Synthesis of Shape-Persistent Polyal Dendrimers – Facile Entry to Polyene and Polyyne Dendrimers

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Keywords: Dendrimers / Polyenes / Polyynes / Sonogashira coupling / Corey–Fuchs reaction

Polyaldehyde (polyal) dendrimers were synthesized by a divergent iterative method using 1,3,5-triethynylbenzene (**1**) as the core unit and 2-bromo-5-*tert*-butyl-1,3-benzenedicarbaldehyde (**2**) as the building block. The polyal dendrimers were further transformed into a new class of polyene and polyyne dendrimers.

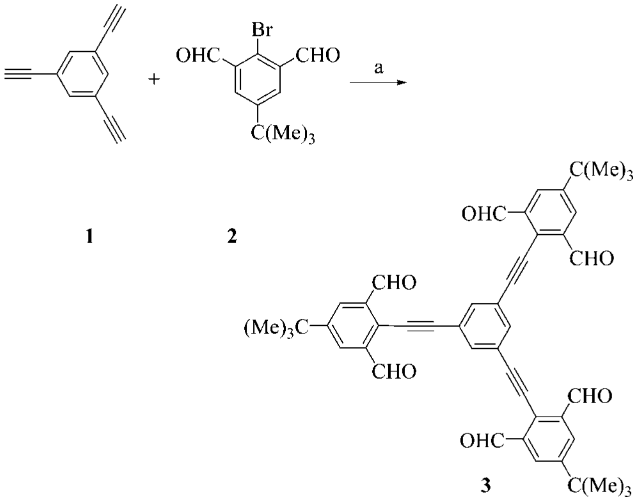
Introduction

The past decade has witnessed an explosive growth in the areas of cyclophynes,[1] cyclo(*n*)carbons,[2] graphyne and graphdiyne segments,[3] carbon-rich organometallics,[4] polyphenylenes,[5] and superacenes[6] with the revival of hydrocarbon chemistry[7] and, in particular, the chemistry of acetylenes.[8] During the same period, the chemistry of dendrimers has also evolved as a major area of research in view of the synthetic challenges and wide range of applications of these molecules in several areas.[9] Acetylenic dendrimers are a special class of compounds with promising utility in the areas of electronics and photonics.[10] The stiff acetylenic units provide a persistent shape and dimension, and acetylenic dendrimers of various shapes and sizes have been reported.[11] Moore and co-workers have made seminal contributions in the area of acetylenic dendrimers, in particular phenylacetylene dendrimers.[12] Their synthetic approaches based on convergent and divergent strategies along with the *SYNDROME* concept have led to the synthesis of large dendrimers of nanodimensions. Phenylacetylene dendrimers find applications in the areas of light-harvesting antenna molecules,[13] nonlinear optical materials,[14] and organic light-emitting diodes.[15]

In this paper we report the synthesis of first- and second-generation polyaldehyde (polyal) dendrimers starting from 1,3,5-triethynylbenzene (**1**) as the core unit and 5-*tert*-butyl-1,3-benzenedicarbaldehyde as the propagating unit. The choice of 2-bromo-5-*tert*-butyl-1,3-benzenedicarbaldehyde (**2**) as the building block is based on the following. It is easily synthesized in multi-gram quantities from a readily available and cheap starting material, namely 1-*tert*-butyl-3,5-dimethylbenzene in three steps, it is very reactive in Sonogashira coupling with several terminal acetylenes, which offers a convenient synthetic methodology for the synthesis of acetylenic dendrimers, the aldehyde functional groups in the resulting dendrimers are amenable to further functional-group transformations to a variety of derivatives, and finally the innocuous *tert*-butyl group should impart high solubility to the dendrimers.

Results and Discussion

The Sonogashira coupling of 1,3,5-triethynylbenzene (**1**) and 2-bromo-5-*tert*-butyl-1,3-benzenedicarbaldehyde (**2**) proceeded smoothly to yield the first-generation hexaaldehyde **3** in 72% yield (Scheme 1). A small amount of poly-



Scheme 1. Synthesis of first.generation polyal. Reagents and conditions: (a) $[PdCl_2(PPh_3)_2]$, PPh_3, CuI, NEt_3, 70 °C, 8 h, 72%.

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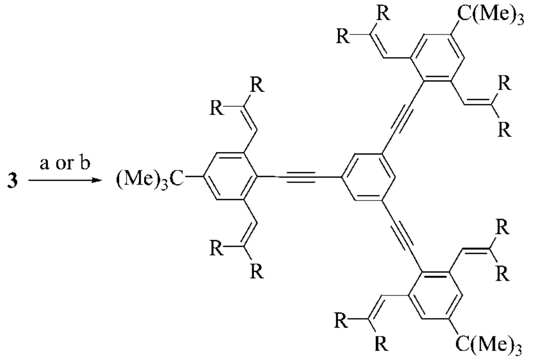
DOI: 10.1002/ejoc.200500055

mer formed from **1** was easily removed during the chromatographic purification of **3**.

