Boron-nitride and aluminum-nitride "Pringles" and flapping motion†

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Motivated by the recent successful synthesis of a new nanocarbon, namely, a warped, double-concave graphene "Pringle" (Nat. Chem., 2013, 5, 739), we investigate properties of warped boron-nitride (BN) and aluminum-nitride (AlN) analogues, i.e., the non-planar B40N40H30 and Al40N40H30 "Pringles" using density functional theory (DFT) calculations. Particular attention is placed on the effect of non-hexagonal rings on the stability and physical properties of BN and AlN Pringles. We find that the warped BN and AlN Pringles with one pentagon and five heptagons are stable without imaginary frequencies. Both the warped B40N40H30 and Al40N40H30 Pringles are expected to be flexible in solution as both can periodically change their shape in a dynamic "flapping" fashion due to their much lower activation barrier of racemization compared to that of the C80H30 counterpart. Since the warped B40N40H30 possesses a smaller HOMO–LUMO gap than the planar B39N39H30, it is expected that incorporating non-hexagonal ring defects by design can be an effective way to modify electronic properties of BN-based nanoplates.

The discovery of the C60 fullerene,1 carbon nanotubes2 as well as monolayer graphene3 has attracted tremendous interest in seeking new members in the nanocarbon family as well as low-dimensional nanomaterials of carbon analogues. Indeed, a variety of structure analogues of nanocarbon sheets without containing carbon elements has been synthesized in the laboratory. Well-known examples are the boron-nitride (BN) nanomaterials which can be viewed as isoelectronic "cousins" to many nanocarbon allotropes.4–10 Unlike the covalent C–C bonds, the partially ionic B–N bonds can significantly affect geometric and electronic structures of BN nanomaterials. For example, a BN monolayer is a wide direct bandgap semiconductor while monolayer graphene is a semimetal with a zero bandgap.11–14 Note however that BN cages are structurally dissimilar to carbon fullerenes. This is because BN clusters with perfect BNBN alternation are energetically preferred due to less strain energy and aromatic destabilization.15,16

It is known that the presence of defects may induce notable changes in nanostructures, thereby modifying nanomaterials' physical properties. As an example, line defects in the hexagonal BN (h-BN) monolayer, characterized by boundaries between fcc domains and a small population of hcp domains, have been observed during the growth of h-BN on the Ni(111) surface.17 The existence of an extended line defect in a BN sheet presents a way to modify electronic or magnetic properties of the BN sheet for potential applications in nanoelectronics and spintronics. A recent theoretical study of line-defect-containing BN sheets, nanoribbons, and single-walled BN nanotubes shows that the bandgaps can be changed by the pentagon–octagon–pentagon line defects created by inserting B3, N3, or C2 dimers.18 Yamijala and Pati found that electronic and magnetic properties of a BN nanoribbon can be modified by adding a number of (odd or even) pentagon–heptagon line defects at the ribbon edges.19 These studies suggest that controlled topological (non-hexagonal rings) defects can be useful to modulate electronic properties of BN nanostructures.

Very recently, a new carbon nanostructure belonging to the nanocarbon family, i.e., the first non-planar nanographene, has been reported.20 Kawasumi et al. successfully synthesized a grossly warped nanographene C80H30 having twenty-six polygons, among which five are heptagons and one is a pentagon. The introduction of five heptagons not only causes the nanographene to warp but also alters its electronic and optical properties. This warped nanographene exhibits many unique features such as a facile bowl-to-bowl inversion of the central corannulene, a unique racemization pathway, as well as a larger gap (3.06 eV) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). In view of many structural similarities between BN and carbon nanostructures, it is expected that the embedding of non-hexagonal rings into a BN nanoplate would provide a new member of BN nanostructures as well. Besides BN, we also investigate a warped...
aluminium-nitride (AlN) nanoplate for the purpose of comparison. AlN nanomaterials are often used in deep ultraviolet optoelectronics, and as building blocks in new nanomaterials.21–24

