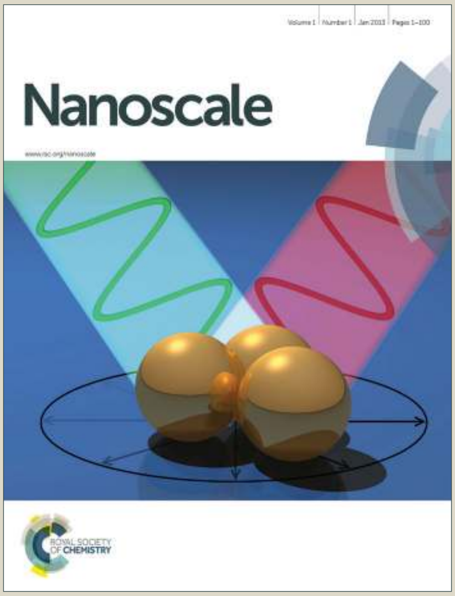
Nanoscale

This article can be cited before page numbers have been issued, to do this please use: A. B. Rahane and V. Kumar, *Nanoscale*, 2015, DOI: 10.1039/C4NR06026A.



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/nanoscale

B_{84}: A quasi-planar boron cluster stabilized with hexagonal holes†

View Article Online
DOI: 10.1039/C4NR06026A

Amol B. Rahane,[a] **and Vijay Kumar,***[a,b‡]

Received Xth XXXXXXXXXX 2014, Accepted Xth XXXXXXXXX 20XX
First published on the web Xth XXXXXXXXXX 20XX
DOI: 10.1039/b000000x

We report the finding of a bowl-shaped quasi-planar structure of B_{84} cluster with four hexagonal holes and a three-chain ring all around the edges using *ab initio* calculations. A large number of other isomers including those explored earlier such as empty cage, filled cage, and disordered structure, have been found to lie significantly higher in energy. A tubular structure, however, lies only about 0.45 eV higher in energy. Calculations of the infrared and Raman spectra show that the quasi-planar structure is dynamically stable. These results suggest that quasi-planar structures may be among the low energy structures for larger clusters as well. Accordingly we have calculated the optimal quasi-planar structures stabilized with 2, 3, 5, 6, and 7 hexagonal holes also. The stability of the quasi-planar structures is discussed in terms of multi-center two-electron bonding and it is shown that with increasing size their binding energy tends to approach the value for α-boron sheet.

1 INTRODUCTION

After the discovery of carbon fullerene (C_{60})[1], and a planar sheet of carbon called graphene[2], much interest has aroused to find stable hollow as well as planar structures of inorganic materials. Boron is just before carbon in the periodic table and great efforts have been made to find its fullerene and tubular structures[3,4]. However, due to the electron deficiency in boron, the existence of B_{60} fullerene similar to C_{60}, was considered unlikely. Boron is known to favour three-center (3c) bonding which prevents the formation of structures with all hexagons without atoms at the center. A triangular lattice arrangement will, however, favour such 3c bonding. Accordingly an intriguing fullerene-type structure in which a boron atom was inserted at the center of each of the 20 hexagons of B_{60} fullerene having the same symmetry (I_h) as C_{60} was proposed for B_{80}[5]. A later study[6], however, reported the I_h symmetry structure not to be an energy minimum in the potential energy surface and that it exhibits a spontaneous symmetry breaking to yield a puckered cage with a rare T_h symmetry. It was also shown[7] that the icosahedral structure (I_h) is vibrationally unstable with seven imaginary frequencies while the T_h symmetry structure is vibrationally stable and has a highest occupied molecular orbital - lowest unoccupied molecular orbital (HOMO-LUMO) gap of 0.96 eV. Later Sadrzadeh *et al.*[8] reported very small energy differences (lower than 30 meV) among the three lowest lying isomers namely those with I_h, and T_h symmetries and another isomer with C_1 symmetry. The fullerene structure with chains of a triangular arrangement of boron atoms and empty pentagons aroused much interest in the study of boron nanostructures[9–12]. However, it was subsequently dismissed as a core-shell structure was found to be lower in energy and it still remains the lowest energy structure for this cluster[13].

These developments spurred further studies of the atomic and electronic structures of small boron clusters and the findings of novel quasi-planar, tubular, and fullerene structures.[14–32] The stability of these structures has been shown to arise from the coexistence of two center (2c) and multi-center bonding. Experimental support based on photoelectron spectroscopy has also been obtained for several clusters up to the size of 40 boron atoms. Recently a highly stable high symmetry quasi-planar structure with a triangular three-chain ring and a hexagonal hole at the center has been predicted for B_{36} from a combined theoretical and experimental study[30]. The authors also suggested the possibility of constructing large size aggregates or infinite sheets of such boron clusters named 'borophene'. Later a planar structure for B_{35} has been suggested to be a more flexible motif for 'borophene'[24]. Interestingly, infinite boron sheets with different arrangements of hexagonal holes on a triangular lattice have been studied for several years[33–40] and a so-called α-boron sheet with higher hexagonal hole density than 'borophene', is lower in energy[38]. Therefore, there is open challenge for generating large size 'ideal' planar clusters for boron. It has been suggested that a transition from planar to fullerene structures occurs around a size of B_{38}, for which a fullerene structure has been proposed[31]. However, combining theory and experiments, the

---

† Electronic Supplementary Information (ESI) available. See DOI: 10.1039/b000000x/

[a] *Dr. Vijay Kumar Foundation, 1969, Sector 4, Gurgaon - 122 001, Haryana, India. Fax: +91 124 407 9369; Tel: +91 124 407 9369; E-mail: amol_rahane2000@yahoo.com, kumar@vkf.in, vijay.kumar@snu.edu.in*
[b] *Center for Informatics, Shiv Nadar University Post Office, NH-91, Gautam Budh Nagar 201314, Uttar Pradesh, India.*

View Article Online
DOI: 10.1039/C4NR06026A

first observation of an all boron fullerene structure has been recently made for B_{40}[32] but a quasi-planar structure with two hexagonal holes arranged in a fashion of β-boron sheet[38] is favoured for anionic B_{40}[32]. For larger size boron clusters, it is unclear which structural growth pattern will be favoured among the several different structures like fullerene, quasi-planar, tubular or core-shell.

