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Synthesis and crystal structures of extremely crowded oligophenylenes as model precursors to 'cubic graphite'

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Abstract—By using drastic conditions for a Diels–Alder cycloaddition reaction, it was possible to synthesize an oligophenylene with an extremely dense packing of the benzene rings. Crystallographic data could be obtained and a projection of the structure on the plane of the central phenyl ring reveals that the molecule retained its theoretical threefold symmetry with only minor deviations. Due to its dense packing of interlocked benzene rings, this oligophenylene could be furthermore used as a suitable precursor for constructing a subunit of 'cubic graphite'.

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1. Introduction

The search for novel three-dimensional polyphenylene structures also includes a carbon phase so-called 'cubic graphite', proposed and attempted to synthesize by Gibson et al.[1] The name cubic graphite implies both, the cubic symmetry of such a phase and the close relationship between its solid-state structure and that of conventional graphite. In such a phase each benzene ring is connected to six other different rings and each benzene ring is part of three equivalent polyparaphenylene chains.

Four neighboring benzene rings are arranged to a tetraphenylene ring with a strong mutual twist between them (Fig. 1). Thus, within such a novel phase, all carbon atoms become equivalent. This material would present the perfect three-dimensional polyphenylene structure[2,3] and should possess high thermal and mechanical stability. These features and the presence of large diffusion channels for lithium cations and its high predicted maximum charge storage capacity make 'cubic graphite' a candidate for rechargeable batteries, battery-like supercapacitors, and electrochromic displays.[2,3]

Although this particular carbon phase might never be accessible due to the extremely crowded three-dimensional arrangement of hexaphenylbenzene (HPB) units, highly dense polycyclic aromatic hydrocarbons, and nanosized dendritic or hyperbranched polyphenylenes have gained even more attention as fascinating synthetic targets.[3–11] The biggest oligophenylene nanostructures from which crystallographic data could be obtained are based on the Diels–Alder cycloaddition between tetraphenylcyclopentadienones and arylacetylenes.[5,6] This approach in combination with palladium-catalyzed Hagihara–Sonogashira coupling reactions[12] leads to a great diversity of higher generation polyphenylene dendrimers, and when applied to a functionalizable core to a versatile synthesis and self-assembly of star-type hexabenzocoronenes.[13] A different strategy to novel three-dimensional polyphenylene structures utilizes the Suzuki coupling reaction of dibromo-hexaphenylbenzene units with complementary bis(boronic acid) derivatives. This route affords a novel oligophenylene

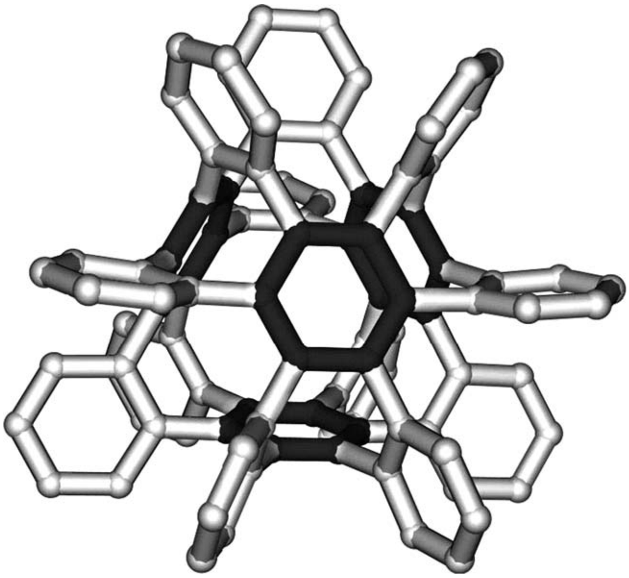

Figure 1. Three-dimensional representation of a subunit of cubic graphite.

Keywords: Cubic graphite; Oligophenylene; Dendrimer; Dense packing; Diels–Alder; Cycloaddition.

