the sulfate solution into neat solvent and subtracting this data from that of the host–guest titration. The data was analyzed and fit by the Origin software (MicroCal).[12]

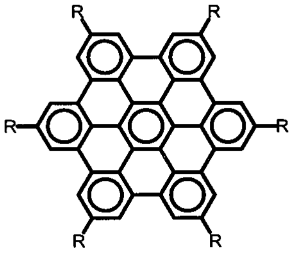
[11] Close inspection of the multidimensional error hypersurface of the NMR binding data in the reaction of **1** and sulfate ions revealed no minimum that would justify accounting for a 1:2 host–guest complex.[6] Recalculation of the primary data with host dimerization and 1:1 host–guest complexation incorporated gave $K_a = 680\ \text{M}^{-1}$, which is in reasonable agreement with the present determination conducted at a slightly higher temperature.

[12] T. Wiseman, S. Williston, L.-N. Lin, *Anal. Biochem.* **1989**, *179*, 131–137.

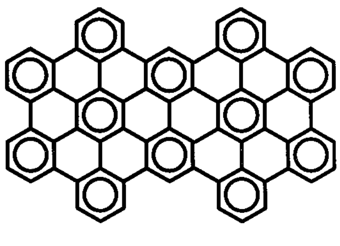
A Soluble C_{60} Graphite Segment[**]

Vivekanantan S. Iyer, Kimihiro Yoshimura,
Volker Enkelmann, Rebekka Epsch, Jürgen P. Rabe,
and Klaus Müllen[*]

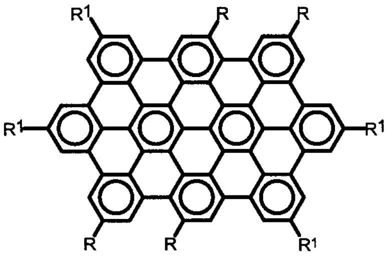
We recently described an efficient cycloaddition-cyclodehydrogenation route to obtain very large polycyclic aromatic hydrocarbons (PAHs) such as **1a** (C_{42}) and **2** (C_{72}).[1–3] Owing to the extremely low solubility of the parent compounds, the soluble hexa-*n*-alkyl derivatives **1b** were synthesized in order to perform complete spectroscopic characterization of these compounds. Discotic meso phases with stacked discs were thereby observed. Physisorption of **1b** onto substrate surfaces gave rise to the formation of monomolecular adsorbate layers, which were characterized by scanning tunneling microscopy (STM).[1–3]