Here we explore the stability of quasi-planar structures for larger sizes and focus our attention on B_{84} which has been extensively studied earlier. We constructed a quasi-planar structure with four hexagonal holes and also studied several other isomers including tubular[41], I_h C_{60} type fullerene cage with B_{12} icosahedral stuffing[9] and twelve B atoms either capping outside on pentagons or inside below the pentagons and connecting the inner B_{12} icosahedron, as well as a D_{2h} B_{84} fullerene cage with four B atoms capping pentagons in B_{80} fullerene[9,42] that have been studied earlier. In addition three types of B_{84} tubular clusters namely, double-ring tubular (DRT), three-ring tubular (TRT), and four-ring tubular (FRT) structures have been studied[41]. Among these, the TRT structure is the most stable one. Further, Yang and co-workers[42] have studied different isomers of B_{84} and suggested amorphous (distorted) structures to be the most stable ones. Here we find a quasi-planar structure with four hexagonal holes (Fig. 1-I) to be even lower in energy than the amorphous structure. Our results thus raise the question if quasi-planar structures would continue to be favourable for even larger sizes. Accordingly we have further explored quasi-planar lowest energy structures with 2, 3, 5, 6, and 7 hexagonal holes.

2 COMPUTATIONAL DETAILS

The calculations have been performed using density functional theory with generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof[43] for the exchange-correlation energy. The electron-ion interaction is treated within projector augmented wave (PAW) pseudopotential method[44,45] in Vienna *Ab initio* Simulation Package (VASP)[46]. The cut-off energy for the plane wave expansion was set to 318.6 eV. The calculations were considered to be converged when the absolute value of the force on each ion was less than 0.005 eV/Å with a convergence in the total energy of about 10^{-5} eV without any symmetry constraint. The gamma point has been used for Brillouin zone integrations. Further calculations have been done for a core-shell fullerene isomer by heating it to 600 K and then cooling to 200 K in steps of 100 K. At each temperature, the cluster was simulated for 2 ps and then finally quenched to 0 K. This led to a lower energy isomer than the starting core-shell configuration.

We also performed calculations on α-boron sheet taking an 8-atom supercell with a lattice vector of 15 Å perpendicular to the sheet. This ensures that there is negligible interaction between the sheet and its periodic images. The Brillouin zone for this calculation has been represented with a dense Monkhrost-Pack[47] **k**-points mesh of 9x9x3. The optimized structure shows that a slightly buckled α-sheet is favoured as it has also been suggested in an earlier study[38]. The calculated lattice parameters in the plane of the sheet (5.058 Å and 5.058 Å) are in agreement with the earlier study[38]. The cohesive energy for this sheet is 6.035 eV/atom and it is used as upper limit to compare the stability of the calculated planar structures.

In order to check the dynamical stability of the quasi-planar structure, we further calculated the vibrational frequencies for the lowest energy quasi-planar isomer of B_{84} using GAUSSIAN09 package[48]. For these calculations we used B3PW91 hybrid exchange-correlation functional[49] and 6-21G basis set[50]. Voronoi charge analysis as implemented in the Bader program[51] has been performed to obtain charge transfer among the different boron atoms.

3 RESULTS and DISCUSSION

We considered all the isomers reported earlier[42] and also some other structures. Our calculations show that the TRT structure (Figure 1-VI) is lower in energy than the FRT (Figure 1-XX) and DRT (Figure 1-XXII) structures as also reported earlier[41]. Further, we performed full optimization of the two core-shell isomers without any symmetry restriction and this led to amorphous structures which are lower in energy than the initial structures with symmetry restricted optimization. We find that the isomer with *outer* capping (Figure 1-XIV) is lower in energy than the one with *inner* capping (Figure 1-XVII). However the TRT isomer is still lower in energy compared with the two core-shell type amorphous structures. In order to further check if the amorphous structures were not a local minimum, we performed a molecular dynamics simulation on the outer capped stuffed boron isomer of B_{84} by heating it to 600 K for 2 ps. Then we lowered the temperature to 200 K in steps of 100 K and at each temperature, the simulation was done for 2 ps. Finally the structure was quenched to 0 K and fully optimized. After the completion of the MD runs we got an amorphous structure which is $\sim$1.3 eV lower in energy than the initial amorphous structure obtained from the optimization of the outer capped isomer and this is shown in Figure 1-V. This structure becomes lower in energy than the TRT isomer.

We further explored planar isomers of B_{84}. It is to be noted that Tang and Ismail-Beigi[34] have studied the electronic structure of a graphene-like hexagonal boron sheet as well as a triangular boron sheet and found the latter to be energetically more favorable. The valence electron configuration of boron is $2s^22p^1$ and one can construct sp^2 hybridized orbitals like in a graphene sheet but it leaves one empty p-orbital and this ren-