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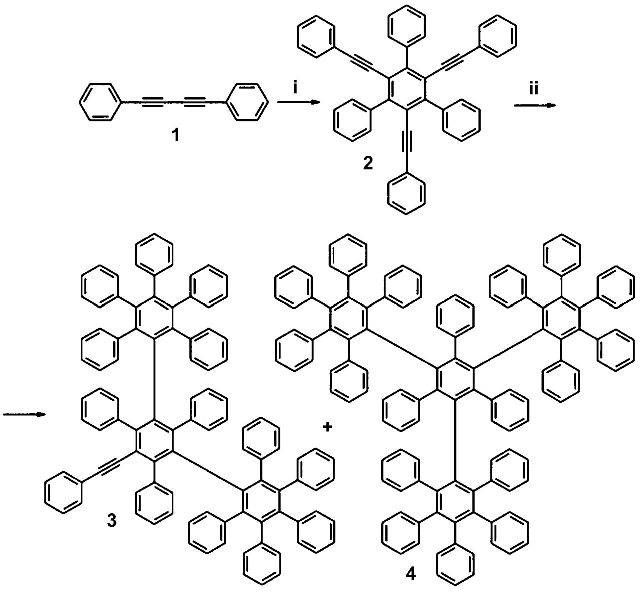
macrocycle related to 'phenylogous cubic graphite' with a large central cavity and the formation of channels within the crystal.[14] A further approach to crowded polyphenylenes is based on the thermal ring opening of biphenylene units with subsequent dimerization to tetraphenylene and leads to 'cubic graphite' related structures.[15]

Herein, we present the straightforward synthesis and crystal structures[16] of the densely packed oligophenylenes **3** and **4**. The 1,3,5-tris-(phenylethynyl)-2,4,6-triphenylbenzene (**2**) was synthesized via a cobaltoctacarbonyl mediated cyclotrimerization of diphenylbutadiyne **1** following a literature procedure[17] (Scheme 1). Looking at the sterical demands of **4**, a threefold Diels–Alder reaction with **2** seemed to be impossible. Indeed, reaction of both components in refluxing diphenyl ether under argon atmosphere proceeded very slowly. The generation of the monoadduct was detected by thin layer chromatography (TLC) and field-desorption mass spectrometry (FDMS) soon after the reaction started. However, the formation of the bisadduct **3** required four days. Under these reaction conditions, target compound **4** was not formed even after an extremely prolonged reaction time of one month. Instead, decomposition became rampant and therefore a rather uncommon preparative method was chosen. A mixture of the acetylene derivative **2** and excess tetraphenylcyclopentadienone was placed in a glass ampoule. After evacuation (10^{-5} mbar), the ampoule was sealed and heated for 72 h at 265 °C. A complex reaction mixture was obtained, which made a full separation and characterization of all components impossible. After column chromatography and washing, only minor amounts of **4** could be isolated, and the amount of double Diels–Alder product **3** was also very modest. Although the yield of **4** was rather low, these conditions seemed to provide an optimum for the formation of **4**. While a decrease in temperature prevented the formation of a melt, and therefore, good mixing, an increase resulted in more drastic conditions, favoring undesired side reactions. These harsh conditions and the resulting low yields stand in contrast to other ethynyl precursor molecules, where the products also show a dense packing of the benzene rings.[6] However, one major difference is that the ethynyl functionalities in these examples were situated spatially less close than for the precursor **2**, which indicates the strong influence of the steric situation upon the Diels–Alder cycloaddition.



Scheme 1. Reaction conditions: (i) $Co_2(CO)_8$, dioxane, 8 h, reflux; (ii) tetraphenylcyclopentadienone, 265 °C, 72 h, **3** (34%), **4** (2%).

