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Synthesis of Rigid Tetrahedral Tetrafunctional Molecules from 1,3,5,7-Tetrakis(4-iodophenyl)adamantane

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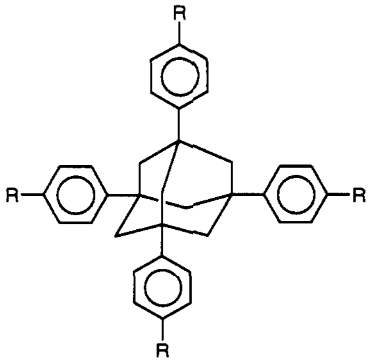
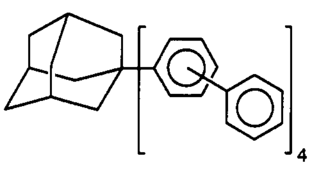
The synthesis of supermolecular organic structures possessing designed architectures has been a longstanding goal of materials scientists and chemists.[2,3] Dendrimers are examples of such macromolecules that possess controlled, highly branched spherical structures. Both divergent (core first) and convergent synthetic approaches to dendritic materials are under investigation by several groups,[4–8] and both an extensive review on their syntheses[3] and a paper discussing theoretical considerations[9] have appeared. However, need still exists for simple synthetic approaches to molecules with the appropriate symmetry and functionality to allow efficient formation of well-defined star, dendritic, and hyperbranched structures.

Incorporation of the rigid, low-strain, and highly symmetrical adamantane molecule into extended-chain materials with enforced three-dimensional architecture may satisfy this need: functionalization of the four tertiary (bridgehead) positions of adamantane gives a rigid tetrahedral array of functional groups. While numerous 1,3,5,7-tetrasubstituted adamantane derivatives have been reported,[10] only a handful can be readily obtained in good yields.[11–13] After greatly improving the synthesis of 1,3,5,7-adamantane tetracarboxylic acid, Newkome and coworkers[14] have recently demonstrated the value of this approach in the divergent synthesis of four-directional cascade polymers with the tetraacid as the core moiety. However, only milligram quantities of the first- and second-generation cascade polymers were synthesized, pointing out the absence of synthetic approaches that can routinely generate gram quantities of the desired starting materials and intermediates.

We report here the facile two-step synthesis of 1,3,5,7-tetrakis(4-iodophenyl)adamantane, **1**, and demonstrate its utility in the synthesis of structures possessing extended tetrahedral symmetry. Aryl compounds containing halide substituents (such as **1**) are especially attractive since the phenyl groups provide a lateral extension of the three-dimensional adamantane core while the halide moieties provide entry into a wide variety of derivatization pathways.



1: R = I **2**: R = H **3**: R = C≡C–C(CH$_3$)$_2$OH
4: R = C≡CH **5**: R = Ph



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Compound **1** was prepared in yields of 60–80% by the iodination[15] of the readily available 1,3,5,7-tetraphenyl adamantane,[16] **2**, which was obtained in high yield from commercially available 1-bromoadamantane. The structure of **1** was confirmed by ^{1}H and ^{13}C NMR, FTIR, and elemental analysis. This key intermediate is easily purified[17] and has been obtained in 10-g quantities. With the availability of large amounts of this key intermediate, a multitude of synthetic opportunities exist that lead to extended chain structures. The chemistry below was developed for analogous aryl halides and allows synthesis of **3–6** using literature methods.[18–20]

Compound **3** was prepared through palladium-catalyzed coupling of **1** with 2-methyl-3-butyn-2-ol in yields of 35–45%.[21] The ^{13}C NMR spectrum is shown in Figure 1 along with the spectrum of **1**. The appearance of the acetylenic

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(2) Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304.

(3) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138.

(4) Kim, Y. H.; Webster, O. W. *J. Am. Chem. Soc.* **1991**, *112*, 4592.

(5) Miller, T. M.; Neenan, T. X.; Zayas, R.; Bair, H. E. *J. Am. Chem. Soc.* **1992**, *114*, 1018.

(6) Hawker, C. J.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638; Wooley, K. L.; Hawker, C. J.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4252.

(7) Moore, J. S.; Xu, Z. *Macromolecules* **1991**, *24*, 5893.

(8) Newkome, G. R.; Moorefield, C. N.; Baker, G. R.; Johnson, A. L.; Behera, R. K. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1176.

(9) Farin, D.; Avnir, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1379.

(10) Fort, R. T. In *Adamantane: The Chemistry of Diamond Molecules*; Gassman, P. G., Ed.; Studies in Organic Chemistry; Marcel Dekker: New York, 1976; Vol. 5.

(11) Setter, H.; Krause, M. *Tetrahedron Lett.* **1967**, 1841.

