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Synthesis and X-Ray Crystal Structures of Poly-Adamantane Molecular Rods

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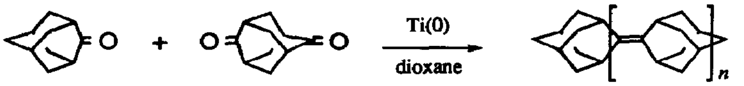
Abstract: End-functionalized molecular rods composed of apically repeating adamantane units linked by double bonds are easily prepared in one step by a mixed McMurry coupling

Recent reports from the groups of Hawthorne and Michl[1b,c] describing the preparation of poly-carborane rods add to the growing list of molecular rods put forth as possible components in a molecular "tinker toy®" construction kit.[1a] We wish to contribute to this area of research by reporting the preparation of torsionally rigid rods composed of apically repeating adamantane units linked by double bonds. The poly-adamantane rods are easily prepared in one step by McMurry coupling and represent the first rods with ketone end groups amenable to further modification.

The McMurry reagent is unparalleled in its ability to efficiently couple ketones.[2] Accordingly, we were intrigued by the possibility of preparing poly-adamantane rods by this method since adamantanone (1) undergoes the Ti(0) mediated coupling in near quantitative yield.[3] Our initial efforts focused on the mixed McMurry coupling of 1 and adamantane-2,6-dione (2) (Scheme 1). The rods 3a-c were prepared, isolated, and characterized.[4] We now present the synthesis of end-functionalized rods by the mixed McMurry coupling of adamantane-2,6-dione *mono*-(ethylene)ketal (4)[5] and 2.[6]



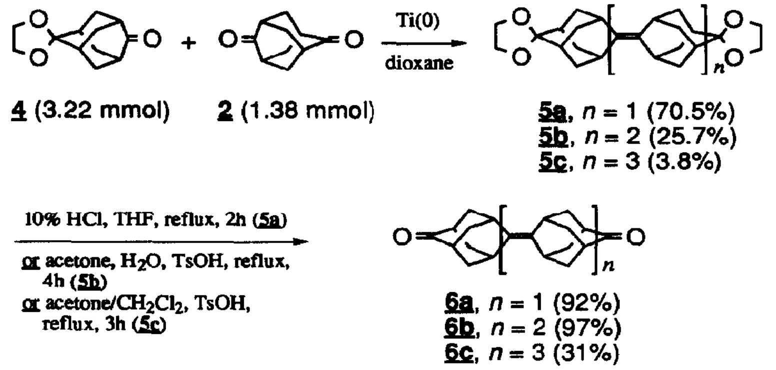
1 (20 mmol) 2 (0.5 mmol)

3a, $n = 1$ (9.17 mmol)
3b, $n = 2$ (0.34 mmol)
3c, $n = 3$ (0.0075 mmol)

Scheme 1

In a typical procedure the Ti(0) reagent (5 equiv) is generated from Na (46.4 mmol) and $TiCl_3$ (17.2 mmol) in refluxing dioxane (50 mL).[4] The mixture of ketones 4 (3.22 mmol) and 2 (1.38 mmol) is added as a solid. After 4 hours at reflux (N_2), the reaction mixture is carefully filtered while hot through a Florisil plug and the solid washed with hexanes. Evaporation of the filtrate leaves the rods 5a-c (0.52, 0.19, and 0.028 mmol respectively) which are easily separated by fractional sublimation.[7] The products account for 45.8% of 4 and

17.8% of 2 used. The melting points of the series increase sharply with increasing rod length, whereas solubility decreases. Ketals **5a,b** are soluble in common solvents, but **5c** is only moderately soluble in CH_2Cl_2 and $CHCl_3$.