View Article Online
DOI: 10.1039/C4NR06026A

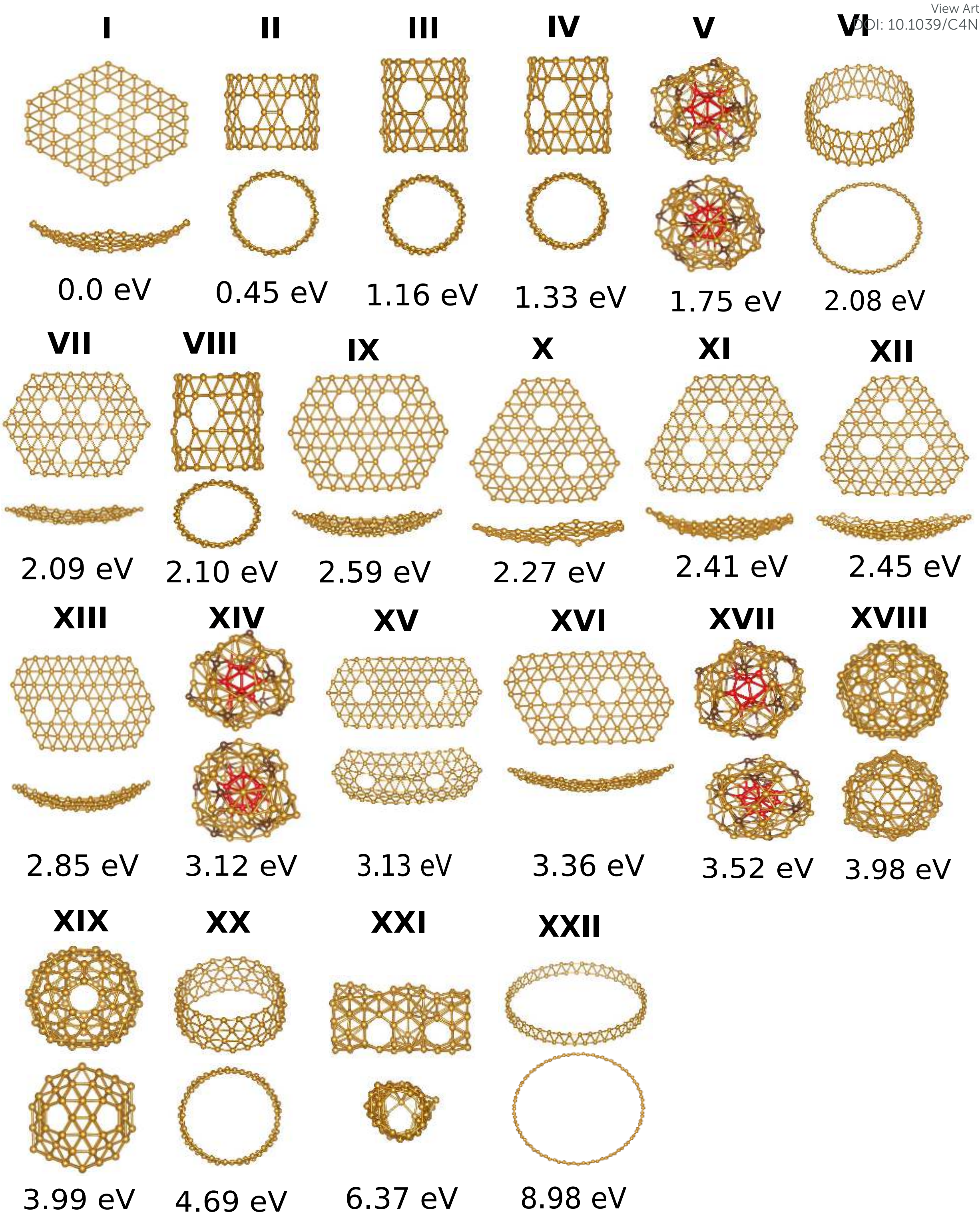


Fig. 1 The lowest energy and some low-lying isomers of B_{84}. For the core-shell isomers the inner B_{12} icosahedron and B atoms capping pentagons of the B_{60} shell in the initial structure are marked with different colors. The energy below each isomer figure is given w.r.t. the lowest energy isomer.

View Article Online
DOI: 10.1039/C4NR06026A

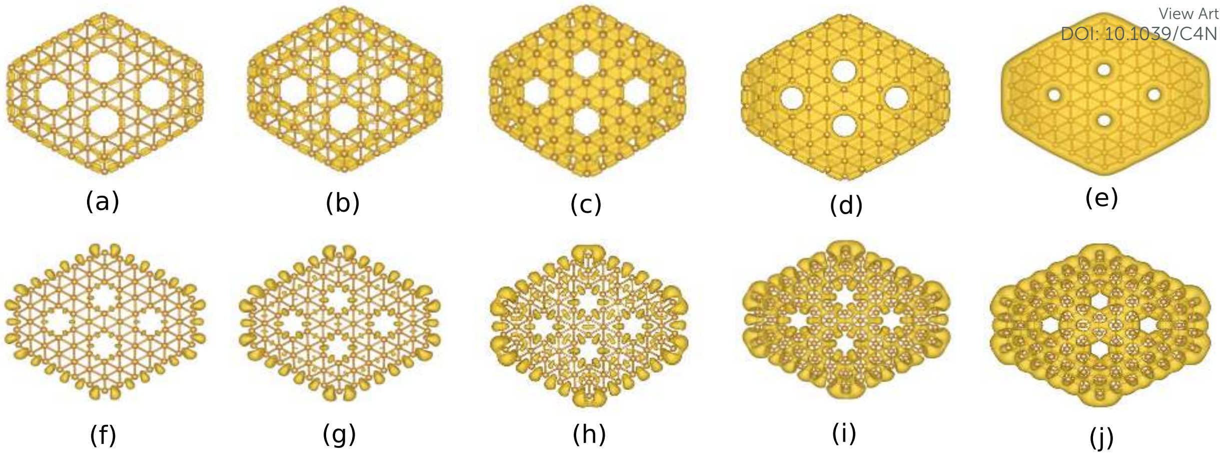


Fig. 2 Total charge density isosurfaces at (a) 0.90 (80 %), (b) 0.86 (76 %), (c) 0.8 (70 %), (d) 0.75 (66 %), and (e) 0.45 (40 %) of the maximum isosurface value, and electron localization function (ELF) at the values (f) 0.84, (g) 0.80, (h) 0.76, (i) 0.70, and (j) 0.65 for the lowest energy isomer of B_{84}.

ders boron electron-deficient as well as makes graphene-like structure unfavorable. Further, they also showed that a model B_{32} cluster with a hexagonal hole is more stable than a double ring structure. Based on this study Wang[30] and co-workers designed a symmetric planar cluster for B_{36} with one hexagonal hole. Here we consider the possibility of the formation of larger sized planar clusters with one or more than one hexagonal holes.

