Single-Crystal Structures of Polyphenylene Dendrimers

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Abstract: A series of first-generation polyphenylene dendrimers based on three different cores were prepared by Diels–Alder cycloaddition and their single-crystal structures were determined. Consisting exclusively of interlocked, twisted phenyl rings, these polyphenylene nanostructures have exciting structural and dynamic properties. Single crystals of dendrimers, suitable for X-ray structure analysis, were grown from different solvent mixtures by slow evaporation at room temperature. It should be pointed out that one of the described polyphenylene dendrimers represents up to now the biggest oligophenylene nanostructure from which crystallographic data is available.

Keywords: dendrimers · nanostructures · polyphenylene dendrimers · structure elucidation

Introduction

The structural determination of dendritic molecules faces a hierarchy of tasks. The perfection and monodispersity of the molecular structures are shown by spectroscopic and chromatographic techniques.[1] Scattering techniques and electron microscopy establish the overall shape of the three-dimensional objects in solution and in the solid state. Scanning probe microscopy has become increasingly important, since it allows direct visualization of dendritic nanostructures[2–4] in real space and tests their shape-persistence under different stimuli. A particularly convincing and aesthetically appealing way of looking at dendrimer structures rests upon the X-ray analysis of single crystals. However, the growth of single crystals of large dendritic molecules of suitable size and perfection has encountered a variety of problems and has so far been restricted to comparatively small molecules. A major obstacle is the conformational flexibility of most dendrimers, which hampers the formation of a perfect long-range order, which is typical for high-quality single crystals. It is characteristic that a propyleneimine dendrimer could be crystallized only after reducing the mobility by the formation of hydrogen bonds at the surface.[5] Another problem stems from the fact that dendrimers often crystallize as solvates or chlatrates, that is, with inclusion of solvent molecules. Crystals of this type are in many cases quite unstable and degrade rapidly by the evaporation of the solvent.

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These difficulties explain the relatively low number of crystallographic works on polyphenylene nanostructures.[6–10] Recently Pascal et al. reported the crystal structure of new oligophenylenes and revealed that with increasing size of the molecules the accuracy of computational methods in predicting conformations is quite unsatisfactory.[11]

Since the beginning of dendrimer research, no convincing evidence has been found about the position of dendrimer branch-ends and in general about the three-dimensional structure of these macromolecules. These issues can not be addressed adequately by classical analytical methods for the determination of the structure of small molecules, like NMR spectroscopy.

We have recently described polyphenylene dendrimers, which possess, for example, pentaphenylbenzene repeat units.[12–13] The synthesis of these polyphenylene dendrimers is possible, both in divergent and in convergent fashion, and utilizes the Diels–Alder cycloaddition between tetraphenylcyclopentadienones and arylacetylenes. Molecular structures with high molecular weight (high generations) are obtained in high perfection by using this preparative method.

The interlocking of twisted phenyl rings has exciting structural and dynamic consequences and can explain the stiffness of the molecular framework. This has been experimentally proven recently by means of solid-state NMR techniques.[14] The measurements clearly support the shape-persistence of highly substituted polyphenylene dendrimers.[2, 3] The detectable free mobility of the phenyl rings in these dendrimers is identified as a restricted rotation of the terminal phenyl rings around their fixed axes. The angular excursions of these phenyl rings is limited to 60° on a millisecond to second timescale and to reorientation up to 20° on a microsecond timescale.

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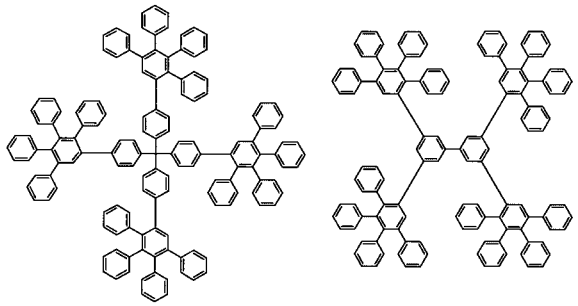
Molecules **1**, **2**, and **3** represent the first generations of branched polyphenylenes; they illustrate the great structural diversity of this dendrimer type that results from the use of



1

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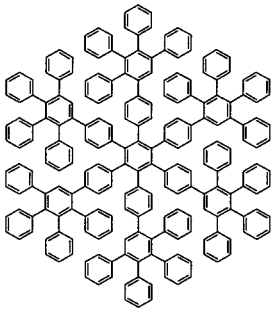
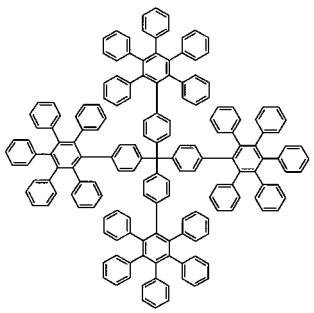
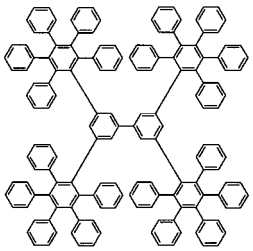


3

different aromatic core units. While we succeeded in growing single crystals of dendrimer **3** containing 37 phenyl rings, crystallization of **1** and **2** was hampered by their low solubility. We therefore have synthesized structures **1-Ph** and **2-Ph**, built up from hexaphenylbenzene units, which form crystals suitable for crystallographic investigations.