Scheme 2

Deprotection of **5a-c** provided the diketones **6a-c** (Scheme 2);[8] the X-ray crystal structures of **6a** and **6b** have been determined (Figures 1 and 2).[9] Diketone **6a** possesses crystallographically imposed inversion symmetry. The O(1)-O(1') and C(6)-C(6') distances are 10.693 Å and 8.304 Å respectively. Diketone **6b** possesses pseudo-D_{2d} symmetry and is bent 22.4° from the line defined by the intersection of planes containing O(1)-C(1)-C(10) and O(2)-C(30)-C(21). The O(1)-O(2) and C(1)-C(30) distances are 15.325 Å and 12.946 Å respectively. Although the distances between the allylic hydrogens in **6a** and **6b** are less than the van der Waals distance of 2.4 Å there is no significant twisting of the double bonds.[10] Trimer **6b** has a slight twist of ~6° along its axis as determined from the intersection of least-squares planes containing the double bonds and their neighboring atoms; however, we attribute the twist and bend in **6b** to deformation of the central adamantane skeleton.[11] Our rods have an average repeat length of 4.9 Å per adamantane unit and a

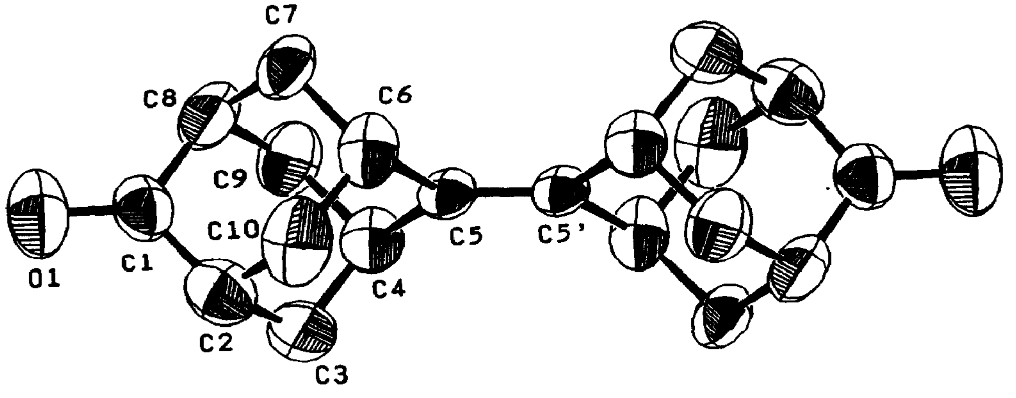


Figure 1. ORTEP representation of dimer **6a**. Hydrogen atoms removed for clarity.

van der Waals diameter of *ca.* 7 Å. Both dimensions are comparable to those of the carborods.[1b,c] Attempts to grow crystals of **6c** have thus far been unsuccessful; however the terminal to terminal C···C length of **6c** is calculated by MM2 to be 18.028 Å.[11]

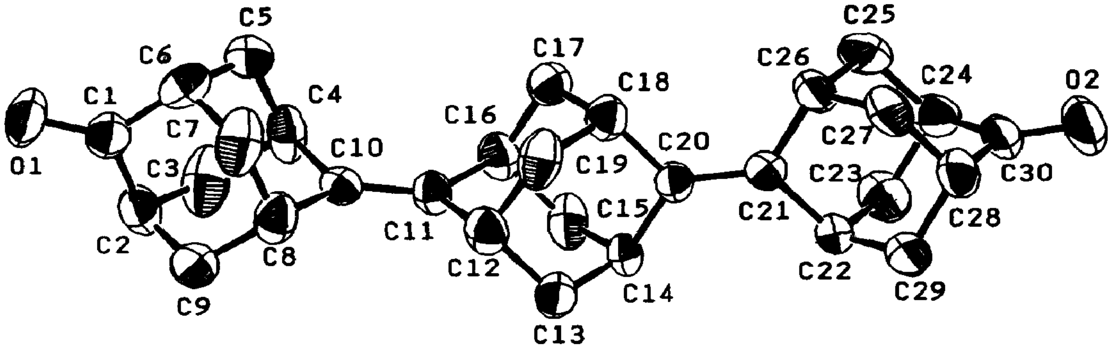


Figure 2. ORTEP representation of trimer **6b**. Hydrogen atoms removed for clarity.

