Heteropolycyclic Aromatics

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B–N versus C–C: How Similar Are They?**

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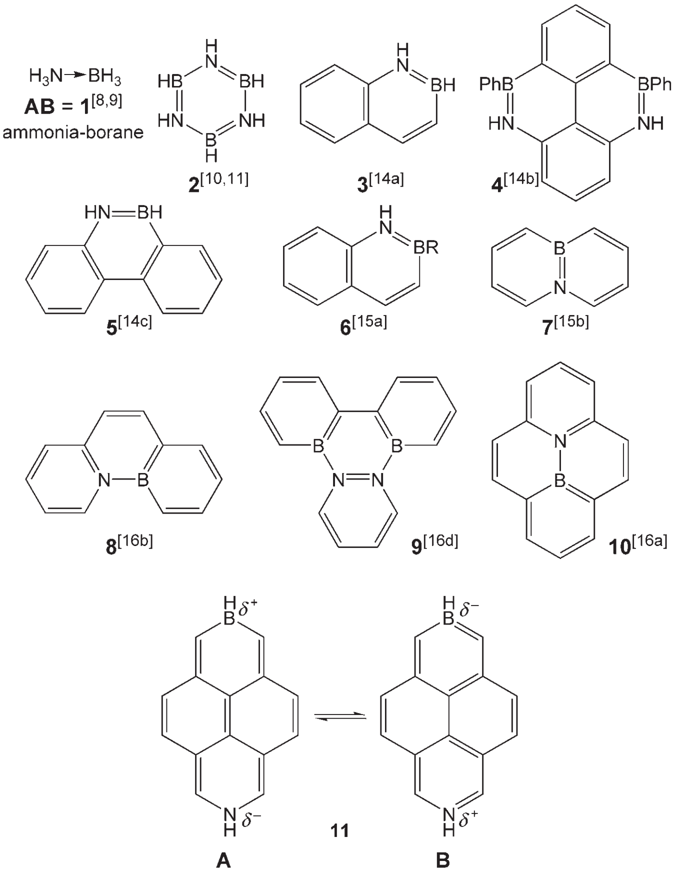
Carbon, of course, forms numerous types of compounds, largely on the basis of its ability to form strong, covalent bonds with itself. Boron, being one element to the left of carbon in the periodic table, has a significantly lower electronegativity, and it possesses one less electron. Likewise, nitrogen, being one element to the right of carbon, has a higher electronegativity and one more electron. Thus, replacement of two carbon atoms by one boron and one nitrogen atom produces systems that are isoelectronic with their all-carbon analogues, yet they possess at least local dipole moments if the two heteroatoms are adjacent, as the bonding now contains a significant ionic component. This polarity can significantly alter both molecular and solid-state electronic and optical properties of the system by modifying the character of the frontier molecular orbitals, the gap between the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO), and the intermolecular interactions present in solid phases.

Elemental carbon exists in several allotropes, including graphite and diamond. Extended Hückel band-structure calculations show that graphite, which has a high conductivity and a metallic structure, is a semimetal, whereas isoelectronic boron nitride, with a graphite structure, is an insulating white solid.[1] Boron nitride also exists as a polymorph with a diamond structure, which is of considerable value as an extremely hard coating.

Similar to the more popular carbon analogues, BN nanotubes can be prepared by direct-current arc,[2] laser ablation,[3] and chemical vapor deposition (CVD)[4] methods. The CVD method uses borazine as the precursor compound, which is decomposed over a NiB_2 catalyst at 1100 °C. The BN nanotubes have similar mechanical properties to the carbon ones, with a Young's modulus of approximately 1 TPa.[5] However, in contrast to carbon nanotubes, which can be semiconducting or metallic, depending on their diameter and chirality, BN nanotubes have a uniform band gap of approximately 5 eV and can be considered to be insulating, regardless of their structure.[6] This field, including both pure and doped BN nanotubes, has attracted much current interest.[7]

The simplest comparison on a molecular scale can be made between ethane and the isoelectronic ammonia-borane adduct (**1**, $H_3N{\cdot}BH_3$, also abbreviated **AB**, Scheme 1), which is attracting considerable attention as a hydrogen-storage material.[8,9] Ethane, a gas at ambient temperature and pressure, has a dipole moment of zero, and all hydrogen atoms are very weakly acidic, as the electronegativity of H is actually between that of boron and carbon. In contrast, **AB** is polar. The boron-bonded hydrogen atoms are hydridic, and the nitrogen-bonded hydrogen atoms are acidic, leading to



Scheme 1. Ammonia-borane (AB) and some cyclic BN-containing π systems.

