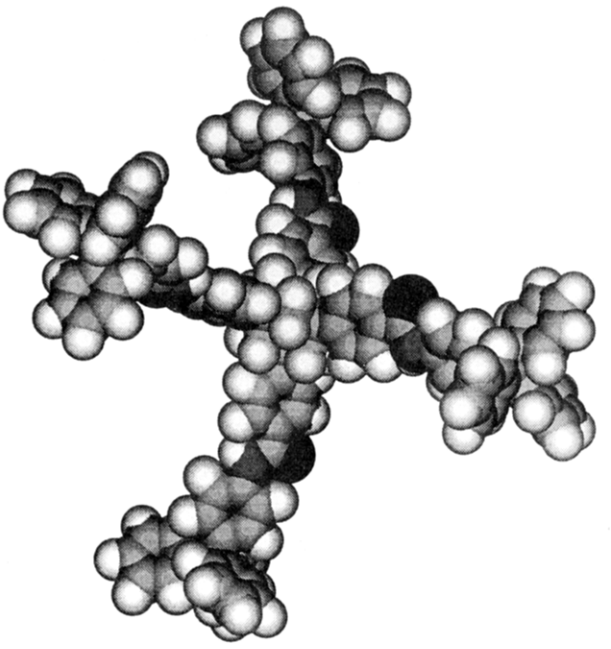

Figure 16. Conformationally minimized molecular model of **14**.

tritylaniline under palladium-catalyzed carbonylation conditions. ^{1}H NMR spectra of this dendrimer (**14**) and that of **13** (both obtained in DMSO-d_6) are shown in Figure 15 (aromatic region only). The splitting patterns are well-defined in both cases, which indicates structural and conformational purity. As was the case with **13** and **12**, elemental analysis of **14** indicated that two water molecules were bound per four amide groups. MMX molecular modeling calculations gave the conformationally minimized structure of **14** shown in Figure 16. While it is hard to visualize how two water molecules can act as hydrogen bond bridges between the amide groups of this family of dendrimers, the fact that exactly two water molecules are bound per four arms suggests that they are bound internally and in a similar fashion for all three compounds, i.e., between the amide groups of pairs of arms in a single dendrimer molecule.

DSC analysis showed that **13** underwent a small endothermic transition at 330 °C followed by a melt (confirmed by visual observation) at 424 °C. No transitions were present on a second DSC run. Dendrimer **14** displayed a small endotherm at 291 °C and then did not melt but slowly decomposed. For comparison, the all-aromatic aramids based on 1,3,5-benzenetricarboxamide melt at 317–321 °C (0th generation, 4 phenyl rings) and 295–309 °C (1st generation, 10 phenyl rings).

Conclusions

The *tert*-butyl bromide–$AlCl_3$ catalyzed arylation of 1-bromoadamantane is apparently not a general synthetic

route to tetraphenyl-substituted adamantane derivatives. The reaction methodology only gives efficient tetrasubstitution with benzene. Tetraphenyl substitution (by aromatics other than benzene) was achieved by Friedel–Crafts reaction of 1,3,5,7-tetrabromoadamantane. 1,3,5,7-Tetrakis(4-iodophenyl)adamantane (5) was formed in good yields by the iodination of the easily formed 1,3,5,7-tetraphenyladamantane. Compound 5 was further functionalized via Grignard and halide coupling reactions to give several expanded tetrahedral molecules which were used to prepare first generation dendrimers with adamantane cores.

Given that 1,3,5,7-tetraphenyladamantane (1) does not melt or decompose until 417–419 °C, we expected that extended derivatives of 1 would also show good thermal stability. The fact that compounds 11 and 11a sublimed at 250 °C with decomposition indicates surprisingly low intermolecular interactions (no hydrogen bonds between molecules) and ready cleavage of the nitrogen–adamantyl carbon bond. The tritylamide compound 14 also decomposed at temperatures above 300 °C, behavior again attributed to the presence of the aliphatic nitrogen bond. In contrast, the aramid derivatives 12 and 13 showed high T_g's and T_m's (when present) and no degradation below 400 °C.