1a: R = H
1b: R = *n*-alkyl



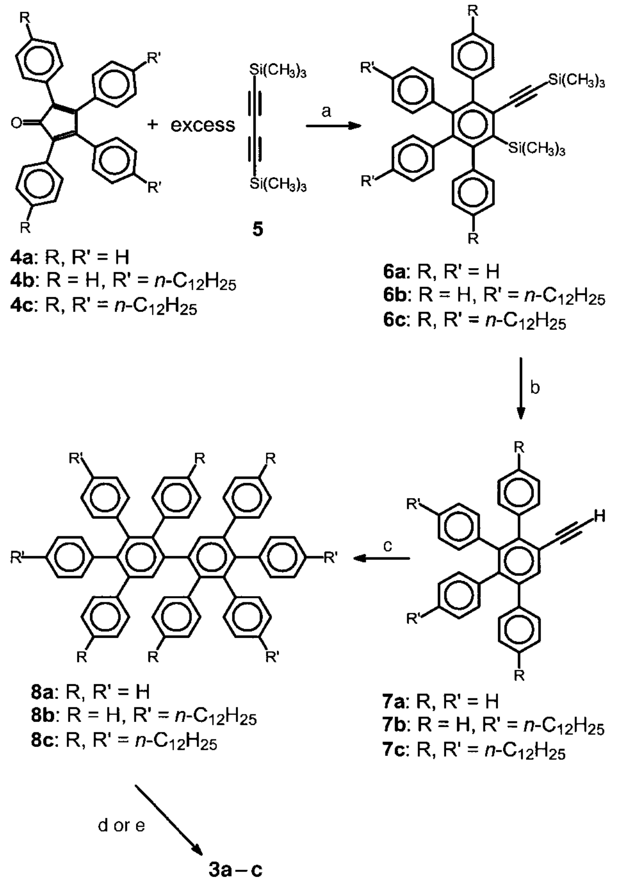
2



3a: R, R1 = H
3b: R = H, R1 = *n*-$C_{12}H_{25}$
3c: R, R1 = *n*-$C_{12}H_{25}$

A comparable protocol is impossible with larger discs (e.g. C_{72}, C_{78}, C_{96}, C_{132}) since the synthetic strategies are not readily transferable to the respective *n*-alkyl derivatives. We describe here the remarkable C_{60} hydrocarbon **3a**,[4, 5] which, as a homologue of **1a**, is predicted to be the most thermodynamically stable of the $C_{60}H_{22}$ PAH isomers.[6] The synthesis of **3a** in gram or even decagram quantities is surprisingly straightforward. More importantly, however, soluble tetra- and octa-*n*-alkyl derivatives (**3b** and **3c**, respectively) of this large disk can be prepared, and the formation of monolayers from solution is possible even with discs of that size. This could prove to be a central step for the electronic characterization of molecular graphite models.

Following the construction principle reported by our group for larger PAHs, an oligophenyl precursor of **3** is available by a twofold Diels–Alder reaction between butadiyne and tetraphenylcyclopentadienone (**4a**, Scheme 1). The reaction of **4a** with a large excess of 1,4 bis(trimethylsilyl)butadiyne (**5**)—both starting materials are commercially available—resulted in the formation of **6a** in nearly quantitative yield.



Scheme 1. a) **4a**, **4b**, or **4c** (1 equiv), 250 °C, Ph_2O, 3–6 h, ca. 100%; b) $n\text{Bu}_4\text{N}^+\text{F}^-$ (10 equiv), THF, **6a**: 85%, **6b**: 86%, **6c**: 88%; c) **4a**, **4b**, or **4c** (1.1 equiv), 250 °C, Ph_2O, 3–6 h, ca. 100%; d) $Cu(OSO_2CF_3)_2$ (60 equiv), $AlCl_3$ (60 equiv), 25 °C, CS_2, **3a**: >90%; e) $FeCl_3$, CH_3NO_2, CH_2Cl_2, Ar, 15–30 min, **1a**: >80%, **3b**: 75%.

---

[*] Prof. Dr. K. Müllen, Dr. V. S. Iyer, K. Yoshimura,
Priv.-Doz. Dr. V. Enkelmann
Max-Planck-Institut für Polymerforschung
Ackermannweg 10, D-55128 Mainz (Germany)
Fax: (+49) 6131-379-350
E-mail: muellen@mpip-mainz.mpg.de

R. Epsch, Prof. Dr. J. P. Rabe
Institut für Physik der Humboldt-Universität, Berlin (Germany)

[**] This work was supported by the Volkswagen-Stiftung, the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie, and the Commission of the European Union. V.S.I. thanks the Max-Planck-Gesellschaft for a scholarship, and K.Y. thanks Canon Inc., Tokyo, for the sabbatical and the financial support of his stay.

Monoadduct **6a** was desilylated with an excess of tetrabutylammonium fluoride to afford **7a** (85%), which subsequently underwent another Diels–Alder reaction with **4a** followed by loss of the CO group to give **8a** (99%). The tetra-*n*-dodecyl (**8b**) and octa-*n*-dodecyl derivatives (**8c**) were prepared analogously from **8a** and the corresponding substituted cyclopentadienones[7] **4b** and **4c** (Scheme 1 and Table 1). All oligophenyls **8** are readily soluble in organic solvents. The crystal structure of **8a** (Figure 1) clearly shows that the phenyl substituents are strongly twisted with respect to the central biphenyl unit (twisting angle = 61°). Furthermore, the outer phenyl rings are in close proximity, which is necessary for the cyclodehydrogenation leading to the planar structure **3a**.[8]

Table 1. Selected spectroscopic data[a] of **3a**, **3c**, and **8a**.