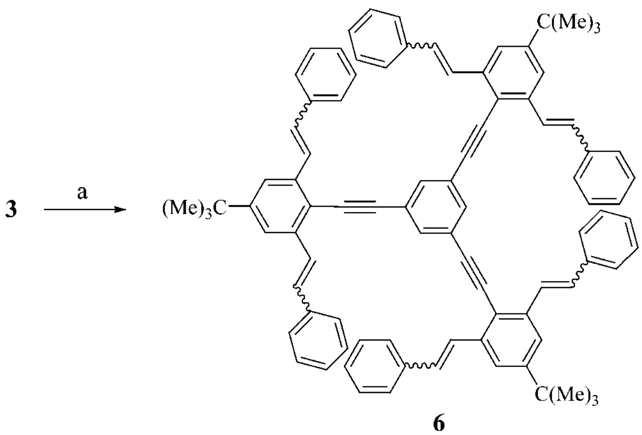
The ^{1}H NMR spectrum of **3** is very simple and shows four singlet resonances in the ratio of 2:2:1:9, corresponding to the aldehyde, peripheral ring, core ring, and *tert*-butyl protons, respectively. The ^{13}C NMR spectrum of **3** displays six signals in the aromatic region, thereby confirming the overall threefold axis of symmetry of the molecule. The energy-minimized structure of **3** based on semi-empirical AM1 calculations[16] shows the molecule to be planar. The hexaaldehyde **3** reacts cleanly with methylenetriphenylphosphorane to yield the corresponding hexaene derivative **4** in near quantitative yield (Scheme 2).



R = H **4**
R = Br **5**

Scheme 2. Synthesis of first-generation polyenes. Reagents and conditions: (a) Ph_3PCH_3Br, *n*BuLi, THF, –78 °C to 0 °C, 2 h, 79%; (b) CBr_4, PPh_3, Zn, CH_2Cl_2, 25 °C, 100%.

A pure sample of **4** was obtained as a colorless solid in 79% yield after column chromatographic purification. The ^{1}H NMR spectrum of **4** confirmed the absence of aldehyde protons. All vinyl protons appear as an AMX pattern, thus confirming the formation of the hexaene derivative **4**. In addition, the ^{13}C NMR spectrum shows six signals due to the aromatic carbons and two signals due to the vinylic carbons, indicating again the overall threefold axis of symmetry of **4**. Treatment of the hexaaldehyde **3** with benzylidenetriphenylphosphorane yielded the corresponding hexastyryl derivative **6** as a colorless solid in 98% yield after column purification (Scheme 3).



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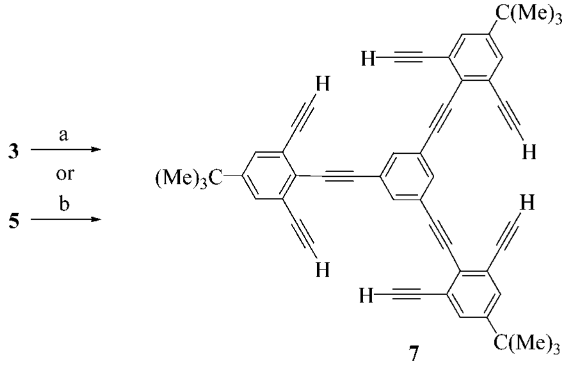
Scheme 3. Synthesis of hexastyryl derivative **6**. Reagents and conditions: (a) Ph_3PCH_2PhCl, *n*BuLi, THF, 25 °C, 3 h, 98%.

The ^{1}H NMR spectrum of **6** is complex and reveals that **6** is formed as a mixture of (*Z*) and (*E*) isomers. From the *tert*-butyl signals it is evident that **6** is a mixture of three major isomers of almost equal proportions. Attempts to separate these isomers by column chromatography on silica gel were unsuccessful as the retention times of the isomers are very similar. The hexastyryl derivative **6** was therefore fully characterized as a mixture of geometrical isomers.

The hexaaldehyde **3** was converted into the corresponding hexaethynyl derivative **7** by two different methods. In the first method ethynylation was carried out in a single step using dimethyl (1-diazo-2-oxopropyl)phosphonate[17] (Scheme 4). This procedure yielded **7**, albeit in a poor yield of only 29%. An alternative two-step methodology involving Corey–Fuchs dibromoolefination[18] followed by the conversion of the dibromoolefin into acetylene by treatment with lithium diisopropylamide was adopted (Schemes 2 and 4). When **3** was subjected to the modified Corey–Fuchs reaction (using CBr_4, PPh_3, and Zn) it yielded the expected hexakis(dibromoethenyl) derivative **5** in quantitative yield (Scheme 2). In the ^{1}H NMR spectrum of **5** the olefinic protons appear as a singlet at δ = 7.84 ppm along with two other singlets at δ = 7.77 and 7.70 ppm for the peripheral and core aromatic ring protons, respectively, in the ratio 2:2:1. In the ^{13}C NMR spectrum the characteristic resonance due to the vinylic CBr_2 carbon appears at δ = 92.3 ppm. The MALDI-TOF mass spectrum of **5** shows the molecular ion peak at *m*/*z* = 1650 and peaks due to the sequential loss of bromine atoms; each of these peaks appears as a cluster of isotope peaks. Peaks due to the loss of *tert*-butyl groups are not observed in the spectrum. The bromo derivative **5** was converted into the hexaethynyl derivative **7** by treatment with an excess of LDA (Scheme 4).



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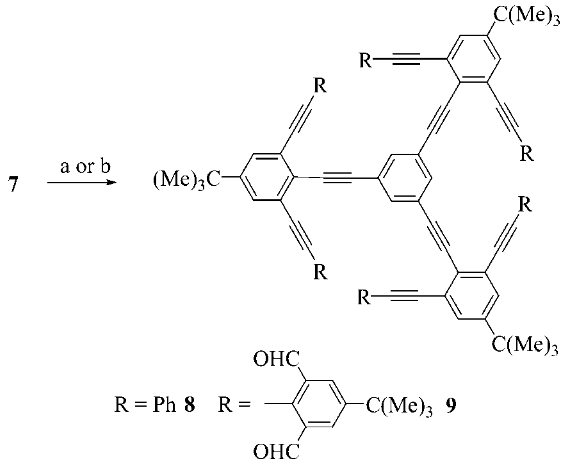
Scheme 4. Synthesis of first generation polyyne. Reagents and conditions: (a) $MeCOC(N_2)P(O)(OMe)_2$, Cs_2CO_3, MeOH, 29%; (b) LDA, THF, –78 °C, 10 min, 84%.