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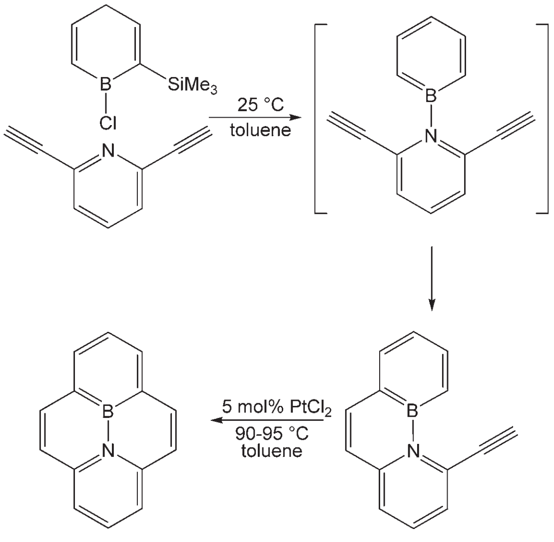
strong intermolecular BH···HN interactions; thus, **AB** is a solid at room temperature. The difference in electronegativity of boron and nitrogen is reflected in a number of very important properties of **AB**, which contrast dramatically with those of ethane.

Another pair of isoelectronic molecules that has long fascinated chemists is benzene and borazine (**2**, $B_3N_3H_6$), which has alternating B and N atoms in the hexagonal ring. The main question which arises is the degree of aromaticity in borazine, which has been studied both experimentally and theoretically for decades. While many earlier studies suggested that borazine is highly aromatic, the most recent theoretical results suggest just the opposite.[10,11] Thus, the matter is still one of debate and study.

Polycyclic aromatic hydrocarbons (PAHs) are attractive, not only because of their intrinsic beauty resulting from structural simplicity and high symmetry, but also owing to their fundamental electronic and optical properties, which are of value in organic optoelectronic materials.[12] The replacement of one or more C–C units in PAHs by isoelectronic B–N units is expected to tune their electronic and photophysical properties.[13] However, since the pioneering work of Dewar and co-workers (i.e. **3**–**5**) in the 1950s and 1960s,[14] few reports on BN-substituted PAHs appeared until the beginning of this century, when the research groups of Paetzold, Ashe, and Piers took on the synthetic challenge of constructing such molecules (i.e. **6** and **7**).[15,16]

The Piers group has focused on the formation of heterocyclic analogues of the PAHs carbazole, phenanthrene (**8**), and triphenylene (**9**).[16] The BN moieties can be "internalized" through an ene–yne cycloisomerization reaction, which they have recently extended to afford a pyrene analogue containing a BN unit at the center (**10**). The photophysical behavior of pyrene is amongst the best understood of all organic compounds, and it remains the subject of much study.[17] Excimer formation occurs even at very low concentrations, and the vibrational fine structure of the emission spectrum can be used to examine solvent polarity. Thus, the synthesis of the BN analogue of pyrene represents a major breakthrough, allowing comparisons to be made with one of the most important hydrocarbon chromophores.

The synthetic strategy (Scheme 2) used to prepare the "internal" BN pyrene started with boroacyclohexadiene and 2,6-dialkynylpyridine derivatives, which form Lewis acid–base complexes. Spontaneous cyclization gave the BN phenanthrene derivatives, but platinum-catalyzed cyclization was required to form the second ring, thus affording the final pyrene analogue in good yield. Subsequent work showed that these strategies are also applicable to the synthesis of a B_2N_2-containing quaterphenyl analogue, which combines two BN pyrene units.[16c]



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Scheme 2. Synthesis of the internal BN pyrene analogue **10** of Piers and co-workers.[16a]