The intermediates and model compounds described here confirm overall synthetic pathways and provide the spectroscopic information necessary for adequate characterization of higher molecular weight dendrimers and star polymers with analogous structures. The DSC results are very promising for this approach, giving thermally stable three-dimensional adamantane-based poly(phenylene) and aramid containing dendrimers.

Experimental Section

General Procedures. All reactions were performed under nitrogen unless otherwise specified. FTIR spectra were obtained using a Perkin-Elmer 1600 spectrometer. Solution NMR spectra were obtained on a Bruker AC300 spectrometer operating at 330.1 MHz for ^{1}H and 75.469 MHz for ^{13}C. Solid-state NMR spectra were acquired on a Bruker MSL200 spectrometer operating at 50.32 MHz for ^{13}C and referenced to the methine peak of adamantane at 29.5 ppm. A DuPont 9900 TA was used to collect the DSC data. Unless otherwise specified, melting points were determined using an electrothermal melting point apparatus. Elemental analysis were performed by MHW Laboratories of Phoenix, AZ.

Chemicals. 1-Bromoadamantane, phenylboronic acid, [bis(trifluoroacetoxy)iodo]benzene (BFIB), $AlCl_3$, $AlBr_3$, carbon monoxide, $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$, iodine, 4-*tert*-butylaniline, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and 4-tritylaniline were used as received from Aldrich Chemical Co. Adamantane (Lancaster) was used as received. Benzene, chloroform, toluene, and tetrahydrofuran (THF) (Fisher) were dried and distilled prior to use. 1-Aminoadamantane (Aldrich) and triphenylphosphine (Eastman) were recrystallized from hexanes and ethanol, respectively. Dimethylacetamide (DMAc; Aldrich) was distilled and stored over molecular sieves. Bromobenzene and 1,3-dibromobenzene (Aldrich) were dried over $MgSO_4$ before use. Carbon dioxide gas, obtained from freshly made dry ice, was passed through a column of calcium sulfate/calcium chloride prior to use. *sec*-Butyllithium (2.0 M in cyclohexane) was obtained from Lithco Co. and titrated against 2,5-dimethoxybenzyl alcohol prior to use.

Modeling. Molecular modeling was performed on an IBM RISC R/S 6000 work station using Polygraph, a software product of Molecular Simulations. MMX molecular mechanics calculations were performed.

1,3,5,7-Tetraphenyladamantane (1). A dry 1000-mL three-neck round-bottom flask was fitted with two condensers, a magnetic stirbar, a nitrogen inlet, and two outlets running to a 30% NaOH solution. The flask was placed in an ice bath and cooled. To this flask was added 1-bromoadamantane (30.0 g, 0.14 mol), benzene (300 mL), and *tert*-butyl bromide (38.2 g, 0.28 mol). $AlCl_3$ (1.6 g, 0.012 mol) was added in four portions over 30 min to the chilled, stirring solution. The ice bath was replaced with a heating mantle and the reaction mixture allowed to warm to room temperature. The solution was then heated at reflux for 1 h, during which time large amounts of a white solid (1,3,5,7-tetraphenyladamantane) formed. The heterogeneous reaction mixture was cooled to room temperature and poured into acidic ice. Benzene (300 mL) was added and the slurry stirred for about an hour. The solution was decanted into a separatory funnel, leaving behind as much of the solid as possible. The layers were separated, and the organic layer was filtered to remove the 1,3,5,7-tetraphenyladamantane. The solids were combined and Soxhlet extracted overnight with chloroform. The desired product was insoluble in chloroform: 32.0–43.0 g (50–70%); mp 417–419 °C; IR (KBr) 3025, 2907, 2848, 1590, 1490, 1349, 1079, 769, 750, 703 cm^{-1}; ^{13}C CP/MAS NMR δ 39.4, 45.3, 124.8, 127.3, 129.2, 149.8.

