



**Boron-nitrogen substituted perylene through
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ARTICLE TYPE

Boron-nitrogen substituted perylene through photocyclisation

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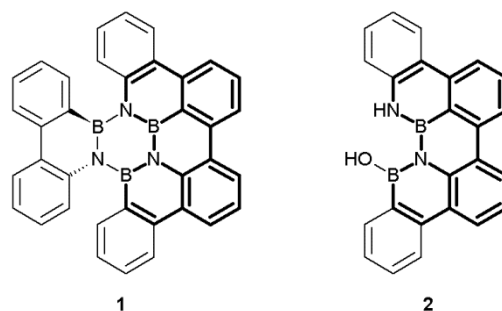
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5 A BN substituted hexabenzotriphenylene (B₃N₃) closes one C-C bond upon irradiation with light of 280 – 400 nm in the presence of iodine to yield a phenanthrene annelated B₃N₃ tribenzoperylene. Upon treatment with methanol a B₂N₂ dibenzoperylene is obtained.

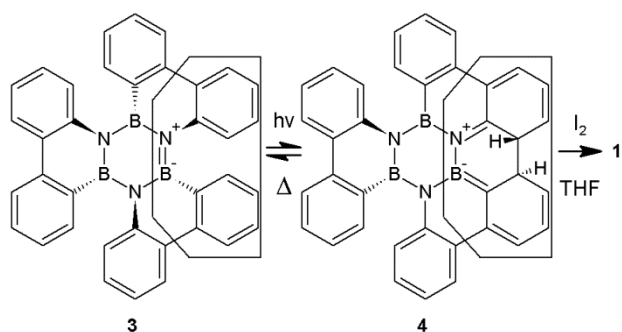
10 Atom-precise built-up of doped graphene (sub)structures is one of the challenging synthetic problems of these days.¹ These polycyclic aromatic hydrocarbons have astonishing properties that could show superior performance^{1a, 2} compared to their all-carbon analogues in industrial applications.³ To tune electronic properties, or to be more accurate the HOMO-LUMO gap,⁴ synthetic tools and handles to implement changes have to be available. While all-carbon PAH only offer the opportunity for alteration at the periphery, substitution of carbon atoms by suitable other elements may provide a means to improve electronics without significantly changing other parameters like bond length,⁵ and crystal packing.⁶ In this regard a long known concept is the isoelectronic substitution of CC units by BN moieties that only alters electronics without changing geometrical properties.⁷ But although several aromatic hydrocarbons with incorporated BN-units are known, there are only very few methods available for their synthesis. While some synthetic methods are restricted to one special BN-PAH without the possibility for extending their scope,⁸ others have proven to be of conceptual relevance as they are useful for a broader range of boron nitrogen aromatics. The oldest known concept to produce BN-PAHs involves hydroboration of suitable alkenes in the key step.^{8a, 9} Another strategy introduced by Piers *et al.* relies on the aromatization of boron containing heterocycles by the extrusion of trimethylsilylchloride when reacted with azaheterocycles (pyridine, pyridazine, ...).^{2, 6, 10} A route that is mainly used for the synthesis of different 1,2-dihydroazaborines utilizes ring closing metathesis.¹¹ Introduction of BN units into aromatic hydrocarbons can also be accomplished by Lewis acid (AlCl₃) assisted Friedel-Crafts reaction of dichloroaminoboranes, which are obtained from the reaction of aromatic amines with boron trichloride. Although long known,¹² this concept has been reintroduced only recently.¹³ Similar to the Friedel-Crafts reaction, the photocyclisation of suitable BN stilbenes has almost been forgotten. Early investigations show that B,B,N-triarylamino-boranes form BN phenanthrenes upon irradiation.¹⁴ As photocyclisations of stilbenoid systems prove to be a versatile tool in all-carbon chemistry,¹⁵ the conceptual transfer to BN

systems may also be a powerful tool for building up BN-PAHs in an atom-precise way. We here reintroduce the concept of photocyclisation for BN-PAHs and expand its scope by presenting two representatives of a new class of extended BN polyaromatic hydrocarbons that are related to perylenes. A photochemical synthesis is carried out to produce **1** whereas **2** is received upon treatment of **1** with methanol.