We carry out a series of density functional theory (DFT) calculations to investigate the structural, electronic, and optical properties of the warped BN and AlN nanoplates. We show that the grossly warped nanostructures of \( \text{B}_{40}\text{N}_{40}\text{H}_{30} \) and \( \text{Al}_{40}\text{N}_{40}\text{H}_{30} \) with multiple odd-membered-ring defects are locally stable and their electronic and optical properties can be modified by the non-hexagonal ring defects. The warped \( \text{B}_{40}\text{N}_{40}\text{H}_{30} \) exhibits a markedly reduced HOMO–LUMO gap compared to \( \text{C}_{80}\text{H}_{30} \), which is 3.85 eV lower in energy than the isomer with 18 BNBN (or AlNAlN) alternation. More specifically, the lowest-energy alternative hexagons, which can be viewed as exchanging a pair of B and N atoms at the edge of the lowest-energy isomer \( \text{B}_{40}\text{N}_{40}\text{H}_{30} \). This result confirms the previous theoretical prediction that the B–B and N–N bonds should be avoided as much as possible in BN clusters as they would result in much less stable isomers.15 Like the warped \( \text{C}_{80}\text{H}_{30} \) with enantiomers of \( \text{MPMPM} \) and \( \text{PMPMP} \) configurations, the presence of five helical hexa[7]ciculene moieties,25 each with \( M \) or \( P \) chirality around the heptagon, also renders the lowest-energy structures having an isoenenergetic enantiomer of \( \text{MPMPM} \) (see below). Computed vibrational spectra of the warped \( \text{B}_{40}\text{N}_{40}\text{H}_{30} \) and \( \text{Al}_{40}\text{N}_{40}\text{H}_{30} \) have a frequency range of 10.6–3622.2 and 3.5–3561.7 cm\(^{-1} \), respectively, and the spectra exhibit a strong peak at 1440 and 930 cm\(^{-1} \), respectively. These strong peaks can be used as a fingerprint to determine the warped nanostructures in future experiments. Note that the highest vibrational frequency of the warped \( \text{B}_{40}\text{N}_{40}\text{H}_{30} \) is higher than that of the \( \text{Al}_{40}\text{N}_{40}\text{H}_{30} \) (3242.3 cm\(^{-1} \)), reflecting stronger B–N bonds than Al–N bonds and C–C bonds (see ESI† Fig. S5).

We find that the warped \( \text{B}_{40}\text{N}_{40}\text{H}_{30} \) and \( \text{Al}_{40}\text{N}_{40}\text{H}_{30} \) not only can flip back and forth between two different conformers through bowl-to-bowl inversion, but also change between two enantiomers through a racemization pathway (see Fig. 2 or ESI† Fig. S6 for an enlarged view). The “flipping” behavior is due to the presence of the central pentagon defect while the five pentagons induce negative curvature. For the bowl-to-bowl inversion as illustrated in Fig. 2 (MPMPM ⇔ TS\(^{\text{flip}} \) ⇔ MPMPM), the computed bowl inversion energy of the \( \text{C}_{80}\text{H}_{30} \) is 1.7 kcal mol\(^{-1} \), in agreement with the result of ref. 20. However, both \( \text{B}_{40}\text{N}_{40}\text{H}_{30} \) and \( \text{Al}_{40}\text{N}_{40}\text{H}_{30} \) exhibit a deeper bowl structure (see Fig. 1) compared to the warped \( \text{C}_{80}\text{H}_{30} \) (with bowl depth 0.37 Å). Hence, for the \( \text{B}_{40}\text{N}_{40}\text{H}_{30} \) and \( \text{Al}_{40}\text{N}_{40}\text{H}_{30} \) nanoplates, the activation energy of the bowl inversion is 27.9 and 23.2 kcal mol\(^{-1} \), respectively, much higher than that of \( \text{C}_{80}\text{H}_{30} \). The \( \text{B}_{40}\text{N}_{40}\text{H}_{30} \) nanoplate possesses the highest bowl inversion energy (27.9 kcal mol\(^{-1} \)) due also to the strong B–N bonds. A recent study shows that the bowl inversion energy of a chiral nitrogen-doped carbon-bowl reaches an extraordinarily high value of 42.2 kcal mol\(^{-1} \) due largely to the strong C–N bonds.26

