Cite this: Phys. Chem. Chem. Phys., 2011, 13, 11575-11578

www.rsc.org/pccp

PCCP

COMMUNICATION

Deciphering the mystery of hexagon holes in an all-boron graphene α -sheet

Timur R. Galeev,^a Qiang Chen,^{bc} Jin-Chang Guo,^{bc} Hui Bai,^{bc} Chang-Qing Miao,^{bc} Hai-Gang Lu,^{bc} Alina P. Sergeeva,^a Si-Dian Li*^{bc} and Alexander I. Boldyrev*^a

Received 20th February 2011, Accepted 3rd May 2011 DOI: 10.1039/c1cp20439d

Boron could be the next element after carbon capable of forming 2D-materials similar to graphene. Theoretical calculations predict that the most stable planar all-boron structure is the so-called α -sheet. The mysterious structure of the α -sheet with peculiar distribution of filled and empty hexagons is rationalized in terms of chemical bonding. We show that the hexagon holes serve as scavengers of extra electrons from the filled hexagons. This work could advance rational design of all-boron nanomaterials.

Recently discovered graphene,^{1,2} a one-atom-thick planar sheet of carbon atoms densely packed in a honeycomb crystal lattice, gave us the opportunity to probe properties of 2D-materials. The isolated layers of graphene were found to exhibit high carrier mobilities (>200 000 cm² V⁻¹ s⁻¹ at electron densities of 2×10^{11} cm⁻²),³⁻⁶ exceptional Young modulus values (>0.5–1 TPa), and large force constants (1–5 Nm⁻¹).^{7–9} Due to these properties graphene is attractive for many potential commercial applications such as energy storage,¹⁰ micro- and optoelectronics.¹¹

Boron, the light neighbour of carbon in the Periodic Table, is an excellent next candidate for acquiring 2D-structures. Indeed, graphite-like material MgB₂, which possesses remarkable superconductivity near 40 K,¹² is composed of planar honeycomb crystal lattices of boron atoms with magnesium atoms located above the center of the hexagons between the layers. Thus, each of the all-boron graphite-like sheets in MgB₂ is an example of a 2D-structure composed of boron atoms. However, boron atoms in MgB₂ have a charge of -1 and thus acquire electronic configuration similar to that of carbon. One can construct a honeycomb crystal lattice of a neutral boron sheet assuming that every boron is sp²-hybridized and forms three two-center-two-electron (2c-2e) σ -bonds. Such a structure was shown to be less stable than the truly remarkable α -sheet structure (Fig. 1), computationally predicted by Tang and

This journal is © the Owner Societies 2011



Fig. 1 (a) Geometric structure of the all-boron α -sheet. (b) The proposed bonding pattern for the all-boron α -sheet: 3c-2e σ -bonds (solid triangles), 4c-2e σ -bonds (solid rhombi) and delocalized π -bonds (circles).

Ismail-Beigi^{13,14} and Yang *et al.*¹⁵ This structure is formed of two types of hexagons: empty hexagons and ones with an additional boron atom at the center. A similar pattern with hexagon holes and filled hexagons was predicted for boron nanotubes.^{15,16} All-boron fullerenes with a similar network of filled hexagons and pentagon holes have also attracted significant attention^{13,16–27} since Szwacki *et al.* predicted a highly spherical buckyball structure for B_{80} .²⁸

The 2D-lattice with hexagon holes and filled hexagon motifs in the α -sheet is puzzling and understanding its chemical bonding pattern could be an important advancement towards future design of all-boron nanostructures. In order to address this issue we performed a chemical bonding analysis for the lattice. To date there is no computational tool capable of analyzing chemical bonding in terms of 2c-2e, 3c-2e or *n*c-2e bonds in general in infinite 2D-lattices, therefore we investigated chemical bonding in fragments of the all-boron α -sheet. For our analysis we chose three α -sheet fragments, which are shown in Fig. 2–4. They were selected in a way to preserve electro neutrality when placed into the 2D- α -sheet. These fragments allowed us to trace all bonding elements in the α -sheet and reduce the influence of the boundary conditions in our fragments upon extension of their size.