3a: MS (LD-TOF): *m/z* (%): 746 (0.6), 745 (5), 744 (20), 743 (65), 742 (100) [M^+] (calcd for $C_{60}H_{22}$: 746.0 (0.7), 745.18 (4.7), 744.17 (22), 743.17 (67), 742.17 (100)); UV/Vis (1,1,2,2-tetrachloroethane): λ_{max} = 290, 425, 450 (shoulder), 550, 590 (shoulder)

3c: MS (MALDI-TOF): *m/z* (%): 2095 (0.5), 2094 (2), 2093 (8), 2092 (22), 2091 (50), 2090 (88), 2089 (100), 2088 (55) [M^+] (calcd for $C_{156}H_{214}$: 2094.69 (0.5), 2093.69 (2.2), 2092.69 (7.6), 2091.68 (22.2), 2090.68 (51.1), 2089.68 (87.8), 2088.67 (100), 2087.67 (56.6)); ^1H NMR (500 MHz, [D$_4$]1,2-dichlorobenzene, 170 °C): $\delta = 9.84$ (s, 2H), 9.55 (s, 2H), 9.42 (m$_c$, 10H), 4.44 (m$_c$, 4H), 3.75 (m$_c$, 12H), 2.73 (m$_c$, 4H), 2.57 (m$_c$, 12H), 2.12–1.10 (m, 168H); UV/Vis ($CHCl_3$): λ_{max} (ε) = 276 (50800), 290 (45600, shoulder), 410 (67700), 450 (28200, shoulder), 482 (12900), 510 (6700)

8a: MS (FD, 8 kV): *m/z* (%): 762.1 (100) [M^+] (calcd for $C_{60}H_{42}$: 762.3); ^{13}C NMR (125 MHz, [D$_2$]1,1,2,2-tetrachloroethane, 140 °C): $\delta = 142.28$, 141.57, 140.79, 140.42, 140.16, 140.03, 139.74, 139.17, 132.88, 131.77, 130.12, 127.44, 126.77, 126.52, 126.08, 125.61, 125.46, 125.19

[a] All LD-TOF and MALDI-TOF mass spectra were calibrated with samples of C_{60} and C_{70} fullerenes. The matrix for the MALDI-TOF measurements was 9-nitroanthracene. FD = field desorption, MALDI = matrix-assisted laser desorption/ionization.

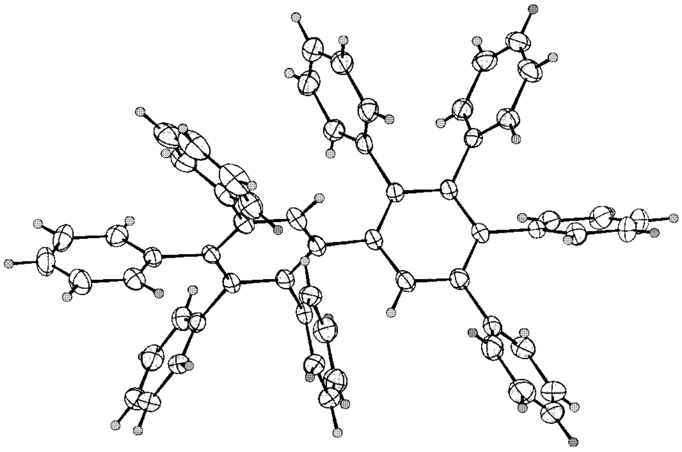


Figure 1. Crystal structure of **8a**.

The cyclodehydrogenation of **8a** with copper(II) trifluoromethanesulfonate and aluminum(III) chloride in carbon disulfide proceeded smoothly and led to **3a** (>90%). High-resolution laser desorption time-of-flight mass spectrometry (LD-TOF) of **3a** (*m/z* = 742, see Table 1 for isotope distribution) was performed and proved the loss of exactly 20 hydrogen atoms. Similar to other large PAHs, the crude burgundy sample of **3a** does not yield a defined X-ray powder diffractogram, which suggests the amorphous character of the solid. Quick sublimation of the crude product under ultrahigh vacuum at 680 °C yielded pure **3a** as a light orange powder[9] which was sufficiently soluble in 1,1,2,2-tetrachloroethane, and a UV/Vis spectrum was obtained (Table 1).

