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## Polybenzoid C<sub>54</sub> Hydrocarbons: Synthesis and Structural Characterization in Vapor-Deposited Ordered Monolayers\*\*

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Basic research aimed at developing molecular electronic devices tends to focus more and more on thin-if possible epitaxially ordered-organic films. Such films are produced preferentially under high-vacuum conditions by vapor deposition onto well-characterized substrate surfaces, with careful control of deposition rate, substrate temperature, and film thickness. This development requires organic compounds that vaporize without decomposition, but for applications they must also have a negligible vapor pressure at room temperature, that is, they must have strong intermolecular binding forces. Moreover, suitable molecules must have a shape and symmetry that allows two-dimensional close packing.<sup>[1, 2]</sup> With the aim of producing adsorbate films composed of molecules that resemble larger sections of graphite layers, we here describe a structure-specific synthesis of the extended polybenzoid hydrocarbons 3 and 13 and report the study of the ordered adsorbate films of 3 by electron diffraction analysis and scanning tunneling microscopy (STM). Evaluation of the shape of larger molecules by ultrahigh-resolution STM and special diffraction methods becomes increasingly important as their characterization by classical spectroscopic methods is impaired by decreasing solubility.

Polybenzoid arenes that can be represented by at least one Kekulé form that consists only of electron sextets as a mesomeric limiting structure<sup>[3]</sup> can be obtained—as has been described previously—by a cycloaddition-cyclodehydrogenation sequence (Scheme 1).<sup>[4]</sup> Starting from the ene-diene component **1**, a double intramolecular Diels–Alder cycloaddition and dehydrogenation leads to the phenylene-bridged bistriphenylene derivative **2**, which exists as two rotamers **2 a** and **2 b**. Therefore the synthesis sequence described<sup>[4]</sup> must lead to the two isomers **3** and **4** as cyclodehydrogenation products.

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Scheme 1. a) 100 °C in toluene. b) DDQ; 140 °C in 1,1,2,2-tetrachloroethane. c) AlCl<sub>3</sub>/CuCl<sub>2</sub>; room temperature in carbon disulfide. For spectroscopic data see Table 1.

Table 1. Physical and spectroscopic data for 3, 5, 7, 10, 12, and 13.

**3**: MS (FD, 8 kV): m/z (%): 670 (100) [ $M^+$ ], 335 (21) [ $M^{2+}$ ]; MS (LD-TOF): m/z (%): 670 (100) [ $M^+$ ] (calibrated with C<sub>60</sub> and C<sub>70</sub>); UV/Vis (vapor-deposited film on quartz):  $\lambda_{max} = 202$ , 241, 285, 392, 486, 521 nm; m.p. > 300 °C

5: <sup>1</sup>H NMR (500 MHz, [D<sub>2</sub>]1,1,2,2-tetrachloroethane, 30 °C):  $\delta = 7.89$  (d, <sup>3</sup>*J*(H,H) = 7.9 Hz, 2 H; H6, H6", terphenyl, outer), 7.65 (s, 2 H; H3', H6', terphenyl, central), 7.44–7.32 (m, 8 H), 7.27–7.08 (m, 18 H), 6.97 (d, <sup>3</sup>*J*(H,H) = 16.3 Hz, 2 H; olefinic AB system). 6.93 (m<sub>e</sub>, 2 H; BC, olefinic ABCD system), 6.82 (d, <sup>3</sup>*J*(H,H) = 16.3 Hz, 2 H; olef. AB system), 6.77 (m<sub>e</sub>, 2 H; BC, olefinic ABCD system), 6.56 (d, <sup>3</sup>*J*(H,H) = 15.4 Hz, 2 H; AD, olefinic ABCD system); MS (FD, 8 kV): *m/z* (%): 690 (100) [*M*<sup>+</sup>]; m.p. (decomp.) > 80 °C