Compound **7** was isolated as a colorless crystalline solid in 84% yield after chromatographic purification. The acetylenic protons appear as a sharp singlet in the ^{1}H NMR spectrum of **7** at δ = 3.37 ppm. The energy-minimized structure of **7** based on semi-empirical calculations (AM1) shows the entire π system to be planar. In order to prepare the hexaphenylethynyl derivative **8**, the hexaethynyl derivative **7** was subjected to a sixfold Sonogashira coupling with iodobenzene (Scheme 5).



Scheme 5. Synthesis of second-generation polyal. Reagents and conditions: (a) PhI (6.25 equiv.), $[Pd(PPh_3)_4]$, PPh_3, CuI, Et_3N, 60 °C, 3 d, 36% (**8**); (b) **2** (7.0 equiv.), $[Pd(PPh_3)_4]$, PPh_3, CuI, Et_3N, 60 °C, 3 d, 34% (**9**).

Compound **8** was obtained as a pale-yellow substance in 36% yield (85% for each coupling step) after column chromatographic purification of the crude product on silica gel. The energy-optimized structure of **8** based on semi-empirical AM1 calculations is propeller shaped. The dihedral angle between the blades of the propeller and the shaft is 29° (Figure 1).

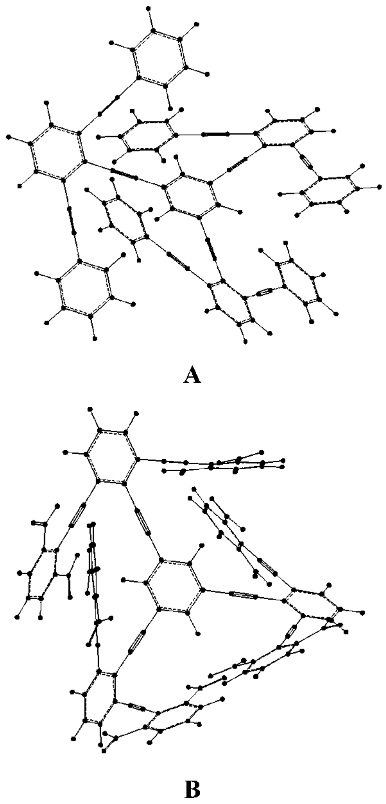
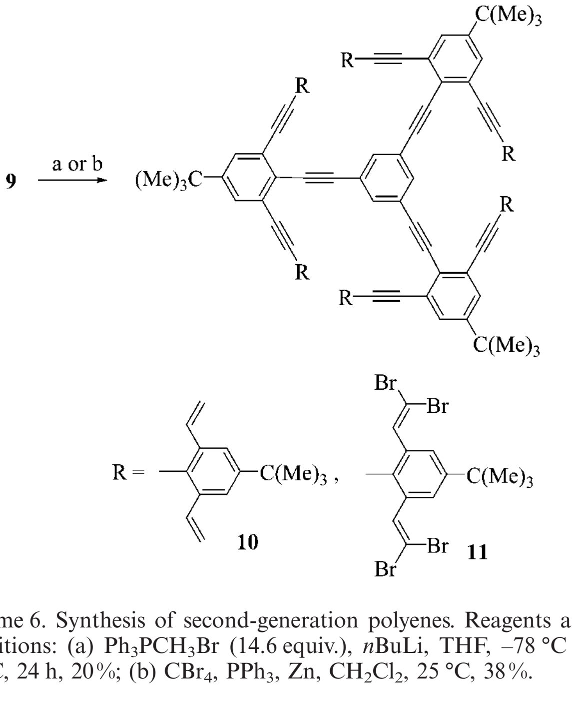


Figure 1. Calculated energy-minimized structures of **8** (A) and **9** (B) shown without the *tert*-butyl groups.

Having successfully demonstrated the synthesis of the first-generation polyal dendrimer, namely the hexaaldehyde **3**, and its conversion into several derivatives (**4**–**8**) in excellent yields, synthesis of the second-generation dendrimer was undertaken. The hexaethynyl derivative **7** was subjected to Sonogashira coupling with the bromodialdehyde **2** in the presence of $[Pd(PPh_3)_4]$ as the catalyst (Scheme 5). The expected sixfold coupling occurred smoothly and the dodecaaldehyde **9** was isolated in 34% yield (84% for each coupling step), after column chromatographic purification, as a colorless amorphous solid. The ^{1}H NMR spectrum of **9** is simple, as expected, with six singlets in the ratio of 4:4:1:2:9:18 corresponding to the aldehyde protons (δ = 10.75 ppm), the second generation aryl protons (δ = 8.05 ppm), the core aromatic protons (δ = 7.73 ppm), the first generation aryl protons (δ = 7.67 ppm), the first generation *tert*-butyl protons (δ = 1.42 ppm), and the second generation *tert*-butyl protons (δ = 1.20 ppm), respectively. The MALDI-TOF mass spectrum of **9** shows the molecular ion peak at m/z = 1818. The energy-minimized structure of **9** obtained by semi-empirical AM1-type calculations is shown in Figure 1. The molecule is propeller shaped as in the case of **8**. More interestingly, however, six of the twelve aldehyde groups are oriented towards the core of the dendrimer, as dictated by the substitution pattern of the building block used, namely **2**. The dodecaaldehyde **9** underwent a 12-fold Witting reaction with methylenetriphenylphosphorane to yield the corresponding dodecaene derivative **10** (Scheme 6).