Mass spectrometric studies of **3a** at higher laser intensities revealed a fragment ion of the formula $C_{54}H_{22}^+$ with a relative intensity (based on [**3a**]$^+$) of up to 45%. The fact that no charged C_6 or C_3 fragments could be observed suggests that **3a** or [**3a**]$^+$ photodegraded to $C_{54}H_{22}^+$ and neutral fragments.[10]

Attempts to perform the analogous cyclodehydrogenation of **8b** resulted in unidentified product mixtures because of the inherently high acidity of the reaction mixture. The use of iron(III) chloride allowed the cyclodehydrogenation to occur under significantly milder conditions and without side reactions (such as alkyl group migrations or chlorinations). Hydrogen chloride was continuously removed from the reaction mixture by a steady flow of argon. Under these conditions, **3b** was obtained from **8b** in 75% yield. The high-resolution mass spectrum of **3b** is shown in Figure 2.

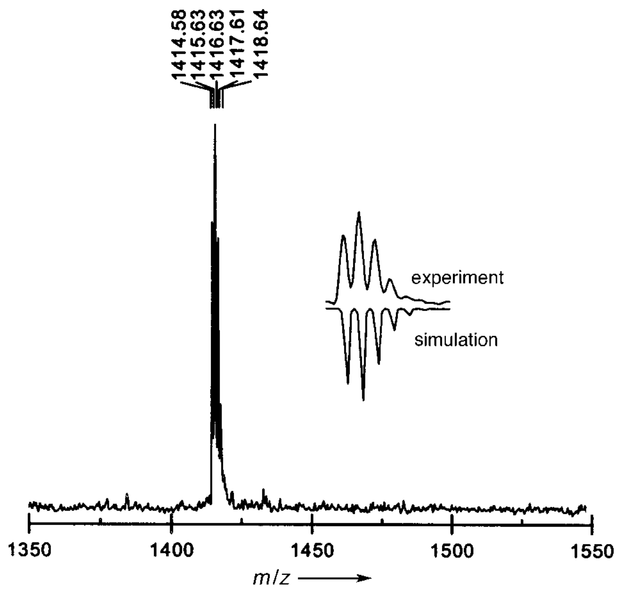


Figure 2. MALDI-TOF mass spectrum of **3b** (molecular-ion area). The insert compares the experimental and the calculated M^+ signal of **3b**.

To further enhance the solubility of **3**, it was intended to synthesize the octa-*n*-alkyl compound **3c**. However, the method successful for the synthesis of **3b** yielded only partially cyclodehydrogenated as well as partially cyclized, chlorinated products rather than **3c**.[11] To our surprise, experiments to dehalogenate the product mixture with potassium in tetrahydrofuran led to completely cyclized octa-*n*-alkyl C_{60} compound **3c** (60%). UV/Vis, mass, and ^1H NMR spectra were obtained for the highly soluble **3c** (Table 1, Figure 3a, b). The spatially most confined aryl protons (H_a) in the bay region show a singlet at $\delta = 9$, and the H_b protons show a singlet at $\delta = 9.55$. The broadening of