The comparison between pyrene and its internal BN analogue is informative. Piers and co-workers suggested different packing modes for pyrene and internal BN pyrene in their single crystals, as the latter structure contained pairs of crystallographically inequivalent molecules stacked in nearly but not perfectly parallel fashion. However, a closer examination of the crystal structure of pyrene itself[18] (which contains only one molecule in the asymmetric unit) shows similar overall packing. Essentially, both structures are comprised of a herringbone of dimers, although for pyrene, the pairs of molecules making up the dimers are crystallographically equivalent and exactly parallel by symmetry. It is therefore interesting that the dimeric units in the BN pyrene case ($Z=8$, $Z'=2$) are not crystallographically equivalent, and we must wonder whether an alternative, more symmetric $Z=4$, $Z'=1$ structure is accessible. Our DFT geometry optimizations (B3LYP, 6-31G*) are in perfect agreement with the crystallographically determined, short B–N bond length of 1.456 Å; calculations by Piers and co-workers support aromatic behavior of the borabenzene ring but suggest a measurable degree of bond localization in the C_4NB rings, as in the flanking rings in pyrene itself.

Interestingly, the absorption and emission bands of the internal BN pyrene are significantly red-shifted relative to those of pyrene. The emission spectrum of BN pyrene also clearly shows the vibrational fine structure characteristic of pyrene. However, the fluorescence quantum yield for the BN pyrene analogue is lower than that of pyrene, whereas the BN-containing phenanthrene analogue **8** shows a higher quantum yield than its hydrocarbon analogue.[16b] Thus, phenanthrene is weakly fluorescent ($\Phi=0.09$ in cyclohexane), while pyrene is highly fluorescent ($\Phi=0.60$ in cyclohexane). However, for the BN-substituted phenanthrene, $\Phi=0.58$ in cyclohexane, whereas for the internal BN pyrene, $\Phi=0.15$ in cyclohexane. The reasons for these variations are not yet clear.

It is interesting to speculate on the properties of isomers of the Piers group's BN pyrene, such as **11**, in which the B and N atoms are shifted to the 2- and 8-positions (i.e. as far apart as possible). Preliminary DFT calculations on such an isomer give a dipole moment of approximately 10.4 D, in contrast to the value of about 2.5 D for the internal isomer, thus reflecting the increased charge separation that occurs upon moving the electropositive B and electronegative N atoms

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further apart. In addition, the 2,8-isomer shows a greater degree of bond localization throughout the π system, which is consistent with a larger contribution from a quinoidal form, **11A** (see Scheme 1), and substantial charge-transfer character is expected upon photoexcitation. We therefore pose the challenge of synthesizing such an isomer, which would require a rather different approach than that described above, and which we anticipate would have interesting linear and nonlinear optical properties.[13]

The realization of the first internal BN-substituted PAH represents a major achievement in organic synthesis and will have a significant impact on the important area of heterocyclic chemistry. This system may be regarded as the smallest internal p–n junction. Future work, both experimental and theoretical, will no doubt be directed toward the elucidation of the electronic structure and photophysical properties of such compounds, along with new synthetic procedures for the preparation of isomers and larger PAH analogues and derivatives.

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[1] J. K. Burdett, *Chemical bonding in solids*, Oxford University Press, New York, **1995**, pp. 71–72.

[2] N. G. Chopra, R. J. Luyken, K. Cherrey, V. H. Crespi, M. L. Cohen, S. G. Louie, A. Zettl, *Science* **1995**, *269*, 966–967.

[3] D. P. Yu, X. S. Sun, C. S. Lee, I. Bello, S. T. Lee, H. D. Gu, K. M. Leung, G. W. Zhou, Z. F. Dong, Z. Zang, *Appl. Phys. Lett.* **1998**, *72*, 1966–1968.

[4] O. R. Lourie, C. R. Jones, B. M. Bartlett, P. C. Gibbons, R. S. Ruoff, W. E. Buhro, *Chem. Mater.* **2000**, *12*, 1808–1810.

[5] N. G. Chopra, A. Zettl, *Solid State Commun.* **1998**, *105*, 297–300.

[6] X. Blase, A. Rubio, S. G. Louie, M. L. Cohen, *Europhys. Lett.* **1994**, *28*, 335–340.

[7] M. Terrones, J. M. Romo-Herrera, E. Cruz-Silva, F. López-Urías, E. Muñoz-Sandoval, J. J. Velázquez-Salazar, H. Terrones, Y. Bando, D. Golberg, *Mater. Today* **2007**, *10*(5), 30–38.