Scheme 6. Synthesis of second-generation polyenes. Reagents and conditions: (a) Ph_3PCH_3Br (14.6 equiv.), *n*BuLi, THF, –78 °C to 25 °C, 24 h, 20%; (b) CBr_4, PPh_3, Zn, CH_2Cl_2, 25 °C, 38%.

Compound **10** was isolated as a pale-orange solid in 20% yield (corresponding to >87% yield in each Wittig step). The absence of signals due to the aldehyde protons and the appearance of vinylic protons as an AMX pattern in the ^{1}H NMR spectrum confirmed the formation of **10**. The MALDI-TOF mass spectrum of **10** shows the molecular ion peak at m/z = 1794. When aldehyde **9** was subjected to a Corey–Fuchs reaction the corresponding dibromovinyl derivative **11** was obtained in 38% yield (>92% yield in each step) as a red solid after column chromatographic purification (Scheme 6). The presence of four singlets in the ratio 4:4:1:2 in the aromatic region and two singlets for the *tert*-butyl protons in the ratio 2:1 in the ^{1}H NMR spectrum of **11** confirmed the formation of the second-generation hexakis(dibromovinyl) derivative. The MALDI-TOF mass spectrum of **11** shows peaks corresponding to the loss of *tert*-butyl groups as well as bromine atoms from the molecular ion, in sharp contrast to the behavior of **5**, where loss of *tert*-butyl groups from the molecular ion was not observed. Attempted synthesis of the corresponding dodecaethynyl derivative by treatment of **11** with an excess of LDA resulted in the formation of intractable material. It is presumed that the dodecaethynyl derivative is unstable and undergoes oxidative decomposition during the workup and isolation process.

Thermal Stability Studies

During the melting-point determination of the hexaene derivative **4** we observed that it did not melt on heating up to 200 °C but underwent a rapid thermal decomposition to a black soot that is insoluble in all common organic solvents. Similarly, the hexaacetylene derivative **7** also rapidly decomposed above 195 °C without any sign of melting. The differential scanning calorimetric studies of both of these compounds showed a single, strong, sharp exotherm at 202 °C for **4** and at 158 °C for **7**. In contrast, the hexastryryl derivative **6** is quite stable even in refluxing diphenyl ether when heated up to 250 °C under nitrogen. It is well known that polyacetylenes undergo thermal decomposition to yield fullerenes[19] and other interesting carbon materials. We are currently investigating this aspect in detail. Although the hexakis(dibromovinyl) derivative **5** is quite stable, the dodecakis derivative **11** decomposes at room temperature and under exposure to light.

Fluorescence Emission Studies

The fluorescence emission spectra of the first generation dendrimers **4**, **6**, and **8** were measured in cyclohexane. In all cases blue fluorescence emission could be observed under UV light. The emission spectra are shown in Figure 2. Compounds **4**, **6**, and **8** were excited at 308, 261, and 292 nm, respectively. The hexastyryl derivative **6** has emission maxima at 408 and 426 nm. The emission maxima of **4** [369, 382, and 395 (sh) nm] and **8** [371, 388, 401 (sh), 421 (sh)] are nearly the same and are blue-shifted in comparison to that of **6**.

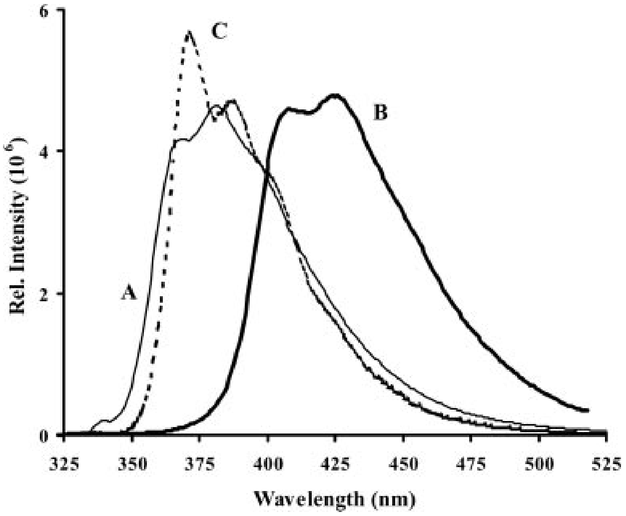


Figure 2. Fluorescence emission spectra of **4** (A), **6** (B), and **8** (C) in cyclohexane (1.0×10^{-5} M).