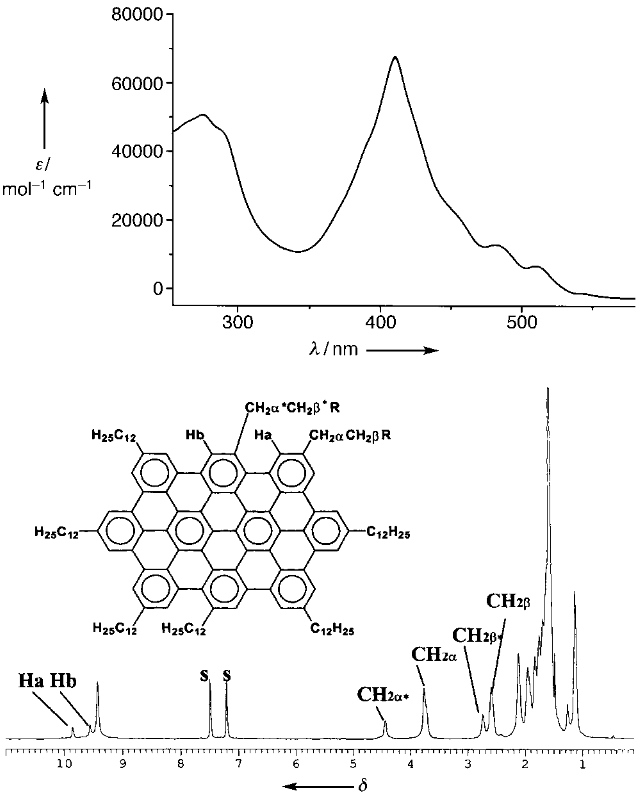


Figure 3. a) UV/Vis spectrum of a solution (1.4×10^{-5} M) of **3c** in chloroform. b) ^{1}H NMR spectrum of **3c** (2 mg) in [D_4]1,2-dichlorobenzene (1.5 mL) at 170 °C.

the signal presumably arises from aggregates of the large molecular discs that may exist even at the high temperatures used to record the spectrum. This clearly demonstrates that the characterization of very large PAHs (size in the nanometer range) reaches the limits of the standard methods in organic chemistry.

As a result of the improved solubility of **3b** and **3c**, it was possible for the first time to prepare highly ordered monolayers (2D crystal) of PAHs larger than **1**. Figures 4a and 5a show STM images of monolayers from **3b** and **3c** which were obtained in situ at the interface between solutions in 1,2,4-trichlorobenzene and the basal surface of graphite. The positions of the aromatic discs correspond to areas of high tunneling currents.[12, 13] The alkyl chains could not be resolved, which is an indication of high conformational mobility of the side chains at room temperature. Both **3b** and **3c** show a double-row structure; however, the orientation of the discs of **3b** alternates from row to row (fishbone pattern), whereas the orientation of **3c** is maintained within the rows and only the distances between them alternate.[14] The parameters of the unit cell of **3b**[15] correspond to a surface area which is in close agreement to the value calculated from the van der Waals circumference of two flat molecules per unit cell. In contrast, the experimentally determined value for the surface area of **3c** is larger than that theoretically calculated, which means that the molecular packing also contains free surface areas. Figures 4b and 5b illustrate packing models, for which only one of the many comparable conformations for the alkyl chains is shown.

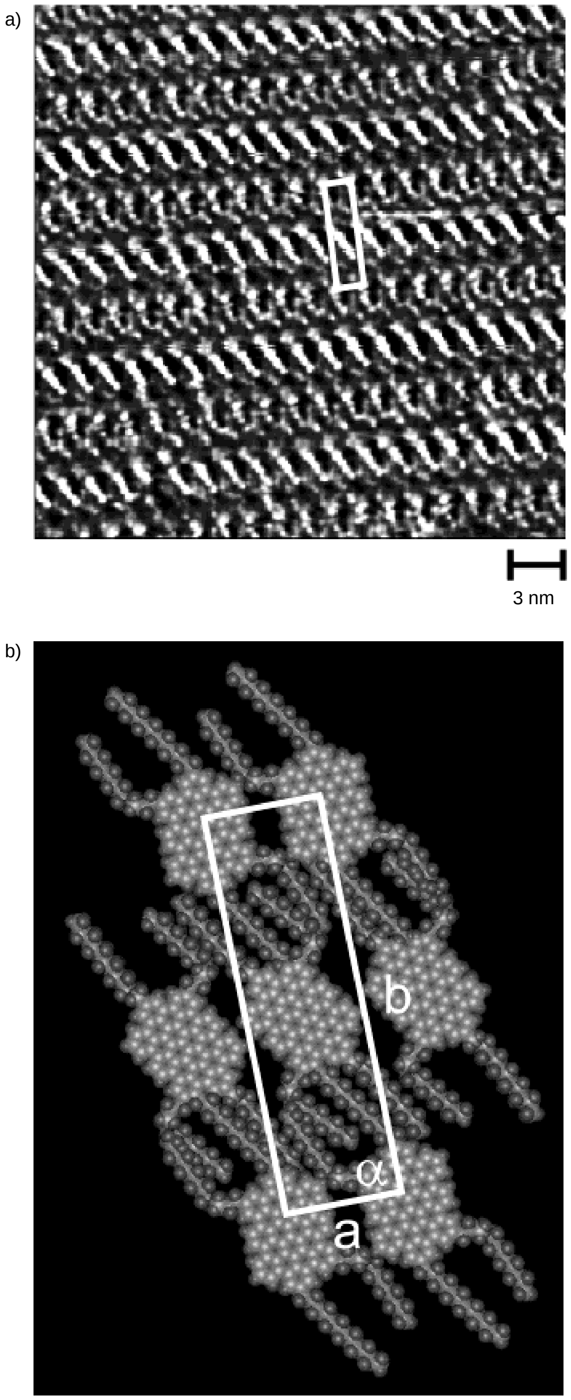


Figure 4. STM image (a) and model (b) of **3b** on the basal surface of graphite.