[8] T. B. Marder, *Angew. Chem.* **2007**, *119*, 8262–8264; *Angew. Chem. Int. Ed.* **2007**, *46*, 8116–8118.

[9] For an excellent, detailed review of **AB** chemistry, see: F. H. Stephens, V. Pons, R. T. Baker, *Dalton Trans.* **2007**, 2613–2626.

[10] a) D. Benker, T. M. Klapötke, G. Kuhn, J. Li, C. Miller, *Heteroat. Chem.* **2005**, *16*, 311–315; b) A. Soncini, C. Domene, J. J. Engelberts, P. W. Fowler, A. Rassat, J. H. van Lenthe, R. W. A. Havenith, L. W. Jenneskens, *Chem. Eur. J.* **2005**, *11*, 1257–1266; c) B. Kiran, A. K. Phukan, E. D. Jemmis, *Inorg. Chem.* **2001**, *40*, 3615–3618.

[11] a) W. Shen, M. Li, Y. Li, S. Wang, *Inorg. Chim. Acta* **2007**, *360*, 619–624; b) I. Fernández, G. Frenking, *Faraday Discuss.* **2007**, *135*, 403–421.

[12] J. E. Anthony, *Chem. Rev.* **2006**, *106*, 5028–5048.

[13] For reviews on the linear and nonlinear optical properties of organoboron compounds, see: a) C. D. Entwistle, T. B. Marder, *Angew. Chem.* **2002**, *114*, 3051–3056; *Angew. Chem. Int. Ed.* **2002**, *41*, 2927–2931; b) C. D. Entwistle, T. B. Marder, *Chem. Mater.* **2004**, *16*, 4574–4585; c) S. Yamaguchi, K. Tamao, *Chem. Lett.* **2005**, *34*, 2–7.

[14] a) M. J. S. Dewar, R. Dietz, *J. Chem. Soc.* **1959**, 2728–2730; b) S. S. Chissick, M. J. S. Dewar, P. M. Maitlis, *Tetrahedron Lett.* **1960**, *1*, 8–10; c) M. J. S. Dewar, V. P. Kubba, R. Pettit, *J. Chem. Soc.* **1958**, 3073–3076; d) K. M. Davies, M. J. S. Dewar, P. Rona, *J. Am. Chem. Soc.* **1967**, *89*, 6294–6297.

[15] a) P. Paetzold, C. Stanescu, J. R. Stubenrauch, M. Bienmüller, U. Englert, *Z. Anorg. Allg. Chem.* **2004**, *630*, 2632–2640; b) X. Fang, H. Yang, J. W. Kampf, M. M. Banaszak Holl, A. J. Ashe III, *Organometallics* **2006**, *25*, 513–518.

[16] a) M. J. D. Bosdet, W. E. Piers, T. S. Sorensen, M. Parvez, *Angew. Chem.* **2007**, *119*, 5028–5031; *Angew. Chem. Int. Ed.* **2007**, *46*, 4940–4943; b) M. J. D. Bosdet, C. A. Jaska, W. E. Piers, T. S. Sorensen, M. Parvez, *Org. Lett.* **2007**, *9*, 1395–1398; c) C. A. Jaska, W. E. Piers, R. McDonald, M. Parvez, *J. Org. Chem.* **2007**, *72*, 5234–5243; d) C. A. Jaska, D. J. H. Emslie, M. J. D. Bosdet, W. E. Piers, T. S. Sorensen, M. Parvez, *J. Am. Chem. Soc.* **2006**, *128*, 10885–10896; e) D. J. H. Emslie, W. E. Piers, M. Parvez, *Angew. Chem.* **2003**, *115*, 1290–1293; *Angew. Chem. Int. Ed.* **2003**, *42*, 1252–1255.

[17] See, for example: M. Perry, C. Carra, M. N. Crétien, J. C. Scaiano, *J. Phys. Chem. A* **2007**, *111*, 4884–4889, and references therein.

[18] a) A. Camerman, J. Trotter, *Acta Crystallogr.* **1965**, *18*, 636–643; b) A. C. Hazell, F. K. Larsen, M. S. Lehmann, *Acta Crystallogr. Sect. B* **1972**, *28*, 2977–2984; c) C. S. Frampton, K. S. Knight, N. Shankland, K. Shankland, *J. Mol. Struct.* **2000**, *520*, 29–32.

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