(12) Mello, R.; Cassidei, L.; Fiorentino, M.; Fusco, C.; Curici, R. *Tetrahedron Lett.* **1990**, *21*, 3067.

(13) Sollott, G. P.; Gilbert, E. E. *J. Org. Chem.* **1980**, *45*, 5405.

(14) Newkome, G. R.; Nayak, A.; Behera, R. K.; Moorefield, C. N.; Baker, G. R. *J. Org. Chem.* **1992**, *57*, 358.

(15) Merkushev, E. B.; Simakhina, N. D.; Koveshnikova, G. M. *Synthesis* **1980**, 486.

(16) Newman, H. *Synthesis* **1972**, 692.

(17) Recrystallized from CHCl$_3$/MeOH. DSC data: endo 290 °C, endo 345 °C; IR (KBr) 3049, 2919, 2848, 1484, 1443, 1390, 1355, 1179, 1076, 1002, 820, 779, 703 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.03 (s, 12 H), 7.64 (d, 8 H), 7.15 (d, 8 H); ^{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.

(18) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627.

(19) Lucotte, G.; Cormier, L.; Delfort, B. *J. Polym. Sci. A* **1991**, *29*, 897.

(20) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513.

(21) Recrystallized from ethanol. DSC data: exo 330.4 °C, endo 333.7 °C; IR (KBr) 3378, 2978, 2931, 2848, 2226, 1508, 1443, 1361, 1273, 1161, 1020, 961, 908, 838, 773 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.59 (s, 6 H), 2.08 (s, 12 H), 7.37 (s, 16 H); ^{13}C NMR (CDCl$_3$) δ 31.5, 39.2, 46.8, 65.6, 81.9, 93.6, 120.7, 124.9, 131.7, 149.2. Anal. Calcd for $C_{54}H_{56}O_4$: C, 84.34; H, 7.34; O, 8.32. Found: C, 84.09; H, 7.13.

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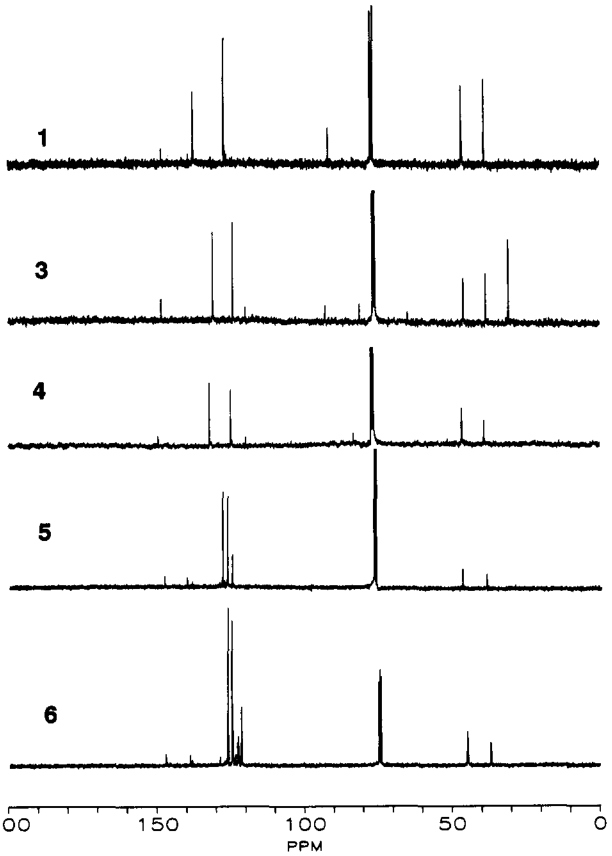

Figure 1. The 75-MHz ^{13}C NMR spectra obtained in CDCl$_3$ of compounds 1 and 3–6 using a Bruker AC-300.

carbons at 81.9 and 93.6 ppm along with the absence of a resonance for the iodine ipso carbon confirm its structure as does ^{1}H NMR and elemental analysis. Deprotection[22] of 3 gave the acetylene, 4, in nearly quantitative yield. The structure of 4 is confirmed by ^{13}C NMR and FTIR. The ^{13}C spectrum (Figure 1) contains peaks corresponding to the deprotected acetylene: substituted acetylenic carbon at 83.7 ppm, aryl carbon ipso to acetylene at 120.0 ppm, and unsubstituted acetylene carbon buried under CDCl$_3$ peaks. In the FTIR spectrum of 4, a strong absorbance is evident at 3284 cm^{-1} (sp carbon–hydrogen stretch) while the less intense sp carbon–sp carbon stretch is at 2108 cm^{-1}. During thermal analysis of 4, an endotherm was observed at 124 °C with no additional transitions up to 400 °C. Thermal transitions were absent during a second heating to 400 °C confirming acetylene group reaction. The cure chemistry is apparently similar to that reported recently for acetylene-terminated polyimides[23] and poly(organophosphazene)s[24] as monitored by solid-state ^{13}C NMR. In fact, diethynyladamantanes have recently been synthesized and shown to undergo thermal polymerization at ca. 210 °C to give highly cross-linked materials with good thermal and oxidative stability.[25] The availability of 1 and extended acetylene derivatives such as 4 offers options for extending the known behavior of acetylene-terminated monomers and oligomers into the realm of three-dimensionally ordered supermolecular structures with symmetry and bonding similar to that of diamond and diamond-like materials.

