Synthesis of a naphthodiazaborole and its verification by planarization with AFM

Zsolt Majzik,*,†,¶ Ana B. Cuenca,‡,¶ Niko Pavliček,† Núria Miralles,‡ Gerhard Meyer,† Leo Gross,† and Elena Fernández*,‡

†*IBM Research - Zurich, 8803 Rüschlikon, Switzerland*
‡*Department Física Química i Inorgànica, University Rovira i Virgili, 43007 Tarragona Spain*
¶*Both authors have contributed equally to this project*

E-mail: zsolt.majzik@gmail.com; mariaelena.fernandez@urv.cat

Abstract

Aiming to develop materials with new functionalities, we designed the synthesis of a naphthodiazaborinine (the BN isoster of the phenalenyl anion) that is bonded to a hindered di-ortho-substituted aryl system (9-anthracene). We used atomic force microscopy (AFM) to verify the structure of the molecule synthesized. To determine it unambiguously, we planarized the originally nonplanar molecule by removing H atoms that cause steric hindrance.

Abbreviations

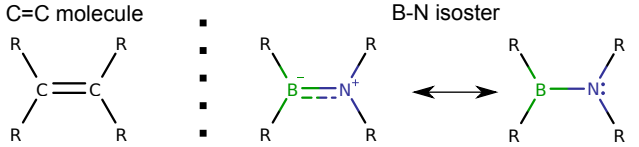
AFM = Atomic Force Microscopy, STM = Scanning Tunneling Microscopy, DFT = Density Functional Theory, Bdan = Boron(1,8)diaminonaphtalene

Keywords

Bdan, AFM, STM, dehydrogentaion, radical, steric hindrance

Introduction

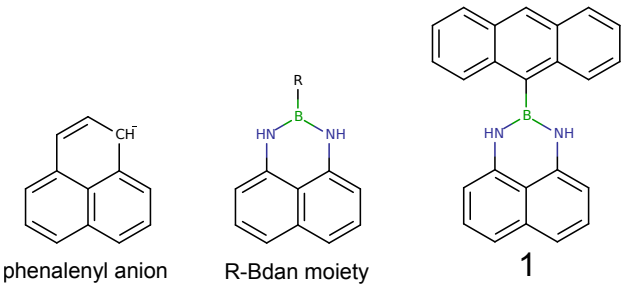
The boron-nitrogen substitution of two adjacent carbon atoms in a C=C bond, referred to as BN/CC isosterism (Scheme 1), increases the chemical diversity of bioactive molecules[1,2] by altering the electronic structure with minimal geometric disruption.[3–7] Furthermore, the conjugated molecules and polymers containing three-coordinate boron exhibit interesting optical and electronic properties, making them appropriate for use in functional materials,[8–11] or as ligands in transition-metal complexes.[12–19] In particular the BN orientation in conjugated molecules with more than one BN unit can develop new antiaromatic systems.[20] It is important to highlight that the BN/CC isosterism can also be used as a molecular design strategy to alter the inherent reactivity patterns, which is consistent with the HOMO orbital coefficients determined in direct comparison with all-carbon structures.[21]



Scheme 1: BN isosterism and comparison with the carbonaceous counterpart.

There is an increasing trend to synthesize new conjugated molecules that contain BN units and in that context the 1,3,2-naphthodiazaborole system (Bdan moiety,

Scheme 2), where the boron is bonded to 1,8-diaminonaphtalene, is a relevant example where the substitution of the N-B-N unit into the aromatic carbonaceous phenalenyl anion[22,23] system changes the topology type of the aromatic system, presumably due to a stronger bond localization.[24,25] Searching for new materials containing the N-B-N unit, we designed the preparation of the 9-anthracene naphthodiazaborinine (**1**), where the Bdan unit is bonded to a hindered di-ortho substituted aryl system (9-anthracene).



Scheme 2: Comparative perspective between R-Bdan species and the corresponding phenalenyl anion. Synthesized 9-anthracene naphthodiazaborinine (**1**) compound.

Atomic resolution of molecules by AFM with functionalized tips[26] enabled identification of individual unknown molecules.[27–29] It also opened the possibility to study reaction products formed by on-surface chemistry[30–35] or atomic manipulation.[36–40] Dehalogenation[38,41] and dehydrogenation[37,40,42–44] by atomic manipulation were demonstrated for several molecular systems.