1-Ph



2-Ph

It should be pointed out that dendrimers **1** and **3** are precursors for large polycyclic aromatic hydrocarbons (PAH), which are formed by a subsequent oxidative cyclodehydrogenation.[15, 16] Sufficient knowledge of shape, supramolecular organization and structural perfection of the dendritic precursors are therefore vital for the proper understanding of the planarization reaction of the dendrimer to the corresponding PAH.

We describe here the synthesis of **1-Ph** and **2-Ph** and present clear single-crystal structures of **1-Ph**, **2-Ph**, and **3**. The important feature at a molecular level is that the tightly packed phenyl rings can fill the space around a core by adopting different degrees of inter-ring torsion and even by a desymmetrization of the molecular frame. At a supramolecular level the formation of porous lattices is remarkable.

Results

Synthesis: Due to their high number of energetically similar conformational isomers, polyphenylene dendrimers generally do not crystallize but instead precipitate as amorphous powders upon attempted crystallization. A notable exception is **3**, which gives small crystals from a solution in tetrachloroethane after about half a year of crystallization. Dendrimer **3** is synthesized by the Diels–Alder addition of tetraphenylcyclopentadienone to the sixfold ethinyl-substituted hexaphenylbenzene.[17, 18] The addition occurs at 190 °C in diphenylether quantitatively.

Whereas molecule **3** possesses a disc-like shape, as molecular mechanics would indicate,[19] dendrimers **1** and **2** are predicted to have a more globular dumbbell shape. Unfortunately, **1** is practically insoluble in organic solvents independent of the temperature and **2** could not be crystallized. Therefore instead of **1** and **2**, two molecules **1-Ph** and **2-Ph** were synthesized. Containing an additional phenyl ring on each dendritic branch, **1-Ph** and **2-Ph** have a good solubility in organic solvents such as tetrachloroethane or tetrahydrofuran. From their better solubility and higher molecular symmetry, one might expect a higher tendency towards crystallization.

The starting point of the synthesis of the molecules is the palladium-catalyzed Hagihara–Sonogashira coupling of phenylacetylene to tetra(4-iodophenyl)methane and 3,3′5,5′-tetrabromobiphenyl, leading to the Diels–Alder active cores **4** and **5**, respectively (Scheme 1). The cycloaddition of tetraphenylcyclopentadienone to **4** and **5** was carried out in diphenyl ether at 200 °C. In both cases the addition was complete in 24 hours. After precipitation in pentane and several washing cycles, products **1-Ph** and **2-Ph** were obtained in yields exceeding 90 %. FD mass spectrometry, ^{1}H and ^{13}C NMR spectroscopy, and elemental analysis confirmed the purity of the synthesized compounds.

The ^{1}H NMR spectra of both **1-Ph** and **2-Ph** show peaks at unusually high-field positions for aromatic protons. This strong high-field shift of aromatic signals arises from the magnetic anisotropy due to the ring currents of the surrounding phenyl rings, which induce a strong deshielding effect. These shifts also suggest that the corresponding protons of the dissolved molecules are immobile on the NMR timescale. Furthermore, a ^{1}H-^{1}H COSY spectrum of **2-Ph** was measured to assign the broad aromatic signal between $\delta = 6.86$ and 6.96 ppm to the protons present in the molecule.

The ^{1}H-^{1}H COSY spectrum shows an ABCDE splitting pattern, composed of three triplets and two doublets. Figure 1 schematically shows the cause of this splitting. The interactions between the protons of the central phenyl rings (A) and the *ortho*-situated protons (e.g., "1") of the surrounding phenyl groups (C) together with the occurring desymmetriza-