The molecular structure of both compounds could be assigned by MS, ^{1}H NMR, and ^{13}C NMR spectroscopy; however, absolute certainty provided their crystal structures. Whereas isolation of **3** via column chromatography did not provide any difficulties, the fraction containing **4** consisted of several components. Field-desorption and MALDI-TOF MS analysis showed the presence of a peak at *m/z* 1706 Da, most likely corresponding to the norbornadienone, which is subsequently transferred to the final product **4** under CO extrusion. The presence of such a norbornadienone is substantiated by a recent publication[10] demonstrating that significant steric crowding supports the stability of that particular class of compounds. Additionally, one has to consider that applying the above described reaction conditions, it is not possible to estimate to what extent partial cyclodehydrogenation will also come into play, making an unambiguous structural assignment even more difficult.

The ^{1}H NMR spectra of both oligophenylenes, **3** and **4**, show resonances at unusually high-field positions for aromatic ring protons implying that they are placed above the centers of neighboring aromatic rings. While the aromatic proton resonances assigned to the 'core' of **3** resonate at δ=5.74, those attributable to core **4** (Fig. 3 b, d, f) appear at δ=4.83. These strong high-field shifts are caused by the magnetic anisotropy as a result of the ring currents of the surrounding *ortho*-phenyl rings of the pentaphenyl units. Similar effects have been reported in the literature.[5,7] The ^{13}C NMR spectrum of **3** indicated a C_{2v} symmetry on the timescale of the solution-based NMR experiment, as it displays 34 resonances. This is consistent with a fast, unrestricted rotation of all phenyl groups including the ones directly connected to the central phenyl ring. Due to the very poor solubility of **4** in all organic solvents, the acquisition of ^{13}C NMR spectral data had to be performed at 373 K using $C_2D_2Cl_4$ as solvent. The spectrum shows 22 signals corresponding to a D_{3h} symmetry of the molecule, which would be expected within the fast exchange limit for all single bond rotations.

Crystals of **3** and **4** were grown from tetrachloroethane and methylenechloride, respectively, by slow evaporation at room temperature (Fig. 2). They crystallize as solvates and especially **3**, which contains five solvent molecules per asymmetric unit, decomposes quickly under ambient conditions.[18] A projection of the structure of **4** on the plane of the central phenyl ring reveals that here the molecule retains its theoretical threefold symmetry with only minor deviations. This can be explained by the rigidity of the intramolecular packing in this overcrowded molecule, which reduces the distortions by outer forces, e.g., packing effects. Thus the molecular shape is almost cylindrical. As a consequence **3** crystallizes in a pseudohexagonal packing ($a\approx c$, $\beta\approx$ 120°), which is expected for an array of disks. Compound **3** appears to be much less rigid owing to its reduced inner

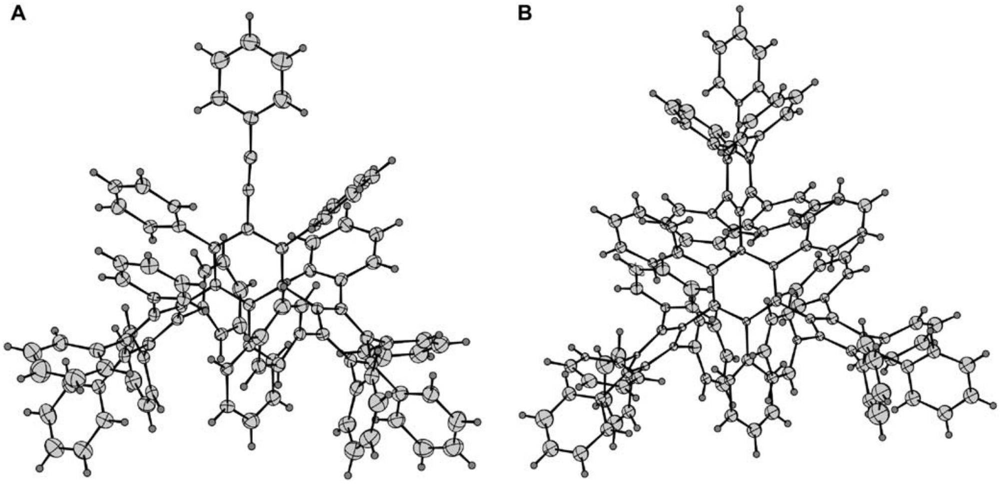


Figure 2. Crystal structures of (A) compound **3** and (B) compound **4** (projection along the central phenyl ring).

packing density and especially the angles, which are determined by the three phenyl substituents (Fig. 3 b, d, f) with the central phenyl ring, seem to be affected considerably by intermolecular contacts.