Conclusions

In the present study it is clearly shown that dialdehyde **2** is a very useful building block for divergent iterative synthesis of polyal dendrimers. These dendrimers, in turn, are useful for the synthesis of polyene and polyyne dendrimers and, presumably, other classes of dendrimers containing functional groups such as imines, acetals etc. The majority of the polyphenylacetylene-based dendrimers reported by Moore[12] and others[20] contain 1,4 and 1,3,5 connectivity of the aromatic units. As a result of this connectivity such dendrimers are dense on the periphery and relatively less dense at the core (e.g. starburst[21] and snowflake[22] type structures). The noteworthy feature of the present contribution is that the arene connectivity is 1,2,6 or 1,2,3 (compounds **4**–**11**). This is due to the fact that the reactive 2-bromo-5-*tert*-butyl-1,3-benzenedicarbaldehyde (**2**) is used as the repeating building block. Therefore in this class of dendrimers both the periphery and the core get progressively crowded due to the encroachment of one arm of the building block into the core (Figure 1). Such steric crowding will surely strongly impose restrictions on the synthesis of higher generations of this class of dendrimers and their stability. We are currently exploring the synthesis of imine-based dendrimers from these polyals and also the use of longer spacers for the synthesis of higher generations of this class of dendrimers to overcome the steric effects. The use of other aromatic core units is also underway.

Experimental Section

General Remarks: ^{1}H and ^{13}C NMR spectroscopy: Bruker AM-400 at 400 MHz and 100 MHz or Bruker AM-200 at 200 MHz and 50 MHz, respectively, in $CDCl_3$ solution, unless otherwise stated, with TMS as internal standard. All reactions were carried out under argon in flame-dried Schlenk flasks unless indicated otherwise. Column chromatography was performed on silica gel (60–120 or 240–400 mesh). TLCs were run on Macherey–Nagel polygram sil

G/UV_{254} plates. Melting points are uncorrected. THF was distilled from potassium. Fluorescence spectra were recorded on a Jobin–Yvon Fluorolog spectrometer.

2-Bromo-5-*tert*-butyl-1,3-dimethylbenzene was synthesized from 1-*tert*-butyl-3,5-dimethylbenzene according to a literature procedure.[23] Oxidation of 2-bromo-5-*tert*-butyl-1,3-dimethylbenzene, according to a literature procedure,[24] with CrO_3 in acetic anhydride, yielded the corresponding acetate of **2** in 65% yield. This was hydrolyzed with 6 N HCl to yield **2** in quantitative yield. 1,3,5-Triethynylbenzene was prepared from 1,3,5-tribromobenzene by a Sonogashira coupling.[25]

CAUTION: The polyenes and polyynes described herein are potentially sensitive to heat and shock and can undergo violent decomposition; they should be handled with caution.

4-*tert*-Butyl-2,6-bis(diacetoxymethyl)bromobenzene: M.p. 165 °C. IR (neat): $\tilde{\nu}$ = 1751 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.97 (s, 2 H), 7.61 (s, 2 H), 2.15 (s, 12 H), 1.35 (s, 9 H) ppm. ^{13}CNMR ($CDCl_3$): δ = 168.2, 151.2, 135.3, 126.2, 119.6, 89.1, 34.8, 31.1, 20.6 ppm. MS (EI, 70 eV): *m/z* (%) = 474 (2) [M^+], 472 (2) [M^+], 393 (5), 291 (44), 255 (98), 253 (100), 227 (32), 225 (30), 207 (66). HRMS calcd. for $C_{20}H_{25}O_8$ [M – Br]: 393.1549; found 393.1550.

2-Bromo-5-*tert*-butyl-1,3-benzenedicarbaldehyde (2): M.p. 93–95 °C. IR (neat): $\tilde{\nu}$ = 1685 cm^{-1} (C=O). UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 240 nm (4.54), 320 (3.24). ^1H NMR ($CDCl_3$): δ = 10.52 (s, 2 H), 8.17 (s, 2 H), 1.37 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 190.9, 151.9, 133.9, 132.5, 128.1, 34.9, 30.8 ppm. MS (EI, 70 eV): *m/z* (%) = 270 (29) [M^+], 268 (30) [M^+], 255 (98), 253 (100), 227 (44), 225 (48), 118 (22), 117 (20), 115 (28). HRMS calcd. for $C_{12}H_{13}O_2{}^{79}Br$: 268.00989; found 268.00950. $C_{12}H_{13}BrO_2$ (268): calcd. C 53.73, H 4.89; found C 53.61, H 4.88.

First-Generation Polyal (Hexaaldehyde) 3: A Schlenk flask was charged with **2** (4.03 g, 15.0 mmol), [$PdCl_2(PPh_3)_2$] (0.53 g, 0.75 mmol), PPh_3 (0.195 g, 0.75 mmol), CuI (0.14 g, 0.75 mmol), and anhydrous Et_3N (150 mL). The mixture was stirred and heated to 70 °C. A solution of **1** (0.75 g, 15.0 mmol) in anhydrous THF (15 mL) was then added dropwise. After 60 min a copious amount of precipitate was observed. The reaction mixture was stirred for 8 h at 70 °C and allowed to stand at room temperature overnight. The solvent was removed under reduced pressure in a rotary evaporator. The dark-brown crude product (4.6 g) thus obtained was dissolved in CH_2Cl_2 and washed with water followed by saturated brine solution. After removal of the solvent the crude product was purified by flash chromatography on silica gel with CH_2Cl_2 to yield **3** (2.6 g, 3.6 mmol, 72%) as a colorless amorphous solid. M.p. 245 °C (decomp). IR (neat): $\tilde{\nu}$ = 2207, 1688 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ = 10.73 (s, 6 H), 8.26 (s, 6 H), 7.88 (s, 3 H), 1.41 (s, 27 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 190.2, 153.5, 153.0, 136.6, 135.1, 130.1, 125.2, 123.4, 115.2, 99.4, 82.9, 35.4, 30.8 ppm. MS (EI, 70 eV): *m/z* (%) = 715 (54) [M^+ + 1], 714 (100) [M^+], 687 (30), 686 (50), 57 (16). HRMS calcd. for $C_{48}H_{42}O_6$: 714.29814; found 714.29818.