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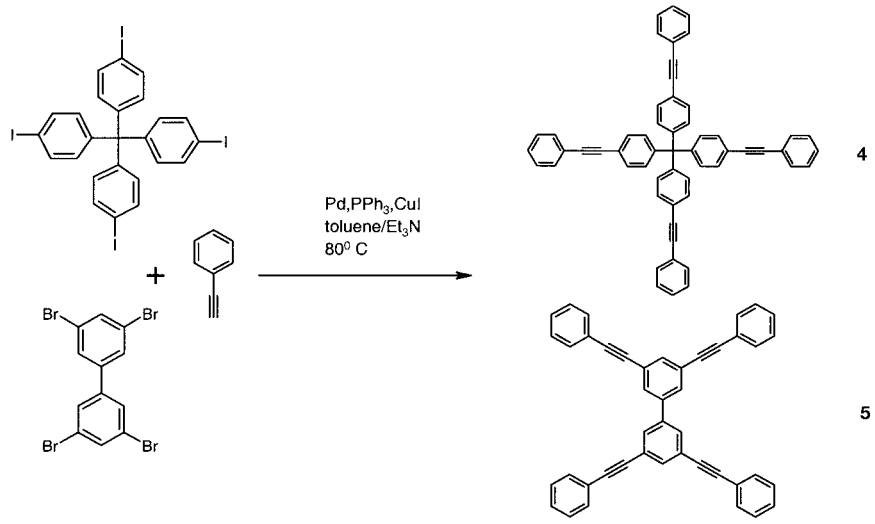

Scheme 1. Cores **4** and **5** used in the synthesis of **1-Ph** and **2-Ph**.

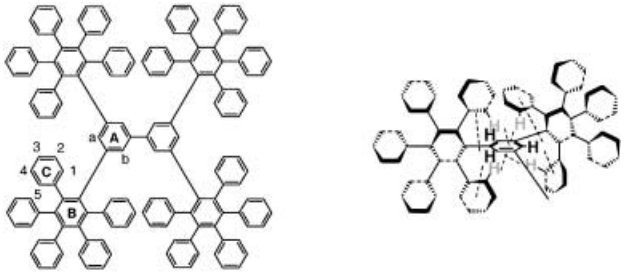

Figure 1. The schematic interaction between the protons of the core with those of the surrounding phenyl groups in the case of **2-Ph**.

tion of the phenyl rings explain the observed ABCDE splitting. The upfield shifts of the a and b protons of the core phenyl rings (A) are induced by the ring currents of the *ortho*-phenyl rings of the pentaphenyl units. Pascal et al. reported similar shifts in their large aromatic propeller molecule.[10] They describe the existence of a doublet at $\delta = 5.68$ ppm close to a singlet at $\delta = 6.25$ ppm in the NMR spectrum of 1,3,5-tris(pentaphenylphenyl)benzene. This is predictable to a certain degree if one considers the similarity between the molecule investigated by Pascal et al. and **2-Ph**.

Discussion

The present study connects to earlier crystallographic works of our group upon oligophenylenes[15, 16, 20] and opens the way toward dendritic channel-forming networks with potential host–guest properties. Single crystals of **1-Ph** and **2-Ph**, suitable for X-ray structure analysis, were grown from CH_2Cl_2/heptane mixtures at room temperature by slow evaporation. The single crystals of **3** were grown from tetrachloroethane.[21] As it has been pointed out before the crystals of all three dendrimers obtained in this way are solvates and contain a large number of solvent molecules. As a consequence the crystals are unstable under ambient conditions. Crystals of **1-Ph** and **3** deteriorate in less than a minute if kept outside the mother liquor. Crystals were immersed rapidly in Riedel de Haën perfluoropolyether type 216, which was kept at dry ice temperatures, and then immediately mounted in sealed capillaries. To prevent crystal decomposition and to increase the resolution, the data collections were carried out at 120 K. Under these experimental conditions the crystals were stable, although **1-Ph** and **3** decompose at room temperature within approximately a day even if kept in a sealed capillary.

Projections of the crystal structures of **1-Ph**, **2-Ph**, and **3** are shown in Figure 2 in comparison. In all three cases the structures are well resolved and exhibit a high rigidity of the packing within each dendritic arm owing to the steric hindrance between the phenyl rings. This is illustrated by the fact that the conformations of the hexaphenylbenzene moiety as defined by the interplanar angles are virtually identical in **1-Ph** and **2-Ph**. The same result has been found for the six pentaphenylbenzene arms in **3**. This demonstrates that in polyphenylene dendrimers the conformation of the dendritic arms is fixed so that they can be regarded in good approximation as rigid groups. In contrast to most other dendritic molecules the conformational flexibility is thus much reduced. The dihedral angles which have been observed in the crystal structures are summarized in Tables 1 and 2.

In Figure 3 the hexaphenylbenzene groups in **1-Ph** and **2-Ph** are shown in equivalent projections in comparison. The studied dendritic molecules possess high symmetry. The theoretical point groups are *mmm*, $\bar{4}$, and 6/*m* for **1-Ph**, **2-Ph**, and **3**, respectively. On the other hand, organic molecules usually loose most of their point group symmetry upon crystallization in order to increase packing density. In this situation, in which the dendritic substituents are, in good approximation, rigid groups, there are only a few degrees of freedom for internal rotations left.