1-Phenyl-, 1,3-diphenyl-, and 1,3,5-triphenyladamantane were isolated as a mixture from the combined benzene and chloroform solutions. 1-Phenyl- and 1,3-diphenyladamantane were very soluble in ether, while 1,3,5-triphenyladamantane was not. Approximately 3.0 g (5.0%) of 1,3,5-triphenyladamantane was isolated by washing the mixture with ether. It was purified by recrystallization from benzene: mp 229–230 °C; IR (KBr) 3060, 3025, 1596, 1496, 1443, 1354, 1343, 1084, 1032, 750, 703 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.0 (d, 6H), 2.1 (br s, 6H), 2.5 (septet, 1H), 7.2 (d, 6H), 7.4 (t, 3H), 7.5 (d, 6H); ^{13}C NMR ($CDCl_3$) δ 30.2, 38.3, 41.4, 48.1, 124.9, 125.9, 128.3, 150.0.

1,3,5-Tris(3-bromophenyl)adamantane (2). A 100-mL three-neck round-bottom flask was equipped with a condenser, nitrogen inlet/outlet, and magnetic stirrer. The flask was placed in an ice bath, and 1-bromoadamantane (5.0 g, 0.0232 mol), *tert*-butyl bromide (6.3 g, 0.046 mol), bromobenzene (25 mL), and $AlCl_3$ (0.25 g, 0.002 mol) were added. Gas formation (HCl/HBr) was evident. The reaction mixture was allowed to warm to room temperature under rapid stirring and nitrogen flow. The flask was then placed in an oil bath and heated at 130 °C for 30 min. The dark red solution was cooled to room temperature and poured onto acidic ice. The layers were separated, and the organic layer was washed with saturated NaCl and dried over $MgSO_4$. The solution was filtered, and the solvent was removed under reduced pressure to give a yellow oil. The oil was dissolved in a 1:1 mixture of hexanes and methylene chloride. A white solid crystallized out, which was identified as 1,3,5-tris(3-bromophenyl)adamantane: mp 216–217 °C; IR (KBr) 3060, 2919, 2848, 1590, 1560, 1478, 1413, 1355, 1079, 985, 891, 785, 767, 697, 679 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.96 (d, 12H), 2.5 (br s, 1H), 7.14, 7.30 (m, 9H), 7.5 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 29.9, 38.5, 41.0, 47.7, 122.8, 123.6, 128.4, 129.3, 129.9, 151.8. Anal. Calcd for $C_{28}H_{27}Br_3$: C, 55.66; H, 4.67; Br, 39.67. Found: C, 56.00; H, 4.68.

1,3,5-Tris(1,3′-biphenylyl)adamantane (6) from 2. A typical palladium-catalyzed phenylboronic acid coupling procedure[29] was as follows. To a two-neck, 50-mL round bottom flask equipped with a condenser and magnetic stirrer was added 1,3,5-tris(3-bromophenyl)adamantane (0.50 g, 0.82 mmol), $Pd(PPh_3)_4$ (0.029 g, 0.025 mmol), and 10 mL of toluene under a nitrogen flush. Once the solids had dissolved, 1 mL of 2 M Na_2CO_3 was added followed by phenylboronic acid [0.33 g (2.7 mmol) in 3 mL of ethanol]. The mixture was heated at reflux under nitrogen overnight. After cooling to room temperature, 0.5 mL of H_2O_2 was added to quench the excess boronic acid. This foaming mixture was stirred for 1 h. Toluene (10 mL) was added and the layers separated. The organic layer was dried over Na_2SO_4 and the toluene removed under reduced pressure to give 0.38 g (76%) of a light yellow solid: mp 70–73 °C; IR (KBr) 3060, 3025, 2896, 2849, 1596, 1572, 1478, 1449, 1408, 1343, 1261, 1096, 1026, 797, 756, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) aromatic/aliphatic integration ratio 2.1 (calc), 2.1 (exp); ^{13}C NMR ($CDCl_3$) δ 30.2, 38.5, 41.5, 48.3, 124.0, 124.1, 125.0, 127.2, 127.3, 128.7, 141.4, 141.7, 150.3.