We build several planar structures for B_{84} with different combinations of hexagonal holes. In Figure 1-I we have shown the lowest energy quasi-planar isomer for B_{84} which has four hexagonal holes that are arranged in the form of a rhombus and around each hole there are six hexagons with a boron atom at the center. Each hole is connected to the other holes through vertex sharing two atom chain as in a perfect α-boron sheet. All around the cluster there is a three atom chain with triangular structure. Our calculations show that this isomer has the lowest energy among all the ordered and disordered structures reported earlier and also considered by us. It is also significantly lower in energy than other tubular and cage structures we considered here which were not considered by earlier studies. For comparison the amorphous structure (shown in Figure 1-V) is a low-lying isomer in our MD calculations and it is 1.75 eV higher in energy than the quasi-planar structure in Figure 1-I that we have obtained here. Interestingly, a group of tubular isomers is also lower in energy than the amorphous structure. A five ring (each with 18 atoms) tubular structure (shown in Figure 1-II) with six equally spaced hexagonal holes in the middle ring is 0.45 eV higher in energy than the lowest energy quasi-planar isomer. This is the second best isomer from our calculations. We have also found several ordered tubular isomers that are lower in energy than the amorphous structure. These results suggest the possibility of symmetric structures to be more favourable than amorphous structures. The TRT structure is 2.08 eV higher in energy than the quasi-planar lowest energy isomer. All the other isomers and their relative energies compared with the lowest energy isomer are given in Figure 1. The optimized core-shell structure with the *outer* capping (Figure 1-XIV), is 3.12 eV higher in energy than the lowest energy structure we have obtained, while the isomer with *inner* capping (Figure 1-XVII) is 3.52 eV higher in energy than the lowest energy isomer. We have shown in Figure 1 several quasi-planar low-lying isomers that are lower in energy than the reported ordered and disordered non-planar structures. These results suggest further possibility of the formation of planar structures for larger boron clusters.

The quasi-planar B_{84} structure has out-of-plane bending as in B_{36}, so as to form a bowl-shaped structure. The B-B bond lengths (See Figure S1, in supporting information for bond distances) for the edges of the hexagonal hole are 1.67 *Å* while for the two borons joining the vertices of the two holes it is 1.75 Å. Other B-B bond lengths near the holes are in the range of 1.69-1.71 *Å*. The B-B bonds in the peripheral chain are relatively short compared to the inner bonds. The shortest bond length of 1.58 Å occurs for the twelve bonds between the six corner B atoms and their nearest neighbours on the outer chain. Further, the length of the next B-B bonds on the outer chain is 1.65 Å while the next-to-next bonds have the value in the range of 1.61-1.62 Å. The shortest bond length of 1.58 Å around the corner B atoms is similar to that in B_{36} cluster[30] while the other bond lengths in the outer chain are shortened as compared to 1.67 Å in B_{36} cluster. The binding energy for the quasi-planar structures of B_{84} and B_{36} clusters is 5.87

View Article Online
DOI: 10.1039/C4NR06026A

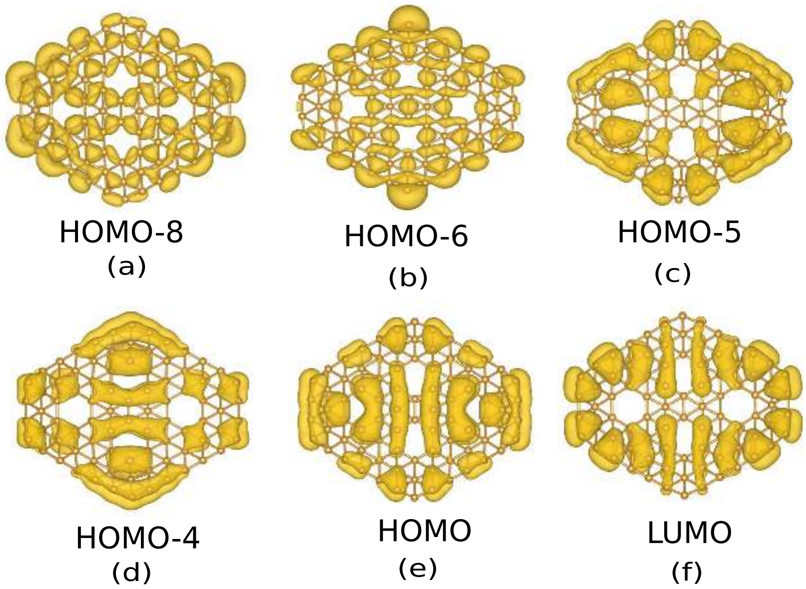


Fig. 3 Some of the molecular orbitals for the lowest energy isomer of B_{84}.

eV/atom and 5.76 eV/atom, respectively indicating that the quasi-planar B_{84} is relatively more stable than B_{36}. The calculated HOMO-LUMO gap for B_{84} is 0.385 eV, compared to 1.077 eV for B_{36}. Note that, the HOMO-LUMO gap is significantly underestimated due to the use of GGA.

We further calculated the total charge density and electron localization function (ELF) to understand the nature of bonding in the lowest energy isomer. Earlier studies[30,37] have suggested multicenter namely 2c, 3c, 4c, 6c, and 7c bonds in boron clusters and sheets. It has been suggested that the conventional 2c two-electron (2e) bonds are not favoured[14,15] in boron due to its electron-deficient character. Figure 2 shows the total charge density isosurfaces and ELF isosurfaces for different values. As there are several short bonds in this cluster, especially for the peripheral chain and edges of the hexagonal holes, the total charge density at the iso-value of 90 % of the maximum value (Figure 2 (a)) shows charge density lobes along such short bonds. The larger the size of the lobe, the shorter and more stronger is the bond. At lower iso-values of the total charge density, the density spreads on the surface of the cluster and several different features can be noticed for different iso-values (Figure 2 (b)-(e)). Following the recent studies on quasi-planar B_{36} cluster[30] and α-boron sheet[37] we analysed the nature of bonding in B_{84} by plotting ELF isosurfaces at different values. At a large value of 0.84 (Figure 2 (f)) the lobes along the B-B bonds on the peripheral chain and B-B bonds along the edges of the hexagonal holes can be noticed. Note that the bonds along the peripheral chain (1.58-1.65 Å) are relatively shorter than the edges of hexagonal holes (1.67 Å). The shortest B-B bonds (1.58 Å) at the six corner atoms on the peripheral chain represent 12 2c-2e bonds. The ELF lobes are also stronger for these bonds. Also there are 18 3c-2e bonds along the peripheral chain, 8 bonds with bond distances 1.61-1.62 Å, while 10 bonds with bond distances of 1.65 Å. In addition 24 3c-2e bonds can be noticed along the edges of the hexagonal holes for this ELF value. With the decrease in the ELF value, other multi-center bonds become also visible. For the ELF value of 0.8 (Figure 2 (g)) the lobes on the B-B bonds joining atoms in the middle chain of the peripheral three chain ring can be seen. The length of these bonds lies in the range of 1.64-1.67 Å. The lengths of the bonds joining the vertices of the two hexagonal holes are also in the same range (1.67 Å). Accordingly the ELF isosurface also shows lobes along these bonds. All these bonds represent 4c-2e bonds. With smaller ELF values the lobes can be seen along all the bonds and the charge becomes delocalized. This is depicted in Figure 2 (h)-(j).

