Boron-nitrogen substituted perylene through photocyclisation

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Boron-nitrogen substituted perylene through photocyclisation

Matthias Müller, a Stefan Behnle, a Cäcilia Maichle-Müssmer b and Holger F. Bettinger a

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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.

Atom-precise built-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 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 and crystal packing. 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. 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, 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 hydrosorbtion of suitable alkynes 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-dihydroazaborines utilizes ring closing metathesis. 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, 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-triarylaminoboranes form BN phenanthrenes upon irradiation. As photocyclisations of stilbenoid systems prove 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 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.

The synthesis of 1 is straightforward and can be accomplished by irradiation of 1,2,3,4,5,6-tris(o,o'-biphenylylene)borazine 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. 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 or DDQ 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.

Fig. 1 Compound 1 is synthesized photochemically and fragments to 2 if treated with MeOH; 1 and 2 both bearing the perylene motif.
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 S1 level and closes the ring upon relaxation in conrotatory manner (6 \( \pi_a \)).20 This assumption is further confirmed by an unsuccessful reaction of 3 in cyclohexane with benzophenone as triplet sensitizer that resulted in the recovery of the starting material.

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

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\(_2\)N\(_2\) 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\(_2\)Cl\(_2\) yields another BN-PAH 2.\(^{1} \)

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 \( \gamma \) motif (P2\(_1\)2\(_1\)2\(_1\)) according to the shortest cell axis definition (2, \( \alpha \): 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°.

Consistent with the known BN substitution effect of increasing the HOMO-LUMO gap\(^{3b} \) is the finding that the BN-perylene 1 and 2 show hypsochromic shifts of around 70 nm for the longest absorbing bands compared to the parent 2:3,10:11-dibenzoperylene (\( \lambda_{\text{max}} \) 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’-biphenyl)ene)borazine 3 yields the ring-closed molecule 1 that belongs to a BN substituted pyrrole 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 methanalysis 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.

Notes and references


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