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COMMUNICATION

Expanding the BN-Embedded PAH Family: 4a-aza-12a-borachrysene

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Previously unknown 4a-aza-12a-borachrysene has been synthesized in only four steps. The reactions of this BN-embedded PAH with bromine and organolithium compounds proceed with complete regioselectivity, resulting in the formation of nine derivatives. One of these, a phenylalkynyl-substituted derivative, exhibits a remarkably high fluorescence quantum yield ($\phi_F = 0.68$).

Formal replacement of a C=C unit in an aromatic compound by an isoelectronic B–N bond leads to BN-aromatic compounds,¹ which maintain their aromaticity and basic structural motifs but have different properties due to the presence of a dipole in the molecule.² BN/CC-isosterism is of particular relevance in the field of polycyclic aromatic compounds (PAHs),³ in which the new optical and electronic properties induced by the presence of this polarized BN unit provide a great opportunity for the design of new materials. Thus, BN-polycyclic aromatic hydrocarbons (BN-PAHs) have been investigated as promising components for improved optoelectronic devices.⁴ Moreover, the azaborine unit has also recently been explored in the search for new ligands for transition-metal-based catalysis,⁵ as well as a new pharmacophore in medicinal chemistry.⁶

Although significant progress has been made in the field of BN-PAHs in the last decade,⁷ there is still a lack of general and mild methodologies for the preparation of these compounds in sufficient quantities and a need for a better understanding of the effects that replacement of a C=C bond by a B–N bond has on their properties.⁸ As such, the basic knowledge obtained from the simplest such systems is highly valuable.

In this regard, several BN-isosteres of benzene,⁹ naphthalene,¹⁰ anthracene¹¹ and phenanthrene¹² have been described. Further studies on these compounds have shown that the position of

the B–N unit plays a crucial role in both their reactivity and their photophysical properties.^{7a,12a-e,13} As far as tetracyclic BN-embedded PAHs are concerned, only examples of triphenylene,¹⁴ pyrene¹⁵ and benzo[*c*]phenanthrene¹⁶ with the replacement of a C=C unit by a B–N bond have been reported (Figure 1). Nevertheless, these molecules cover only a small number of the total possible permutations of this BN/CC-isosterism and, for instance, BN-embedded analogs of tetracene, tetraphene or chrysenes have not yet been described. In this context, herein we report an efficient synthesis of the previously unknown 4a-aza-12a-borachrysene (**1**), as well as a study of its reactivity and main optical properties.

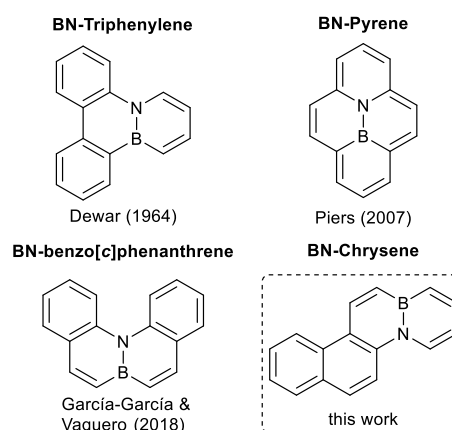


Figure 1. Reported tetracyclic BN-embedded arenes.

The synthesis of **1** (Scheme 1) started with a high-yielding Buchwald–Hartwig amination reaction, using [PdCl(allyl)]₂ and JohnPhos as catalytic system, between easily accessible 2-bromo-1-vinylnaphthalene (**2**)¹⁷ and commercially available 3-butenylamine to give **3**. This substrate was efficiently cyclized via a highly efficient annulation/aromatization process¹⁸ using potassium vinyltrifluoroborate to yield BN-phenanthrene derivative **4**. Subsequent ring-closing metathesis using the second-generation Grubbs catalyst afforded **5**, which was finally oxidized in decane at 140 °C in the presence of Pd/C to give the

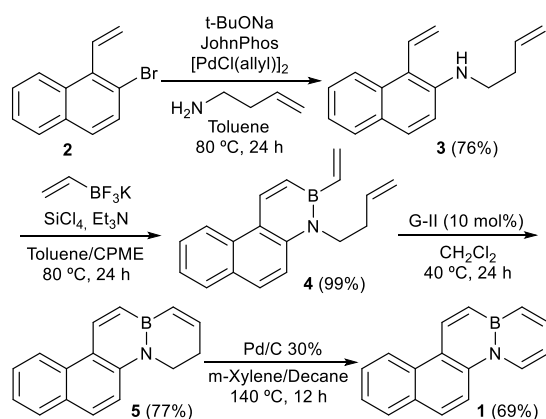
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desired compound **1**. Overall, this novel BN-chrysenes was prepared in only four steps with a 40% overall yield.