1,3,5,7-Tetrakis(4-iodophenyl)adamantane (5) from 1. 1,3,5,7-Tetraphenyladamantane (2.0 g, 0.0045 mol) and iodine (2.3 g, 0.009 mol) were ground together with a mortar and pestle. The finely ground pink solid was transferred to a 100-mL one-neck round-bottom flask containing a magnetic stirbar and equipped with a nitrogen inlet. The mortar was rinsed with 20

mL of chloroform which was also transferred to the flask. [Bis(trifluoroacetoxy)iodo]benzene (BFIB; 3.9 g, 0.009 mol) was added and the reaction mixture flushed with nitrogen. A static atmosphere of nitrogen was maintained while the dark red mixture stirred for 4 h, after which the mixture was filtered to remove a pink solid (mix of product and starting material). The solid was Soxhlet extracted with chloroform overnight. The chloroform solutions were combined and washed sequentially with 5% $NaHSO_3$ (to remove the iodine), water, and saturated NaCl solution. The solvent was removed under reduced pressure to give a yellow solid which was recrystallized from $CHCl_3$/MeOH (9:1) to give 50–70% of the white crystalline product: DSC 290 °C (endo), 345 °C (endo); IR (KBr) 3049, 2919, 2848, 1484, 1443, 1390, 1355, 1179, 1076, 1002, 820, 779, 703 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.03 (s, 12H), 7.15 (d, 8H), 7.64 (d, 8H); ^{13}C NMR ($CDCl_3$) δ 39.0, 46.6, 91.7, 127.1, 137.5, 148.4. Anal. Calcd for $C_{34}H_{28}I_4$: C, 43.25; H, 2.99; I, 53.76. Found: C, 43.24; H, 3.08; I, 53.66.

1,3,5,7-Tetrakis(1,4′-biphenylyl)adamantane (8) from 5. The phenylboronic acid coupling procedure for **6** was employed on **5**. The toluene was removed under reduced pressure, leaving a beige solid which upon recrystallization from toluene gave 0.50–0.70 g (50–65%) of a light tan crystalline solid: mp 135–138 °C; IR (KBr) 3060, 3025, 2919, 2848, 1596, 1496, 1484, 1443, 1355, 1261, 1079, 1032, 761, 703 cm^{-1}; ^1H NMR ($CDCl_3$) aromatic/aliphatic integration ratio 3.0 (calc), 2.94 (obs) with peaks at δ 2.29 (s), 7.18 (d), 7.33 (d), 7.43 (t), 7.58, 7.60 (overlap s, d); ^{13}C NMR ($CDCl_3$) δ 39.2, 47.4, 125.5, 127.0, 127.1, 128.8, 139.1, 142.0, 148.4.

1,3,5,7-Tetrakis(3/4-bromophenyl)adamantane (3). A dry 250-mL three-neck flask was fitted with a water condenser, a magnetic stirbar, a nitrogen inlet, and an outlet to a 30% NaOH solution. The flask was placed in an ice bath. To this chilled flask was added 1,3,5,7-tetrabromoadamantane (5.0 g, 0.011 mol), bromobenzene (100 mL), and $AlBr_3$ (1.3 g, 0.005 mol). The reddish-brown mixture was stirred at 0 °C for 6 h, allowed to warm to room temperature, and finally heated at 60 °C for 4 h. The mixture was then poured onto acidic ice. After the ice melted, the layers were separated and the organic layer was washed with water and a saturated NaCl solution. The product was isolated by precipitation into methanol. Trituration with methanol gave 4.20 g (50%) of a light tan solid: mp 230–237 °C; IR (KBr) 3059, 2926, 2896, 2851, 1589, 1559, 1477, 1445, 1442, 1354, 1076, 1006, 992, 874, 829, 772, 693 cm^{-1}; ^1H NMR ($CDCl_3$) aromatic/aliphatic integration ratio 1.33 (calc), 1.37 (obs) with peaks at δ 2.08 (br s), 7.22 (m) 7.36 (m), 7.49 (d), 7.55 (s); integration ratio of the 7.5 ppm peak to the other aromatic peaks indicated ca. 55–70% "meta", *m*, to "para", *p*, isomer formation; ^{13}C NMR ($CDCl_3$) δ 39.1 *p*, 39.4 *m*, 46.8 *m*/*p*, 120.3 *p*, 122.9 *m*, 123.6 *m*, 126.8 *p*, 128.4 *m*, 129.6 *m*, 130.1 *m*, 131.5 *p*, 147.1 *p*, 151.0 *m*.