In this paper, we report the synthesis of **1** and its structural verification via AFM. The molecule was produced in a metal-catalyzed reaction. The synthesized molecule is nonplanar. The AFM-based identification of **1** included the transformation of **1** into a planar molecule by removing those hydrogen atoms that induce steric hindrance. This route represents a direct method for scanning probe microscopy techniques to identify the structure of nonplanar molecules.[32,45]

Results and discussion

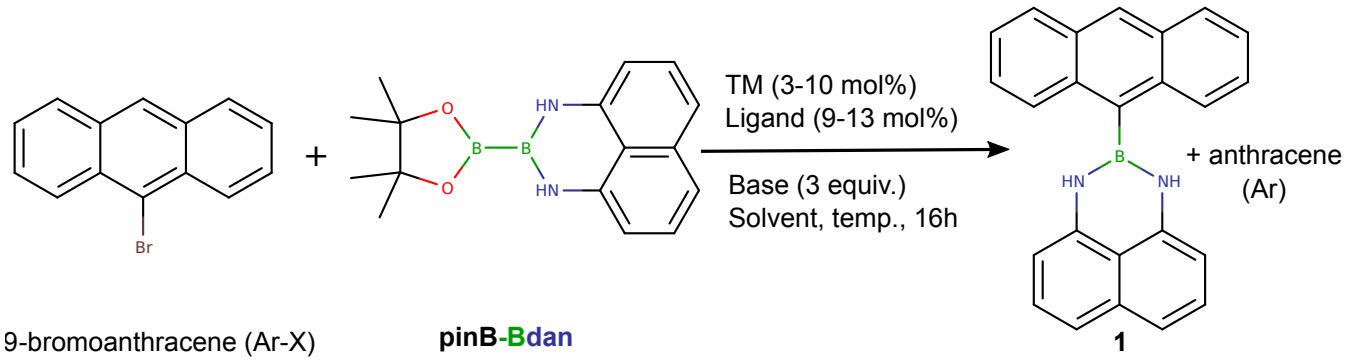
Synthesis of 9-anthracene naphthodiazaborinine

In contrast to the well-established Miyaura borylation of aryl halides with diboronate esters as reagents (bis(pinacolato)diboron = B_2pin_2 and others),[46–56] the analogous direct introduction of Bdan boryl units from HBdan is much less explored.[57] In fact, it was only recently that a chemoselective transfer of Bdan units from (pin)B-B(dan) to a series of aryl halides has been reported.[58] However, as far as we are aware, not a single example of Bdan transfer to a bulky di-ortho-substituted aryl halide has been described. Hence, a series of metal-catalyzed direct Bdan borylation reactions of 9-bromoanthracene were conducted to prepare 9-anthracene naphthodiazaborinine (**1**). Initial catalytic conditions were examined with 3 mol% of $Pd_2(dba)_3$, 9 mol% of the Buchwald ligand XPhos, and KOAc as the base (Table 1, entry 1). This catalytic system promoted a complete conversion of the diboron reagent and the formation of **1** in 66% NMR yield. The reaction also produced anthracene (Ar) as byproduct. Attempts to increase the percentage of product **1** formation by changing the reaction temperature (from 100 °C to 70 °C) or using an stoichiometric amount of 9-bromoanthracene versus (pin)B-B(dan), were unsuccessful (Table 1, entries 2,3). Adjusting the 9-bromoanthracene/(pin)B-B(dan) ratio to 1/1.5 led to an improved NMR yield formation of **1** (82%), with 76% of isolated yield (Table 1, entry 4). Notably, the CuI/nBu_3P/KOtBu combination, an alternative, well-established borylation method in the literature,[59] did not show significant catalytic activity even when the more reactive 9-iodoanthracene was used (Table 1, entries 5 and 6). Noteworthy, **1** is the first Bdan-borylated compound arising from a di-ortho-substituted aryl halide.

AFM analysis

Compound **1** was deposited onto a Cu(1 1 1) single crystal, which was partially covered

Table 1: Conditions for the metal-catalyzed Bdan transfer to 9-bromoanthracene.[a]



entry	metal	ligand	base	ArX/(pin)B-B(dan)	temp. (°C)	conv. [%]	Ar NMR yield(%)[b]	**1** NMR yield [%][b]
1	$Pd_2(dba)_3$	XPhos	KOAc	1/0.8	100	100	27	66
2	$Pd_2(dba)_3$	XPhos	KOAc	1/0.8	70	77	23	51
3	$Pd_2(dba)_3$	XPhos	KOAc	1/1	100	70	22	48
4	**$Pd_2(dba)_3$**	**XPhos**	**KOAc**	**1/1.5**	**100**	**85**	**3**	**82[76]**[c]
5	CuI	nBu_3P	KOtBu	1/1.5	r.t.	62	54	8
6[d]	CuI	nBu_3P	KOtBu	1/1.5	r.t.	84	73	9

[a]Reaction conditions: 9-bromoanthracene (0.2 mmol), (pin)B-B(dan) (0.8-1.5 equiv.), $Pd_2(dba)_3$ (3 mol%), XPhos (9 mol%), KOAc (3 equiv.), 1,4-dioxane (0.86 mL), at 100 °C for 16 h.; [b]Yields were determined by ^{1}H NMR analysis of the crude reaction mixture using ferrocene as an internal standard.; [c]Isolated yield. [d]9-iodoanthracene was used as ArX.

by double layer NaCl islands (referred to as NaCl(2ML)).