Figure 3 shows the isosurfaces for the HOMO and LUMO along with some of the other molecular orbitals below (above) HOMO (LUMO). The HOMO-8 and HOMO-6 shown in Figures 3 (a) and (b), respectively, have σ-bonding whereas HOMO-5 and HOMO-4 are π-bonded molecular orbitals which are seen in Figures 3 (c) and (d), respectively. The plots for HOMO and LUMO have π-bonding character. The molecular orbitals show typical 2c and 3c bonding which is the characteristic feature of these quasi-planar structures.

Further we have calculated the vibrational modes for the lowest energy quasi-planar isomer of B_{84} cluster. We found that all the frequencies are positive indicating that our structure is dynamically stable. Figure 4 shows the calculated IR

View Article Online
DOI: 10.1039/C4NR06026A

and Raman spectra for this isomer. In the IR spectrum there are three peaks at 766.89 cm^{-1}, 992.32 cm^{-1}, and 1026.43 cm^{-1} with high intensities . The highest intensity peak at 1026.43 cm^{-1} corresponds to a combination of the stretching and bending vibrations (see Fig. S2 in supporting information). For the Raman spectra there is a broad peak in the range of 1050-1075 cm^{-1}, the maximum intensity peak being at 1053.09 cm^{-1}. There are two more frequencies (1222.20 cm^{-1} and 1350.43 cm^{-1}) which also have high intensities. The Raman active modes are the combination of the stretching, bending as well as breathing vibrations. The highest frequency peak around 1350.43 cm^{-1} is due to the stretching vibrations along the peripherial chain (See Fig. S2 in supporting information).

The Gaussian broadened electronic spectrum for the lowest energy isomer for B_{84} is shown in Figure 5. The HOMO and LUMO are π-bonded states which are shown in Figure 3. The Voronoi analysis shows charge transfer from some sites such as the hexagons with the center occupied (see Fig. S3 in supporting information). There is excess of charge on sites forming the hexagonal holes and on outer edge atoms.

In order to further explore planar structures with different number of holes and different number of atoms, we considered several planar structures having different number and combination of holes. We found that the optimized structures in all cases are quasi-planar. Among the different planar structures we studied, the one with four hexagonal holes has the lowest energy for B_{84} as discussed above. We also tried different combinations of four holes arranged in different ways as well as with different inner and outer chains. Also we tried quasi-planar structures with 2 and 3 holes as shown in Figure 1 but they all lie higher in energy. We find that a three-atom outer chain adds to the stability of the lowest energy quasi-planar structure.

For clusters with different number of atoms, we can cut α-boron sheet (Figure 6) in different shapes and sizes and build several planar structures by truncating outer edges with chains. We first considered the possibility of forming a single hexagonal hole. We can build a two atom chain to form a single hole, similar to the two atom chain as in α-boron sheet. However, such a chain will leave some of the outer boron atoms less bonded than in the perfectly periodic boron sheet. To compensate the charge, we can add more chains over the two atom chain in the same plane, to form three- or four-atom chains. Our calculations show that the isomers with two- or four-atom outer chains are less stable than the isomer with three-atom outer chain. This also explains why the perfectly symmetric planar B_{36} structure[30] with three-atom chain around the hexagonal hole is more stable in terms of binding energy per atom than the planar B_{32} structure[35] with two atom chain on one of the edges of hexagon.

For the configurations with two hexagonal holes, we can start with several possibilities, such as facing the two vertices of the hexagonal holes towards each other as in the perfect α-sheet, facing edges of the holes, or sharing an edge of the hexagon, or sharing the vertices of the two holes, as in the modified α-, β- or γ– sheets.[38,39] Previous studies on boron sheets indicate that the structure with two holes facing the vertices (similar to α sheet) is more favourable. We thus tried quasi-planar structures for other sizes with one to seven holes having vertices facing holes and three-member outer chain. The optimized structures are shown in Figure 6. The structure for B_{120} with 7 holes has hexagonal symmetry. The inner part of these isomers resembles with the atomic structure in α-boron sheet. All these structures are likely to be among the low-lying isomers for the respective cluster sizes. The binding energies for B_{36}, B_{56}, B_{70}, B_{84}, B_{98}, B_{112} and B_{120} are 5.76 eV/atom, 5.82 eV/atom, 5.84 eV/atom, 5.87 eV/atom, 5.88 eV/atom, 5.89 eV/atom, and 5.90 eV/atom, respectively. This shows that with increasing cluster size the binding energy increases as shown in Figure 7 and it tends to approach the value for α-boron sheet.

4 CONCLUSIONS

In summary, we have shown that a novel quasi-planar structure with four hexagonal holes is the lowest in energy compared with all earlier reported isomers for B_{84} cluster. We have presented results of infrared and Raman spectra as well as of electronic states. We hope that this will encourage experimentalists to perform experiments to confirm our prediction. We also found several ordered structures that are lower in energy than the earlier predicted lowest energy amorphous structures. Our study suggests that the quasi-planar structures with hexagonal holes are also likely to be favoured for larger sizes or at least these will be amongst the lowest energy isomers. Accordingly we have further explored the possibility of forming quasi-planar boron clusters for large sizes consisting of one or more hexagonal holes. Our study shows that a combination of hexagonal holes and two-atom as well as three-atom chain around the holes are energetically very favorable and can be used to build planar structures for other sizes. We hope that the suggested planar structures for different sizes will encourage experimentalists to explore large clusters.