1,3,5,7-Tetrakis(1,3′/4′-biphenylyl)adamantane (7) from 3. The phenylboronic acid coupling procedure for **6** was used on intermediate **3**. Isolation of the solid product and recrystallization from toluene gave a light yellow crystalline material: 50–55% yield; mp 126–131 °C; IR (KBr) 3022, 2925, 2848, 1519, 1481, 1410, 1351, 1259, 1074, 1004, 789, 700 cm^{-1}; ^1H NMR ($CDCl_3$) aromatic/aliphatic integration ratio 3.0 (calc), 2.78 (obs); ^{13}C NMR ($CDCl_3$) δ 39.3, 39.5, 47.4, 124.0, 124.2, 125.1, 125.5, 127.4, 128.4, 128.7, 131.3, 141.2, 141.5, 149.8.

1,3-Dibromo-4/5-(1-adamantyl)benzene. To a 50-mL two-neck round-bottom flask equipped with a condenser and nitrogen inlet/outlet was added 1,3-dibromobenzene (8.23 g, 0.035 mol) and 1-bromoadamantane (1.50 g, 0.007 mol). The stirring solution was placed in an ice bath, and $AlBr_3$ (0.37 g, 0.0014 mol) was added. The orange reaction mixture was allowed to warm to room temperature and stirred overnight. The mixture was poured onto ice which contained 2 mL of concentrated HCl. The layers were separated, and the organic layer was washed with water and saturated sodium chloride. After drying over $MgSO_4$ the excess dibromobenzene was distilled off, leaving a yellow solid. Recrystallization from toluene gave a white crystalline solid: 1.40 g (53%). A 1:4 mixture of "ortho", *o*, and "meta", *m*, isomers was determined based on NMR data. The isomers were not separated. The DSC trace showed endothermic peaks at 107–109 and 135–137 °C: IR (KBr) 3060, 2907, 2848, 1578, 1549, 1443, 1402, 1102, 849, 738, 685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.7 (d, 6H), 1.8 (d, 6H), 2.1 (br s, 3H), 7.3, 7.5 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 28.7, 29.1, 35.3, 36.5, 36.6, 41.7, 42.8, 48.4, 122.8 *m*, 123.0 *o*, 127.2 *o*/*m*, 131.1 *o*/*m*, 131.6 *o*, 154.0 *o*, 155.4 *m*.

1,3-Diphenyl-4/5-(1-adamantyl)benzene. The phenylboronic acid coupling procedure was used on 1,3-dibromo-4/5-(1-adamantyl)benzene to give an orange solid. Recrystallization from toluene gave a light yellow solid: 0.32 g (65%); ^1H NMR ($CDCl_3$) δ 1.8 (br s, 6H), 1.9 (s, 6H), 2.3 (br d, 3H), 7.4, 7.6 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 2.91, 29.6 36.9, 37.8, 42.5, 43.4, 48.4, 123.2, 123.7, 124.0, 127.3, 127.5, 128.8, 141.6, 141.8.

1,3,5,7-Tetrakis(1,3-dibromophenyl)adamantane (4). The procedure given for the reaction of bromobenzene with 1,3,5,7-tetrabromoadamantane was followed with the exception that 1,3-dibromobenzene was used in place of bromobenzene to give 1.5 g of **4** (80%): DSC, no transitions up to 450 °C; IR (KBr) 3060, 2931, 2849, 1578, 1560, 1549, 1449, 1408, 1355, 1008, 991, 855, 738, 685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.04 (br s, 12H), 7.45 (br apparent t, 12H); ^{13}C NMR ($CDCl_3$) δ 41.4, 46.6, 123.6, 125.4, 126.8, 127.3, 128.3, 130.2, 130.6, 131.7, 132.4, 133.7, 150.8.