Since chemical bonding in the all-boron α -sheet was anticipated to involve delocalized bonding we selected the Adaptive Natural Density Partitioning (AdNDP) method as a tool for our chemical bonding analysis. This method was recently developed by Zubarev and Boldyrev²⁹ and used to analyze chemical bonding in boron clusters,^{29–31} prototypical aromatic

^a Department of Chemistry and Biochemistry, Utah State University, Old Main Hill 0300, Logan, UT 84322-0300, USA. E-mail: a.i.boldyrev@usu.edu; Fax: +1 435-797-3390;

Tel: +1 435 7971630

^b Institute of Molecular Sciences, Shanxi University, Taiyuan 030006, People's Republic of China

^c Institute of Materials Science and Department of Chemistry, Xinzhou Teacher's University, Xinzhou 034000, Shanxi, People's Republic of China. E-mail: lisidian@xztc.edu.cn; Fax: +86 0350-3031845; Tel: +86 0350-3048202



Fig. 2 (a) Geometric structure of the B_7^{+7} fragment, six 3c-2e σ -bonds, and one 7c-2e π -bond. (b) Geometric structure of the $B_7H_6^+$ fragment, six 2c-2e B–H σ -bonds superimposed on a single framework, six 3c-2e σ -bonds superimposed on a single framework, and one 7c-2e π -bond.



Fig. 3 (a) Geometric structure of the B_{22}^{+16} fragment, eighteen 3c-2e σ -bonds (inside of peripheral triangles) superimposed on a single framework, three 4c-2e σ -bonds (inside of rhombus motifs) superimposed on a single framework, and four 7c-2e π -bonds located on filled hexagons. (b) Geometric structure of the $B_{22}H_{12}^{+4}$ fragment, twelve 2c-2e B-H σ -bonds, eighteen 3c-2e σ -bonds superimposed on a single framework, three 4c-2e σ -bonds superimposed on a single framework, and four 7c-2e π -bonds superimposed on a single framework, three 4c-2e σ -bonds superimposed on a single framework, and four 7c-2e π -bonds superimposed on a single framework, and four 7c-2e π -bonds.

organic molecules³² and gold clusters.³³ The AdNDP method analyzes the first-order reduced density matrix in order to obtain its local block eigenfunctions with optimal convergence properties for electron density description. The obtained local blocks correspond to the sets of *n* atoms (*n* ranging from one to the total number of atoms in the molecule) that are tested for the presence of two-electron objects (*n*-center two electron (*n*c-2e) bonds, including core electrons and lone pairs as a special case of n = 1) associated with this particular set of *n* atoms. AdNDP initially searches for core electron pairs and lone



Fig. 4 Geometric structure of the B_{30}^{+16} fragment of the α -sheet, twenty-four 3c-2e σ -bonds (inside of peripheral triangles and triangles bordering upon the hole) superimposed on a single framework, six 4c-2e σ -bonds (inside of rhombus motifs) superimposed on a single framework, one 6c-2e π -bond located on the hexagon hole, and six 7c-2e π -bonds located on filled hexagons.

pairs (1c-2e), then 2c-2e, 3c-2e,... and finally nc-2e bonds. At every step the density matrix is depleted of the density corresponding to the appropriate bonding elements. User-directed form of the AdNDP analysis can be applied to specified molecular fragments and is analogous to the directed search option of the standard Natural Bond Orbital (NBO) code.^{34,35} AdNDP accepts only those bonding elements whose occupation numbers (ON) exceed the specified threshold values, which are usually chosen to be close to 2.00 |e|. When all recovered *n*c-2e bonding elements are superimposed onto the molecular frame the overall pattern always corresponds to the point-group symmetry of the system. Thus, AdNDP recovers both Lewis bonding elements (1c-2e and 2c-2e objects, corresponding to the core electrons and lone pairs, and two-center two-electron bonds) and delocalized bonding elements, which are associated with the concepts of aromaticity and antiaromaticity. From this point of view, AdNDP achieves seamless description of systems featuring both localized and delocalized bonding without invoking the concept of resonance. Essentially, AdNDP is a very efficient and visual approach to interpretation of the molecular orbital-based wave functions.

