

Synthesis of a Giant 222 Carbon Graphite Sheet

Christopher D. Simpson, J. Diedrich Brand, Alexander J. Berresheim, Laurence Przybilla, Hans Joachim Räder, and Klaus Müllen*^[a]

Abstract: In this paper we present the synthesis and characterization of the so far largest polycyclic aromatic hydrocarbon (PAH), containing 222 carbon atoms or 37 separate benzene units. First a suitable three-dimensional oligophenylene precursor molecule is built up by

a sequence of Diels–Alder and cyclo-trimerization reactions and then planar-

Keywords: carbon • cyclodehydrogenation • graphite • mass spectrometry • polycycles

ized in the final step by oxidative cyclodehydrogenation to the corresponding hexagonal PAH. Structural proof is based on isotopically resolved MALDI-TOF mass spectra and electronic characteristics are studied by UV/Vis spectroscopy.

Introduction

Extremely large polycyclic aromatic hydrocarbons (PAHs) are for long being used by theoreticians as model compounds for graphite.^[1–5] Not so long ago the synthesis of such huge PAHs seemed out of reach due to decreasing solubility with increasing size of the molecules. Hexa-*peri*-hexabenzocoronene, described for the first time by Halleux, was for a long time with its 42 carbon atoms the largest fully characterized PAH.^[6, 7] Applying the synthetic concept recently introduced by us, it has been possible to produce a variety of extremely large PAHs with up to 132 carbon atoms.^[8–13] This was achieved employing a synthetic concept based on two key steps. In the first step a fully characterizable, soluble oligophenylene precursor was synthesized, which was then in the second step planarized by oxidative cyclodehydrogenation to the corresponding PAH. For the synthesis of the oligophenylene precursors, the cobaltoctacarbonyl-catalyzed cyclotrimerisation of symmetrical diphenylacetylene derivatives as well as the Diels–Alder reaction of a phenyl- or diphenylacetylene containing molecule and a tetraphenylcyclopentadienone have proven to be useful. While the cyclotrimerisation leads exclusively to hexagonal structures, a range of different PAHs of varying structure and size are accessible through the Diels–Alder route. In this article we describe two different synthetic routes to an oligophenylene precursor (**1**) containing 37 separate benzene units as well as its subsequent oxidative cyclodehydrogenation to the corre-

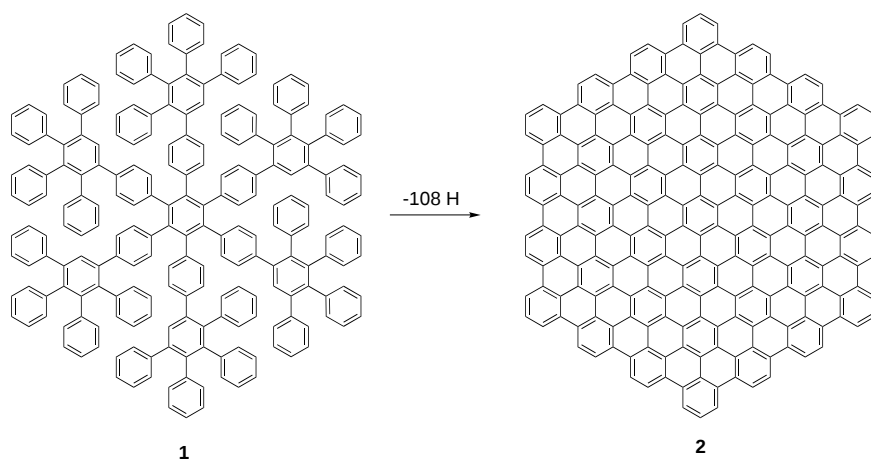
sponding hexagonal, 222 carbon containing PAH (**2**). This PAH, which up to now has only been considered in theoretical articles,^[4] is presently the biggest fully condensed aromatic system actually having been prepared. Its diameter is approximately 3 nm (Scheme 1).