7: <sup>1</sup>H NMR (500 MHz,  $[D_2]1,1,2,2$ -tetrachloroethane, 130 °C):  $\delta = 8.94$  (s, 2H; H1, H1'), 8.58 (d, <sup>3</sup>*J*(H,H) = 8.5 Hz, 2H; H6, H6'), 8.47 (d, <sup>3</sup>*J*(H,H) = 7.9 Hz, 2H; H5, H5'), 7.63 (d, <sup>3</sup>*J*(H,H) = 8.4 Hz, 2H; H7, H7'), 7.51 (dd, <sup>3</sup>*J*(H,H) = 7.7 Hz, <sup>3</sup>*J*(H,H) = 7.2 Hz, 2H; H4, H4'), 7.34–7.28 (m, 8H; H3, H3', 4H *m*-phenyl-1, 2H *p*-phenyl-1), 7.24 (d, <sup>3</sup>*J*(H,H) = 7.2 Hz, 4H; 4H *o*-phenyl-1), 7.17–7.13 (m, 8H; H2, H2', 4H *m*-phenyl-2, 2H *p*-phenyl-2), 6.99 (d, <sup>3</sup>*J*(H,H) = 7.5 Hz, 4H; 4H *o*-phenyl-2); MS (FD, 8 kV): *m/z* (%): 682 (100) [*M*<sup>+</sup>]; m.p. > 300 °C

**10**: (crude mixture) MS (FD, 8 kV): m/z (%): 690 (100) [ $M^+$ ]

**12**: <sup>1</sup>H NMR (500 MHz, [D<sub>2</sub>]1,1,2,2-tetrachloroethane, 130 °C):  $\delta = 9.79$  (s, 2H; H1, H1'), 8.92 (d, <sup>3</sup>*J*(H,H) = 8.4 Hz, 2H; H6, H6'), 8.78 (d, <sup>3</sup>*J*(H,H) = 8.4 Hz, 2H; H2, H2'), 7.74 (d, <sup>3</sup>*J*(H,H) = 8.4 Hz, 2H; H7, H7'), 7.62 (d, <sup>3</sup>*J*(H,H) = 7.9 Hz, 2H; H5, H5'), 7.49 (dd, <sup>3</sup>*J*(H,H) = 8.3 Hz, <sup>3</sup>*J*(H,H) = 7.6 Hz, 2H; H3, H3'), 7.21–7.13 (m, 16H; 4H *o*-phenyl-1, 4H *m*-phenyl-1, 2H *p*-phenyl-1, 4H *m*-phenyl-2, 2H *p*-phenyl-2), 7.08 (d, <sup>3</sup>*J*(H,H) = 7.9 Hz, 4H; 4H *o*-phenyl-2), 7.01 (dd, <sup>3</sup>*J*(H,H) = 7.6 Hz, 2H; H4, H4'); MS (FD, 8 kV): *m/z* (%): 682 (100) [*M*<sup>+</sup>], 341 (16) [*M*<sup>2</sup>+]; m.p. > 300 °C

**13**: MS (FD, 8 kV): m/z (%): 674 (100) [ $M^+$ ]; MS (LD-TOF): m/z (%): 674 (100) [ $M^+$ ] (calibrated with C<sub>60</sub> and C<sub>70</sub>); m.p. > 300 °C

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In view of this problem, we decided on a new synthesis route that is structure-specific. If the 1,4-di(2'-iodo-*trans*-styryl)benzene<sup>[4]</sup> needed to form the ene-diene component 1 as the central building block is replaced by 1,4-dibromo-2,5-di-*trans*styrylbenzene (8), double hetero-aryl-aryl coupling with 9 leads to the *para*-terphenyl derivative 5. This opens up a new cycloaddition-cyclodehydrogenation route (Scheme 2) which, in contrast to the earlier route (Scheme 1), no longer permits rotation of the two outer phenyl rings about the central *para*-terphenyl unit after the double intramolecular [4+2] cycloaddition to 6. Consequently, the formation of a different isomer of the cyclodehydrogenation product 3 is prevented.



Scheme 2. a) Tetrakis(triphenylphosphane)palladium(0); reflux in toluene/ethanol/ water mixture (50.25/25 vol%); exclusion of light. b) 135 $^{\circ}$ C in 1,1,2,2-tetrachloroethane. c) DDQ; 135 $^{\circ}$ C in 1,1,2,2-tetrachloroethane. d) AlCl<sub>3</sub>/CuCl<sub>2</sub>; room temperature in carbon disulfide. For spectroscopic data see Table 1.