We performed the AdNDP analysis of the all boron α -sheet fragments with geometric parameters (B–B distance of 1.67 Å) of the predicted lattice structure.^{13,15} We used a hybrid density functional method known in the literature as B3LYP with the 6-31G basis set. AdNDP is an extension of the NBO analysis^{34,35} and it was shown before^{29,36} that AdNDP is not sensitive to the level of theory or the basis set. All calculations were performed using the AdNDP program and the Gaussian 03 software package.³⁷ Molecular visualization was performed using Molekel 5.4.³⁸

First, we analyzed the seven-atom (the filled hexagon) fragment of the α -sheet (Fig. 2a). The charge of +7 was selected for the bare B₇ cluster from a few trial AdNDP runs which allowed us to have a symmetric chemical bonding picture with bonding elements, which will be shown later to be present in the 2D α -sheet lattice. The AdNDP analysis revealed six 3c-2e σ -bonds and one 7c-2e π -bond in the B₇⁺⁷ fragment. In order to reduce external charge we ran AdNDP calculations for the B₇H₆⁺ cluster. The analysis revealed the same chemical bonding pattern with additional six 2c-2e B–H

 σ -bonds (Fig. 2b), showing robustness of the chemical bonding picture.

The second model system was chosen in order to understand how the chemical bonding picture changes upon addition of three neighbouring filled hexagons to the B₇ motif (Fig. 3a). The AdNDP analysis of the B₂₂⁺¹⁶ cluster revealed a 3c-2e σ -bond in every peripheral triangle while a 4c-2e σ -bond was found in every rhombus motif at the junction of two hexagons (Fig. 3a). In addition, a 7c-2e π -bond on every filled hexagon was revealed using the user-directed form of the AdNDP method. It will be shown below that the newly found 4c-2e σ -bonds are present in the α -sheet at all junctions of the filled hexagons. Again, in order to test the robustness of this chemical bonding pattern we performed the same analysis for the B₂₂H₁₂⁺⁴ system (Fig. 3b). We found that the bonding picture is the same as that for the B₂₂⁺¹⁶ cluster with additional twelve 2c-2e B–H σ -bonds.

The B_{30}^{+16} cluster was chosen as a fragment of the all-boron α -sheet containing a hexagonal hole (Fig. 4). The AdNDP analysis revealed twenty-four 3c-2e σ -bonds at the peripheral triangles and triangles bordering upon the hole. Again, a 4c-2e σ -bond was found in every rhombus motif at the junction of two hexagons. Then a 7c-2e π -bond was revealed on every filled hexagon using the user directed AdNDP method as well as the new bonding element in this cluster: a 6c-2e π -bond over the hexagon hole at the center. The analysis of the largest studied fragment allowed us to recover the last missing bonding element—the 6c-2e π -bond over the hexagon hole.

From the chemical bonding analyses of the model fragments we now can propose the following chemical bonding picture (Fig. 1b) for the infinite all-boron α -sheet. On every filled hexagon we found three 3c-2e σ -bonds (solid triangles), which are bordering upon the holes, three 4c-2e σ -bonds (solid rhombi) at the junction of two filled hexagons, and one 7c-2e π -bond (circles). With this chemical bonding for each B₇ fragment we have six valence electrons coming from three 3c-2e σ -bonds, three electrons coming from three 4c-2e σ -bonds and two electrons coming from the 7c-2e π -bond with the total number of eleven electrons. On the other hand, if we consider a filled hexagon as a part of the lattice we can calculate the total number of valence electrons as follows: each of the six peripheral boron atoms brings half of its valence electrons (9 electrons in total) and the central atom brings all its valence electrons (3 electrons) resulting in the total of twelve electrons per filled hexagon. Thus, there is one extra electron on each filled hexagon motif not involved in the bonding presented above. As one can see from the whole lattice picture the extra electron on a filled hexagon (an electronic donor) is shared by three hexagonal holes (three electronic acceptors) evenly distributed around it, while each hole is surrounded by six filled hexagons, resulting in two 'extra' electrons per hole. Those two electrons form the 6c-2e π -bond (Fig. 1b, circles over hexagon holes), which was revealed in our B_{30}^{+16} model system. It is interesting to notice that, unlike graphene, which contains in-plane 2c-2e C-C σ-bonds, the all-boron graphene α -sheet studied in this work possesses no localized 2c-2e B–B σ -interactions.