Results and Discussion

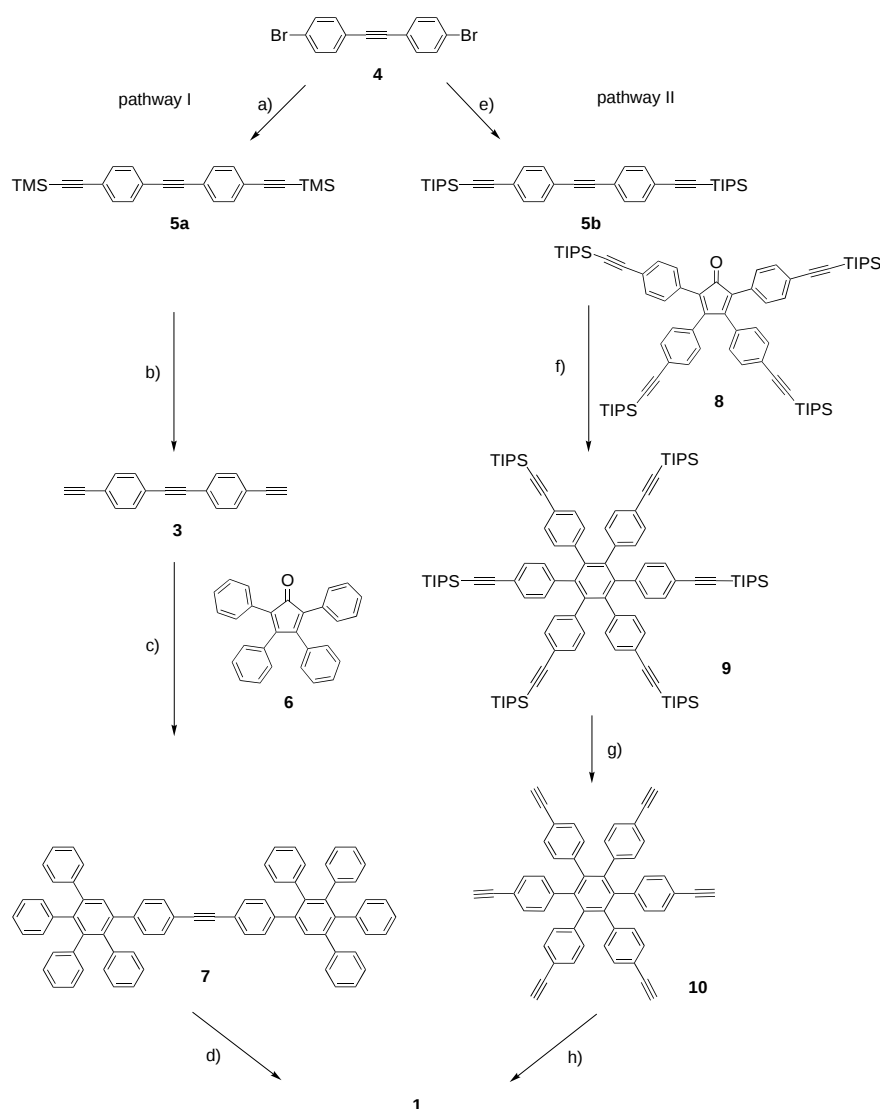
The two synthetic approaches to the precursor molecule **1** (pathway I and II, see Scheme 2) are based on the selectivity of the Diels–Alder reaction regarding acetylenes carrying substituents of varying steric demand. While mono-substituted phenylacetylenes react at temperatures around 160 °C with reasonable rates, diphenylacetylenes require a temperature of or above 200 °C to obtain an adequate reaction rate. Triisopropylsilyl groups serve as protective groups for acetylenes, preventing the Diels–Alder reaction from occurring. This circumstance has been used by us recently in the synthesis of polyphenylene dendrimers.^[14]

The first pathway (I) of obtaining **1** is the combination of the Diels–Alder reaction with the cobaltoctacarbonyl-catalyzed cyclotrimerisation.^[15–17] According to Scheme 2 the diphenylacetylene derivative **3** can be obtained by coupling 4,4'-dibromophenylacetylene (**4**) with trimethylsilylacetylene^[18–20] followed by the removal of the silyl protection groups using potassium fluoride. Compound **3** reacts in a Diels–Alder reaction at 190 °C in diphenyl ether with two equivalents of tetraphenylcyclopentadienone (**6**) exclusively at the outer acetylene units to give **7** in 66 % yield. Despite the large substituents on the triple bond, the cobaltoctacarbonyl-catalyzed cyclotrimerisation of **7** can be carried out with a yield of 71 % obtaining the precursor oligophenylene **1**.

[a] Prof. Dr. K. Müllen, Dipl.-Chem. C. D. Simpson, Dr. J. D. Brand, Dr. A. J. Berresheim, Dr. L. Przybilla, Dr. H. J. Räder
Max-Planck-Institute for Polymer Research
Ackermannweg 10, 55128 Mainz (Germany)
Fax: (+49) 6131-379100
E-mail: muellen@mpip-mainz.mpg.de



Scheme 1. Oxidative cyclodehydrogenation of the precursor molecule **1** to the PAH **2**.



Scheme 2. The two different synthetic routes to the precursor molecule **1**: a) trimethylsilylacetylene, $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$, CuI , PPh_3 , $\text{NEt}_3/\text{toluene}$, 80°C , 93%; b) KF , DMF , RT, 83%; c) tetraphenylcyclopentadienone, Ph_2O , 190°C , 11 h, 66%; d) $[\text{Co}_2\text{CO}_8]$, dioxane, 100°C , 5 d, 71%; e) triisopropylsilylacetylene, $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$, CuI , PPh_3 , $\text{NEt}_3/\text{toluene}$, 80°C , 74%; f) Ph_2O , 200°C , 11 d, 72%; g) Bu_4NF , THF , RT, 89%; h) tetraphenylcyclopentadienone, Ph_2O , 190°C , 11 h, 89%.

The second synthetic pathway (II) to **1** was opened by the use of the sterically very demanding triisopropylsilyl groups as substituents on the outer triple bonds of **5b**. Thus, when treating **5b** with the cyclopentadienone **8**, only the central, sterically less hindered triple bond of **5b** underwent a Diels–Alder reaction to afford **9** in 72% yield. The reaction was carried out in diphenyl ether at 200°C , however, in this case it took 11 days for the starting materials to react completely. This extended reaction time is explained by the increased steric demand of the reaction compared with pathway (I) where the outer triple bonds of **3** undergo the Diels–Alder reaction. On treating **9** with tetrabutylammonium fluoride, the hexaethynyl-substituted hexaphenylbenzene (**10**) was obtained with a yield of 89% which was then reacted further with tetraphenylcyclopentadienone (**6**) to obtain the targeted precursor molecule **1** in 90% yield. Even though being a very large oligophenylene, **1** is very well soluble in solvents such as dichloromethane, chloroform, tetrahydrofuran. It was possible to completely characterize this molecule including assigning the proton and carbon signals in the corresponding NMR spectra.