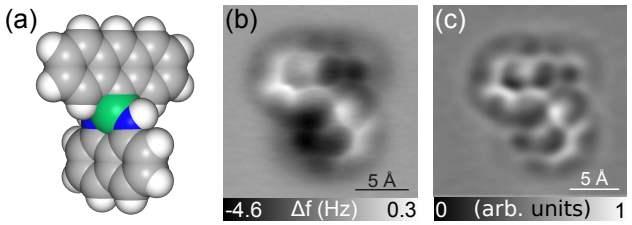


Figure 1: (a) Molecular model, owing to steric hindrance **1** is nonplanar. (b) Constant-height (Δz = +1.2 Å) AFM frequency shift map recorded with CO tip at 5 K and V = 0. (c) Laplace-filtered image of (b).

A constant-height AFM image of **1** adsorbed on Cu(1 1 1) is shown in Fig. 1b. The image was recorded in constant-height mode with a CO-functionalized tip (CO tip)[26,60] at Δz = +1.2 Å. The tip height Δz is defined with respect to the STM set-point at I_t = 1 pA and V = 0.1 V above Cu(1 1 1). In Fig. 1b, the left edge of the anthracenyl head and the right part of the naphthodiazaborinine unit appear with bright contrast, indicating repulsive interactions because of an increased adsorption height.[37,45] Owing to the steric hindrance between the H atoms bound to the N atoms and the closest hydrogens of the anthracenyl unit, the molecule is nonplanar (see model in Fig. 1a). Because of the 3D shape of the molecule, its structure could not be determined unambiguously from the image presented in Fig. 1b alone. The structure even remained unclear after Laplace filtering (see Fig. 1c). Only after planarization of the molecule as described in the next section could we conclude that the molecule imaged in Fig. 1b is **1** adsorbed in the geometry indicated in Fig. 1a.

Tip-induced dehydrogenation

To planarize the molecule and to determine its structure unambiguously, we decided to remove the H atoms that cause steric hindrance (see Fig. 2). Dehydrogenation was induced by

increasing the bias voltage in constant-height mode until a sudden change in the tunneling current occurred. We positioned the tip with open feedback loop at $\Delta z = -4.5$ Å above the center of the molecule and ramped the bias voltage from +0.1 V to +4 V. At typically $V = +3.0$ V we observed a sudden drop in the tunneling current indicating a manipulation event.

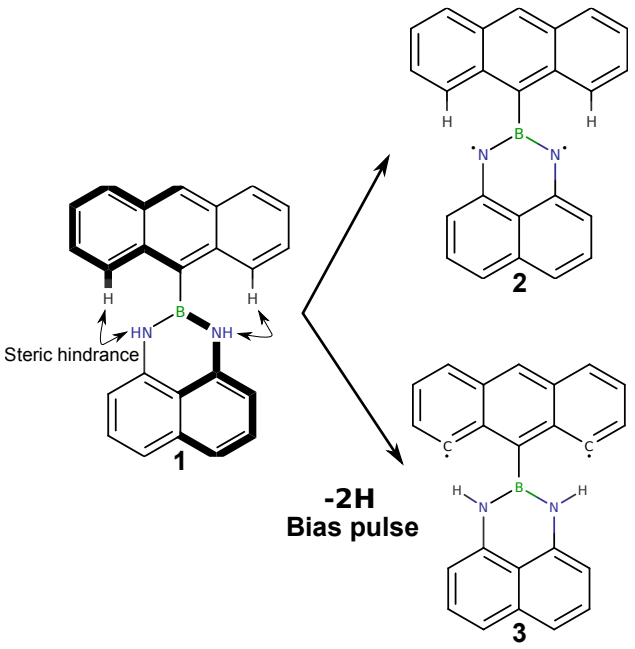


Figure 2: Radical formation and planarization via dehydrogenation: removal of the hydrogen atoms allows the molecule to adapt a planar adsorption geometry.

After the tip-induced reaction, to investigate the outcome, constant-height AFM imaging with a CO tip was performed. As a result of the manipulation the entire molecule could be imaged with atomic resolution and the symmetric appearances of the anthracenyl and the naphthodiazaborinine groups indicate a planar adsorption geometry (see Fig. 3). The steric hindrance could have been eliminated by removing the hydrogens either from the N atoms or from the closest C atoms of the anthracenyl unit (see **2** and **3** in Fig. 2, respectively). However, the exact location of the dehydrogenation cannot be explicitly determined from Fig. 3.