In summary, the results presented herein show that, by using rather drastic synthetic conditions, highly dense oligophenylenes are accessible. Compound **4**, due to its dense packing of benzene rings, is furthermore a suitable precursor for constructing a subunit of 'cubic graphite'. The key structural motif comprises of a HPB subunit having in ortho- and ortho′-positions each of the three alternating (Fig. 3 a, c, e) benzene rings connected with further two benzene rings. The latter ones would allow for the formation of six alternating tetraphenylene rings in a final cyclodehydrogenation step involving the other three alternating (Fig. 3 b, d, f) benzene rings of the central HPB unit. After the formation of the red dotted bonds in Figure 3A, one would obtain a subunit of 'cubic graphite', represented schematically in Figure 3B.

However, the extremely low yield towards **4** forces us to seek for more efficient synthetic approaches to create suitable precursors of this extremely challenging carbon framework. This will also promote efforts into the creation of related[14,15] and new, intriguing graphite models. A promising approach to achieve the latter goal includes spatial restricted cyclodehydrogenations applied to polyphenylene dendrimers. Thus, a suitable arrangement of the dendrons, predetermined by the core, would just allow for oxidative cyclodehydrogenation within the wings and not between them. This concept might create not only giant propeller-shaped molecules with blades comprised of PAHs, but also large channels and cages for storage and transport are feasible.[19]

2. Experimental

2.1. General

Freshly powdered 1,3,5-tris(ethynylphenyl)-2,4,6-trisphenylbenzene (**2**) (75 mg, 0.124 mmol) and tetraphenylcyclopentadienone (245 mg, 0.637 mmol) were placed in a glass ampoule. The mixture was thoroughly mixed, and the ampoule afterward evacuated to 10^{-5} mbar. After sealing,

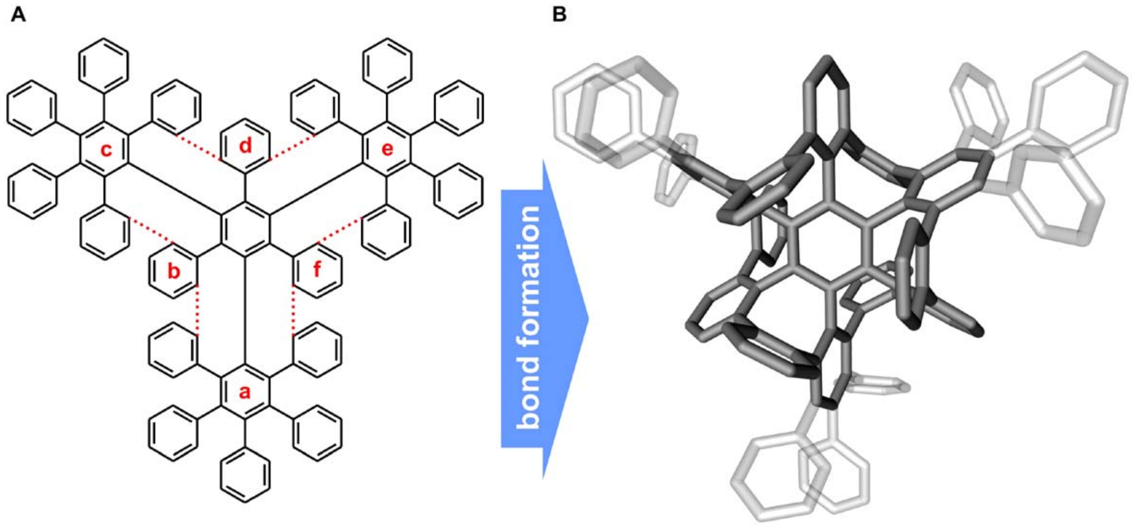


Figure 3. (A) Necessary bond formations from **4** (red dotted lines) towards a subunit of 'cubic graphite'; (B) schematic representation of the theoretically formed product (semi-empirical AM1 calculation).

