Heterocycles

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Construction of an Internally B_3N_3-Doped Nanographene Molecule**

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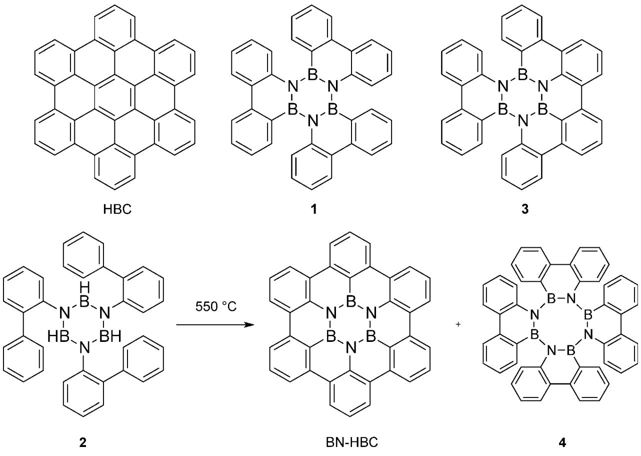
In memory of Paul von Ragué Schleyer

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 isotypic with that of the parent HBC. Scanning tunneling microscopy shows that BN-HBC lies flat on Au(111) in a two-dimensional pattern.*



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

Nanographene molecules are well-defined polycyclic aromatic hydrocarbons (PAHs) that resemble a segment of graphene.[1] Progress in synthetic and analytic methodologies has made disk-like nanographene molecules of unprecedented size available. Owing to their geometric confinement, their electronic structures differ from that of graphene. They have finite energy gaps and may thus be considered to be carbon-based quantum dots. Owing to their high thermal and chemical stability, good film-forming properties, and high charge-carrier mobility, nanographene molecules are sought after as materials for organic electronics in applications such as organic field-effect transistors (OFET), organic photovoltaics (OPV), 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 since high-yielding syntheses for this PAH and efficient strategies for its chemical functionalization were missing for a long time.[3] Substitution at the periphery of HBC allows tailoring of the properties to achieve liquid crystals that self-organize into nanoscale objects and that can be applied in OFET and OPV.[1]

An alternative and attractive means of modifying the intrinsic electronic properties of nanographenes without changing the molecular size is the substitution of C–C units by isoelectronic B–N 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 by segregation of the carbon and hexagonal boron nitride phases or they provide only an undefined and unpredictable means of incorporating BN units. Well-defined BN-doped nanographenes may offer an alternative means for modification and may be a feedstock for chemical vapor deposition (CVD) synthesis of BN-doped graphene.[7] Only a small number of molecules are known for which boron and nitrogen atoms are fully surrounded by carbon hexagons, and these include BN-pyrene and a B_2N_2 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 since reliable strategies for the incorporation of BN units into this nanographene are unknown. The oxidative cyclodehydrogenation methods that have proven so successful in the synthesis of HBC failed to produce BN-HBC from hexaphenylborazine.[5] The overcrowded propeller-like B_3N_3-hexabenzotriphenylene **1**, which has three of the six required C–C bonds already installed, is accessible either by treating 10-chloro-10,9-borazarophenanthrene with bulky bases or by heating *N*,*N*′,*N*″-tris(2-biphenylyl)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]

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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 derivative (**4**), which we isolated earlier in very small amount as a byproduct of the same reaction run at 405 °C. Separation of BN-HBC from the crude reaction mixture is challenging. Extraction of the dichloromethane-soluble byproducts followed by high-vacuum sublimation gave samples that still contain some **4** according to MS, solid-state ^{11}B NMR, and powder diffraction (see the Supporting Information).

BN-HBC is obtained after sublimation as a 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, which is associated with the BN stretching vibration ν(BN). The energy of this vibration continuously increases in the series **1** (1366 cm^{-1}),[9c,d] **3** (1375 cm^{-1}),[10] and BN-HBC (1384 cm^{-1}), thus indicating that along with planarization, stiffening of the B–N 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 $P2_1/a$ and the lattice constants of HBC as starting values showed that the solid-state structure of BN-HBC and HBC are isotypic (see the Supporting Information). The packing of HBC molecules in the solid state 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 provided 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)) were in good agreement with values computed at the B3LYP/6-31G* level of theory (calc. (B3LYP/6-31G*): $C_Q = 2.9$ 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, deviates somewhat from the computed value (31 ppm, with the chemically related hexaphenyl borazine as a reference). It was shown that the chemical shift of hydrogen atoms in solid HBC depend strongly on the stacking arrangement owing to ring current effects.[12] Computational modeling using an aggregate consisting of at least three molecules was shown to improve agreement considerably.[12a] When 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 upfield by 2 ppm on average. 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 under 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; Figure 1 c) is comparable to 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 in Figure 1 b), with a minority also adsorbed on the fcc regions of the surface. It is apparent that the symmetries of the molecule and the substrate align, in a manner similar to unsubstituted HBC on Au(111).