The high demands towards the efficiency and selectivity of the now following cyclodehydrogenation reaction can be understood by looking at the computer-generated model of **1** in Figure 1. It shows the three-dimensional structure of the dendritic molecule which has to be completely planarized by aryl–aryl bond formation to obtain the flat PAH **2**. The depicted conformation, resembling a six-bladed propeller, can be assumed to be one of the thermodynamically most likely arrangements of the molecule

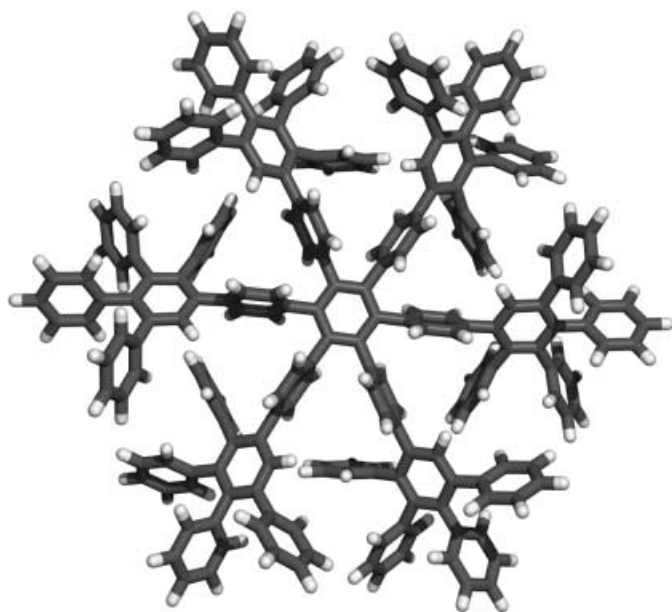


Figure 1. Computer-simulated model of the three-dimensional structure of **1** (using the molecular-mechanics force field of Wavefunction Spartan Pro 1.0.5).

in solution. Single-crystal X-ray studies, which give an insight into the molecular structure in the solid-state, confirm the calculated shape in general, however, of the dendritic arms only five are oriented almost perpendicular to the central ring, while the sixth one is almost parallel to it. Details of these X-ray studies will be published separately.^[21]

The oxidative cyclodehydrogenation method used to convert the oligophenylene **1** to the PAH **2** has been described previously.^[8–11] Due to the extremely low solubility of **2** in all solvents, the successful cyclodehydrogenation could not be proven by conventional analysis methods. For instance solution NMR spectroscopy was completely out of the question, but also solid-state ¹³C NMR spectroscopy resulted only in broad unidentifiable signals, giving no further information about the detailed structure of the analyte. Also elementary analysis, a method usually very well suitable for solid materials, could not be used since incomplete combustion under soot formation of this high carbon content type of molecule leads to inaccurate results. Even leaving the combustion problem aside, the accuracy of the method is not high enough to distinguish between a molecular composition of C₂₂₂H₄₄ (**1**) and for instance a molecule with a C₂₂₂H₄₆ composition or a mixture of the two.

The problems mentioned above led to the burden of structural proof resting mainly on mass spectrometry. In the case of smaller PAHs, laser desorption time of flight (LD-TOF) mass spectrometry was shown to be a useful method.^[22] However, in the case of **2** only unstructured extremely broad signals were detectable with LD-TOF, rendering the clear proof of **2** impossible. This is due to the high molecular weight of **2** (2708 g mol⁻¹) which cannot be detected by laser desorption mass spectrometry without fragmentation and clustering phenomena.

A reliable and detailed characterization of **2** was not possible until a new method of sample preparation was

developed for MALDI-TOF mass spectrometry. This new method, as well as a detailed characterization of **2** was recently published in a separate paper.^[23] The key feature of this method is a modified way of sample preparation for MALDI-TOF mass spectrometry. Until quite recently only soluble samples could be characterized by MALDI-TOF mass spectrometry, since the traditional method of sample preparation required a dissolving step for homogenization of sample and matrix prior to analysis.^[24]

Within the new method of sample preparation the use of solvents could be avoided completely, which opened the application of MALDI-TOF MS also for insoluble samples in general. Only with the novel method of sample preparation did it become possible to obtain well resolved mass spectra of PAH **2** without fragmentation and cluster signals which is a severe necessity for a reliable characterization of reaction products by mass spectrometry, especially when no other methods can provide supplemental information to prove the results.

Figure 2a shows the MALDI-TOF mass spectrum of PAH **2**. The most intense signal at 2708 g mol⁻¹ represents exactly the mass of the target molecule, whereas a series of low intensity signals in the higher molecular region up to 2900 g mol⁻¹ are due to trace amounts of side products.

These additional signals are due to intermediates during synthesis which result from an incomplete cyclodehydrogenation and a partial chlorination. However, it should be emphasized, that the signal intensities of the side products are highly overestimated in relation to the signal of the desired structure **2**. A quantification approach, which is described thoroughly in ref. [22], reveals that the side products have a much higher desorption and ionization efficiency than PAH **2** which leads to an overestimation of the impurities by a factor of 285 in the MALDI-TOF mass spectrum. Thus the purity of **2** can be calculated from the corrected peak areas in Figure 2a to be 99%.