It is remarkable that the submolecularly resolved pictures of **3c** show three similarly directed strips with a distance of 0.4 ± 0.02 nm over each molecule. The latter do not result from the graphite lattice of the support layer since they are seen only over the aromatic discs and not in the entire picture. Furthermore, the distance of 0.246 nm[16] between equivalent graphite atoms is significantly lower than the distance between the individual strips. This value, however, is in good agreement with the distance between the benzene subunits of

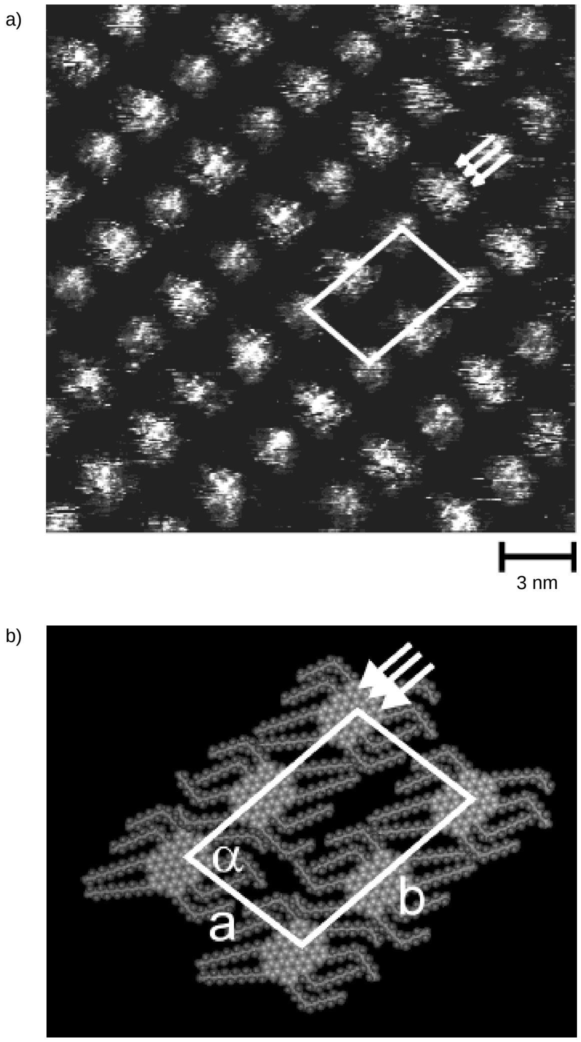


Figure 5. STM image (a) and model (b) of **3c** on the basal surface of graphite.

the aromatic discs (0.38 nm). In addition, this distance also occurs in the pattern of the electronic state density of the frontier orbitals of the free molecules, which are believed to create the contrast between molecular adsorbates on graphite.[13, 17] Therefore, one can assign the submolecular contrast to the local electronic state densities of the conjugated systems. Based upon this, it is possible to determine the orientation of the aromatic discs on the substrate.

To date, it is unclear whether a transition to a graphite-like electronic behavior can be observed with increasing size of the PAH discs.

Received: April 21, 1998 [Z11760 IE]
German version: *Angew. Chem.* **1998**, *110*, 2843–2846

Keywords: cyclodehydrogenations · graphite segments · nanostructures · polycycles · scanning tunneling microscopy

---

[1] V. S. Iyer, M. Wehmeier, J. D. Brand, M. A. Keegstra, K. Müllen, *Angew. Chem.* **1997**, *109*, 1675–1679; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1604–1607.

[2] M. Müller, V. S. Iyer, C. Kübel, V. Enkelmann, K. Müllen, *Angew. Chem.* **1997**, *109*, 1679–1682; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1607–1610.