5 Acknowledgements

We are thankful to N. Sukumar for discussions. We gratefully acknowledge the use of the high performance computing facility of the Shiv Nadar University (SNU) and ITC-PAC for financial support.

View Article Online
DOI: 10.1039/C4NR06026A

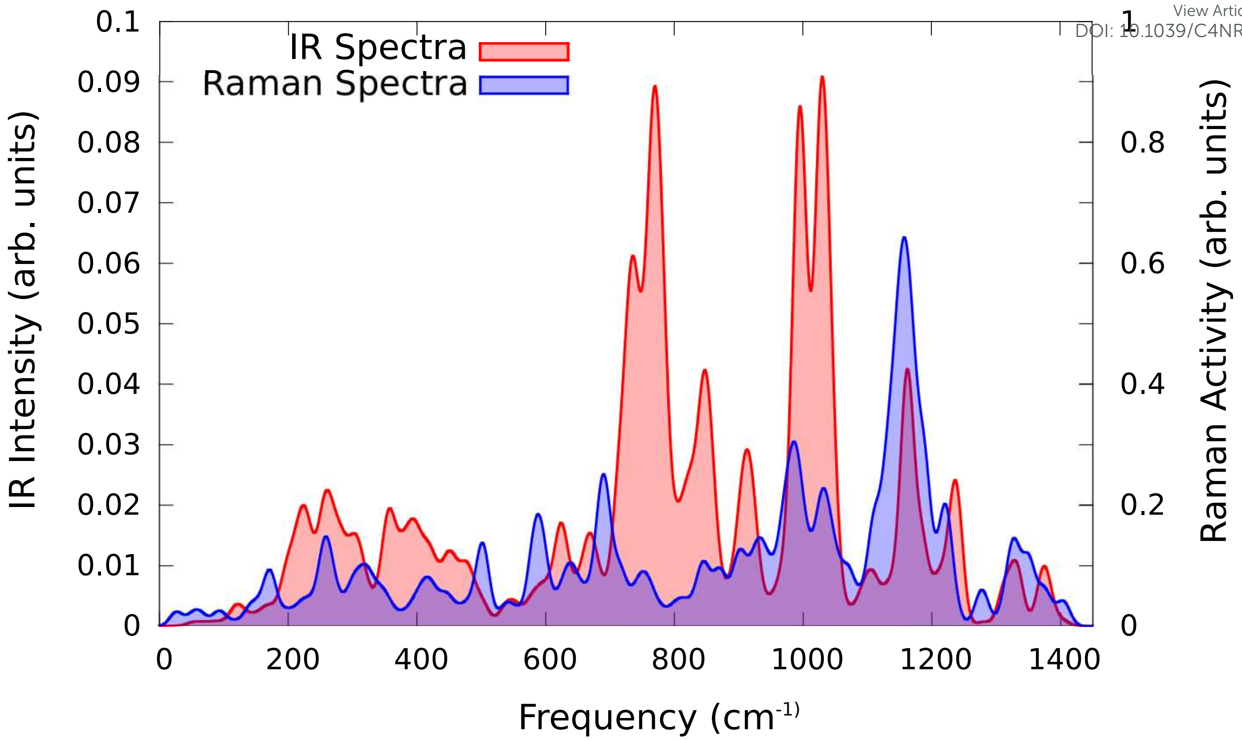


Fig. 4 The calculated IR and Raman spectra for the lowest energy quasi-planar isomer of B_{84}.

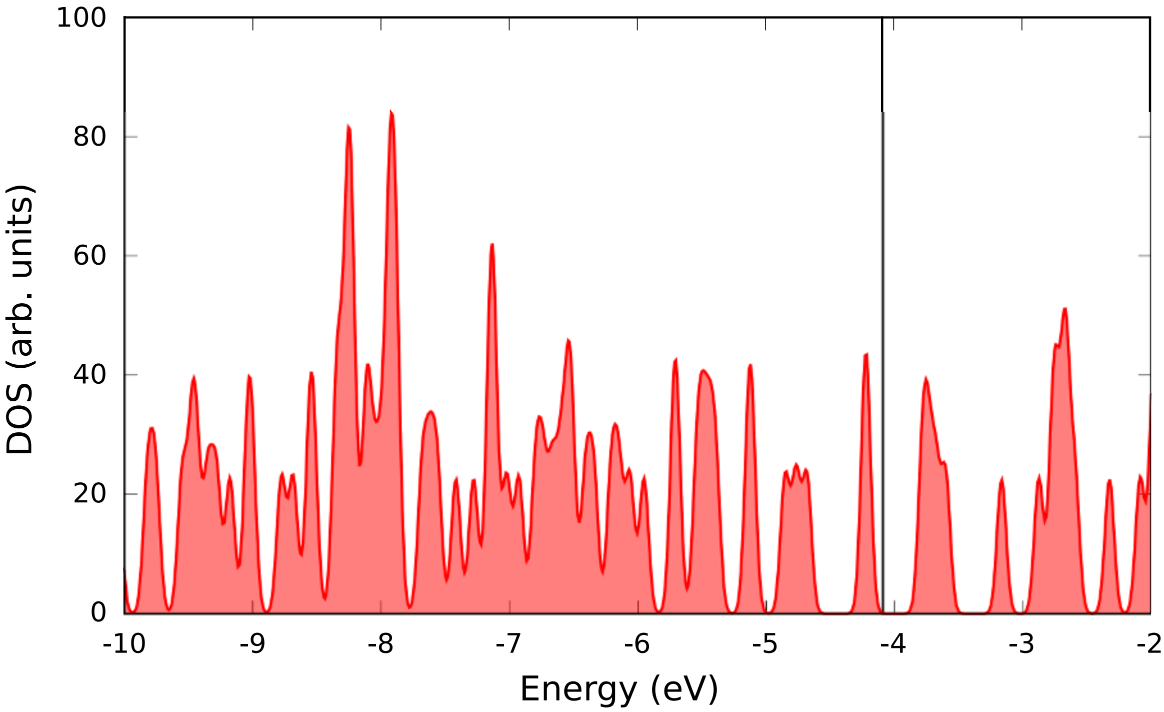


Fig. 5 The Gaussian broadened electronic spectra for the lowest energy quasi-planar isomer of B_{84}. The HOMO is shown by the vertical line.