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2. McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513.
3. a) McMurry, J. E.; Fleming, M. P. *J. Org. Chem.* **1976**, *41*, 896. b) Fleming, M. P.; McMurry, J. E. *Org. Synth.* **1981**, *60*, 113. c) Tolstikov, G. A.; Lerman, B. M.; Belogaeva, T. A. *Syn. Commun.* **1991**, *21*, 877. d) For an improvement see reference 4a.
4. a) Shen, D., Ph.D. dissertation, University of California, Los Angeles, 1990. b) Chapman, O. L., to Mobil Oil Corp., U.S. Pat. 5,053,434, 1991.
5. a) Mono-deprotection of adamantane-2,6-dione *bis*-(ethylene)ketal in acetone with *p*-TsOH gave **4** in 69% yield after column chromatography (SiO$_2$, 3:2 hexanes/EtOAc); R_f = 0.59 (3:2 hexanes/ EtOAc); mp 95.0-95.5 °C; IR (KBr) υ 2933, 2864, 1723, 1696, 1454, 1382, 1305, 1288, 1236, 1211, 1137, 1085, 1038, 1013, 996, 944 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 4.00 (s, 4 H), 2.45 (br s, 2 H), 2.30 (br d, J_{AB} = 11.3 Hz, 4 H), 1.91- 1.89 (6 H, m); ^{13}C NMR (90.6 MHz, CDCl$_3$) δ 216.80, 109.08, 64.49, 45.14, 35.83, 35.78; HRMS (EI) calcd for $C_{12}H_{16}O_3$ 208.1099, found 208.1093. b) See also reference 6.
6. Ayres, F. D.; Khan, S. I.; Chapman, O. L.; Kaganove, S. N. *Tetrahedron Lett.* in press.
7. Characterization of **5a**: (sublimes ~210 °C, 0.1 mmHg) mp 275.0-275.5 °C (sealed tube); IR (KBr) υ 2954, 2929, 2901, 2859, 1450, 1399, 1385, 1313, 1216, 1118, 1085, 1042, 941 cm^{-1}; ^{1}H NMR (360 MHz, CDCl$_3$) δ 3.97 (s, 8 H), 2.82 (br s, 4 H), 2.06 (br d, J_{AB} = 11.7 Hz, 8 H), 1.86 (br s, 4 H), 1.61 (br d, J_{AB} = 11.7 Hz, 8 H); ^{13}C NMR (90.6 MHz, CDCl$_3$) δ 132.35, 111.09, 64.23, 36.72, 36.64, 30.28; HRMS (EI) calcd for $C_{24}H_{32}O_4$ 384.2300, found 384.2282. **5b**: (sublimes

~320 °C, 0.1 mmHg) mp 308-310 °C (darkens); IR (KBr) υ 2927, 2905, 2855, 2843, 1448, 1384, 1310, 1222, 1126, 1103, 1088, 1078, 1039, 1012, 995, 986, 944 cm^{-1}; ^{1}H NMR (360 MHz, CDCl$_3$) δ 3.97 (s, 8 H), 2.95 (br s, 4 H), 2.84 (br s, 4 H), 2.07 (br d, J_{AB} = 11.8 Hz, 8 H), 1.87 (br s, 4 H), 1.77 (br s, 8 H), 1.64 (br d, J_{AB} = 11.8 Hz); ^{13}C NMR (90.6 MHz, CDCl$_3$) δ 133.09, 132.22, 111.16, 64.22, 41.45, 36.75, 36.65, 32.02, 30.33; HRMS (EI) calcd for $C_{34}H_{44}O_4$ 516.3240, found 516.3247. **5c**: mp >390 °C (sealed tube, darkens ~370 °C); IR (KBr) υ 2950, 2924, 2903, 2841, 1448, 1384, 1310, 1214, 1206, 1125, 1100, 1086, 1043, 1014, 997, 987, 962, 934 cm^{-1}; ^{1}H NMR (360 MHz, CDCl$_3$) δ 3.98 (s, 8 H), 2.97 (br s, 8 H), 2.85 (br s, 4 H), 2.08 (br d, J_{AB} = 11.7 Hz), 1.88 (br s, 4 H), 1.79 (br s, 16 H), 1.65 br d, J_{AB} = 11.7 Hz, 8 H); ^{13}C NMR (90.6 MHz, CDCl$_3$) δ 133.24, 133.00, 132.15, 111.19, 64.23, 41.50, 36.77, 36.67, 32.10 (2 peaks), 30.34; HRMS (EI) calcd for $C_{44}H_{56}O_4$ 648.4179, found 648.4163.