Figure 2b shows an expanded region of the molecular ion of PAH **2** with isotopic resolution. The black bars below the measured signals indicate the theoretical isotopic distribution of PAH **2** which is calculated for the elemental composition of the perfect structure (C₂₂₂H₄₂).

The close agreement of theoretical and measured signal intensities is a strong proof for the desired structure, since it proves the complete removal of 108 hydrogen atoms during the formation of 54 new carbon bonds.

Although a mass spectrum is certainly not a definitive structure proof in the customary sense, the existence of the desired structure of PAH **2** can be assumed with high certainty in this case because there is no reasonable other structure which can be formed by the given reaction conditions to yield an elemental composition of C₂₂₂H₄₂. Any defect structure which may result from rearrangement reactions or incomplete cyclodehydrogenation give rise to a higher number than 42 hydrogens in the molecule, leading to additional or overlapping isotopic distributions. An incomplete cyclodehydrogenation reaction for example, where only one C–C bond remains unclosed would result in an elementary composition of C₂₂₂H₄₄ instead of C₂₂₂H₄₂ for PAH **2**, thus resulting in an isotopic pattern similar to that in Figure 2b but shifted by two mass units to higher molecular weight. Thus, the signal

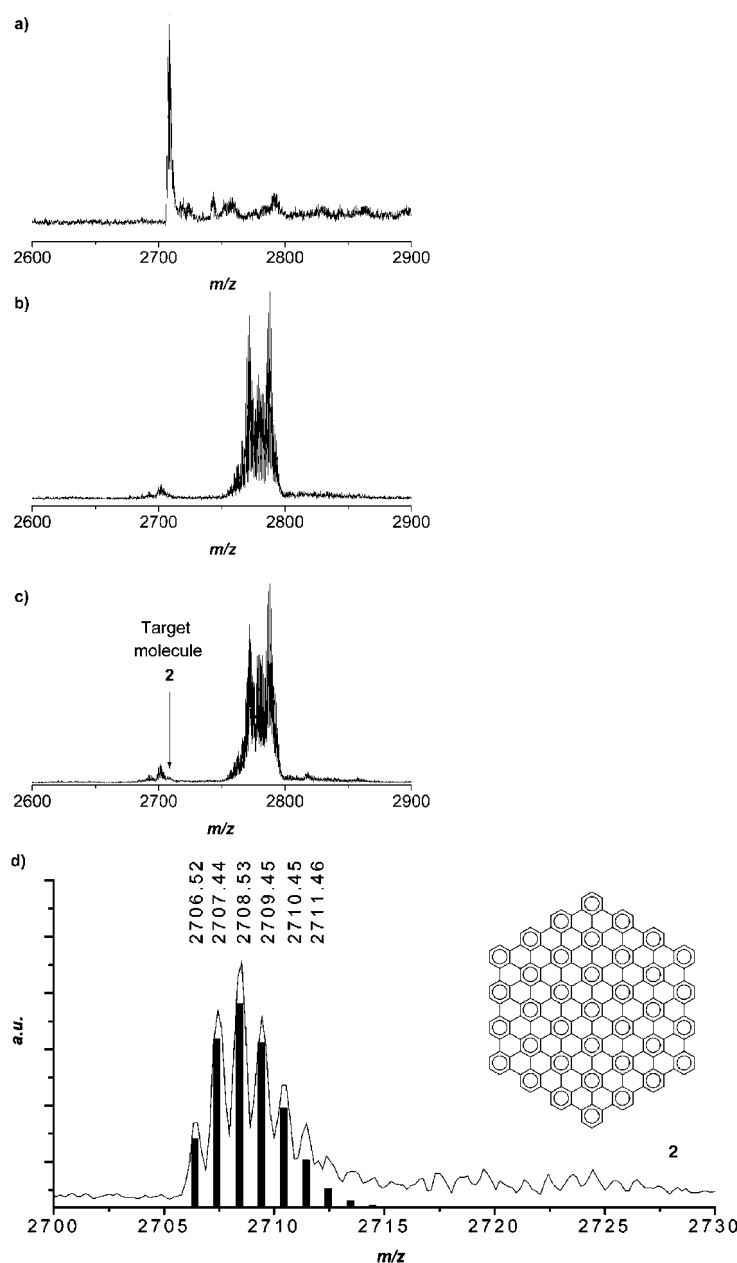


Figure 2. a) MALDI-TOF mass spectra obtained by applying the dry sample preparation with tetracyanoquinodimethane (TCNQ) as matrix to a) sample containing a significant amount of target molecule **2** (cyclodehydrogenation reaction with copper(II) triflate/aluminum(III) chloride); b) sample containing only side products (cyclodehydrogenation reaction with iron(III) chloride); c) mixture of the two preceding samples in a mass ratio 1:1; d) isotopically resolved MALDI-TOF spectrum of **2**. The bars underneath the signal represent the calculated spectrum for $C_{222}H_{42}$ (enlargement of spectrum 2).

intensities within the isotopic distribution of the perfect structure in Figure 2b would increase starting at the isotopic peak at $2708.5 \text{ g mol}^{-1}$ towards higher molecular weight and therefore destroying the agreement of measured and simulated signal intensities of the isotopic pattern of the pure molecular ion of structure **2**.