Occupation numbers (ONs) revealed for every bonding element are very close to the ideal value of 2.00 |e| (see Fig. 2–4) giving additional credibility to the presented chemical bonding picture for the all-boron α -sheet.

Table 1	Calculated	NICS _{zz}	values	(ppm)
---------	------------	---------------------------	--------	-------

$R_{\rm z}{}^a/{ m \AA}$	Filled hexagon ^b	Hexagon hole ^b	Benzene ^c
0.0	_	-51.5	-14.5
0.2	-100.4	-53.0	-16.3
0.4	-75.3	-56.9	-20.6
0.6	-70.8	-61.7	-25.2
0.8	-66.3	-66.1	-28.3
1.0	-60.8	-68.9	-29.2
1.2	-55.2	-69.9	-28.2
1.4	-49.9	-69.0	-26.0
1.6	-45.2	-66.8	-23.2
1.8	-41.0	-63.6	-20.2
2.0	-37.3	-59.8	-17.4
^{<i>a</i>} Distance $6-311 + G$	e from the hexagon *. ^c Calculated at B3LY	centre. ^b Calculated $P/6-311++G^{**}$.	at B3LYP/

The AdNDP method revealed a delocalized π -bond on every filled hexagon and every hexagon hole. Each π -bond is responsible for local π -aromaticity in the corresponding fragment. We further probed the revealed π -aromaticity using one of the most popular ways of evaluating aromaticity in planar species, the nuclear independent chemical shift (NICS_{zz}), which was introduced by Schleyer and co-workers.³⁹ In this method negative NICS_{zz} values indicate aromaticity and positive values indicate antiaromaticity. NICS_{zz} calculations were performed above the center of the filled and empty hexagons in the B₃₀⁺¹⁶ model system using the B3LYP/6-311+G* level of theory. We also calculated the same set of the NICS_{zz} values for the prototypical aromatic system, benzene, using the B3LYP/6-311++G** level of theory. Results of all the calculations are summarized in Table 1.

One can see that the NICS_{zz} values above the filled hexagons and hexagon holes are significantly more negative than the corresponding values of benzene, thus, confirming the presence of local π -aromaticity in the hexagons.

From our overall chemical bonding picture we get a 1/3ratio for the numbers of valence π - and σ -electrons in the all-boron α -sheet, which was obtained from the fact that out of a total of twelve valence electrons on each filled hexagon motif (including the one it donates to the holes) three form π -bonds and nine form σ -bonds. We would like to stress that this ratio is close to that of the so far largest planar boron clusters studied both experimentally and theoretically: B_{16}^{2-} (the valence π - to σ -ratio is 0.25)³⁰ and B₁₉⁻ (the valence π - to σ -ratio is 0.26).³¹ The presence of holes as well as their amount relative to the number of filled hexagons in the all-boron α -sheet is determined by this π - to σ -electrons ratio: the holes in the all-boron α -sheet absorb the third π -electron of each filled hexagon, which cannot be accepted by the motif. Interestingly, the ratio of 1/9 between the number of the donated π -electrons (1 electron) and the number of total σ -electrons (9 electrons) in a filled hexagon equals the hexagon hole density of 1/9 in the infinite all-boron α -sheet.¹³ This analysis agrees with the proposed chemical bonding pattern demonstrated in Fig. 1b for a building block of the α -sheet boron.

Now it is clear why the hypothetical honeycomb crystal lattice of a neutral boron sheet where each boron atom acquires sp²-hybridization and forms three 2c-2e σ -bonds but no π -bonds is not energetically favourable. In order for the neutral all-boron 2D-structure to be energetically