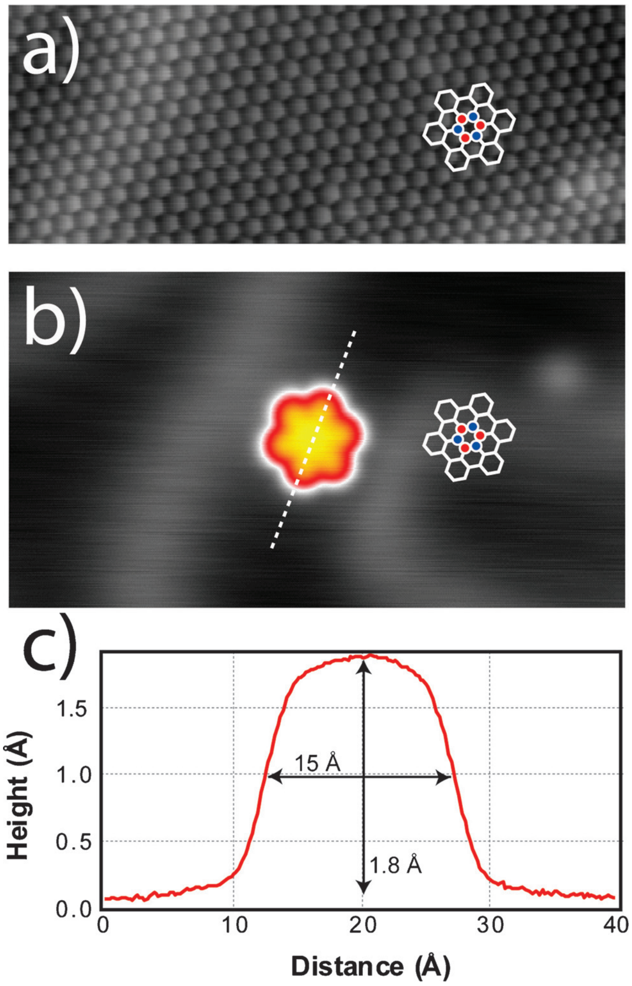

Figure 1. STM images and height profile of BN-HBC/Au(111) acquired in constant-current mode at 4 K. a) Atomically resolved image of the clean Au(111) surface prior to deposition ($V_t = -0.06$ V; $I_t = 1.0$ nA; 90×35 Å). b) STM image of a BN-HBC molecule adsorbed at an elbow of the Au(111) herringbone reconstruction ($V_t = -1.7$ V; $I_t = 0.8$ nA; 90×50 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), which indicates 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.

Keywords: arenes · graphene · heterocycles · scanning probe microscopy

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[1] a) A. C. Grimsdale, K. Müllen, *Angew. Chem. Int. Ed.* **2005**, *44*, 5592; *Angew. Chem.* **2005**, *117*, 5732; b) A. C. Grimsdale, J. Wu, K. Müllen, *Chem. Commun.* **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; *Angew. Chem.* **2012**, *124*, 7758; 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; *Angew. Chem.* **1995**, *107*, 1768.

[4] a) P. G. Campbell, A. J. V. Marwitz, S.-Y. Liu, *Angew. Chem. Int. Ed.* **2012**, *51*, 6074; *Angew. Chem.* **2012**, *124*, 6178; 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; *Angew. Chem.* **2008**, *120*, 248.

[5] a) C. Tönshoff, M. Müller, T. Kar, F. Latteyer, T. Chassé, K. Eichele, H. F. Bettinger, *ChemPhysChem* **2012**, *13*, 1173; b) S. Sanyal, A. K. Manna, S. K. Pati, *J. Mater. Chem. C* **2014**, *2*, 2918.

[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; DOI: 10.1038/am.2012.10; 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; *Angew. Chem.* **2014**, *126*, 2430; f) Y. Gong, G. Shi, Z. Zhang, W. Zhou, J. Jung, W. Gao, L. Ma, Y. Yang, S. Yang, G. You, R. Vajtai, Q. Xu, A. H. MacDonald, B. I. Yakobson, J. Lou, Z. Liu, P. M. Ajayan, *Nat. Commun.* **2014**, *5*, 3193.

[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; e) T. Hatakeyama, S. Hashimoto, T. Oba, M. Nakamura, *J. Am. Chem. Soc.* **2012**, *134*, 19600; f) S. Hashimoto, T. Ikuta, K. Shiren, S. Nakatsuka, J. Ni, M. Nakamura, T. Hatakeyama, *Chem. Mater.* **2014**, *26*, 6265.

[8] a) M. J. D. Bosdet, W. E. Piers, T. S. Sorensen, M. Parvez, *Angew. Chem. Int. Ed.* **2007**, *46*, 4940; *Angew. Chem.* **2007**, *119*, 5028; 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. Int. Ed. Engl.* **1965**, *4*, 695; *Angew. Chem.* **1965**, *77*, 719; b) R. Köster, K. Iwasaki, S. Hattori, Y. Morita, *Justus Liebigs Ann. Chem.* **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**, 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. Krüger, 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*, 063716.

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