Dendrimer **2-Ph** has in this respect the smallest conformational flexibility. As we have shown in one of our earlier studies,[14] only rotations within a limited range about the bonds to the central C atom are possible such that the overall spherical shape of the molecule does not change. It is therefore not surprising that **2-Ph** behaves similarly to many other tetraphenylmethane derivatives and retains its ideal tetrahedral symmetry in the crystal. The molecule is located on a four-fold inversion axis of the body centered tetragonal cell with the space group $I\bar{4}$. The asymmetric unit contains one dendritic arm. The packing, which is shown in Figure 4, can be regarded as a distorted body centered cubic (bcc) lattice that is typical for the crystallization of solid spheres. The distortions from this ideal symmetry result from the deviation of **2-Ph** from a true spherical shape and from the fact that the interstitial volume between the dendrimers is filled with solvent molecules. This crystal structure can be characterized

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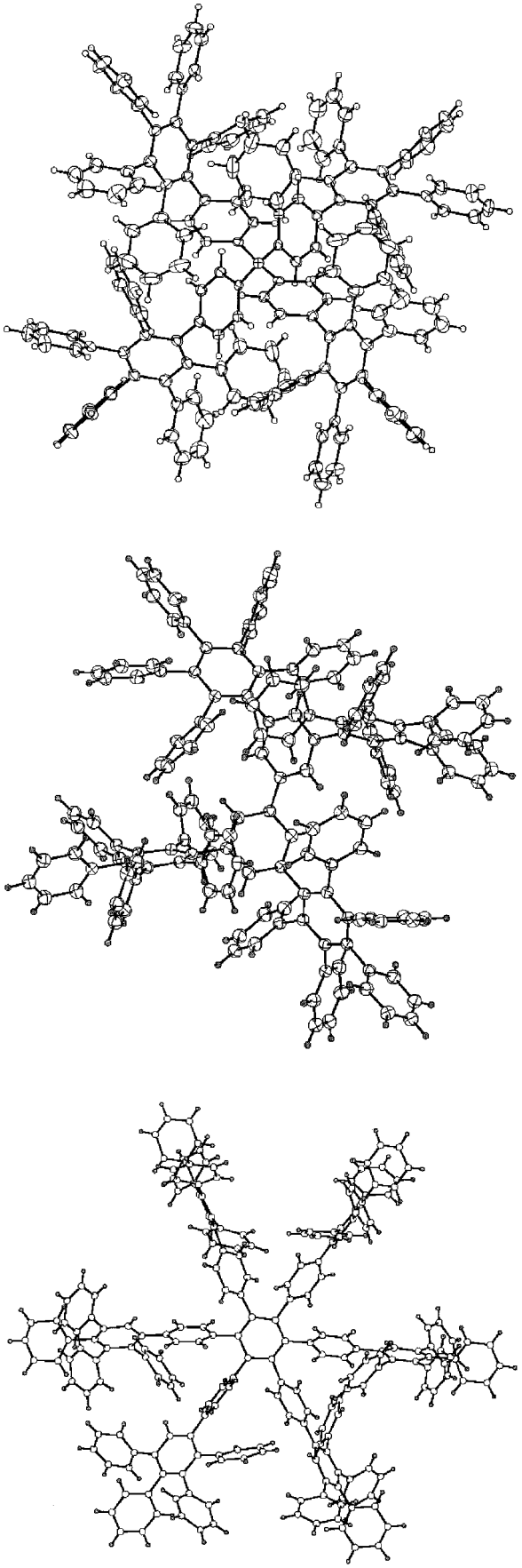

Figure 2. Crystallographic structures of **1-Ph** (top), **2-Ph** (middle), and **3** (bottom).

Table 1. Interplanar angles between phenyl rings in the dendritic arms: angles observed in the hexaphenylbenzene groups in **1-Ph** and **2-Ph**.

Planes[a]	**1-Ph** (arm 1)	**1-Ph** (arm 2)	**1-Ph** (arm 3)	**1-Ph** (arm 4)	**2-Ph**
1–2	120.1	114.3	107.9	124.5	115.1
1–3	92.7	115.1	106.6	103.9	115.6
1–4	94.4	112.8	123.0	103.2	113.2
1–5	107.1	116.6	122.2	111.3	116.4
1–6	111.5	121.6	111.1	113.7	117.4
1–7	112.4	112.6	105.1	118.3	115.3

[a] Plane 1 denotes the central plane, plane 2 is oriented to the center of the molecule, and the other planes are arranged in a clockwise manner

Table 2. Interplanar angles between phenyl rings in the dendritic arms: angles observed in the six pentaphenylbenzene groups of **3**.