Scheme 1 Synthesis of BN-chrysenes **1**.

The structure of **1** was confirmed by an X-ray diffraction study (Figure S1).¹⁹ The B–N bond length (1.451(3) Å) is similar to those reported for other BN-aromatic compounds.²⁰ In contrast to the BN-embedded benzo[*c*]phenanthrene,¹⁶ which adopts a twisted conformation with an angle between the non-BN rings of 38.9°, this heterocycle is planar, with angles between the rings ranging from 0.2° to 1.8°. The molecules are associated in pairs by $\pi\cdots\pi$ interactions with a perpendicular distance of 3.40 Å, and they are aligned in an antiparallel orientation with respect to the B–N bond. These pairs of molecules are connected by C–H $\cdots\pi$ and hydrophobic interactions, thus resulting in an alternating pattern (Figure 2).

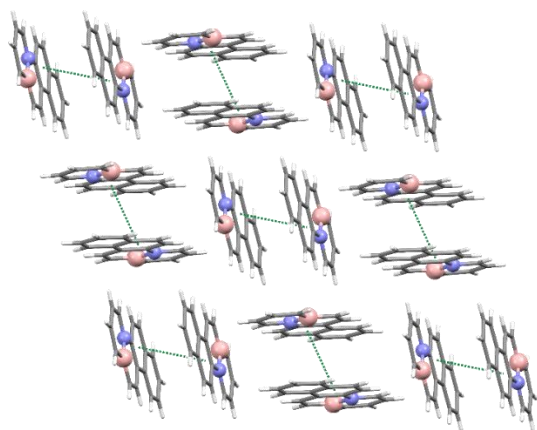
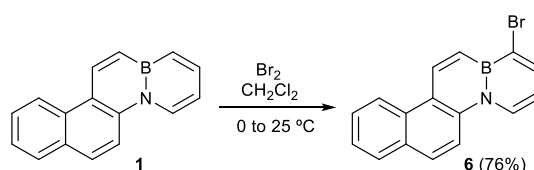


Figure 2. Pattern of the pairs of molecules in the crystal packing for **1**.

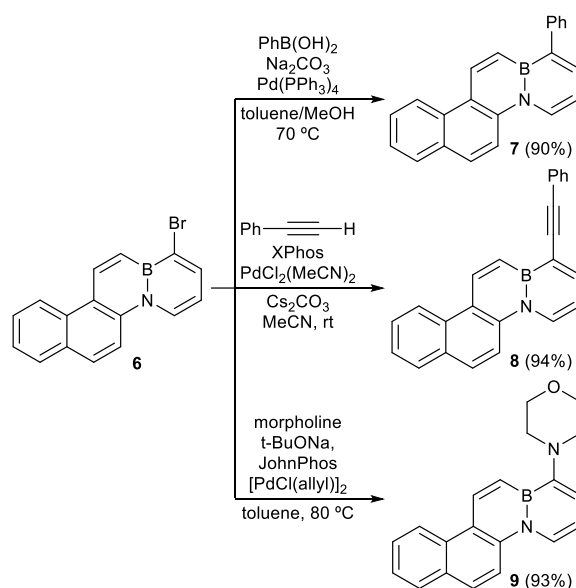
The reactivity of BN-chrysenes **1** was evaluated in order to gain an insight into the properties of this compound and to develop new possibilities for obtaining functionalized derivatives. We began our investigation by exploring its behaviour in an electrophilic aromatic substitution, a type of reaction that has proven to be a useful tool for the functionalization of BN-aromatic compounds.^{7a} Thus, regioselective bromination of **1** at the C1 position (next to the boron)^{12c,21} was achieved by treatment with 1.7 equivalents of bromine in CH_2Cl_2 at 25 °C (Scheme 2). It is worth noting that **6** was the only product

isolated under these conditions; no traces of other regioisomers or dibrominated compounds were observed.