The fact that the progress and the efficiency of the cyclodehydrogenation reaction can now be monitored by MALDI-TOF mass spectrometry allowed us to optimize the experimental conditions for the cyclodehydrogenation reaction.

The conditions applied for cyclodehydrogenation are listed in Table 1. Best results were obtained using a combination of copper(II) triflate/aluminum(III) chloride in carbon disulfide as cyclodehydrogenation reagents. Experiment 1, with just one hour of reaction time, resulted in a broad distribution of products with various degrees of dehydrogenation. Increasing the reaction time to one day and the temperature to 30°C led

Table 1. Reaction conditions employed in the conversion from **1** to **2**.

Experiment no.	Reaction conditions
1	$\text{AlCl}_3/\text{Cu}(\text{SO}_3\text{CF}_3)_2/\text{CS}_2/\text{RT}/1 \text{ h}$
2	$\text{AlCl}_3/\text{Cu}(\text{SO}_3\text{CF}_3)_2/\text{CS}_2/30^\circ\text{C}/24 \text{ h}$
3	$\text{AlCl}_3/\text{Cu}(\text{SO}_3\text{CF}_3)_2/\text{CS}_2/30^\circ\text{C}/10 \text{ d}$
4	$\text{AlCl}_3/\text{Cu}(\text{SO}_3\text{CF}_3)_2/\text{CS}_2/\text{RT}/21 \text{ d}$
5	$\text{AlCl}_3/\text{CuCl}_2/\text{CS}_2/\text{RT}/10 \text{ d}$
6	$\text{FeCl}_3/\text{nitromethane}/\text{CH}_2\text{Cl}_2/\text{RT}/2 \text{ d}$

to an almost complete formation of **2** (Experiment 2), which turned out to be the best conditions.

Other experiments using copper(II) chloride/aluminum(III) chloride as oxidizing agents only lead to the increased formation of chlorinated and partially dehydrogenated side products next to our desired compound. Iron(III) chloride on the other hand only yielded partially cyclized products.

Special attention was also directed to a efficient removal of metal ions during the workup procedure. The precipitate was washed repeatedly and thoroughly with ammonium hydroxide to remove copper ions and with hydrochloric acid to remove aluminium ions. Analysis by transmission electron microscopy (TEM) using energy dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS) methods showed no significant amount of inorganic residues.^[25]

Previous work in our group has shown, that UV/Vis spectra of insoluble molecules, which are not accessible to solution spectroscopy, can be recorded as thin films smeared onto a quartz substrate.^[26] The UV/Vis spectrum of **2**, depicted in Figure 3, was measured by the same method. It shows

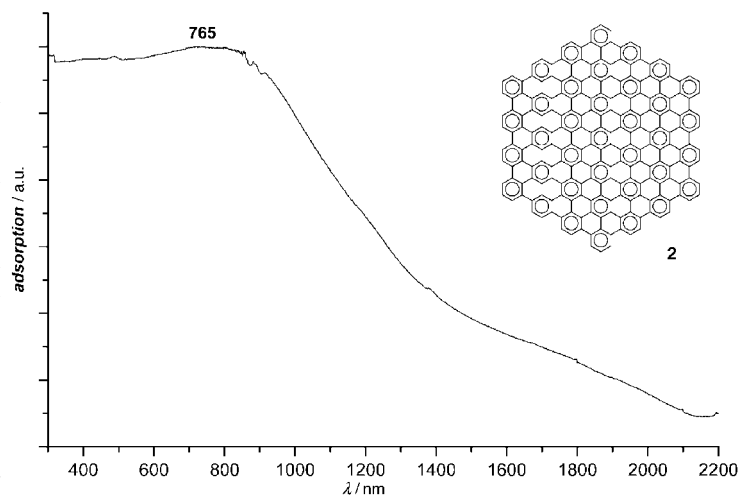


Figure 3. UV/Vis spectrum of **2**, measured of a thin film on a quartz substrate.

absorption over the complete visible range of the electronic spectrum, with a maximum of the band at approximately 765 nm. The broad and unstructured pattern of the band can be explained by the large number of electronic transitions taking place in this giant PAH, which leads to the continuum-like appearance in the visible range.

In summary, this successful synthesis of the so far largest polycyclic aromatic hydrocarbon represents an important step towards improved graphite model structures. It shows on one side the efficiency but on the other side also the limits of the synthetic concept employed, of planarizing large soluble oligophenylene precursors to polycyclic aromatic hydrocarbons. The removal of 108 hydrogens from one molecule represented a challenge in its own right but being able to analyze and characterize the resulting product precisely by MALDI-TOF mass spectrometry was also a prerequisite, showing how strongly synthetic chemistry depends on the advances of analytical methods.

Experimental Section

General methods: ^1H NMR and ^{13}C NMR were recorded in CDCl_3 and CD_2Cl_2 on a Bruker DPX 250, Bruker 300 AMX and Bruker 500 DRX 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. MALDI-TOF mass spectra were measured on a Bruker Reflex II-TOF spectrometer using a 337 nm nitrogen laser and 7,7,8,8-tetracyanoquinodimethane (TCNQ) as matrix. UV/Vis spectra were recorded on a Perkin–Elmer Lambda 9 machine. Elemental analysis was carried out on a Foss Heraeus Vario EL. Chemicals were obtained from Fluka, Aldrich and Strem and used as received.