55 Fig.1 Compound **1** is synthesized photochemically and fragments to **2** if treated with MeOH; **1** and **2** both bearing the perylene motif

The synthesis of **1** is straightforward and can be accomplished by irradiation of 1,2:3,4:5,6-tris(o,o'-biphenylylene)borazine **3**¹⁶ in the presence of iodine/THF as oxidant-scavenger system using a high pressure mercury vapour lamp in an overnight (15 hr) reaction. Following the stilbene photocyclization reaction path the *trans*-dihydro intermediate **4** can also be assumed (Scheme 1). For best results, the reaction is done with 3 eq. of iodine (43 % yield). Lowering the iodine load to 1 eq. results in a decrease to 27 % yield, while raising it to 30 eq. mainly returns the starting material with only traces of **1**. For safety and performance reasons, THF is preferred over propylene oxide as scavenger of the formed hydrogen iodide prohibiting unwanted reaction interference.¹⁷ The reaction works well in toluene and cyclohexane, but owing to the low solubility of **3** in cyclohexane, suspensions of **3** have to be irradiated nearly 3 times longer than the solutions in toluene. Cyclohexene¹⁸ or DDQ¹⁹ have also been reported as oxidants in photocyclizations but they do not lead to product formation here. Higher concentrations (above 0.7 mM) are counterproductive and only lead to a 20 % yield of **1** with still some 25 % of starting material **3** left unreacted.



Scheme 1 Reaction of **3** with light to yield the trans-dihydro derivative **4** that is being oxidized by iodine to receive the final product **1**. The black box tracks the transformation of the stilbenoid system

The reaction mechanism is investigated by irradiating solutions of **1** in toluene with different wavelength ranges. Irradiation with light of 240 – 255 nm almost exclusively excites the solvent toluene and does not lead to product formation. Low conversion is obtained when the absorption bands of iodine are addressed (420 – 630 nm). Reasonable yields can only be achieved with light of 280 – 400 nm where toluene and iodine are almost transparent and **3** absorbs energy. This is in support of the proposed mechanism where **3** is directly excited to the S_1 level and closes the ring upon relaxation in conrotatory manner (6π).

Although stilbene photocyclisations are known for substrates with bromine substituents,²¹ the tribromo derivative **5**^{16c} cannot be cyclised as irradiation leads to an almost complete decomposition of the starting material. Nevertheless there are quite a number of all-carbon molecules known that, without satisfying explanation, do not undergo stilbene photocyclisations.²²

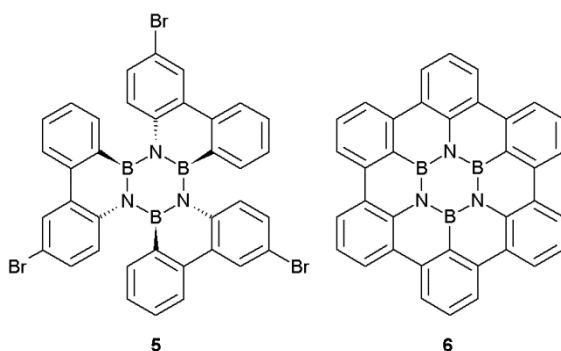


Fig. 2 Tribromo derivative (**5**) of **3** and the ring closed planar hexa-peri-benzocoronene derivative **6**

As the photocyclization works reasonably well for closing one C-C-bond in our system, the idea was to investigate the possibility of forming three new C-C-bonds. But the synthesis of the BN-HBC derivative **6** was unsuccessful, even after irradiation of **1** for 62 hours and of **3** for 160 hours.