8. Characterization of **6a**: mp 332.0-332.5 °C (partially sublimes); IR (KBr) υ 2976, 2922, 2860, 1751, 1720, 1712, 1695, 1560, 1457, 1451, 1433, 1348, 1325, 1304, 1269, 1233, 1198, 1085, 1033, 987, 956 cm^{-1}; ^{1}H NMR (360 MHz, CDCl$_3$) δ 3.09 (br s, 4 H), 2.63 (br s, 4 H), 2.15 (br d J_{AB} = 11.7 Hz), 2.04 (br d J_{AB} = 11.7 Hz, 8 H); ^{13}C NMR (90.6 MHz, CDCl$_3$) δ 217.40, 132.25, 46.92, 40.87, 31.01; HRMS (EI) calcd for $C_{20}H_{24}O_2$ 296.1776, found 296.1761. **6b**: mp >390 °C (darkens at 370 °C); IR (KBr) υ 2918, 2851, 1726, 1449, 1345, 1304, 1264, 1128, 1085, 1029, 983, 962, 945, 698 cm^{-1}; ^{1}H NMR (360 MHz, CDCl$_3$) δ 3.08 (br s, 4 H), 3.04 (br s, 4 H), 2.62 (br s, 4 H), 2.12 (br d, J_{AB} = 11.7 Hz, 8 H), 2.04 (br d, J_{AB} = 11.7 Hz, 8 H), 1.86 (br s, 8 H); ^{13}C NMR (90.6 MHz, CDCl$_3$) δ 218.11, 134.97, 130.25, 47.14, 41.31, 41.03, 32.21, 30.87; HRMS (EI) calcd for $C_{30}H_{36}O_2$ 428.2715, found 428.2709. **6c**: mp >360 °C; IR (KBr) υ 2952, 2913, 2845, 1730, 1447, 1401, 1385, 1343, 1304, 1204, 1086, 1030, 984, 965 cm^{-1}; ^{1}H NMR (360 MHz, CDCl$_3$) δ 3.08 (br s, 4 H), 3.02 (br s, 8 H), 2.62 (br s, 4 H), 2.12 (br d, J_{AB} = 12.9 Hz, 8 H), 2.04 (br d, J_{AB} = 12.9 Hz, 8 H), 1.84 (br s, 16 H); ^{13}C NMR (90.6 MHz, CDCl$_3$) δ 218.31, 135.49, 132.94, 129.86, 47.19, 41.42, 41.07, 32.37, 32.04, 30.84; HRMS (EI) calcd for $C_{40}H_{48}O_2$ 560.3654, found 560.3629.

9. Crystals of **6a** were grown by slow crystallization from hexanes/CH_2Cl_2. Monoclinic space group $P2_1/n$; a = 10.384(5) Å, b = 11.228(5) Å, c = 6.953(3) Å, α = 90.00°, β = 100.50(2)°, γ = 90.00°, V = 797.2(7) Å^3, Z = 2; unique data ($I > 3\sigma(I)$), 424; $R(R_w)$ = 5.7% (6.0%). Crystals of **6b** were grown from EtOAc/CH_2Cl_2. $P2_1/n$; a = 13.129(2) Å, b = 12.184(2) Å, c = 14.308(2) Å, α = 90.00°, β = 90.98(1)°, γ = 90.00°, V = 2288.5(5) Å^3, Z = 4; unique data ($I > 3\sigma(I)$), 1433; $R(R_w)$ = 6.1% (6.4%). All calculations were performed on the DEC VAX 3100 cluster of the J. D. McCullough Crystallography Laboratory with the UCLA crystallographic package.

10. Allylic H···H and C···C distances for **6a**: H(4)···H(6') 1.90 Å, C(4)···C(6') 3.06 Å. For **6b**: H(4)···H(16) 1.93 Å, C(4)···C(16) 3.08 Å, H(8)···H(12) 1.87 Å, C(8)···C(12) 3.05 Å, H(14)···H(22) 1.84 Å, C(14)···C(22) 3.06 Å, H(18)···H(26) 1.95 Å, C(18)···C(26) 3.06Å. S. C. Swen-Walstra and G. J. Visser have also commented on the absence of deformation around the double bond in the X-ray crystal structure of adamantylideneadamantane, *Chem. Comm.* **1971**, 83.

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