Unlike the ene-diene component 1, the *para*-terphenyl derivative 5, which takes part in the double intramolecular Diels-Alder reaction, is not synthesized by aryl-aryl coupling involving zincates, but from boronates, in accordance with the method of Suzuki.<sup>[5]</sup> Here, the distyrylbenzene 8 is treated with 2-(4'-phenyl-*trans*,*trans*-buta-1',3'-dienyl)phenylboronic acid (9) in 92% yield to form 5. The formation of 8 proceeds very readily by a double Wittig reaction of benzaldehyde with  $\alpha, \alpha'$ -bis(triphenylphosphonio)-2,5-dibromo-*para*-xylene dibromide, and the preparation of the boronic acid 9 proceeds via the

known 2'-iodo-1,4-diphenyl-*trans*, *trans*-buta-1,3-diene<sup>[4]</sup> by lithiation with *n*-butyllithium followed by transmetalation with the trimethyl ester of boric acid.

In the aryl-aryl coupling according to Suzuki to give 5, no intramolecular [4+2] cycloaddition takes place even after a reaction time of several days in a mixture of toluene, ethanol, and water (50:25:25 vol%) at boiling point (about 100 °C). However, the double intramolecular Diels-Alder reaction of 5 takes place quantitatively in  $[D_2]1,1,2,2$ -tetrachloroethane at 135 °C within 1 h (monitored by NMR). On the laboratory scale, the yield for the double [4+2] cycloaddition is 98%. The mixture of isomers of 6 caused by of the formation of eight new chirality centers is not separated. Instead, dehydrogenation of the cyclohexene structures of the crude mixture of 6 formed by the cycloaddition is carried out with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). All the isomers lead to the tetraphenyltetrabenzoanthracene derivative 7 (96% yield).

The oxidative cyclodehydrogenation of 7 is carried out with copper dichloride and aluminum trichloride in carbon disulfide at room temperature (99% yield). The removal of twelve hydrogen atoms can be demonstrated by field desorption (FD) and laser desorption time-of-flight (LD-TOF) mass spectrometry, which show that six new aryl-aryl bonds are formed, with complete planarization of the four phenyl substituents of 7 in the plane of the tetrabenzoanthracene structure. However, unlike the cyclization of **2**, this leads exclusively to the formation of the polybenzoid arene tribenzo-[*hi*, *o*, *uv*]triphenylene[2,1,12,11-*bcdef*]ovalene (**3**)<sup>[6]</sup> with  $D_{2p}(2/mmm)$  symmetry.

The versatility of the cycloaddition-cyclodehydrogenation route described here is shown by the ability to form not only the *para*-terphenyl derivative **5** but also the *para*-terphenyl derivative **10** in which the positions of the styryl and phenylbutadienyl substituents are reversed relative to those in the ene-diene compound **5** (Scheme 3).

The preparation of 10 is also achieved by a double heteroaryl-aryl coupling of the Suzuki type, in which 1,4-dibromo-2,5-di(4'-phenyl-*trans,trans*-buta-1',3'-dienyl)benzene (14) is treated with *trans*-stilbene-2-boronic acid 15. The formation of the dibromobenzene 14 proceeds in analogy to the synthesis of 8 by the double Wittig reaction of *trans*-cinnamic aldehyde with  $\alpha, \alpha'$ -bis(triphenylphosphonio)-2,5-dibromo-*para*-xylene dibromide, and the preparation of the stilbeneboronic acid 15 proceeds in analogy to the synthesis of 9 from 2-iodo-*trans*-stilbene.

Because of its low solubility in the usual solvents, the crude product 10 of the Suzuki reaction is not purified by column chromatography. Instead, it is separated from the inorganic palladium catalyst residues by a Soxhlet extraction with 1,1,2,2tetrachloroethane, during which the double intramolecular [4+2] cycloaddition of 10 also takes place. The mixture of isomers of 11 is dehydrogenated with DDQ without prior purification (as in the case of the mixture of isomers of 6), to form the tetraphenyltetrabenzoanthracene derivative 12, which is then recrystallized several times from 1,1,2,2-tetrachloroethane (53% yield over all reactions).<sup>[7]</sup>

In the oxidative cyclodehydrogenation of 12 with copper dichloride and aluminum trichloride (98% yield), only eight hydrogen atoms can be removed because of the positions of the four phenyl substituents, so that only four new aryl-aryl bonds are formed, as can be shown by LD-TOF mass spectrometry. As in the synthesis of the arene 3, the intramolecular Diels-Alder reaction prevents the rotation of the outer phenyl rings of the central *para*-terphenyl unit of 10 after the first cycloaddition stage. The synthesis therefore leads exclusively to the formation of the polybenzoid hydrocarbon 13, which has  $C_{2h}$  (2/m) symmetry.

