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Boron–nitrogen substituted perylene obtained through photocyclisation†

Cite this: *Chem. Commun.*, 2014, **50**, 7821

Received 24th February 2014,
Accepted 20th May 2014

DOI: 10.1039/c4cc01424c

www.rsc.org/chemcomm

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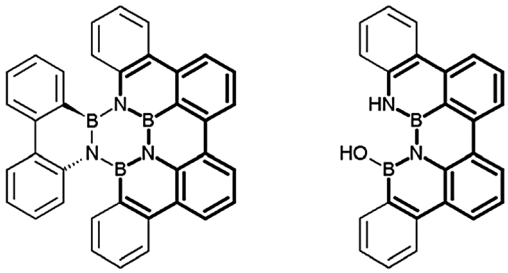
A BN substituted hexabenzotriphenylene (B_3N_3) closes one C–C-bond upon irradiation with light of 280–400 nm in the presence of iodine to yield a phenanthrene annelated B_3N_3 tribenzoperylene. Upon hydrolysis a B_2N_2 dibenzoperylene is obtained.

Atom-precise build-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 PAHs only offer the opportunity for alteration at the periphery, substitution of carbon atoms by other suitable 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, which 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 of 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 aza-heterocycles (pyridine, pyridazine,...).[2,6,10] A route that is mainly used for the synthesis of different 1,2-dihydro-1,2-azaborines utilizes ring closing metathesis.[11] Introduction of BN units into aromatic hydrocarbons can also be accomplished by Lewis acid ($AlCl_3$) 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 photo-cyclisation of stilbenoid systems proves 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 reintroduce here 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 obtained upon hydrolysis of **1** (Fig. 1).

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 an oxidant-scavenger system using a high pressure mercury vapour lamp in an overnight (15 h) reaction. Following the stilbene photocyclization reaction path the *trans*-dihydro intermediate **4** can also be assumed (Scheme 1). For best



1 **2**

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

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† Electronic supplementary information (ESI) available: Detailed experimental procedures and spectra of **1** and **2**, and the Raman spectrum of **3**. CCDC 987402. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc01424c

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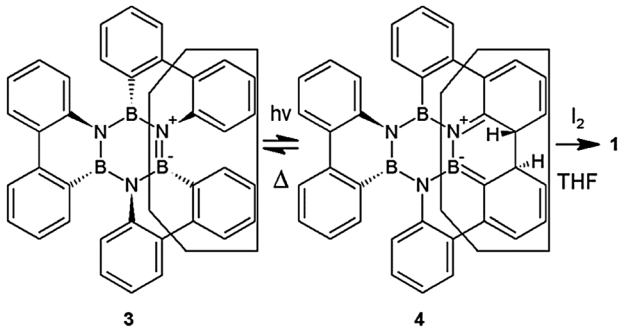

Scheme 1 Reaction of **3** with light to yield the *trans*-dihydro derivative **4** that is being oxidized by iodine to obtain the final product **1**. The black box tracks the transformation of the stilbenoid system.

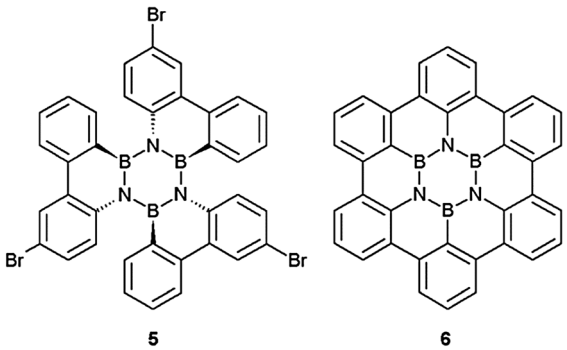

Fig. 2 Tribromo derivative (**5**) of **3** and the ring closed planar hexa-peri-benzocoronene derivative **6**.

results, the reaction was carried out with 3 eq. of iodine (43% yield). Lowering the iodine load to 1 eq. resulted in a decrease to 27% yield, while raising it to 30 eq. mainly returned the starting material with only traces of **1**. For safety and performance reasons, THF is preferred over propylene oxide as a 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. Cyclohexene[18] and DDQ[19] have also been reported as oxidants in photocyclizations but they did not lead to product formation here. Higher concentrations (above 0.7 mM) were counterproductive and only led to a 20% yield of **1** with still some 25% of starting material **3** left unreacted.