The computed energy barrier for the racemization of the \( \text{B}_{40}\text{N}_{40}\text{H}_{30} \), as shown in Fig. 2 (MPMPM ⇔ TS\(^{\text{rac}} \) ⇔ PMPMP), is merely 4.3 kcal mol\(^{-1} \), which is much lower than that (18.9 kcal mol\(^{-1} \)) for the \( \text{C}_{80}\text{H}_{30} \) nanographene. To simulate

Fig. 1 Optimized warped structures of (a) \( \text{B}_{40}\text{N}_{40}\text{H}_{30} \) and (b) \( \text{Al}_{40}\text{N}_{40}\text{H}_{30} \) nanoplates. Top and side views are on the left and right panels, respectively. B, Al, and N atoms are represented by light pink, dark pink, and navy blue balls, respectively. All hydrogen atoms at the perimeter are omitted for clarity. M represents a left-handed helix around the seven-membered ring, while P denotes a right-handed helix. The bowl depth, labeled by red arrows, is calculated as an averaged depth between the centroid of the central pentagon and second-nearest neighboring atoms to the pentagonal vertices.

Fig. 2 Bowl-to-bowl inversion (left, MPMPM ⇔ TS\(^{\text{flip}} \) ⇔ MPMPM) and racemization (right, MPMPM ⇔ TS\(^{\text{rac}} \) ⇔ PMPMP) pathways for \( \text{B}_{40}\text{N}_{40}\text{H}_{30} \). The computed energy barriers at the B3LYP/6-31G(d) level. All hydrogen atoms at the perimeter are omitted for clarity. Values (in unit of kcal mol\(^{-1} \)) are relative Gibbs free energies at 298.15 K and 1 atm.
Al40N40H30 nanoplates are expected to exhibit "flapping" features with at least four well-resolved peaks located at 226, 244, 200 and 213 nm, respectively; the second peak has a shoulder at 207 nm. The spectrum of the warped B40N40H30 exhibits richer transitions between the warped and planar BN nanostructures.

As expected, the addition of non-hexagonal rings modifies electronic and optical properties of the B40N40H30 and Al40N40H30 Pringles. For example, data for the comparison between the warped B40N40H30 and a planar and fully BNNN alternating B39N39H30 nanoplate (see the inset image in Fig. 3[b]) clearly show that the HOMO-LUMO gap can be appreciably reduced via embedding non-hexagonal rings into the BN nanoplate. The HOMO-energy (E_HOMO = −5.777 eV) of the B40N40H30 is shifted upward compared to that of the planar B39N39H30 (E_HOMO = −6.487 eV), while the LUMO is shifted downward (E_LUMO = −0.763 versus −0.016 eV), leading to a narrower HOMO-LUMO gap (5.01 eV) for the warped structure than that (6.47 eV) of the planar B39N39H30. Based on this result, we expect that the introduction of non-hexagonal rings into the BN sheet, a wide-gap semiconductor, can also reduce the bandgap due in part to the narrower HOMO–LUMO gap.

The effect of the non-hexagonal rings on optical properties is illustrated in Fig. 3, where the computed optical absorption spectra of the warped B40N40H30 and planar B39N39H30 are shown. A major difference between the two spectra is the peaks in the ultraviolet region. The planar B39N39H30 exhibits two sharp peaks at 200 and 213 nm, respectively; the second peak has a shoulder at 207 nm. The spectrum of the warped B40N40H30 exhibits richer features with at least four well-resolved peaks located at 226, 244, 260, and 288 nm, respectively. Compared to the feature peaks of the planar B39N39H30, the peaks of warped B40N40H30 can be viewed as red-shifted due in part to the narrower HOMO–LUMO gap of the warped structure. These features can be used to differentiate the warped and planar BN nanostructures.

In summary, we investigate structural and electronic properties of warped B40N40H30 and Al40N40H30 nanoplates or Pringles. Both B40N40H30 and Al40N40H30 nanoplates are local minima on the potential energy surfaces without imaginary frequencies. Compared to the C40H30 counterpart, the B40N40H30 and Al40N40H30 nanoplates have much higher bowl inversion energy due to their deeper bowl depth and relatively stronger chemical bonds B–N (or Al–N) bonds. More interestingly, the B40N40H30 and Al40N40H30 nanoplates are expected to exhibit "flapping" motion in solution due to the much lower energy barrier of the racemization compared to that of the C40H30 counterpart. Finally, embedding non-hexagonal rings in BN nanoplates can reduce the HOMO–LUMO gap. Such a bandgap-reduction by introduction of non-hexagonal rings can exploit electronic properties of BN nanostructures for nanoelectronic applications.