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Scheme 3. a) Tetrakis(triphenylphosphane)palladium(o); reflux in toluene/ethanol/ water mixture (50/25/25 vol%); exclusion of light. b) 135°C in 1,1,2,2-tetrachloroethane. c) DDQ; 135°C in 1,1,2,2-tetrachlorethane. d) AlCl<sub>3</sub>/CuCl<sub>2</sub>; room temperature in carbon disulfide. For spectroscopic data see Table 1.

For structural characterization of **3** and for the production of thin films by vacuum vapor deposition, the crude product was first subjected to a fractionating high vacuum sublimation in a fused silica tube using a temperature step program. At an evaporation temperature of 600 °C, a bright orange, microcrystalline material (maximum crystal size  $100 \times 10 \times 1 \ \mu\text{m}^3$ ) deposited, which displayed an orange-red fluorescence in high yield when irradiated with UV light.

For investigations by low-energy electron diffraction (LEED), a monomolecular film (approximately 3 Å thick) of **3** was deposited at a rate of 20 Å h<sup>-1</sup> onto a freshly cleaved (0001) surface of a single crystal of the layer chalcogenide MoS<sub>2</sub> (molybdenite) pretreated by heating to 450 °C for about 5 min in ultrahigh vacuum (UHV). Film thickness was monitored by a vibrating quartz balance. Only with very low energy electrons (in the region of 10 eV) could useful electron diffraction diagrams be obtained displaying the very small reciprocal lattice vectors 0.071(3) and 0.105(3) Å<sup>-1</sup>. Taking into account the directions of the latter and their multiplication (induced by the substrate symmetry, with the consequence of multiple domain formation), the very large unit mesh a = 14.2(5) Å,  $p = 84.9(1.4)^{\circ}$  in direct space was derived, with an area of 201 Å<sup>2</sup>. The appearance of discrete diffraction spots

indicates a well-ordered growth of 3 on the MoS<sub>2</sub> substrate. The large unit mesh with an area that corresponds closely to the (estimated) van der Waals area of the planar molecule 3 indicates a close-packed arrangement (Z = 1) of molecules that lie flat (cf. Ref. [8]). In situ thermodesorption spectroscopy with detection by mass spectrometry showed that the molecular mass of the molecules that could be resublimed from the monomolecular film was 670 u, in agreement with the formula  $C_{54}H_{22}$ .

For direct investigation of the molecular size and shape by scanning tunneling microscopy (STM) (see Ref. [2]), a suitably prepared sample was removed from the UHV and scanned in air. The STM images obtained thus clearly showed molecules of rhombic shape and of the expected size (Fig. 1). Here, too, the

molecules were found to lie flat on the substrate surface. The intermolecular distances in the STM image are, however, somewhat larger than those that correspond to the close molecular packing concluded from the LEED patterns. One should be aware, however, that the LEED image reflects the dominant packing across a large surface area (about  $1 \text{ mm}^2$ ), whereas the STM image gives very local information. It is known from STM investigations of monolayers of other systems that competition between intermolecular interactions (tending to give



Fig. 1. STM image of a nominally 3 Å thick vapor-deposited layer of 3 on a (0001) face of a MoS<sub>2</sub> single crystal, taken in constant height mode (bias:  $\pm 1.8$  V at the sample; tunneling current: 90 pA; image area: 100 Å × 100 Å). A regular arrangement of rhombic molecules can be discerned.

close pack-ing) and strongly ordering local interactions with the substrate can lead to more than one structure.<sup>[9]</sup>

With the compound 3, we were successful in synthesizing a large aromatic molecule with remarkable thermal stability, high fluorescence yield, and high symmetry that allows dense surface coverage; these properties render 3 an extremely useful and promising model system for further investigations aimed at the development of a molecular electronics system on the basis of ultrathin epitaxial organic films.

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