it was heated in an electric oven at 2 °C/min to 265 °C. This temperature was maintained for 72 h. The ampoule was cooled to room temperature and carefully opened. The solid red-brownish residue was removed from the ampoule and subjected to column chromatography (silica gel, *n*-hexane/dichloromethane 2:1) to yield, after removal of the solvent by rotary evaporation and careful washings with *n*-pentane, the double- and triple-Diels–Alder product **3** (55 mg, 0.042 mmol, 34%) and **4** (5 mg, 0.003 mmol, 2%), respectively.

2.1.1. Compound 3. Colorless solid; mp>300 °C; ^{1}H NMR (700 MHz, $C_2D_2Cl_4$, 306 K): δ=7.16–6.93 (m, 16H), 6.88–6.73 (m, 12H), 6.72–6.55 (m, 27H), 6.54–6.41 (m, 8H), 6.28 (s, 3H), 5.74(w, 4H); ^{13}C NMR (176 MHz, $C_2D_2C_{14}$, 318 K): δ=144.32, 142.59, 141.97, 141.52, 141.26, 141.16, 141.03, 139.98, 139.69, 138.35, 137.64, 136.54, 133.89, 133.37, 132.45, 131.92, 131.73, 131.57, 131.02, 128.23, 127.88, 127.02, 126.62, 126.49, 126.37, 126.01, 125.83, 125.41, 124.96, 124.74, 123.86, 123.74, 96.10, 92.05; FDMS (8 kV): *m*/*z* (%): 1320 (100%) [M^+].

2.1.2. Compound 4. Colorless solid; mp>300 °C; ^{1}H NMR (700 MHz, $C_2D_2Cl_4$, 306 K): δ=6.95 (t, ^3J=7.3 Hz, 6H), 6.88 (d, ^3J=7.7 Hz, 7H), 6.85 (t, ^3J=7.3 Hz, 7H), 6.78 (t, ^3J=7.7 Hz, 9H), 6.58 (d, ^3J=6.0 Hz, 12H), 6.52 (w, 20H), 6.38 (d, ^3J=5.1 Hz, 9H), 6.16 (d, ^3J=8.5 Hz, 14H), 4.83 (w, 6H); ^{13}C NMR (176 MHz, $C_2D_2C_{14}$, 373 K): δ=142.15, 141.89, 141.72, 141.66, 141.54, 139.75, 139.59, 138.69, 137.90, 135.89, 135.79, 132.29, 131.62, 131.52, 126.49, 126.24, 126.01, 125.55, 125.15, 124.97, 124.71, 124.22; FDMS (8 kV): *m*/*z* (%): 1676 (100%) [M^+].

Acknowledgements

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16. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CSD 285923 and CSD 285924 and can be obtained free of charge, on application to: CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).
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18. Crystals were mounted in closed capillaries and the data collections were carried out at 120 K on a Nonius KappaCCD diffractometer with graphite monochromated Mo Kα radiation. 19,149 and 19,089 unique reflections were collected for **4** and **3**, respectively, of which 4121 and 14,881 reflections were considered observed (I>22(I)). The structures were solved by direct methods and refined by full-matrix least squares analyses on F^2 with anisotropic temperature factors for all non-hydrogen atoms. The H atoms were refined with fixed isotropic temperature factors in the riding mode. Final R values for all reflections were 0.115 (R_w 0.194) (**4**) and 0.068 (R_w 0.117) (**3**). The R values for the observed reflections were 0.069 (R_w 0.107) (**4**) and 0.055 (R_w 0.099) (**3**).
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