Synthesis

4,4'-Di(trimethylsilylethynyl)tolane (5a): 4,4'-Dibromotolane (**4**; 10 g, 29 mmol), copper(I) iodide (1.13 g, 5.9 mol), triphenylphosphine (0.77 g, 2.93 mmol) and bis(triphenylphosphine)palladium(II) dichloride (0.7 g) were dissolved under inert atmosphere in piperidine (200 mL). Trimethylsilylacetylene (8.76 g, 89.3 mmol) was added and the reaction mixture was stirred for 5 h at 80 °C. After cooling, the solution was poured into CH_2Cl_2 (300 mL) and 6 M HCl (200 mL). The organic phase was separated, washed with saturated ammonium chloride solution and water, and dried over magnesium sulfate. After evaporating the solvent, the crude product was purified by column chromatography on silica gel with petroleum ether/ethylacetate (9:1) to afford **5a** (5.9 g, 93 %) as colorless crystals. M.p. 133 °C; ^1H NMR (200 MHz, CDCl_3): δ = 7.44 (s, 4H), 7.43 (s, 4H), 0.25 (s, 18H); ^{13}C NMR (125 MHz, CDCl_3): δ = 132.0, 131.5, 123.2, 123.1, 104.7, 96.5, 91.0, 0.0; FD-MS: m/z (%): 369.9 (100) [M] $^+$.

4,4'-Di(ethynyl)tolane (3): 4,4'-Di(trimethylsilylethynyl)tolane (**5a**; 2 g, 5.4 mmol) was dissolved in dimethylformamide (400 mL). After adding potassium fluoride (0.78 g), dissolved in water (1 mL), the reaction mixture was stirred for 1 h at room temperature. Then CH_2Cl_2 (400 mL) was added, the organic phase washed with 6 M HCl and saturated ammonium chloride solution and dried over MgSO_4 . After evaporating the solvent, the crude product was purified by column chromatography on silica gel with CH_2Cl_2 to afford **3** (1.0 g, 83 %) as colorless crystals. M.p. 188 °C; ^1H NMR (250 MHz, CDCl_3): δ = 7.47 (m, 8H), 3.17 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ = 132.6, 132.0, 123.9, 122.7, 91.3, 83.7, 79.5; FD-MS: m/z (%): 226.1 (100) [M] $^+$; elemental analysis calcd (%) for $\text{C}_{18}\text{H}_{10}$: C 95.55, H 4.45; found: C 93.43, H 3.75.

Di-(4',5',6'-triphenyl-1,1':2',1''terphenyl)acetylene (7): 4,4'-Di(ethynyl)tolane (**3**; 520 mg, 2.48 mmol) and tetraphenylcyclopentadienone (**6**; 1.9 g, 4.95 mmol) were dissolved in diphenyl ether (10 mL) and heated under an argon atmosphere for 11 h at 170 °C. After cooling heptane (100 mL) was added, the precipitate filtered and repeatedly washed with heptane. After drying in vacuo, **7** (1.54 g, 66 %) was afforded as pale yellow solid. M.p. > 300 °C; ^1H NMR (300 MHz, CDCl_3): δ = 7.40 (s, 2H), 7.22–6.60 (m,

48H); ^{13}C NMR (75 MHz, CDCl_3): δ = 157.7, 142.2, 142.0, 141.30, 140.27, 140.1, 131.9, 131.8, 131.6, 131.2, 130.3, 130.1, 128.0, 127.5, 127.3, 127.0, 126.7, 126.2, 125.8, 123.6, 119.3, 90.1; FD-MS: m/z (%): 938.1 (100) [M] $^+$; elemental analysis calcd (%) for $\text{C}_{74}\text{H}_{50}$: C 94.63, H 5.37; found: C 92.01, H 5.22.

1,2,3,4,5,6-Hexakis(4',5',6'-triphenyl-1,1':2',1''terphenyl)benzene (1) by cyclotrimerization: Di(4',5',6'-triphenyl-1,1':2',1''terphenyl)acetylene (**7**; 500 mg, 0.533 mmol) was dissolved in dioxane (100 mL) and degassed. Then dicobaltoctacarbonyl (118 mg, 0.35 mmol) was added under argon and the reaction mixture was refluxed for 15 h. After evaporating the solvent, the crude product was purified by column chromatography on silica gel with petroleum ether/ethylacetate (8:2) to afford **1** (355 mg, 71 %) as colorless solid. M.p. > 300 °C; ^1H NMR (500 MHz, CDCl_3): δ = 7.44 (s, 6H), 7.14–7.11 (m, 30H), 6.90–6.60 (m, 90H), 6.62 (d, 3J = 8.14 Hz, 12H), 6.36 (d, 3J = 8.14, 12H); ^{13}C NMR (125 MHz, CDCl_3): δ = 141.78, 141.67, 140.63, 140.54, 140.45, 140.08, 140.01, 139.92, 139.12, 139.00, 138.44, 138.13, 131.65, 131.56, 131.53, 131.17, 129.96, 128.33, 127.51, 126.85, 126.74, 126.53, 126.18, 125.51, 125.26; FD-MS: m/z (%): 2815.4 (100) [M] $^+$; elemental analysis calcd (%) for $\text{C}_{222}\text{H}_{150}$: C 94.63, H 5.37; found: C 94.05, H 5.83.

