

Atom precise bottom-up construction of an internally B₃N₃ doped nanographene molecule

Matthias Krieg,^[a] Florian Reicherter,^[a] Peter Haiss,^[a] Markus Ströbele,^[b] Klaus Eichele,^[b] Michael-John Treanor,^[c] Renald Schaub,^[c] Holger F. Bettinger*^[a]

In memory of Paul von Ragué Schleyer

Abstract: The synthesis of a hexa-*peri*-hexabenzocoronene (HBC) with a central borazine core is described. The solid state structure of this BN doped HBC (BN-HBC) is isotopic with that of parent HBC. Scanning tunneling microscopy shows that BN-HBC is lying flat on Au(111) and is two-dimensional.

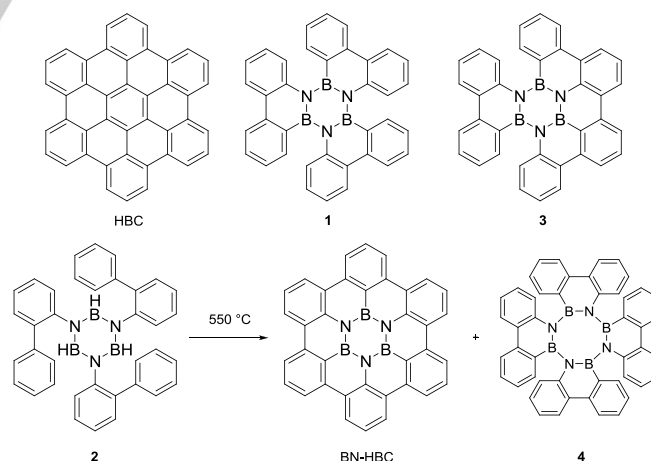
Nanographene molecules are well-defined polycyclic aromatic hydrocarbons (PAH) that resemble a segment of graphene.^[1] Progress in synthetic and analytic methodologies made disk-like nanographene molecules of unprecedented size available. Due to their geometric confinement, their electronic structures differ from that of graphene. They do have finite energy gaps and nanographene molecules may indeed be considered carbon based quantum dots. Due to their high thermal and chemical stability, good film forming properties and high charge carrier mobility nanographene molecules are sought as materials for organic electronics in applications such as organic field effect transistors, organic photovoltaics, and organic light emitting diodes.^[1]

An iconic representative of nanographene molecules is hexa-*peri*-hexabenzocoronene (HBC, Scheme 1), sometimes called "super-benzene".^[1d] Though long known,^[2] its potential in organic electronics could only more recently be studied as high-yielding syntheses of this PAH and efficient strategies for its chemical functionalization were missing for a long time.^[3] Substitution at the periphery of HBC allowed for tailoring the properties and achieving liquid crystallinity, self-organization into nanoscale objects, and application in OFET and OPV.^[1]

An alternative and attractive means of modifying the intrinsic electronic properties of nanographenes without changing molecular size is the substitution of CC units by isoelectronic BN units.^[4] Theory suggests that BN doping increases the HOMO-

LUMO and optical gap of HBC,^[5] and similarly that of graphene. Consequently, BN doping has been investigated as a possible means of introducing a band gap in graphene.^[6] Such approaches are often plagued with segregation of carbon and hexagonal boron nitride phases or allow only an undefined and unpredictable way of incorporating BN units. Well-defined BN doped nanographenes may offer an alternative means for modification and may be a feedstock for CVD synthesis of BN doped graphene.^[7] Only a small number of molecules are known where boron and nitrogen atoms are fully surrounded by carbon hexagons, and these include BN-pyrene and a B₂N₂ derivative of perylene that were reported by the Piers group.^[8]

The atom precise bottom up synthesis of extensively BN doped HBC poses a challenging problem as reliable strategies for incorporation of BN units into this nanographene are unknown. The oxidative cyclodehydrogenation methods that proved to be so successful for the synthesis of HBC failed to produce BN-HBC from hexaphenylborazine.^[5] The overcrowded propeller-like B₃N₃-hexabenzotriphenylene **1** with three of the six required C–C bonds already installed is accessible either by treatment of 10-chloro-10,9-borazarophenanthrene with bulky bases or by heating N,N',N''-tris(2-biphenyl)borazine **2** to 405 °C.^[9] Unfortunately, attempts to close **1** to BN-HBC under Scholl conditions were unsuccessful and oxidative photocyclization closes only one of the three missing C–C bonds to give **3**.^[10]



Scheme 1. Synthesis of BN-HBC and **4** from **2**.