View Article Online
DOI: 10.1039/C4NR06026A

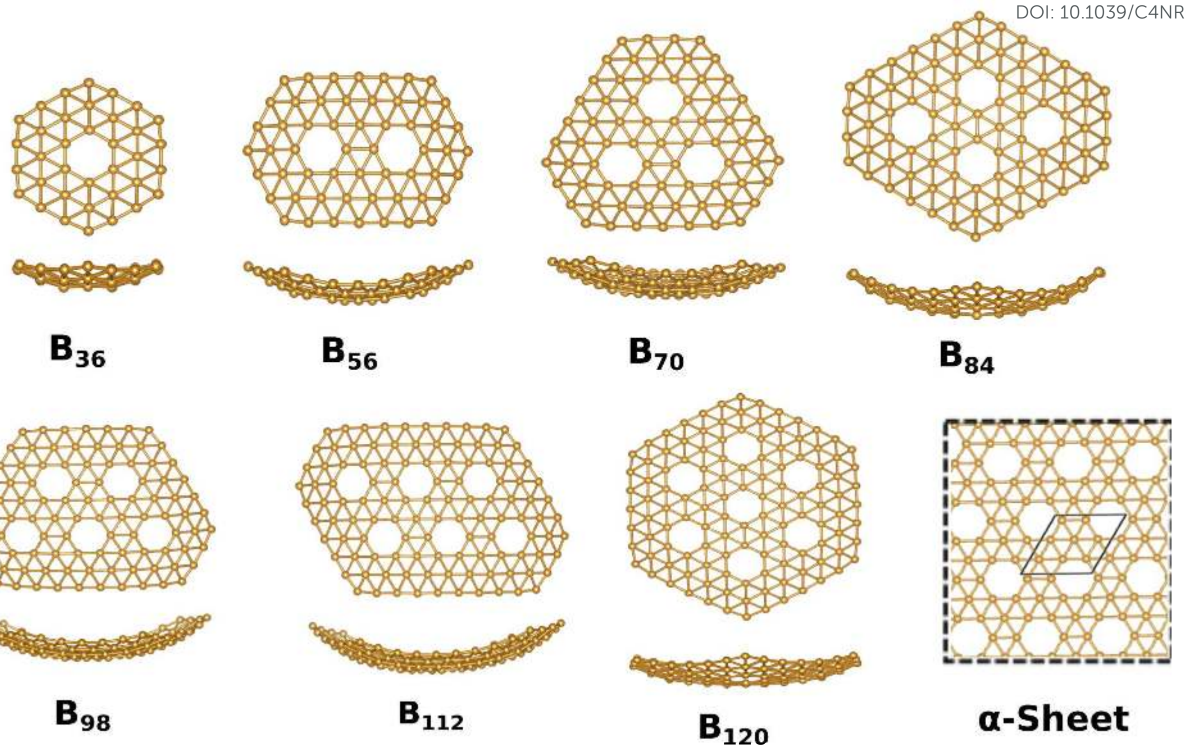


Fig. 6 Predicted quasi-planar optimal structures with 2-7 hexagonal holes and a three-atom outer chain. The optimal cluster size is 36, 56, 70, 84, 98, 112, and 120 for 2, 3, 4, 5, 6, and 7 hexagonal holes, respectively. The edges have 4, 7, and 10 boron atoms. The atomic structure of α-boron sheet is also shown.

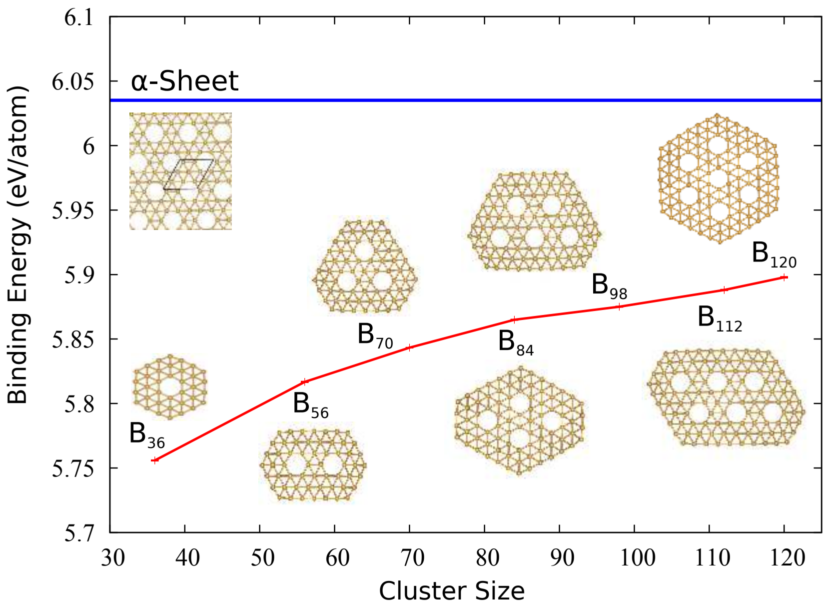


Fig. 7 Binding energy (eV/atom) for the quasi-planar structures with different number of holes. The horizontal line (blue) shows the cohesive energy (eV/atom) for an infinite α-sheet.

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 K. Novoselov, A. Geim, S. Morozov, D. Jiang, M. Katsnelson, I. Grigorieva, S. Dubonos and A. Firsov, *Nature*, 2005, **438**, 197–200.