1,3,5,7-Tetrakis(1,3-terphenylyl)adamantane (9) from 4. The phenylboronic acid coupling procedure was used on **4** with THF as the solvent instead of toluene to give a white solid: 0.53 g (91%); DSC, no transitions up to 450 °C; IR (KBr) 3060, 2931, 2849, 1596, 1561, 1449, 1408, 1355, 1261, 1079, 1008, 861, 808, 761, 697 cm^{-1}; ^{13}C NMR (THF with DMSO-d_6 insert) δ 45.8, 122.5, 123.5, 127.1, 128.0, 141.2, 150.0; ^{13}C CP/MAS NMR δ 39.9, 46.9, 128.0 (br), 142.6, 151.3.

1,3,5,7-Tetrakis(4-carboxylatophenyl)adamantane (10) from 5. A chilled three-neck, 250-mL round-bottom flask, equipped with a mechanical stirrer and under nitrogen purge, was charged with **5** (5.0 g, 5.3 mmol) in 30 mL of dry THF. *sec*-Butyllithium (4.5 mol as a 1.37 M cyclohexane solution) was added via a syringe over a 2-h period with rapid stirring. The orange reaction mixture was stirred for an additional 2 h at room temperature. The nitrogen purge was replaced with a carbon dioxide line, and dry carbon dioxide was bubbled through the reaction mixture for 1 h. A yellow/white precipitate formed immediately upon CO_2 addition. The mixture was poured into 4 N HCl/ice and the solid isolated by suction filtration. The crude product was recrystallized from acetic acid: 2.7 g (70%); mp 380 °C (dec); IR(KBr) 3060, 2931, 2849, 1725, 1690, 1607, 1413, 1279, 1184, 1102, 756, 703 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.14 (br s, 12H), 7.42 (br d, 8H), 7.81 (d, 8H), 12.8 (br s, 4H); ^{13}C NMR (DMSO-d_6) δ 40.1, 125.1 (impurity), 125.5, 128.2 (impurity), 128.5, 129.3, 154.3, 167.3.

1,3,5,7-Tetrakis[(1-adamantylcarbamoyl)phenyl]adamantane (11) from 10. A literature procedure[30] for amide synthesis that employed a solvent mix of tetramethylurea and pyridine (7:3) was used with **10**, except that the reaction mixture was stirred for 24 h. Upon recrystallization from CH_2Cl_2, a yellow solid was isolated: 0.31 g (35%); mp 247–255 °C (sub); FTIR (KBr) 3425, 3025, 2907, 2849, 1719, 1660, 1607, 1496, 1443, 1355, 1279, 1184, 1102, 908, 755, 732, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.69 (br s, 22H), 2.01 (br s, 42H), 7.35, 7.80 (m, 16H), 8.00 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 29.4, 36.3, 39.3, 41.6, 46.9, 52.2, 125.0 (impurity), 126.8, 128.5 (impurity), 130.3, 133.9, 152.0, 166.2.

1,3,5,7-Tetrakis[(1-adamantylcarbamoyl)phenyl]adamantane (11a) from 5. A typical carbonylation procedure (1 atm of CO) was as follows.[31] To a two-neck 50-mL round-bottom flask, equipped with a magnetic stirrer, condenser, and gas inlet/outlet was added **5** (0.50 g, 0.53 mmol), 1-aminoadamantane (0.31 g, 2.12 mmol), palladium(II) chloride bis(triphenylphosphine) (0.022 g, 0.032 mmol), triphenylphosphine (0.017 g, 0.64 mmol), and 15 mL of DMAc. The mixture was flushed with nitrogen and then with carbon monoxide. Under an atmosphere of carbon monoxide, the reaction mixture was stirred and heated to about 50 °C, at which time DBU (0.39 g, 2.5 mmol) was added. The mixture was stirred under 1 atm of carbon monoxide and heated at 100 °C overnight. After cooling to room temperature, the mixture was filtered, the filtrate was washed with 5 mL of DMAc, and the combined organic portions were then poured into methanol. The yellow solid was recrystallized from CH_2Cl_2 to give 0.40 g (60%) of a white solid; mp 250–254 °C (sub); IR (KBr) 3342, 3060, 2908, 2849, 1707, 1625, 1560, 1496, 1443, 1355, 1355, 1296, 1184, 1102, 1014, 755 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.63 (br d, 22H), 2.03 (br t, 42H), 7.48 (m, 8H), 7.67 (m, 8H), 8.03 (m, 4H);

^{13}C NMR ($CDCl_3$, both *cis* and *trans* isomers) δ 29.4, 36.3, 39.2, 42.4, 46.5, 50.7, 124.9, 126.8, 128.5, 130.2, 131.9, 133.9, 151.7, 153.9, 166.3, 169.3.