4,4'-Di-(triisopropylsilylethynyl)tolane (5b): 4,4'-Dibromotolane (**4**; 8 g, 23.8 mmol), copper(I) iodide (0.91 g, 4.8 mol), triphenylphosphine (1.25 g, 4.77 mmol) and bis(triphenylphosphine)palladium(II) dichloride (1.7 g, 2.3 mmol) were dissolved under inert atmosphere in triethylamine (140 mL) and toluene (70 mL). Triisopropylsilylacetylene (10.42 g, 57.13 mmol) were added and the reaction mixture was stirred for 5 h at 80 °C. After cooling, the solution was poured into CH_2Cl_2 (300 mL) and 6 M HCl (200 mL). The organic phase was separated, washed with saturated ammonium chloride solution and water, and dried over magnesium sulfate. After evaporating the solvent, the crude product was purified by column chromatography on silica gel with petroleum ether to afford **5b** (9.53 g, 74 %) as colorless solid. M.p. 108 °C; ^1H NMR (500 MHz, CD_2Cl_2): δ = 7.51 (m, 8H), 1.20 (m, 42H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 135.1, 134.5, 126.7, 125.9, 109.6, 96.3, 94.1, 21.8, 14.4; FD-MS: m/z (%): 538.2 (100) [M] $^+$; elemental analysis calcd (%) for $\text{C}_{36}\text{H}_{50}\text{Si}_6$: C 80.23, H 9.35; found: C 80.01, H 9.50.

1,2,3,4,5,6-Hexakis[4-(triisopropylsilylethynyl)phenyl]benzene (9): 4,4'-Di(triisopropylsilylethynyl)tolane (**5b**; 565 mg, 1.05 mmol) and 2,3,4,5-tetrakis[4-(triisopropylsilylethynyl)phenyl]-cyclopentadienone (**8**; 1.26 g, 1.15 mmol) were dissolved in diphenyl ether (7 mL) and heated under an argon atmosphere for 11 d at 200 °C. After cooling CH_2Cl_2 (10 mL) was added, the solution was slowly poured into methanol (100 mL) and the precipitate was filtered. The crude product was again dissolved in CH_2Cl_2 (10 mL) and precipitated in methanol (250 mL). After drying in vacuo, **9** (1.23 g, 72 %) was afforded as pale yellow solid. M.p. > 300 °C; ^1H NMR (200 MHz, CDCl_3): δ = 7.05 (d, J = 8.0 Hz, 12H), 6.73 (d, J = 8.0 Hz, 12H), 1.10 (m, 126H); ^{13}C NMR (50 MHz, CDCl_3): δ = 140.5, 140.4, 131.4, 121.2, 107.8, 90.8, 19.1, 11.8; FD-MS: m/z (%): 1617.3 (100) [M] $^+$; elemental analysis calcd (%) for $\text{C}_{108}\text{H}_{150}\text{Si}_6$: C 80.23, H 9.35; found: C 80.01, H 9.42.

1,2,3,4,5,6-Hexakis[4-ethynylphenyl]benzene (10): 1,2,3,4,5,6-Hexakis[4-(triisopropylsilylethynyl)phenyl]benzene (**9**; 400 mg, 0.25 mmol) was dissolved in THF (30 mL). To this solution tetrabutylammonium fluoride trihydrate (700 mg, 2.23 mmol) in THF (10 mL) was added. After 2 h, CH_2Cl_2 (500 mL) was added, the organic phase washed with water (2 $\times$ 200 mL) and dried over MgSO_4 . After evaporating the solvent, the crude product was purified by column chromatography on silica gel with petroleum ether/ CH_2Cl_2 (1:1) to afford **10** (150 mg, 89 %) as colorless solid. M.p. > 300 °C; ^1H NMR (200 MHz, CD_2Cl_2): δ = 7.04 (d, J = 8.0 Hz, 12H), 6.73 (d, J = 8.0 Hz, 12H), 3.00 (s, 6H); ^{13}C NMR (50 MHz, CD_2Cl_2): δ = 141.3, 140.6, 131.9, 131.5, 120.3, 84.0, 77.9; FD-MS: m/z (%): 678.3 (100) [M] $^+$; elemental analysis calcd (%) for $\text{C}_{54}\text{H}_{30}$: C 95.53, H 4.45; found: C 95.08, H 4.29.

1,2,3,4,5,6-Hexakis(4',5',6'-triphenyl-1,1':2',1''terphenyl)benzene (1) by Diels–Alder: 1,2,3,4,5,6-Hexakis[4-ethynylphenyl]benzene (**10**; 1.13 g, 1.67 mmol) and tetraphenylcyclopentadienone (**6**; 5.77 g, 15.00 mmol) were dissolved in diphenyl ether (40 mL) and heated under an argon atmosphere for 2 h at 190 °C. After cooling CH_2Cl_2 (30 mL) was added, the solution was slowly poured into methanol (500 mL) and the precipitate was filtered. After soxhlet extraction over night with pentane, **1** (4.2 g, 90 %) was afforded as white solid (for spectroscopical data see above).