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Notes and references

1. H. W. Kroto, J. R. Heath, S. C. O’Brien, R. F. Curl and R. E. Smalley, Nature, 1985, 318, 162–163.
2. S. Iijima, Nature, 1991, 354, 56–58.
3. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, Science, 2004, 306, 666–669.
4. N. G. Chopra, R. J. Luyken, K. Cherrey, V. H. Crespi, M. L. Cohen, S. G. Louie and A. Zettl, Science, 1995, 269, 966–967.
5. W. Mickelson, S. Aloni, W. Q. Han, J. Cumings and A. Zettl, Science, 2003, 300, 467–469.
6. A. Loiselle, F. Willaime, N. Demoney, G. Hug and H. Pascard, Phys. Rev. Lett., 1996, 76, 4737–4739.
7. X. Xia, D. A. Jelski, J. R. Bowser and T. F. George, J. Am. Chem. Soc., 1992, 114, 6493–6496.
8. F. Jensen, Chem. Phys. Lett., 1993, 209, 417–422.
9. D. L. Strout, J. Phys. Chem. A, 2001, 105, 261–263.
10. M. Monajemi and J. E. Boggs, J. Phys. Chem. A, 2013, 117, 1670–1684.
11. Y. B. Zhang, Y. W. Tan, H. L. Stormer and P. Kim, Nature, 2005, 438, 201–204.
12. K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. K. Khotkevich, S. V. Morozov and A. K. Geim, Proc. Natl. Acad. Sci. U. S. A., 2005, 102, 10451–10453.
13. A. Nag, K. Raidongia, K. P. S. Hembram, R. Datta, U. V. Waghmare and C. N. R. Rao, ACS Nano, 2010, 4, 1539–1544.
14. D. Golberg, Y. Bando, Y. Huang, T. Terao, M. Mitome, C. Tang and C. Zhi, ACS Nano, 2010, 4, 2979–2993.
15. F. Jensen and H. Toftlund, Chem. Phys. Lett., 1993, 201, 89–96.
16. H. Y. Zhu, T. G. Schmalz and D. J. Klein, Int. J. Quantum Chem., 1997, 63, 393–401.
17. W. Auwärter, M. Muntwiler, J. Osterwalder and T. Greber, Surf. Sci., 2003, 545, L735–L740.
18. X. Li, X. Wu, X. C. Zeng and J. Yang, ACS Nano, 2012, 6, 4104–4112.
19. S. S. Yamijala and S. K. Pati, J. Phys. Chem. C, 2013, 117, 3580–3594.
20. K. Kawasaki, Q. Zhang, Y. Segawa, L. T. Scott and K. Itami, Nat. Chem., 2013, 5, 739–744.
21. C. Liu, Z. Hu, Q. Wu, X. Wang, Y. Chen, H. Sang, J. Zhu, S. Deng and N. Xu, J. Am. Chem. Soc., 2005, 127, 1318–1322.
22. X. H. Ji, S. P. Lau, S. F. Yu, H. Y. Yang, T. S. Hershey, A. Sedhain, J. Y. Lin, H. X. Jiang, K. S. Teng and J. S. Chen, Appl. Phys. Lett., 2007, 90, 193118.
23. H. Wang, Z. Xie, Y. Wang, W. Yang, Q. Zeng, F. Xing and L. An, Nanotechnology, 2009, 20, 025611.
24. Y. Mei, D. J. Thurmer, C. Deneksa, S. Kiravittaya, Y. F. Chen, A. Dadgar, F. Bertram, B. Baster, A. Krost, J. Christen, T. Reindl, M. Stoffel, E. Coric and O. G. Schmidt, Nature, 2012, 493, 1663–1668.
25. P. J. Jessup and J. A. Reiss, Aust. J. Chem., 1976, 29, 173–176.
26. Q. Tan, S. Higashibayashi, S. Karanjit and H. Sakurai, Nat. Commun., 2012, 3, 891.