To clarify the mechanism of the planarization, we probed the orbital structure of the manipulated molecule. A two-monolayer-thick NaCl

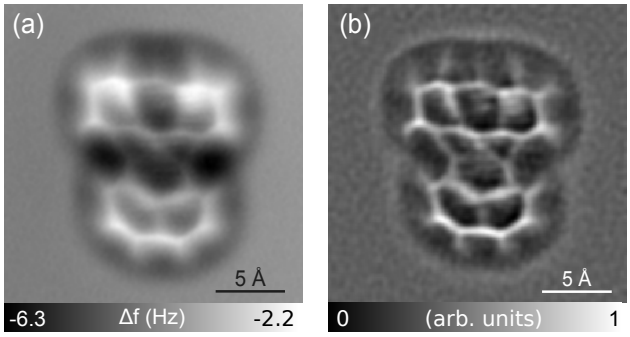


Figure 3: (a) Constant-height ($\Delta z = +2.5$ Å) AFM image with CO tip at $V = 0$ taken after the tip-induced reaction of **1** on Cu(1 1 1). (b) The same image after Laplace filtering.

film was used to electronically decouple the molecule from the metal substrate.[61] On NaCl the molecule could be also dehydrogenated at a similar bias as on Cu(1 1 1). We were able to image the manipulated molecule at its first negative ion resonance. At increased negative biases, the molecule started to move before the bias voltage reached the energy of its positive ion resonance. The negative ion resonance started to dominate the STM contrast at voltages higher than $V = +1.3$ V (see Fig. 4). In the measurement, the highest orbital density is observed above the naphthodiazaborinine part, whereas the anthracenyl head of the molecule exhibits only a faint contrast. Our DFT calculations show that the orbitals with the lowest unoccupied character are located at the naphthodiazaborinine in the case of **2**, whereas they shift to the anthracenyl head in the case of **3**

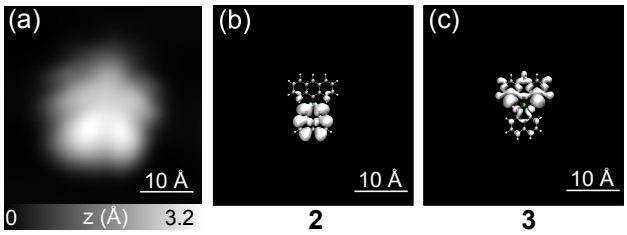


Figure 4: (a) STM measurement of product after dehydrogenation of **1** on NaCl(2ML)/Cu(1 1 1) with a metal tip ($V = +1.3$ V and $I = 0.5$ pA). (b, c) Calculated density of lowest unoccupied orbitals of the dehydrogenated molecule **2** and **3**, respectively.

(for more details, see supplementary informations). Therefore we can conclude that the dehydrogenation took place at the N sites. With this knowledge we can unambiguously assign the compound imaged in Fig. 3 as **2** and the compound imaged in Fig. 1 as **1**.

The Laplace-filtered image (Fig. 3b) shows apparent bonds between the N atoms and the closest C atoms of the anthracene unit. The contrast at this position is unlikely to originate from any kind of bonding configuration. Therefore, we attribute this feature to artifacts that are related to the CO tilting at the tip, which is known to produce sharp features that appear similar as bonds at the positions of ridges of the potential.[45,62–65]

Conclusion

We presented the synthesis of a naphthodiazaborole, namely, 9-anthracene naphthodiazaborinine (**1**), from a di-ortho substituted aryl halide. The yield has been maximized by adjusting the 9-bromoanthracene/(pin)B-B(dan) stoichiometry. The structure of the molecule synthesized was verified via atomic force microscopy.

We demonstrated that planarization by atomic manipulation is a possible route for extending molecular identification by AFM to nonplanar molecular systems that are difficult to be probed with AFM directly.

Experimental

Measurements were performed using a home-built combined STM and AFM operating in ultrahigh vacuum (base pressure below 10^{-10} mbar) at a temperature of 5 K. The bias voltage V was applied to the sample. The AFM is based on a qPlus sensor[66] (stiffness $k = 1800$ N/m, eigenfrequency $f_0 = 29664$ Hz, quality factor $Q = 2 \times 10^5$) operated in frequency-modulation mode.[67] The PtIr tip was cut to length and sharpened using a focused ion beam setup. The oscillation amplitude was 0.5 Å to maximize the lateral resolution.[68] A Cu(111) single crystal was cleaned by several sputtering and annealing cycles. Ultrathin NaCl films were grown by thermal evaporation of NaCl on Cu(111) at a sample temperature of about 270 K. Defect-free (100)-terminated islands of mainly two atomic layers were formed.[69] Low coverages of **1** and CO molecules were adsorbed at sample temperatures below 10 K. CO tips were prepared by picking up a single CO molecule from NaCl.[26]

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