First-Generation Hexaene 4: *n*BuLi (5.2 mL of a 1.6 M hexane solution, 8.32 mmol) was added, at –78 °C, to a stirred suspension of methyltriphenylphosphonium bromide (2.97 g, 8.32 mmol) in THF (50 mL), After addition the solution was warmed to 0 °C and stirring was continued for 60 min to obtain the ylide as a clear, bright-yellow solution, which was added to a solution of **3** (0.9 g, 1.26 mmol) in THF (200 mL) at –78 °C. After addition the mixture was warmed to 0 °C and stirred for 2 h. The reaction was quenched by addition of saturated brine solution. The organic layer was separated, dried over anhydrous $MgSO_4$, and the solvent was removed. The crude product was dissolved in CH_2Cl_2 (100 mL) and filtered through a short column of silica gel to remove the Ph_3PO formed in the reaction. Compound **4** (0.70 g, 79%) was obtained as a colorless solid that was recrystallized from a mixture of CH_2Cl_2/hexane. M.p. 214–215 °C (decomp). IR (neat): $\tilde{\nu}$ = 2204, 1576 cm^{-1} (C=C). UV/Vis (hexane): λ_{max} (log ε) = 205 nm (4.883), 263 (5.117), 308 (4.993), 326 (4.933). ^1H NMR ($CDCl_3$): δ = 7.69 (s, 3 H), 7.58 (s, 6 H), 7.35 (dd, *J* = 17.6, 11.0 Hz, 6 H), 5.85 (dd, *J* = 17.6, 0.98 Hz, 6 H), 5.42 (dd, *J* = 11.0, 0.94 Hz, 6 H), 1.37 (s, 27 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 151.6, 139.5, 135.6, 133.6, 124.3, 121.2, 117.5, 115.7, 96.8, 87.3, 35.0, 31.1 ppm. MS (70 eV, EI): *m/z* (%) = 702 (10) [M^+], 688 (24), 687 (46), 533 (24), 57 (100). HRMS calcd. for $C_{54}H_{54}$: 702.4225; found 702.4225.

First-Generation Hexastyryl Derivative 6: The reaction was carried out as described for the synthesis of **4**. A mixture of **3** (0.5 g, 0.7 mmol), the ylide from benzyltriphenylphosphonium chloride (1.8 g, 4.62 mmol), and *n*BuLi (2.88 mL of a 1.6 M hexane solution, 4.62 mmol) was allowed to react for 3 h at 20 °C. Column chromatographic purification of the crude product on silica gel using CH_2Cl_2/pentane (1:4) yielded **6** (0.809 g, 98%) as a colorless solid, as a mixture of three major products that are geometric isomers. Attempted separation of the isomers by column chromatography with CH_2Cl_2/diethyl ether/pentane as eluent were unsuccessful. IR (neat): $\tilde{\nu}$ = 2198 cm^{-1}, 1575. UV/Vis (hexane): λ_{max} (log ε) = 192 nm (5.148), 229 (4.945), 261 (sh, 4.886), 308 (5.234). ^1H NMR ($CDCl_3$): δ = 7.70–7.85 (m, 6 H), 7.69 (s, 3 H), 7.45–7.65 (m, 9 H), 7.05–7.40 (m, 27 H), 6.90–7.00 (m, 3 H), 6.60–6.80 (m, 3 H), 1.45, 1.16, 0.88 (all singlet, total relative integration 27 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 118–151 (57 signals due to aromatic and olefinic carbons of the three isomers), 97.8, 97.7, 97.4, 97.3, 88.0, 87.9, 87.8, 35.1, 34.7, 34.3, 31.2, 30.8, 30.5 ppm. MS (70 eV, EI): *m/z* = 1160 (12) [M^+ + 2], 1159 (15), 1158 (17) [M^+], 1145 (8), 1144 (16), 1143 (17), 1103 (6), 1102 (10), 1101 (12), 438 (26), 362 (24), 305 (70), 180 (38), 91 (22), 78 (60), 57 (100). $C_{90}H_{78}$ (1158.6): calcd. C 93.26, H 6.73; found C 93.05, H 6.80.

First-Generation Hexakis(dibromovinyl) Derivative 5: A Schlenk flask was charged with CBr_4 (2.79 g, 8.4 mmol), PPh_3 (2.20 g, 8.4 mmol), Zn (0.55 g, 8.4 mmol), and dry CH_2Cl_2 (100 mL). The slurry was stirred at room temperature overnight to yield a strawberry colored suspension. Hexaaldehyde **3** (0.25 g, 0.35 mmol) was added in one portion and stirring was continued for 3 d at 20 °C. The reaction mixture was filtered through a pad of silica gel and the solvent was removed to obtain the crude product as an orange solid. It was further purified by column chromatography on silica gel eluting with a CH_2Cl_2/pentane mixture (1:3, v/v) to yield **5** as a pale-orange solid (0.57 g, 100%). The substance obtained from the column chromatographic purification was washed twice more with pentane to obtain a nearly colorless solid that was analytically pure. M.p. 219–220 °C. IR (neat): $\tilde{\nu}$ = 2207 cm^{-1}, 2165, 1576. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 279 nm (5.0168), 319 (4.874). ^1H NMR ($CDCl_3$): δ = 7.84 (s, 6 H), 7.78 (s, 6 H), 7.70 (s, 3 H), 1.36 (s, 27 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 151.5, 137.7, 135.8, 134.2, 125.7, 123.9, 118.4, 98.3, 92.3, 86.8, 35.2, 31.0 ppm. MALDI-TOF MS: *m/z* = 1650 [M^+] 1570 [M^+ – Br], 1490 [M^+ – 2Br], 1410 [M^+ – 3Br], 1330 [M^+ – 4Br], 1250 [M^+ – 5Br], 1170 [M^+ – 6Br]; each peak appeared as a cluster of isotope peaks. $C_{54}H_{42}Br_{12}$ (1650.3): calcd. C 39.31, H 2.57; found C 39.34, H 2.63.