Scheme 2 Regioselective bromination of **1**.

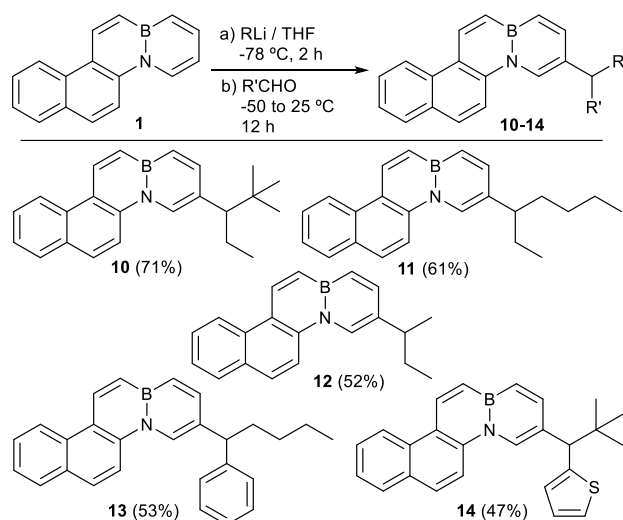
Interestingly, **6** is suitable for further functionalization by different palladium-catalyzed cross-coupling reactions (Scheme 3). Thus, its treatment under standard Suzuki, Sonogashira and Buchwald-Hartwig amination coupling conditions afforded functionalized derivatives **7**, **8** and **9** in excellent yields.



Scheme 3 Cross-coupling reactions.

The reactivity of **1** with organolithium compounds was also studied. Very recently, our group reported the regioselective C–H functionalization of a BN-phenanthrene with embedded B and N atoms via coordination of the organolithium to the boron atom followed by addition of a carbonyl compound.^{13d} In this regard, when using BN-chrysenes **1** under the same reaction conditions optimized in that previous study (2 equiv. of RLi and an excess of carbonyl compound), we achieved derivatives **10–14**, functionalized at the position β to the N atom, in moderate to good yields (Scheme 4), thus demonstrating that our methodology may be useful for the functionalization of higher BN-aromatics.

Once we had developed an efficient synthesis of BN-chrysenes **1**, and examined its reactivity, in which various functionalized derivatives were synthesised, we focused on studying their main photophysical properties. The absorption and emission data for the parent compound **1**, and a selection of its substituted derivatives (**6–9**), in cyclohexane are summarized in table 1.



Scheme 4 Reactivity with organolithium compounds.

The UV/Vis spectra exhibited high-intensity absorption in the 260 and 300 nm region and some lower intensity structured bands that extended from 300 nm up to 400 nm (Figure S2). A bathochromic displacement for the absorption maxima of **1** (~278 nm) with respect to chrysene (~268 nm)²³ was also observed. Derivatives **7** and **8** exhibited the largest molar absorptivities. The morpholinyl-functionalized derivative **9** showed its maximum, as expected, slightly shifted to the blue (at 259 nm).

Table 1. UV/Vis and fluorescence data for BN-phenanthrenes **1**, **6-9**^[a]

compound	ϵ ($M^{-1}cm^{-1}$)	$\lambda_{abs\ max}$ (λ_{exc}) (nm)	λ_{em} (nm)	$\phi_F^{[b]}$	τ [c] (ns)
1	3340	278 (334)	371	0.19	6.0
6	2850	282 (321)	373	0.01	5.3
7	12360	284 (323)	381	0.10	2.7
8	18160	288 (348)	391	0.68	1.0
9	9830	259 (319)	378 (489)	0.16	3.7(2.7)

[a] All experiments were performed using cyclohexane solutions. [b] Quantum yields reported relative to 9,10-diphenylanthracene in cyclohexane ($\phi_F = 0.93$).²² [c] Fluorescence lifetimes were obtained upon 335 nm Nanoled excitation by fixing the emission at λ_{em} .