Thermolysis of **2** at 550 °C produces BN-HBC (Scheme 1) according to laser desorption ionization time of flight mass spectrometry (LDI-TOF-MS). The major product is tetraazatetraborocine **4** that we isolated earlier in very small amount as by-product of the same reaction run at 405 °C. Separation of BN-HBC from the crude reaction mixture is

[a] Dr. M. Krieg, F. Reicherter, Dr. P. Haiss, Prof. Dr. H. F. Bettinger
Institut für Organische Chemie
Universität Tübingen
Auf der Morgenstelle 18, 72076 Tübingen, Germany
E-mail: Holger.Bettinger@uni-tuebingen.de

[b] Dr. M. Ströbele, Dr. K. Eichele
Institut für Anorganische Chemie
Universität Tübingen
Auf der Morgenstelle 18, 72076 Tübingen, Germany

[c] M.-J. Treanor, Prof. Dr. R. Schaub
EaStCHEM and School of Chemistry
University of St Andrews
St Andrews, KY16 9ST, UK

Supporting information for this article is given via a link at the end of the document.

challenging. Extraction of the dichloromethane soluble by-products followed by high-vacuum sublimation allows achieving samples that still contains some **4** according to MS, solid state ^{11}B NMR, and powder diffraction.

BN-HBC is obtained after sublimation as yellow powder that is very poorly soluble in organic solvents. Diagnostic of the borazine core is the strong absorption at 1384 cm^{-1} in the infrared spectrum of the compound that is associated with the BN stretching vibration $\nu(\text{BN})$. The energy of this vibration continuously increases in the series of **1** (1366 cm^{-1}),^[9c,d] **3** (1375 cm^{-1}),^[10] and BN-HBC (1384 cm^{-1}) indicating that along with planarization a stiffening of the BN bonds occurs.

A microcrystalline sample obtained from molten pyrene, as described for the crystallization of HBC,^[11] was studied by powder diffraction. A Le Bail refinement with the space group (P $2_1/a$) and lattice constants of HBC as starting values shows that the solid state structure of BN-HBC and HBC are isotopic (see Supporting Information). The packing of HBC that crystallizes in the γ motif was discussed comprehensively by Goddard et al.^[11] We have reported earlier that the BN-HBC molecule is planar at the B3LYP/6-31G* level of theory.^[5]

Solid state ^{11}B magic angle spinning NMR provides further information on the environment of the boron atoms. The quadrupolar coupling constant C_Q (2.93(1) MHz) and the asymmetry parameter η (0.35(1)) are in good agreement with values computed at the B3LYP/6-31G* level of theory (calc. (B3LYP/6-31G*): $C_Q = 2.9\text{ MHz}$, $\eta = 0.38$). We have observed earlier that measured and computed (B3LYP/6-31G*) NMR parameters are in good agreement for BN functionalized aromatic hydrocarbons.^[5,9c] The isotropic ^{11}B chemical shift δ_{iso} of 27 ppm, however, is found to deviate somewhat from the computed value (31 ppm, using the chemically related hexaphenyl borazine as reference). It was shown that the chemical shift of hydrogen atoms of solid HBC depend strongly on the stacking arrangement due to ring current effects.^[12] Computational modeling using an aggregate consisting of at least three molecules was shown to improve agreement considerably.^[12a] Using a trimer of HBC molecules from the published single crystal X-ray structure,^[11] it is found that the carbon atoms comprising the central six-membered ring are shifted on average to higher field by 2 ppm. Assuming a similar influence of the π system of neighboring molecules on the boron atoms in BN-HBC, reasonably good agreement is obtained between experiment (27 ppm) and theory (29 ppm).

BN-HBC sublimation onto a gold single crystal of (111) orientation was achieved in vacuum at approximately 400°C as monitored by low-temperature Scanning Tunneling Microscopy. High-resolution images (Figure 1) reveal the presence of adsorbates with a six-fold symmetric shape and a lateral size of 15 Å. The molecular topography reflects the expected chemical structure of BN-HBC, and is in all aspects similar to that observed for unsubstituted HBC adsorbed on Au(111).^[13] The measured electronic height of the molecule, 1.8 Å (Fig. 1c), is comparable with previous reports for other two-dimensional polyaromatic hydrocarbon molecules on a Au(111) surface.^[14] This suggests that BN-HBC is flat-lying and two-dimensional. Larger scale STM images reveal that upon adsorption, the BN-HBC molecules are preferentially adsorbed at the elbows of the herringbone reconstruction (as is the case in Fig. 1b), with a

minority also adsorbed on the fcc regions of the surface. It is apparent that the symmetries of the molecule and of the substrate align, similarly to unsubstituted HBC/Au(111).