Planes[a]	arm 1	arm 2	arm 3	arm 4	arm 5	arm 6
1–2	128.5	132.0	132.6	135.3	140.3	138.9
1–3	122.6	123.5	123.7	124.1	119.1	117.5
1–4	117.6	123.8	113.3	119.1	120.1	117.8
1–5	118.4	114.7	116.0	112.1	116.5	113.1
1–6	110.8	125.4	121.1	118.1	121.8	124.3

[a] Plane 1 denotes the central plane, plane 2 is oriented to the center of the molecule, and the other planes are arranged in a clockwise manner

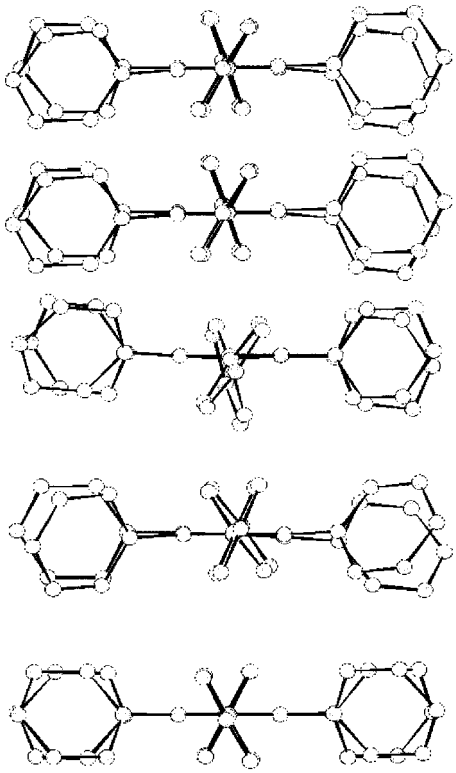

Figure 3. Conformations found in the hexaphenylbenzene groups in **1-Ph** (top four) and **2-Ph** (bottom). Projections parallel to the central ring from top to bottom corresponding to the columns in Table 1.

as a clathrate in which the solvent molecules are trapped in separate cavities. The higher stability of these crystals relative to **1-Ph** and **3** can be attributed to this fact.

This packing is ideal for the formation of ordered supramolecular assemblies in which the trapped solvent molecules

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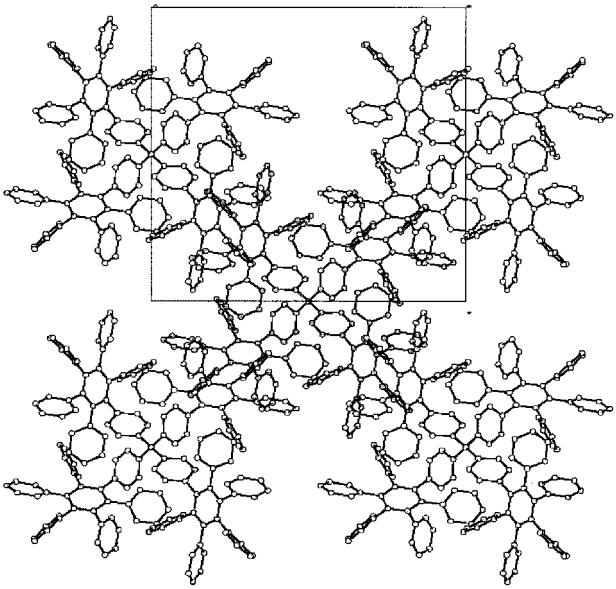

Figure 4. Packing of dendrimer **2-Ph**. The central molecule is above the four others at ½, ½, ½.

can be exchanged with spherical guest molecules. Therefore one can expect that by cocrystallization with suitable partners there is a high possibility for forming complexes in which the structure and composition can be controlled by the ratio of radii of the components. Thus, **2-Ph** was crystallized in the presence of adamantine and tetraphenylbenzene. However, so far we have found no evidence for the formation of mixed crystals. One explanation for this failure may be the large solubility difference of the two components. In both cases crystallization of the guest was observed after the crystallization of the dendrimer was completed. However, there is evidence that the composition of the solvate can be influenced in this manner. While crystals grown from CH_2Cl_2/heptane contained predominantly CH_2Cl_2, the crystals from the cocrystallization experiments contained exclusively heptane. Also comparatively large variations of the lattice parameters of crystals from different batches indicate that the number and nature of the included molecules is not fixed in the structures of dendrimer **2-Ph**.