The presence of an aryl halide in 1 lends itself to other metal catalyzed coupling reactions. For example, 1 was reacted with phenyl boronic acid under Suzuki coupling conditions to give 5 (45–55%).[26] This all para-substituted biphenyl compound is CHCl$_3$ soluble, readily purified, and easily characterized. ^{1}H NMR integration gives the expected ratio of aliphatic to aromatic protons. The ^{13}C NMR spectrum of 5 is included in Figure 1. The peaks at 139.1 and 142.0 ppm correspond to the carbons of the biphenyl link while the absence of the ipso iodine carbon of 1 confirms coupling. Compound 5 can be compared to 6 which was prepared by an alternative route in which 1,3,5,7-tetrabromoadamantane[11] was reacted with excess bromobenzene in the presence of AlBr$_3$ to give 1,3,5,7-tetrakis(3/4-bromophenyl)adamantane[27] (70% meta isomer by ^{1}H NMR integration: ratio of peak at 7.5 ppm to other aromatics). Coupling with phenyl boronic acid under Suzuki conditions gave 6.[28] Present in the ^{13}C NMR spectrum of 6 (Figure 1) are resonances associated with meta- (124.0, 124.4, 128.4 ppm) and para- (125.5, 127.0, 128.7 ppm) substituted biphenyl rings. Two resonances (39.2 and 39.5 ppm) are present for the two types of phenyl-substituted quaternary adamantane carbons while a broad peak at 47.2 ppm is seen for the adamantane secondary carbons.

The syntheses of 3–5 demonstrate the utility of the easily prepared 1,3,5,7-tetrakis(4-iodophenyl)adamantane as a core for extension to three-dimensional structures. The synthesis of dendrimers based on this approach is in progress along with the preparation of a variety of additional adamantane based structures. Compound 1 promises to be a general synthetic starting point or coupling node for a vast array of designed and tailored structures possessing enforced tetrahedral symmetry.

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(22) Recrystallized from MeOH/CCl$_4$. DSC data: endo 123 °C; IR (KBr) 3284, 3083, 2931, 2848, 2108, 1684, 1608, 1508, 1443, 1355, 1261, 832, 797 cm^{-1}; ^{13}C NMR (300 MHz, CDCl$_3$) δ 39.2, 48.6, 83.5, 120.5, 125.0, 132.2, 149.6 ppm.

(23) Swanson, S. A.; Fleming, W. W.; Hofer, D. C. *Macromolecules* **1992**, *25*, 582.

(24) Chang, J. Y.; Rhee, S. B.; Cheong, S.; Yoon, M. *Macromolecules* **1992**, *25*, 2666.

(25) Archibald, T. G.; Malik, A. A.; Baum, K.; Unroe, M. R. *Macromolecules* 1991, *24*, 5261.

(26) Recrystallized from toluene. Mp 135–138 °C; IR (KBr) 3060, 3025, 2919, 2848, 1596, 1496, 1484, 1443, 1355, 1261, 1079, 1032, 761, 703 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) aromatic/aliphatic 3.0 (calc), 2.94 (obs), 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.

(27) Washed with methanol, 54% yield. 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}; ^{1}H NMR (300 MHz, CDCl$_3$) aromatic/aliphatic: 1.33 (calc), 1.37 (obs), δ 2.08 (broad s), 7.22 (d), 7.36, 7.38 (overlap d), 7.51 (d), 7.55 (s); ^{13}C NMR (CDCl$_3$) δ 39.1, 39.4, 46.8, 120.3, 122.9, 123.6, 126.8, 128.4, 129.6, 130.1, 131.5, 147.1, 151.0.

(28) Recrystallized from toluene, 50% yield. Mp 126–131 °C; IR (KBr) 3022, 2925, 2848, 1549, 1481, 1443, 1410, 1351, 1259, 1074, 1004, 789, 700 cm^{-1}; ^{1}H NMR (CDCl$_3$) aromatic/aliphatic 3.0 (calc), 2.78 (obs), δ 2.3 (broad s), 7.25–7.59 (overlap m); ^{13}C NMR (CDCl$_3$) δ 39.3, 39.5, 47.4, 124.0, 124.2, 125.1, 125.5, 127.0, 127.4, 128.4, 128.7, 131.3, 141.2, 141.5, 149.8.