[3] A. Stabel, P. Herwig, K. Müllen, J. P. Rabe, *Angew. Chem.* **1995**, *107*, 1768–1770; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1609–1611.

[4] E. Clar, *The Aromatic Sextet*, Wiley, London, **1972**.

[5] A graphite disc was originally believed to be a plausible structure of [60]fullerene. According to this model, it was calculated that such a stable structure would require 20 or more hydrogen atoms in the periphery: H. Kroto, *Angew. Chem.* **1997**, *109*, 1648–1664; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1578–1593.

[6] J. R. Dias, *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 89–96.

[7] A general procedure for the synthesis of substituted cyclopentadienone derivatives has been reported.[1]

[8] The crystal structure analysis was performed on a Nonius-CAD4 diffractometer with graphite-monochromated $Cu_{K\alpha}$ radiation ($\lambda = 1.5418$ Å) at room temperature. The lattice parameters were determined by least-squares analysis from the angles of 25 reflections ($\theta > 20\,^{\circ}$C). The intensities were measured with $\theta/2\theta$ scans. The structures were solved with direct methods, and the C atoms were refined with anisotropic directional parameters, the H atoms were considered to be in a riding model. Empirical absorption correction; programs used: Molen, SIR92, and CRYSTALS. **6**: orthorhombic, *Fdd*2, $a = 6.5306(4)$, $b = 30.765(2)$, $c = 42.623(1)$ Å, $V = 8563.4(9)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.183\ \mathrm{g\,cm^{-3}}$, $\mu = 4.74\ \mathrm{cm^{-1}}$; of 2079 reflections, 1579 were observed ($I > 3\sigma(I)$), $R = 0.042$, $R_w = 0.047$. Further details on the crystal structure analysis can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-391072.

[9] We thank Professor Dr. N. Karl (Universität Stuttgart) for the sublimation experiments.

[10] The time delay between laser desorption and detection is on the order of microseconds. For structure elucidation of small carbon clusters, see for example H. J. Hwang, A. Van Orden, K. Tanaka, E. W. Kuo, J. R. Heath, R. J. Saykally, *Mol. Phys.* **1993**, *79*, 769–776, and references therein.

[11] The partial cyclodehydrogenation could be a result of the strain caused by the alkyl substituents in the bay region. We have observed this phenomenon in previous cyclodehydrogenations.[2]

[12] D. P. E. Smith, H. Hörber, C. Gerber, G. Binnig, *Science* **1989**, *245*, 43–45.

[13] R. Lazzaroni, A. Calderone, J. L. Brédas, J. P. Rabe, *J. Chem. Phys*, **1997**, *107*, 99–105.

[14] According to Figure 4a, the tunnel current through the aromatic discs of **3b**, the longer axis of which is tilted with respect to the *b* axis of the unit cell, is higher than that through the molecules, which are oriented almost parallel to the *b* axis. To explain the differing contrasts, it is assumed that the aromatic discs opposite to the graphite substrate which are tilted against the *b* axis, are like an additional graphite layer, whereas the molecules in the other rows are rotated relative to the graphite lattice.

[15] **3b**: Unit cell: $a = (1.71 \pm 0.15)$ nm, $b = (5.69 \pm 0.17)$ nm, $\alpha = 87 \pm 2^{\circ}$; surface demand $A = (9.72 \pm 1.15)$ nm^2 (experimental) and $A = 9.86$ nm^2 (calculated from van der Waals circumferences); **3c**: unit cell: $a = (3.41 \pm 0.20)$ nm, $b = (5.45 \pm 0.32)$ nm, $\alpha = 79 \pm 2^{\circ}$; surface demand $A = (18.24 \pm 2.26)$ nm^2 and $A = 15.26$ nm^2 (calculated from van der Waals circumferences).

[16] D. Tománek, S. G. Louie, H. J. Mamin, D. W. Abraham, R. E. Thomson, E. Ganz, J. Clarke, *Phys. Rev. B* **1987**, 35, 7790–7793.

[17] Individual benzene units along the long axis of the aromatic discs could not be resolved, which is probably due to a (albeit small) molecular mobility.