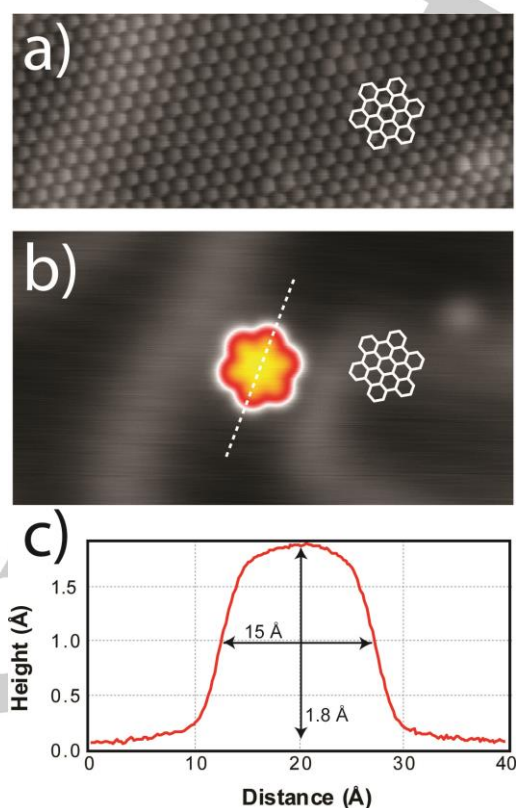


Figure 1. STM images and height profile of BN-HBC/Au(111) acquired in constant-current mode at 4K. a) Atomically resolved image of the clean Au(111) surface prior to deposition ($V_t = -0.06\text{ V}$; $I_t = 1.0\text{ nA}$; $90\text{ Å} \times 35\text{ Å}$). b) STM image of a BN-HBC molecule adsorbed on an elbow of the Au(111) herringbone reconstruction ($V_t = -1.7\text{ V}$; $I_t = 0.8\text{ nA}$; $90\text{ Å} \times 50\text{ Å}$). The molecular structure of BN-HBC is superimposed on the STM image for reference. c) STM height profile of the BN-HBC molecule acquired along the dashed line shown in b), indicating an apparent height of 1.8 Å and a lateral size of 15 Å.

In summary, we have discovered a pathway to a novel BN doped hexa-*peri*-hexabenzocoronene nanographene molecule that has a central borazine six-membered ring. The BN-HBC molecule is expected to be of use for synthesizing BN-doped graphene. Further investigations of its spectral and chemical properties and reactivity are underway in our laboratories.

Acknowledgements

This work was supported in part by the Deutsche Forschungsgemeinschaft and the Fonds der chemischen Industrie. We thank Prof. Michael Hunger (Institute of Chemical Technology, University of Stuttgart) for additional solid state NMR measurements.