First-Generation Hexaethynyl Derivative 7. Method A: A Schlenk flask was charged with MeOH (100 mL, dried over molecular sieves) and was degassed by bubbling argon for 30 min. Hexaaldehyde **3** (2.0 g, 2.8 mmol) and Cs_2CO_3 (10.95 g, 33.6 mmol) were added and the mixture was stirred at room temperature for 5 min and then cooled to –40 °C. A solution of dimethyl-1-diazo-2-oxopropyl phosphonate (3.55 g, 18.5 mmol) in MeOH (10 mL) was added slowly to the reaction mixture with stirring over 5 min. The reaction mixture was then allowed to attain room temperature over a period of 4 h, after which time it was diluted with diethyl ether (100 mL), washed with saturated $NaHCO_3$, and dried over $MgSO_4$. The solvent was removed on a rotary evaporator at 25 °C under reduced pressure. The crude product thus obtained was purified by column chromatography on silica gel and eluted with a 1:4 (v/v) mixture of CH_2Cl_2 and pentane. The desired hexaacetylene **7** was obtained (0.56 g, 29%) as a colorless solid.

Method B: A solution of LDA [freshly prepared from *i*Pr_2NH (0.52 g, 5.1 mmol) and *n*BuLi (1.6 M solution in hexane, 3.18 mmol, 5.1 mL) in THF (10 mL) at –78 °C] was added to a solution of **5** (0.4 g, 0.24 mmol) in dry THF (20 mL) at –78 °C. After 10 min the reaction was quenched with saturated NH_4Cl solution (10 mL) and the mixture was allowed to attain room temperature. The organic layer was removed and the aqueous layer was extracted with CH_2Cl_2. The combined organic phase was washed with saturated brine solution and dried over $MgSO_4$. Removal of the solvent under reduced pressure on a rotary evaporator yielded a crude product which, after chromatographic purification over silica gel with a 1:4 (v/v) CH_2Cl_2/pentane mixture as eluent, yielded the desired hexaacetylene **7** as a colorless solid (0.14 g, 84%). M.p. 195 °C (decomposed violently!). IR (neat): $\tilde{\nu}$ = 3267 cm^{-1}, 2960, 2207, 2107, 1574. UV/Vis (CH_3CN): λ_{max} (log ε) = 245 nm (5.0174), 250 (5.0176), 256 (5.001), 264 (4.9335), 309 (4.9051), 329 (4.90). ^1H NMR ($CDCl_3$): δ = 7.76 (s, 3 H), 7.56 (s, 6 H), 3.38 (s, 6 H), 1.32 (s, 27 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 151.5, 134.7, 130.2, 125.6, 124.8, 123.9, 95.2, 87.7, 82.1, 81.1, 34.7, 30.9 ppm. MS (70 eV, EI): *m*/*z* (%) = 691 (6) [M^+ + 1], 690 (12) [M^+], 603 (1), 292 (9), 202 (4), 101 (28), 72 (52), 57 (88). $C_{54}H_{42}$ (690.32): calcd. C 93.87, H 6.13; found C 92.12, H 6.12.

First-Generation Hexaphenylethynyl Derivative 8: A Schlenk flask was charged with iodobenzene (0.46 g, 2.25 mmol), [$Pd(PPh_3)_4$] (0.13 g, 0.11 mmol), PPh_3 (0.03 g, 0.11 mmol), CuI (0.021 g, 0.11 mmol), and anhydrous Et_3N (50 mL). The mixture was stirred at 60 °C and a solution of hexaacetylene **7** (0.25 g, 0.36 mmol) in THF (15 mL) was added. The reaction was protected from room light. After 3 d the mixture was cooled to room temperature and worked up as described in the synthesis of **3**. Chromatographic purification of the crude product on silica gel with a 1:3 (v/v) CH_2Cl_2/pentane mixture as eluent yielded the desired product **8** as a pale-yellow solid (0.15 g, 36%). M.p. 204–205 °C. IR (neat): $\tilde{\nu}$ = 2209 cm^{-1}, 1596, 750, 685. UV/Vis ($CHCl_3$): λ_{max} (log ε) = 292 nm (5.23). ^1H NMR ($CDCl_3$): δ = 7.84 (s, 3 H), 7.57 (s, 6 H), 7.47–7.45 (m, 12 H), 7.25–7.13 (m, 18 H), 1.39 (s, 27 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 151.5, 134.3, 131.6, 128.7, 128.5, 128.4, 126.2, 124.8, 124.5, 122.8, 95.2, 93.7, 88.8, 88.2, 34.9, 31.0 ppm. MS (70 eV, EI): *m*/*z* (%) = 1148 (15) [M^+ + 2], 1147 (18) [M^+ + 1], 1146 (20) [M^+], 1091 (5), 1090 (8), 1089 (10), 277 (16), 178 (16), 167 (36), 149 (72), 78 (100), 57 (60). MALDI-TOF MS: *m*/*z* = 1146 [M^+], 2292 [$2M^+$]. $C_{90}H_{66}$ (1146.5): calcd. C 94.20, H 5.80; found C 93.38, H 5.76.

