A BN substituted hexabenzotriphenylene (B$_3$N$_3$) closes one C–C-bond upon irradiation with light of 280–400 nm in the presence of iodine to yield a phenanthrene annelated B$_3$N$_3$ tribenzoperylene. Upon hydrolysis a B$_3$N$_2$ dibenzoperylene is obtained.

Atom-precise build-up of doped graphene (sub)structures is one of the challenging synthetic problems of these days. These polycyclic aromatic hydrocarbons have astonishing properties that could show superior performance compared to their all-carbon analogues in industrial applications. To tune electronic properties, or to be more accurate the HOMO–LUMO gap, 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 and crystal packing. In this regard a long known concept is the isoelectronic substitution of CC units by BN moieties, which only alters electrons without changing geometrical properties. 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, 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. 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, …). A route that is mainly used for the synthesis of different 1,2-dihydro-1,2-azaborines utilizes ring closing metathesis. 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, this concept has been reintroduced only recently. 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 phenanthenes upon irradiation. As photocyclisation of stilbenoid systems proves to be a versatile tool in all-carbon chemistry, 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′-biphenylyl)borazine 3′ 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

![Fig. 1](image-url)  
Compound 1 is synthesized photochemically and fragments to 2 if treated with MeOH; 1 and 2 both bearing the perylene motif.
S1 level and closes the ring upon relaxation in a conrotatory manner (6 p),\(^2\) according to the shortest cell axis definition (2, (a): 5.2893(3) Å; 4.6 Å < γ < 5.4 Å) given by Desiraju and Gavezzotti.\(^3\) 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\(^4\) 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-dibenzoperylenyl (\(\lambda_{\text{max}}\) 440 nm).\(^5\) 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′-biphenylence)borazine 3 yields the ring-closed molecule 1 that

![Scheme 1](image)

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](image)

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

![Fig. 3](image)

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

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Notes and references

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