Dendrimer **1-Ph** has one degree of freedom to avoid steric repulsion between the dendritic arms. In the crystal the two phenyl rings of the central biphenyl unit are twisted by 37.2°. Dendrimer **1-Ph** crystallizes in the triclinic space group $P\bar{1}$ on a common position, that is, without any inherent symmetry. It is interesting to note that these twist angles as well as the interplanar angles given in Table 1 agree well with the results of molecular dynamics calculations.[22] Here for dendrimer **1** a twist of 36° was predicted. This shows that we are close to the equilibrium conformation and that the crystal packing effects play only a minor role. The crystals contain six molecules of CH_2Cl_2 per asymmetric unit that separate the dendrimers.

Dendrimer **3** is built from 37 phenyl rings. It crystallizes with inclusion of a large number of tetrachloroethane molecules and represents the largest oligophenylene nanostructure for which it has been possible to solve the crystal structure. Dendrimer **3** has six degrees of freedom by rotation of the dendritic arms about the bonds to the central six-membered ring. It can be expected that unlike the schematic view shown in Figure 2 steric repulsion will force the pentaphenylbenzene groups in a perpendicular orientation so that the shape of a six-bladed propeller results. Inspection of Figure 2 (bottom) shows that this is indeed the case. Dendrimer **3** crystallizes without any inherent symmetry in the triclinic space group $P\bar{1}$; this allows for six individual twist angles for the dendritic arms. Five of these are oriented almost perpendicular to the central ring, the last one is oriented almost parallel to it. The perpendicular arms are oriented in a regular fashion so that the hydrogen in the pentaphenylbenzene substituents points alternatingly up and down.

Dendrimer **3** organizes in its crystal structure in an unexpected and fascinating fashion. A projection of the structure on the [100] plane is shown in Figure 5. The structure is built up by columns, which are formed by the parallel dendritic arms. This arrangement places the five perpendicular arms in such a way that they form a pseudohexagonal honeycomb framework. Thus large rhombic channels are formed that extend through the crystal along the *a* direction. These channels contain 18 molecules tetrachloroethane per unit cell. The diameter of these channels is in the range of

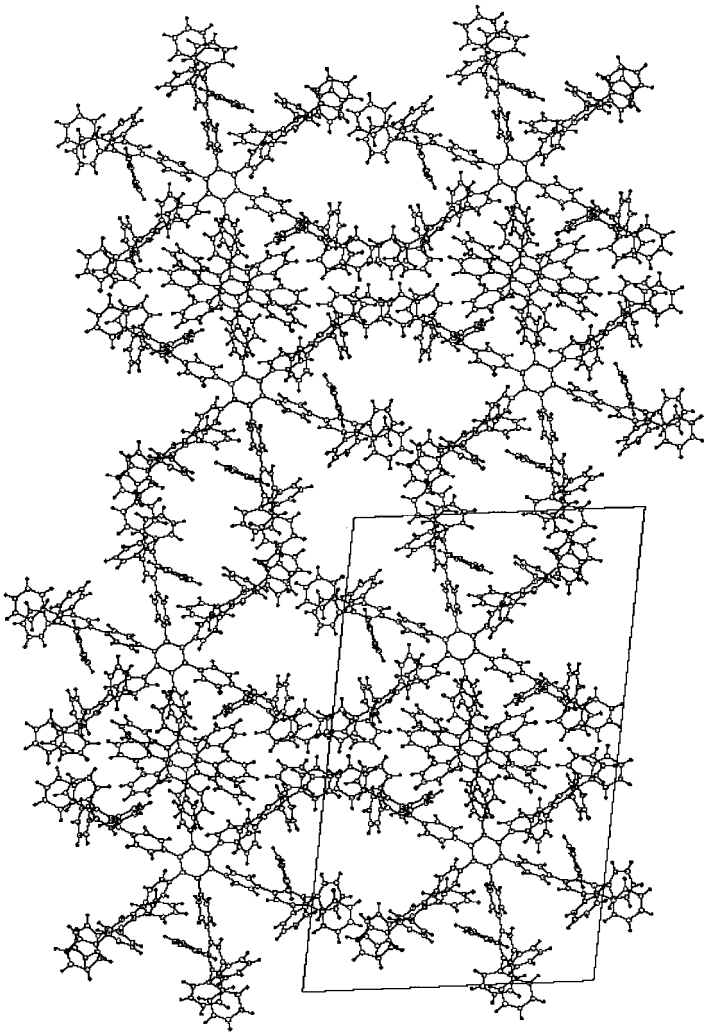

Figure 5. Projection of the crystal structure of **3** along the *a* axis.