The fluorescence spectra observed for **1**, **6-9** derivatives (Figure S3), more or less structured, showed features similar to chrysene (a main band with peaks at 361, 378 and 403 nm).²³ The maxima emission bands for **7** and **8** were also shifted to the red relative to chrysene, **1** or **9**. However, the morpholinyl containing derivative **9** displayed an additional wide fluorescence band near 490 nm whose intensity (and band location) depended on the solvent nature. Its intensity relative to the band centered at 378 nm also increased with concentration. This band may likely be attributed to the presence of rather stable π - π stacking aggregates in solution (see SI for confirmation). Fluorescence decay profiles for all derivatives were mono-exponential with lifetimes ranging from 6.0 ns for **1** to 1.0 ns for **8**. Notice that the decays for **9** measured at λ_{em} of 278 and 489 nm were also mono-exponential with

lifetimes of 3.7 and 2.7 ns respectively. Fluorescence quantum yields for **1**, with respect to chrysene ($\phi_F = 0.14$),²³ experimented a small increase ($\phi_F = 0.19$). Other derivatives differed significantly in their fluorescence quantum yields. Thus, while Br-, Ph- and morpholinyl-functionalized derivatives **6**, **7** and **9** showed a lower value than that of the parent (**1**), phenylalkynyl-substituted derivative **8** exhibited a markedly higher quantum yield ($\phi_F = 0.68$). A similar effect of alkynyl substituents on the fluorescence of BN-aromatic compounds has been reported previously.^{13b}

Finally, we investigated the ability of **1** to react with fluoride, as it is known that the p-orbital of the boron center in BN-PAHs can accept an electron pair from Lewis bases such as F^{-12d,24} and we have shown the coordination of organolithiums to the boron of this BN-chrysene. Thus, we tested the response of **1** to fluoride anions by performing fluorescence titration experiments (Figure 3), which was carried out using a solution of *n*-tetrabutylammonium fluoride (TBAF), synthesized by us.²⁵ Upon addition of fluoride aliquots to a solution of **1** in cyclohexane, the emission intensity at the maximum at 371 nm gradually decreased and a new emission band centered at ~470 nm slightly increased in intensity. An isoemissive point appeared at ~430 nm, thus indicating the formation of a fluoroborate complex. A similar isosbestic point was also observed in the absorption spectra (Figure S8). The Stern-Volmer plots of I_0/I and τ_0/τ (Figure S10) demonstrated that the fluorescence intensity decreasing was not the consequence of a dynamic quenching of **1** fluorescence by F⁻, but rather of the formation of a complex whose estimated constant was $19200 \pm 2100 M^{-1}$ (Figure S11) as described in the SI.

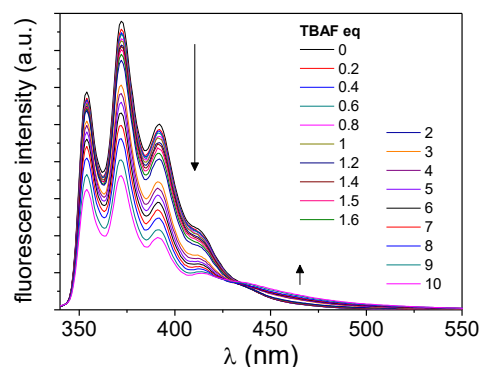


Figure 3. Titration of **1** with 0-10 eq. of TBAF (in cyclohexane).

In conclusion, synthesis of the previously unknown 4a-aza-12a-borachrysene has been described in only four steps with a 40% overall yield. In order to gain an insight into its properties, the reactivity of this BN-chrysene with an activated electrophile (bromine) and organolithium compounds was tested. Bromination proceeded with complete regioselectivity at C1, thus allowing a subsequent straightforward derivatization based on palladium-catalyzed cross-coupling reactions under standard conditions. Regarding the addition of organolithium compounds, BN-chrysene **1** undergoes a regioselective C-H functionalization at C3 via an initial coordination of RLi to the boron atom, followed by addition of a carbonyl compound. The fluorescence of this BN-chrysene and some of its derivatives

was also evaluated. The parent compound **1** was observed to undergo a slight bathochromic shift along with a small increase in the quantum yield ($\phi_F = 0.19$) with respect to chrysene. Phenylalkynyl-substituted derivative **8** exhibited a remarkably higher quantum yield ($\phi_F = 0.68$). Finally, we have demonstrated the ability of **1** to react with fluoride anion by performing a fluorescence titration experiment.

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Conflicts of interest

There are no conflicts to declare.

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