C222-PAH (2): Copper(II) triflate (416 mg, 1.16 mmol) was dried completely under vacuum and heating. After cooling aluminium(III) chloride

(153 mg, 1.15 mmol) and dry CS₂ (50 mL) were added under an argon atmosphere. The mixture was suspended by intense stirring for 15 min, warmed to 30 °C and then 1,2,3,4,5,6-hexakis(4',5',6'-triphenyl-1,1':2',1''-terphenyl)-benzene (**1**; 10 mg, 3.55 × 10⁻³ mmol) dissolved in CS₂ (5 mL) was injected through a septum. After being stirred for 24 h, the reaction was quenched by adding methanol (50 mL). The residue was collected by filtration, washed successively with ammonium hydroxide solution, HCl, water, ethanol, CS₂, and CH₂Cl₂, and subsequently dried in vacuo to afford **2** (6 mg, 62%) as black powder. M.p. > 300 °C; MS (MALDI-TOF): *m/z*: calcd for C₂₂₂H₄₂: 2706.3; found: 2706.5 (see main text for detailed discussion).

Acknowledgement

The authors would like to thank Lileta Gherghel for measuring the UV/Vis spectra and for the fruitful discussions. Financial support of the European Commission (TMR-Programs SISITOMAS and DISCEL) is gratefully acknowledged.

-
- [1] E. Clar, *Aromatische Kohlenwasserstoffe—Polyzyklische Systeme*, Springer, Berlin, **1952**.
- [2] E. Clar, *The Aromatic Sextet*, Wiley, London, **1972**.
- [3] M. Zander, *Polycyclische Aromaten*, Teubner, Stuttgart, **1995**.
- [4] S. E. Stein, R. L. Brown, *J. Am. Chem. Soc.* **1987**, *109*, 3721.
- [5] S. E. Stein, R. L. Brown, *Pathways to Graphite: Properties of Very Large Polybenzoid Hydrocarbons*, Vol. 2, VCH, Weinheim, **1987**.
- [6] A. Halleux, R. H. Martin, G. S. D. King, *Helv. Chim. Acta* **1958**, *41*, 1177.
- [7] A. J. Berresheim, M. Müller, K. Müllen, *Chem. Rev.* **1999**, *99*, 1747.
- [8] P. Herwig, M. Müller, K. Müllen in NATO-ASI-Series C, *Mathematical and Physical Science*, Vol. 499 (Ed.: J. Michl), Kluwer, Dordrecht, **1997**, p. 167.
- [9] V. S. Iyer, M. Wehmeier, J. D. Brand, M. A. Keegstra, K. Müllen, *Angew. Chem.* **1997**, *109*, 1675; *Angew. Chem. Int. Ed.* **1997**, *36*, 1604.
- [10] V. S. Iyer, K. Yoshimura, V. Enkelmann, R. Epsch, J. P. Rabe, K. Müllen, *Angew. Chem.* **1998**, *110*, 2843; *Angew. Chem. Int. Ed.* **1998**, *37*, 2696.
- [11] F. Morgenroth, K. Müllen, *Tetrahedron* **1997**, *53*, 15349.
- [12] M. Müller, H. Mauermann-Düll, M. Wagner, V. Enkelmann, K. Müllen, *Angew. Chem.* **1995**, *107*, 1648; *Angew. Chem. Int. Ed.* **1995**, *34*, 1583.
- [13] M. Müller, V. S. Iyer, C. Kübel, V. Enkelmann, K. Müllen, *Angew. Chem.* **1997**, *109*, 1680; *Angew. Chem. Int. Ed.* **1997**, *36*, 1607.
- [14] U. M. Wiesler, A. J. Berresheim, F. Morgenroth, G. Lieser, K. Müllen, *Macromolecules* **2001**, *34*, 187.
- [15] R. Diercks, K. P. C. Vollhardt, *J. Am. Chem. Soc.* **1986**, *108*, 3150.
- [16] K. P. C. Vollhardt, *Acc. Chem. Res.* **1977**, *10*, 1.
- [17] K. P. C. Vollhardt, *Angew. Chem.* **1984**, *106*, 525; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 539.
- [18] H. A. Dieck, F. R. J. Heck, *Organomet. Chem.* **1975**, *93*, 259.
- [19] L. Cassar, *J. Organomet. Chem.* **1975**, *93*, 253.
- [20] S. Takahashi, Y. Koroyama, K. Sonogashira, N. Hagihara, *Synthesis* **1980**, 627.
- [21] R. Bauer, U. Wiesler, A. Berresheim, V. Enkelmann, K. Müllen, unpublished results.
- [22] K. Yoshimura, L. Przybilla, S. Ito, J. D. Brand, M. Wehmeier, H. J. Räder, K. Müllen, *Macromol. Chem. Phys.* **2001**, *202*, 215.
- [23] L. Przybilla, J. D. Brand, K. Yoshimura, J. Räder, K. Müllen, *Anal. Chem.* **2000**, *72*, 4591.
- [24] H. J. Räder, W. Schrepp, *Acta Polymerica* **1998**, *49*, 272.
- [25] C. Kübel, Ph. D. thesis, Johannes-Gutenberg-University, Mainz, Germany, **1998**; C. Kübel, K. Eckhardt, V. Enkelmann, G. Wegner, K. Müllen, *J. Mater. Chem.* **2000**, *10*, 879.
- [26] F. Dötz, J. D. Brand, S. Ito, L. Gherghel, K. Müllen, *J. Am. Chem. Soc.* **2000**, *122*, 7698.

Received: June 22, 2001

Revised: November 14, 2001 [F3361]