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10 Å and much larger than the included solvent molecules. These represent about 25% of the total mass; the free cross section of the channels can be assessed to be approximately 20% of the *bc* plane. Unlike many other channel forming organic structures the channels are comparatively large, and the walls of the channels are formed by the rigid pentaphenylbenzene side groups. The low stability of the crystals can be attributed to this result; the solvent molecules are much smaller than the channel diameter and are not fixed by intermolecular forces like, for example, hydrogen bonds. Thus it can be expected that diffusion along the wide and extended channels may be quite unhindered.

Conclusion

Crystal structures, suitable for X-ray structure analysis of three polyphenylene dendrimers were grown, whereas **3** represents the up to now biggest oligophenylene nanostructure from which crystallographic data is available. In the three crystal structures the solvent molecules are included without specific interaction within the framework of the dendritic molecules and fill the voids. With the exception of the unsuccessful experiments to build host–guest complexes of **2-Ph**, no attempts have been made to exchange the solvent molecules with specific guests. This would be of particular interest in the channel-forming crystal structure of **3**. Here interesting composite structures could be obtained, for example, by incorporation of large rod-like molecules. This could be done either by cocrystallization as discussed above for **2-Ph** or by an in situ exchange reaction.

Experimental Section

General methods: All starting materials were obtained from commercial suppliers (Aldrich, Fluka, Fischer, Strem, Acros, Riedel de Haën) and were used without purification. Solvents were used in HPLC grade purity as purchased. All atmosphere-sensitive reactions were performed under argon by using Schlenck techniques. Analytical thin-layer chromatography (TLC) was performed on commercial Merck plates coated with silica gel F-254. Flash chromatography was carried out with silica gel 60 (230–400 mesh) from Merck. Dry triethylamine was obtained by vacuum transfer from calcium hydride. ^{1}H and ^{13}C NMR spectra were recorded in $C_2D_2Cl_4$ and [D_8]tetrahydofuran on Bruker DPX250, 300 AMX, and 500 DRX spectrometers with use of the solvent proton or carbon signal as internal standard. FD mass spectra were obtained on a VG Instruments ZAB 2-SE-FPD spectrometer. MALDI-TOF mass spectra were measured on a Bruker Reflex II-TOF spectrometer with a 337 nm nitrogen laser and 7,7,8,8-tetracyanoquinodimethane (TCNQ) as matrix. Elemental analysis was carried out on a Foss Heraeus Vario EL. Because of the high carbon content in some molecules, the combustion may have been incomplete (sooting), resulting in lower values than expected for the carbon content.

X-ray crystallographic analysis:[21] Crystal structure determinations were carried out on an Nonius KCCD diffractometer with graphite monochromated $Mo_{K\alpha}$ radiation. The structures were solved by direct methods (SHELXS-97). Refinement was done with anisotropic temperature factors for C and Cl, the hydrogen atoms were refined with fixed isotropic temperature factors in the riding mode. Some of the solvent molecules are disordered. These were refined with fixed isotropic temperature factors and occupancy factors which were fixed according to the geometry of disorder.

Refinements gave: **1-Ph**: $a = 21.7012(7)$, $c = 18.4737(6)$ Å; $V = 8700.0(8)$ Å^3; $R = 10\%$; **2-Ph**: $a = 17.733(3)$, $b = 5.1771(7)$, $c = 18.266(1)$ Å; $\alpha = 75.785(9)^\circ$, $\beta = 80.236(9)^\circ$ $\gamma = 65.219(9)^\circ$; $V = 6832.8(3)$ Å^3; $R = 15\%$; **3**: $a = 11.0245(2)$, $b = 23.8982(6)$, $c = 42.406(1)$ Å; $\alpha = 89.194(1)^\circ$, $\beta = 95.702(1)^\circ$, $\gamma = 90.194(1)^\circ$; $V = 11002(1)$ Å^3; $R = 20\%$.

General procedure for the aryl-ethynyl coupling to aromatic bromo compounds:[23–25] The aromatic bromine compound was dissolved in a degassed mixture of two parts of triethylamine and one part of toluene (about 30–40 mL of solvents per gram of bromo compound) under argon. After that, bis(triphenylphosphine)palladium(II) dichloride (5 mol%), copper(I) iodide (10 mol%), and triphenylphosphine (10 mol% with respect to the contained in the halogenated compound) were added under a flow of argon. The flask was then sealed with a septum and the reaction mixture stirred at 50–60 °C for about 10 min, after which the ethynyl compound (1–1.1 molar equiv per bromine) was injected. The reaction mixture was stirred further at 80–90 °C and monitored by TLC until no further conversion could be observed (usually 2–5 h). After allowing the solution to cool, it was poured into an equivalent volume of dichloromethane and filtered. Hydrochloric acid, about 6 M, was carefully added to the filtrate until the aqueous phase became slightly acidic (pH < 5). After that, the organic phase was removed, washed twice with distilled water, extracted with a saturated solution of ammonium chloride, washed again several times with distilled water, and dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude product purified by column chromatography on silica gel.