1,3,5,7-Tetrakis[(4-biphenylylcarbamoyl)phenyl]adamantane (12) from 5. The above carbonylation procedure was used on **5** with 4-biphenylaniline to give 0.60 g (92%) of a white solid which was recrystallized from DMAc; first DSC run to 400 °C showed transitions at 249 °C (endotherm) and 368 °C (endotherm), while a second run displayed a T_g-like transition centered at 215 °C: IR (KBr) 3284, 3025, 2919, 2848, 1660, 1631, 1596, 1525, 1484, 1402, 1319, 1244, 1014, 834, 761, 697 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.11 (s, 12H), 7.18 (t, 4H), 7.30 (t, 8H), 7.53 (d, 16H), 7.67 (d, 8H), 7.75 (d, 8H), 7.87 (d, 8H), 10.2 (s, 4H); ^{13}C NMR (DMSO-d_6) δ 45.8, 120.7, 125.4, 126.3, 126.8, 127.1, 127.8, 128.9, 132.6, 135.2, 138.7, 136.7, 153.2, 165.5. Anal. Calcd for $C_{86}H_{68}N_4O_4 \cdot 2H_2O$: C, 82.14; H, 5.77; N, 4.45. Found: C, 81.83; H, 5.76; N, 4.37.

1,3,5,7-Tetrakis[[(*tert*-butylphenyl)carbamoyl]phenyl]adamantane (13) from 5. The carbonylation procedure used for the synthesis of **11a** was employed on **5** and 4-*tert*-butylaniline. A dark gray solid was isolated, dissolved in toluene/methanol (9:1), and treated with activated carbon. The solution was filtered to remove the activated carbon. The solvent was removed under reduced pressure to give the product as a white solid: 0.35 g (58%); DSC 330 °C (endo), 425 °C (endo) (melt with some decomposition); IR (KBr) 3284, 2954, 2931, 2919, 2848, 1666, 1631, 1602, 1531, 1519, 1402, 1325, 1267, 1014, 838 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.13 (s, 12H), 2.10 (s, 12H), 7.20 (d, 8H), 7.53 (d, 8H), 7.63 (d, 8H), 7.82 (d, 8H), 10.1 (s, 4H); ^{13}C NMR (DMSO-d_6) δ 31.3, 34.1, 45.9, 120.2, 125.2, 125.4, 127.7, 132.8, 126.7, 146.0, 153.0, 165.2. Anal. Calcd for $C_{78}H_{84}N_4O_4 \cdot H_2O$: C, 79.56; H, 7.53; N, 4.76; O, 8.15. Found: C, 80.00; H, 7.56.

1,3,5,7-Tetrakis[[(tritylphenyl)carbamoyl]phenyl]adamantane (14) from 5. The carbonylation procedure was used on **5** with 4-tritylaniline to give a light orange solid upon precipitation into methanol. The product was washed with methanol and recrystallized from $CHCl_3$ to give white crystals: 0.61 g (61%); DSC 291 °C (endo) (followed by slow decomposition); IR (KBr) 3354, 3060, 3025, 2931, 2849, 1678, 1596, 1507, 1490, 1443, 1408, 1320, 750, 703 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.12 (s, 12H), 7.20, 7.30 (m, 56H), 7.50 (t, 12H), 7.67 (d, 8H), 7.77 (d, 8H), 7.87 (d, 8H), 10.20 (s, 4H); ^{13}C NMR (DMSO-d_6) δ 45.8, 64.0, 119.6, 125.3, 125.9, 127.7, 130.4, 130.7, 132.6, 137.0, 141.5, 146.5, 153.1, 165.4. Anal. Calcd for $C_{138}H_{108}N_4O_4 \cdot 2H_2O$: C, 86.22; H, 5.87; N, 2.91; O, 4.99. Found: C, 86.34; H, 6.11.

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