Keywords: arenes • heterocycles • graphene • scanning probe microscopy

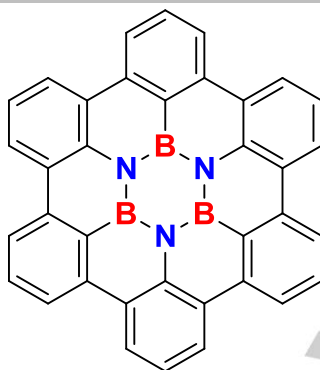
- [1] a) A. C. Grimsdale, K. Müllen, *Angew. Chem. Int. Ed.* **2005**, *44*, 5592; b) A. C. Grimsdale, J. Wu, K. Müllen, *Chem. Comm.* **2005**, 2197; c) L. Schmidt-Mende, A. Fechtenkötter, K. Müllen, E. Moons, R. H. Friend, J. D. MacKenzie, *Science* **2001**, *293*, 1119; d) J. Wu, W. Pisula, K. Müllen, *Chem. Rev.* **2007**, *107*, 718; e) H. Seyler, B. Purushothaman, D. J. Jones, A. B. Holmes, W. W. H. Wong, *Pure Appl. Chem.* **2012**, *84*, 1047; f) M. D. Watson, A. Fechtenkötter, K. Müllen, *Chem. Rev.* **2001**, *101*, 1267; g) L. Chen, Y. Hernandez, X. Feng, K. Müllen, *Angew. Chem. Int. Ed.* **2012**, *51*, 7640; h) K. Müllen, J. P. Rabe, *Acc. Chem. Res.* **2008**, *41*, 511.
- [2] E. Clar, C. T. Ironside, M. Zander, *J. Chem. Soc.* **1959**, 142.
- [3] A. Stabel, P. Herwig, K. Müllen, J. P. Rabe, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1609.
- [4] a) P. G. Campbell, A. J. V. Marwitz, S.-Y. Liu, *Angew. Chem. Int. Ed.* **2012**, *51*, 6074; b) M. J. D. Bosdet, W. E. Piers, *Can. J. Chem.* **2008**, *86*, 8; c) Z. Liu, T. B. Marder, *Angew. Chem. Int. Ed.* **2008**, *47*, 242.
- [5] C. Tönshoff, M. Müller, T. Kar, F. Lattayer, T. Chassé, K. Eichele, H. F. Bettinger, *ChemPhysChem* **2012**, *13*, 1173.
- [6] a) L. S. Panchakarla, K. S. Subrahmanyam, S. K. Saha, A. Govindaraj, H. R. Krishnamurthy, U. V. Waghmare, C. N. R. Rao, *Adv. Mater.* **2009**, *21*, 4726; b) L. Ci, L. Song, C. Jin, D. Jariwala, D. Wu, Y. Li, A. Srivastava, Z. F. Wang, K. Storr, L. Balicas, F. Liu, P. M. Ajayan, *Nat. Mater.* **2010**, *9*, 430; c) D. Jariwala, A. Srivastava, P. M. Ajayan, *J. Nanosci. Nanotechnol.* **2011**, *11*, 6621; d) R. Quhe, J. Zheng, G. Luo, Q. Liu, R. Qin, J. Zhou, D. Yu, S. Nagase, W.-N. Mei, Z. Gao, J. Lu, *NPG Asia Mater* **2012**, *4*, e6; e) S.-M. Jung, E. K. Lee, M. Choi, D. Shin, I.-Y. Jeon, J.-M. Seo, H. Y. Jeong, N. Park, J. H. Oh, J.-B. Baek, *Angew. Chem. Int. Ed.* **2014**, *53*, 2398.
- [7] a) X.-Y. Wang, F.-D. Zhuang, X.-C. Wang, X.-Y. Cao, J.-Y. Wang, J. Pei, *Chem. Commun.* **2015**, *51*, 4368; b) X.-Y. Wang, J.-Y. Wang, J. Pei, *Chem. Eur. J.* **2015**, *21*, 3528; c) G. Li, W.-W. Xiong, P.-Y. Gu, J. Cao, J. Zhu, R. Ganguly, Y. Li, A. C. Grimsdale, Q. Zhang, *Org. Lett.* **2015**, *17*, 560; d) X.-Y. Wang, F.-D. Zhuang, R.-B. Wang, X.-C. Wang, X.-Y. Cao, J.-Y. Wang, J. Pei, *J. Am. Chem. Soc.* **2014**, *136*, 3764.
- [8] a) M. J. D. Bosdet, W. E. Piers, T. S. Sorensen, M. Parvez, *Angew. Chem. Int. Ed.* **2007**, *46*, 4940; b) M. J. D. Bosdet, W. E. Piers, T. S. Sorensen, M. Parvez, *Can. J. Chem.* **2010**, *88*, 426.
- [9] a) R. Köster, S. Hattori, Y. Morita, *Angew. Chem.* **1965**, *77*, 719; b) R. Köster, K. Iwasaki, S. Hattori, Y. Morita, *Lieb. Ann.* **1968**, *720*, 23; c) S. Biswas, M. Müller, C. Tönshoff, K. Eichele, C. Maichle-Mössmer, A. Ruff, B. Speiser, H. F. Bettinger, *Eur. J. Org. Chem.* **2012**, *24*, 4634; d) M. Müller, C. Maichle-Mössmer, P. Sirsch, H. F. Bettinger, *ChemPlusChem* **2013**, *78*, 988.
- [10] M. Müller, S. Behnle, C. Maichle-Mössmer, H. F. Bettinger, *Chem. Commun.* **2014**, *50*, 7821.
- [11] R. Goddard, M. W. Haenel, W. C. Herndon, C. Krueger, M. Zander, *J. Am. Chem. Soc.* **1995**, *117*, 30.
- [12] a) C. Ochsenfeld, S. P. Brown, I. Schnell, J. Gauss, H. W. Spiess, *J. Am. Chem. Soc.* **2001**, *123*, 2597; b) W. Pisula, Z. Tomovic, M. D. Watson, K. Müllen, J. Kussmann, C. Ochsenfeld, T. Metzroth, J. Gauss, *J. Phys. Chem. B* **2007**, *111*, 7481.
- [13] C. Wagner, D. Kasemann, C. Golnik, R. Forker, M. Esslinger, K. Müllen, T. Fritz, *Phys. Rev. B* **2010**, *81*, 035423.
- [14] K. Manandhar, J. B. Sambur, B. A. Parkinson, *J. Appl. Phys.* **2010**, *107*.

Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

The borazine derivative of hexa-peri-hexabenzocoronene forms in a high temperature reaction by multiple dehydrogenation of a borazine.



*Matthias Krieg, Florian Reicherter, Peter Heiss, Markus Ströbele, Klaus Eichele, Michael-John Treanor, Renald Schaub, Holger F. Bettinger**

Page No. – Page No.

Atom precise bottom-up construction of an internally B₃N₃ doped nanographene molecule