The reaction mechanism is investigated by irradiating solutions of **1** in toluene with light of different wavelength ranges. Irradiation with light of 240–255 nm almost exclusively excites the solvent toluene and did not lead to product formation. Low conversion was obtained when the absorption bands of iodine were addressed (420–630 nm). Reasonable yields could 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 a conrotatory manner ($6\pi_a$).[20] This assumption was further confirmed by an unsuccessful reaction of **3** in cyclohexane with benzophenone as a triplet sensitizer that resulted in the recovery of the starting material.

Although stilbene photocyclisation is known for substrates with bromine substituents,[21] the tribromo derivative **5**[16c] (Fig. 2) could not be cyclised as irradiation led to an almost complete decomposition of the starting material. Note that there are quite a number of all-carbon molecules known that, without a satisfying explanation, do not undergo stilbene photocyclisation.[22]

As the photocyclization worked reasonably well for closing one C–C-bond in our system, the possibility of forming three new C–C was investigated. But the synthesis of the BN-HBC derivative **6** (Fig. 2) 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 is expected to impose on the borazine core. And indeed, treatment of **1** with methanol or wet CH_2Cl_2 yielded another BN-PAH **2** (Fig. 3).‡

Crystals of **2** grew 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 in 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 the *c* direction by 70° and to the nearest stack in the *b* direction by 78° (Fig. 3).

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 (Fig. 4). A direct comparison of the spectra of **1** and **2** with those of the corresponding all-carbon analogues is not possible as, to our knowledge, they are not known.

We have shown that the irradiation of 1:2;3:4;5:6-tris(*o*,*o*′-biphenylylene)borazine **3** yields the ring-closed molecule **1** that

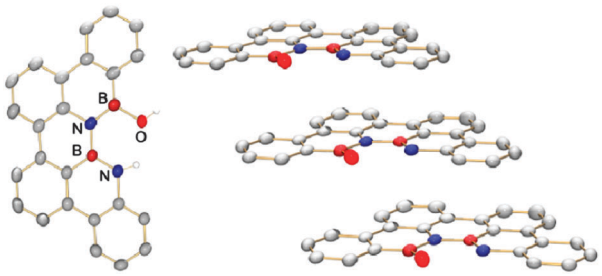

Fig. 3 X-ray crystal structure of **2**. Hydrogen atoms omitted for clarity.

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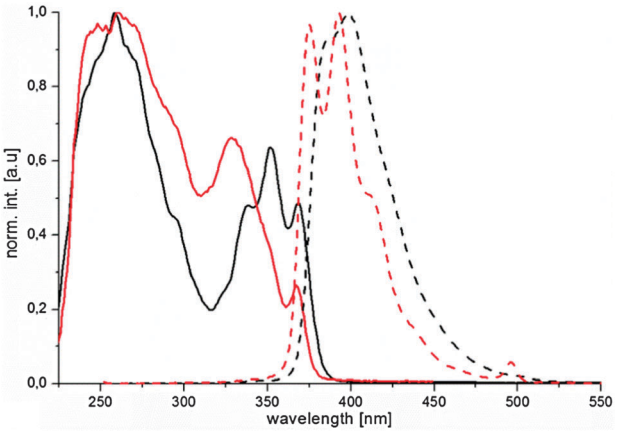

Fig. 4 Fluorescence spectra in dichloromethane (red: **1**; black: **2**): excitation (solid lines, both 0 order) and emission (dotted lines, ex. 247 nm (red), 250 nm (black)).

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 hydrolysis of **1** another representative (**2**) of the aforementioned PAH class is formed.

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der chemischen Industrie through a fellowship to M.M.

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‡ Reaction of **1** with methanol also produces **2**, presumably due to instability of the expected methoxy derivative to H_2O.

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