General procedure for the aryl-ethynyl coupling to aromatic iodo compounds: The procedure is the same as stated above in the case of the aromatic bromo compounds with the difference of the reaction temperature: In case of the aromatic iodo compounds the reactions were carried out at room temperature.

General procedure for the Diels–Alder cycloaddtion of phenylethynyl- and tetraphenylcyclopentadiene derivatives: A mixture of the phenylethynyl derivative and tetraphenylcyclopentadienone (1.5 molar equivalents per phenylethynyl bond) was refluxed for 48 h in diphenyl ether (10 mL per gram of the starting material) under an argon atmosphere. The cooled reaction mixture was added dropwise to pentane (100 mL). The precipitated product was filtered under suction and re-precipitated several times in ethanol until the red color of the cyclopentadienone disappeared. Finally, the product was dried in vacuo.

For a detailed synthetic pathway and physical data of dendrimer **3** please see this journal.[26]

Tetra(4-phenylethinylphen-1-yl)methane (4): Colorless solid; m.p. > 300 °C; ^{1}H NMR (300 MHz, $C_2D_2Cl_4/CS_2$, 303 K): $\delta_H = 7.52–7.44$ (m, 8H), 7.42 (d, $^3J = 8.7$ Hz, 8H), 7.35–7.27 (m, 8H), 7.18 (d, $^3J = 8.7$ Hz, 8H), 3.33 ppm (s, 2H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4/CS_2$, 303 K): $\delta_C = 146.1$, 131.9, 131.4, 131.0, 128.6; 123.3, 121.5, 90.3, 89.5, 65.0 ppm; FD-MS: *m/z* (%):720.1 (100) [M^+]; elemental analysis calcd (%) for $C_{57}H_{36}$:C 94.97, H 5.03; found: C 93.58, H 5.02.

3,3′,5,5′-Tetraphenylethinylbiphenyl (5): Colorless solid; m.p. > 300 °C; ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 303 K): $\delta_H = 7.74–7.69$ (m, 6H), 7.68–7.50 (m, 8H), 7.38–7.29 ppm (m, 12H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 303 K): $\delta_C = 140.3$, 134.1, 132.0, 130.3, 129.0, 124.6, 123.0, 90.9, 88.7 ppm; FD-MS: *m/z* (%): 553.3 (100) [M^+]; elemental analysis calcd (%) for $C_{44}H_{26}$: C 95.28, H 4.72; found: C 94.60, H 4.70.

Cascade: Tetraphenylmethane[4-4,4′,4″,4‴]:(4′,5′-diphenyl-1,1′:2′,1″-terphenyl-6′-yl) (1-Ph): Colorless solid: m.p. > 300 °C; ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 383 K): $\delta_H = 6.88–6.66$ (m, 8H), 6.39 (d, $^3J = 8.4$ Hz, 8H), 5.89 ppm (d, $^3J = 8.4$ Hz, 8H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 383 K): $\delta_C =$ 143.8, 141.0, 140.5, 140.3, 140.2, 138.0, 131.8, 129.9, 129.5, 126.6, 126.4, 125.1, 124.9, 124.9 ppm; FD-MS: *m/z* (%): 2146.0 (100) [M^+], 1073.0 (8) [M^{2+}]; elemental analysis calcd (%) for $C_{169}H_{116}$:C 94.55, H 5.45; found: C 93.49, H 5.15.

Cascade: Biphenyl[4-3,3′,5,5′]:(4′,5′-diphenyl-1,1′:2′,1″-terphenyl-6′-yl) (2-Ph): Colorless solid: m.p. > 300 °C; ^{1}H NMR (300 MHz, [D_8]tetrahydofuran, 303 K): $\delta_H = 6.96–6.56$ (m, 100H), 6.53 (s, 2H), 6.16 (d, 4H), 5.67 ppm (d, 4H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 383 K): $\delta_C = 141.2$, 141.0, 140.9, 140.1, 139.7, 139.6, 138.2, 137.7, 134.1, 131.7, 130.6, 127.5, 127.2, 126.9, 126.6, 125.1, 124.9, 141.0, 140.9, 140.1, 139.7, 139.6, 138.2, 137.7 134.1, 131.7, 130.6, 127.5, 127.2, 126.9, 126.6, 125.1, 124.9 ppm; FD-MS: *m/z* (%): 1980.1 (100) [M^+], 990.1 (5) [M^{2+}]; elemental analysis calcd (%) for $C_{156}H_{106}$: C 94.61, H 5.39; found: C 93.91, H 5.39.

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