3 I. Boustani and A. Quandt, *Europhys. Lett.*, 1997, **39**, 527–532.

4 A. Gindulyt, W. Lipscomb and N. L. Massa, *Inorg. Chem.*, 1998, **37**, 6544–6545.

5 N. G. Szwacki, A. Sadrzadeh and B. I. Yakobson, *Phys. Rev. Lett.*, 2007, **98**, 166804.

6 G. Gopakumar, N. M. T. and A. Ceulemans, *Chem. Phys. Lett.*, 2008, **450**, 175–177.

7 T. Baruah, M. R. Pederson and R. R. Zope, *Phys. Rev. B*, 2008, **78**, 045408.

8 A. Sadrzadeh, O. V. Pupysheva, A. K. Singh and B. I. Yakobson, *J. Phys. Chem. A*, 2008, **112**, 13679.

9 D. L. V. K. Prasad and E. D. Jemmis, *Phys. Rev. Lett.*, 2008, **100**, 165504.

10 X.-Q. Wang, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, **82**, 153409–153412.

11 H. Li, N. Shao, B. Shang, L.-F. Yuan, J. Yang and X. C. Zeng, *Chem. Commun.*, 2010, **46**, 3878–3880.

12 S. De, A. Willand, M. Amsler, P. Pochet, G. L. and S. Goedecker, *Phys. Rev. Lett.*, 2011, **106**, 225502–225505.

13 F. Li, P. Jin, D.-e. Jiang, L. Wang, S. B. Zhang, J. Zhao and Z. Chen, *J. Chem. Phys.*, 2012, **136**, 074302–074309.

14 H. J. Zhai, A. N. Alexandrova, K. A. Birch, A. I. Boldyrev and L. S. Wang, *Angew. Chem. Int. Ed.*, 2003, **42**, 6004–6008.

15 H. J. Zhai, B. Kiran, J. Li and L. S. Wang, *Nat. Mater.*, 2003, **2**, 827–833.

16 B. Kiran, *Proc. Natl Acad. Sci. USA*, 2005, **102**, 961–964.

17 W. Huang, *Nat. Chem.*, 2010, **2**, 202–206.

18 I. A. Popov, Z. A. Piazza, W. L. Li, L. S. Wang and A. I. Boldyrev, *J. Chem. Phys.*, 2013, **139**, 144307.

19 E. Oger, *Angew. Chem. Int. Ed.*, 2007, **46**, 8503–8506.

20 S. Chacko, D. G. Kanhere and I. Boustani, *Phys. Rev. B*, 2003, **68**, 035414.

21 L. Cheng, *J. Chem. Phys.*, 2012, **136**, 104301–104304.

22 A. G. Arvanitidis, T. B. Tai, M. T. Nguyen and A. Ceulemans, *Phys. Chem. Chem. Phys.*, 2014, **16**, 18311.

23 W.-L. Li, Y.-F. Zhao, H.-S. Hu, J. Li and L. S. Wang, *Angew. Chem. Int. Ed.*, 2014, **53**, 1–6.

24 W.-L. Li, Q. Chen, T. W.-J., Y.-F. Zhao, H.-S. Hu, J. Li, H. Zhai, S.-D. Li and L. S. Wang, *J. Am. Chem. Soc.*, 2014, **136**, 12257–12260.

25 A. P. Sergeeva, D. Y. Zubarev, H. J. Zhai, A. I. Boldyrev and L. S. Wang, *J. Am. Chem. Soc.*, 2008, **130**, 7244–7246.

26 A. P. Sergeeva, B. B. Averkiev, H. J. Zhai, A. I. Boldyrev and L. S. Wang, *J. Chem. Phys.*, 2011, **134**, 224304.

27 A. P. Sergeeva, *J. Am. Chem. Soc.*, 2012, **134**, 18065–18073.

28 A. P. Sergeeva, I. A. Popov, Z. A. Piazza, W.-L. Li, C. Romanescu, L. S. Wang and A. I. Boldyrev, *Acc. Chem. Res.*, 2014, **47**, 1349–1358.

29 Z. A. Piazza, *J. Chem. Phys.*, 2012, **136**, 104310.

30 Z. A. Piazza, H.-S. Hu, W.-L. Li, Y.-F. Zhao, J. Li and L.-S. Wang, *Nature Commun.*, 2014, **5**, 3113.

31 J. Lv, Y. Wang, L. Zhua and Y. Ma, *Nanoscale*, 2014, **6**, 11692–11696.

32 H.-J. Zhai, Y.-F. Zhao, W.-L. Li, Q. Chen, H. Baim, H.-S. Hu, Z. A. Piazz, W.-J. Tian, H.-G. Lu, Y.-B. Wu, M. Y.-W., G.-F. Wei, Z.-P. Liu, J. Li, S.-D. Li and L.-S. Wang, *Nature*, 2014, **6**, 727–731.

33 K. C. Lau and R. Pandey, *J. Phys. Chem. C*, 2007, **111**, 2906–2912.

34 H. Tang and S. Ismail-Beigi, *Phys. Rev. Lett.*, 2007, **99**, 115501.

35 X. Yang, Y. Ding and J. Ni, *Phys. Rev. B*, 2008, **77**, 041402.

36 C. Ozdogan, S. Mukhopadhyay, W. Hayami, G. Z. B, R. Pandey and I. Boustani, *J. Phys. Chem. C*, 2010, **114**, 4362–4375.

37 T. R. Galeev, Q. Chen, J.-C. Guo, H. Bai, C.-Q. Mian, H.-G. Lu, A. P. Sergeeva, S.-D. Li and A. I. Boldyrev, *Phys. Chem. Chem. Phys.*, 2011, **13**, 11575–11578.

38 X. Wu, *ACS Nano*, 2012, **6**, 7443–7453.

39 X. Yu, L. Li, X.-W. Xu and C.-C. Tang, *J. Phys. Chem. C*, 2012, **116**, 20075–20079.

40 E. S. Penev, S. Bhowmick, A. Sadrzadeh and B. I. Yakobson, *Nano Lett.*, 2012, **12**, 2441–2445.

41 F. Y. Tian and Y. X. Wang, *J. Chem. Phys.*, 2008, **129**, 024903.

42 B. Shang, L.-F. Yuan, X. C. Zeng and J. Yang, *J. Phys. Chem. A*, 2010, **114**, 2245–2249.

43 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.

44 P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953.

45 G. Kresse and J. Joubert, *Phys. Rev. B*, 1999, **59**, 1758.

46 G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169.

47 H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188.

48 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, . Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian09 Revision D.01*, Gaussian Inc. Wallingford CT 2009.

49 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

50 J. S. Binkley, J. A. Pople and W. J. Hehre, *J. Am. Chem. Soc.*, 1980, **102**, 939.

51 W. Tang, E. Sanville and G. Henkelman, *J. Phys.: Condens. Matter.*, 2009, **21**, 084204.