Second-Generation Polyal (Dodecaaldehyde) 9: A Schlenk flask was charged with **2** (0.79 g, 2.94 mmol), [$Pd(PPh_3)_4$] (0.17 g, 0.15 mmol), PPh_3 (40 mg, 0.15 mmol), CuI (28 mg, 0.15 mmol), and anhydrous Et_3N (50 mL). The mixture was stirred and heated to 60 °C. A solution of **7** (0.29 g, 0.42 mmol) in anhydrous THF (15 mL) was added dropwise. The reaction mixture was stirred for 3 d at 60 °C then cooled and the solvent removed under reduced pressure on a rotary evaporator. The crude product thus obtained was dissolved in CH_2Cl_2 and washed with water followed by saturated brine solution. After removal of the solvent the crude product was purified by flash chromatography on silica gel and eluted with CH_2Cl_2 to yield **9** (0.26 g, 0.14 mmol, 34%) as a colorless amorphous solid. M.p. >272 °C (decomp). IR (neat): $\tilde{\nu}$ = 2199 cm^{-1}, 1687 (C=O). UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 246 nm (5.33), 308 (5.09), 323 (5.08). ^1H NMR ($CDCl_3$): δ = 10.75 (s, 12 H), 8.05 (s, 12 H), 7.73 (s, 3 H), 7.67 (s, 6 H), 1.42 (s, 27 H), 1.20 (s, 54 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 190.6, 152.8, 152.1, 136.5, 130.5, 129.4, 126.3, 125.3, 123.1, 100.5, 96.5, 87.5, 84.7, 35.2, 34.9, 30.99, 30.74 ppm. MALDI-TOF MS: *m*/*z* = 1818 [M^+]. $C_{126}H_{114}O_{12}$ (1818.9): calcd. C 83.14, H 6.31; found C 82.59, H 6.21.

Second-Generation Dodecaene Derivative 10: The procedure described for the synthesis of **4** was followed using **9** (0.1 g, 0.055 mmol), Ph_3PCH_3Br (0.26 g, 0.73 mmol), and *n*BuLi (1.6 M solution in hexane, 0.73 mmol, 0.45 mL). The reaction was carried out for 24 h at room temperature. Chromatographic purification of the crude product on silica gel with a 1:4 (v/v) CH_2Cl_2/pentane mixture as eluent yielded the desired product **10** (0.02 g, 20%). M.p. >145 °C (decomp). IR (neat): $\tilde{\nu}$ = 2200 cm^{-1}, 1579, 908, 879. UV/Vis (CH_3CN): λ_{max} (log ε) = 269 nm (5.17), 300 (5.03), 316 (4.98). ^1H NMR ($CDCl_3$): δ = 7.73 (s, 3 H), 7.56 (s, 6 H), 7.42 (s, 12 H), 7.35 (dd, *J* = 17.5, 11.0 Hz, 12 H), 5.67 (d, *J* = 17.5 Hz, 12 H), 5.12 (d, *J* = 11.0 Hz, 12 H), 1.39 (s, 27 H), 1.21 (s, 54 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 151.2, 151.17, 139.4, 135.5, 135.3, 128.9, 126.7, 123.6, 123.4, 121.0, 117.7, 115.8, 97.1, 94.8, 90.2, 88.6, 34.8, 34.7, 31.1, 31.0 ppm. MALDI-TOF MS: *m*/*z* = 1794 [M^+].

Second-Generation Dibromovinyl Derivative 11: The procedure described for the synthesis of **5** was followed. Compound **9** (0.22 g, 0.12 mmol) was treated with CBr_4 (1.93 g, 5.81 mmol), PPh_3 (1.52 g, 5.81 mmol), and Zn powder (0.38 g, 5.81 mmol) in CH_2Cl_2 (100 mL). The mixture was stirred at 25 °C overnight. Chromatographic purification of the crude product on silica gel with a 1:4 (v/v) CH_2Cl_2/pentane mixture as eluent yielded **11** (0.17 g, 38%) as a red solid. M.p. 80 °C. IR(neat): $\tilde{\nu}$ = 2188 cm^{-1}, 2166, 1580, 829, 743. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 285 nm (5.27), 320 (4.998). ^1H NMR ($CDCl_3$): δ = 7.80 (s, 12 H), 7.73 (s, 12 H), 7.72 (s, 3 H), 7.59 (s, 6 H), 1.39 (s, 27 H), 1.26 (s, 54 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 151.6, 151.1, 137.4, 135.8, 129.8, 125.8, 125.7, 123.6, 123.55, 118.7, 98.6, 95.4, 92.1, 89.1, 88.1, 35.1, 34.8, 31.01, 30.97 ppm. MALDI-TOF MS: *m*/*z* = 3633 [M^+ – 57 (*t*Bu)], 3576 [M^+ – 114 (2× *t*Bu)], 3481, 3401, 3321, 3241, 3081 (due to sequential loss of Br atoms, each peak appears as a cluster of isotope peaks).

Acknowledgments

We gratefully acknowledge financial support from the Volkswagen Stiftung and the Fonds der Chemischen Industrie, Germany. We thank Dr. T. Pradeep and Mr. D. M. David Jaba Singh (IIT Madras) for MALDI-TOF MS measurements, Ms. T. Shyamala (IIT Madras) for fluorescence measurements, and Mr. Harald Berger (TU-BS, Germany) for DSC measurements.

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Received: January 24, 2005