Compound **1** can be regarded as a BN phenanthrene fused to a B_2N_2 substituted dibenzoperylene. The geometrical constraint imposed by the dibenzoperylene unit imposes considerable strain

on the borazine core. And indeed, treatment of **1** with methanol and wet CH_2Cl_2 yields another BN-PAH **2**.[‡]

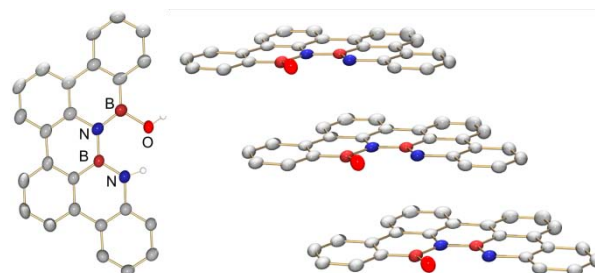


Fig. 3 X-ray crystal structure of **2**

Crystals of **2** grow from a solution of **1** in a mixture of methanol and dichloromethane. They show positional disorder as the boron, nitrogen and oxygen sites are occupied with 0.33:0.66 probability by these elements. Molecule **2** crystallizes in the γ motif ($P2_12_12_1$) according to the shortest cell axis definition (**2**, (a): 5.2893(3) Å; 4.6 Å $< \gamma <$ 5.4 Å) given by Desiraju and Gavezzotti.²³ The essentially planar molecules form parallel displaced stacks with pronounced overlap and only small contribution of C-H interactions from neighbouring stacks. The distance between two molecules in a stack is 3.34 Å, while the displacement is 3.80 Å (long axis of **2**) and 2.20 Å (short axis). Every stack is tilted toward the nearest stack in c direction by 70° and to the nearest stack in b direction by 78°.

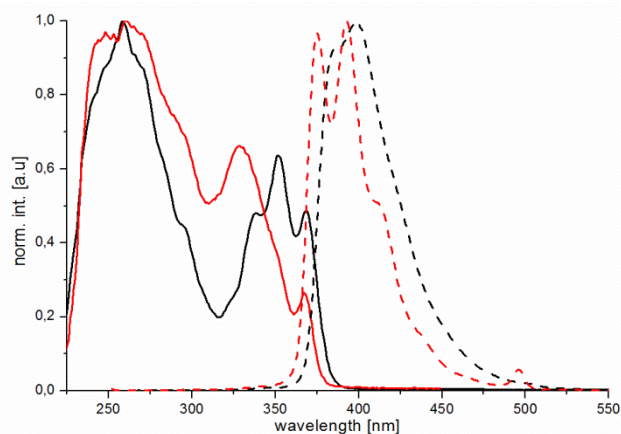


Fig. 4 Fluorescence spectra in dichloromethane (red: **1**; black: **2**): excitation (solid lines, both 0. Order) and emission (dotted lines, ex. 247 nm (red), 250 nm (black))

Consistent with the known BN substitution effect of increasing the HOMO-LUMO gap^{8b} is the finding that the BN-perylenes **1** and **2** show hypsochromic shifts of around 70 nm for the longest absorbing bands compared to the parent 2:3,10:11-dibenzoperylene (λ_{max} 440 nm).²⁴ The fluorescence spectrum of **1** with its maxima at 371 and 389 nm is blue-shifted compared to **2** (386 and 399 nm) and shows a pronounced fine structure in contrast to the excitation spectrum as well as the UV-vis spectrum. A direct comparison of the spectra of **1** and **2** with the corresponding all-carbon analogues is not possible as, to our knowledge, they are not known.

Conclusions

We have shown that the irradiation of 1:2;3:4;5:6-tris(o,o'-biphenylene)borazine **3** yields the ring-closed molecule **1** that belongs to a BN substituted perylene series. Although the mechanism of its formation is still under investigation it seems reasonable to assume a stilbene like photocyclisation reaction that proceeds by direct excitation of the precursor molecule **3**. Upon methanolysis of **1** another representative (**2**) of the aforementioned PAH class is formed.

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Notes and references

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† Electronic Supplementary Information (ESI) available: detailed experimental procedures and spectra for **1** and **2**, Raman spectrum of **3**.

²⁰ See DOI: 10.1039/b000000x/

‡ Reaction of **1** with methanol also produces **2**, presumably due to instability of the expected methoxy derivative to H₂O.

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