This journal is © the Owner Societies 2011

favourable it should have a certain amount of electron density in the π -system. If we transfer some amount of electrons from the 2c-2e σ -bonds in the honeycomb crystal lattice to the π -system it breaks the connectivity in the σ -framework and that makes the whole structure energetically unfavourable. Similarly, the all-boron neutral 2D-structure composed of boron equilateral triangles (or of filled hexagons but with no holes), the so-called triangular sheet, should be unstable too. There are two ways to construct the triangular boron sheet in accordance with our bonding model. First, if one tried to build it with every triangle carrying a 3c-2e σ -bond, there would be not enough electrons even for such σ -bonding, since every boron atom belongs to six triangles and therefore can contribute $3 \times (1/6) = 1/2$ electrons to the triangle with the total of 1.5 electrons per triangle only.. Alternatively, we can construct the neutral all-boron 2D-sheet of filled hexagons with the presence of six 4c-2e σ -bonds (they are shared with the neighbouring hexagons) and six π -orbitals on each filled hexagon. This structure is also unfavourable since the ratio of π - to σ -electrons is 0.5, which was not observed for the lowest energy planar boron clusters.^{30,31,40–42}

The unprecedented chemical bonding model presented in the current work widens our understanding of chemical bonding in general and we believe that the presented bonding picture could be an advance toward rational design of future all-boron nanomaterials.

Acknowledgements

The theoretical work at Utah State University was supported by the National Science Foundation (CHE-1057746). An allocation of computer time from the Center for High Performance Computing at the University of Utah is gratefully acknowledged. Computer time from the Center for High Performance Computing at Utah State University is also gratefully acknowledged.

The theoretical work performed in China was jointly supported by the National Foundation of China (No. 20873117) and Shanxi Natural Science Foundation (No. 2010011012-3).

Notes and references

- 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.
- 2 K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos and A. A. Firsov, *Nature*, 2005, **438**, 197.
- 3 S. Unarunotai, Y. Murata, C. E. Chialvo, N. Mason, I. Petrov, R. G. Nuzzo, J. S. Moore and J. A. Rogers, *Adv. Mater.*, 2010, 22, 1072.
- 4 K. I. Bolotin, K. J. Sikes, Z. Jiang, M. Klima, G. Gudenberg, J. Hone, P. Kim and H. L. Stormer, *Solid State Commun.*, 2008, 16, 351.
- 5 S. V. Morozov, K. S. Novoselov, M. I. Katsnelson, F. Schedin, D. C. Elias, J. A. Jaszcnak and A. K. Geim, *Phys. Rev. Lett.*, 2008, **100**, 016602.
- 6 X. Du, I. Skachko, A. Barker and E. Y. Andrei, *Nat. Nanotechnol.*, 2008, **3**, 491.
- 7 I. W. Frank, D. M. Tanenbaum, A. M. van der Zanda and P. L. McEuen, J. Vac. Sci. Technol., A, 2007, 25, 2558.
- 8 F. Scarpa, S. Adhikari and A. S. Phani, *Nanotechnology*, 2009, 20, 065709.
- 9 R. Faccio, P. A. Denis, H. Pardo, C. Goyenola and A. W. Mombru, J. Phys.: Condens. Matter, 2009, 21, 285304.

- 10 M. D. Stoller, S. Park, Y. Zhu, J. An and R. S. Ruoff, Nano Lett., 2008, 8, 3498.
- 11 K. Mullen and J. P. Rabe, Acc. Chem. Res., 2008, 41, 511.
- 12 J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani and J. Akimitsu, *Nature*, 2001, **410**, 63.
- 13 H. Tang and S. Ismail-Beigi, Phys. Rev. Lett., 2007, 99, 115501.
- 14 H. Tang and S. Ismail-Beigi, Phys. Rev. B, 2009, 80, 134113.
- 15 X. Yang, Y. Ding and J. Ni, Phys. Rev. B, 2008, 77, 0414402
- 16 N. G. Szwacki and C. J. Tymczak, Chem. Phys. Lett., 2010, 494, 80.
- 17 G. Gopakumar, M. T. Nguyen and A. Ceulemans, *Chem. Phys. Lett.*, 2008, **450**, 175.
- 18 T. Baruah, M. R. Pederson and R. R. Zope, *Phys. Rev. B*, 2008, 78, 045408.
- A. Sadrzadeh, O. V. Pupysheva, A. K. Singh and B. I. Yakobson, J. Phys. Chem. A, 2008, 112, 13679.
 S. Botti, A. Castro, N. N. Lathiotakis, X. Andrade and M. A. L.
- 20 S. Botti, A. Castro, N. N. Lathiotakis, X. Andrade and M. A. L. Marques, *Phys. Chem. Chem. Phys.*, 2009, **11**, 4523.
- 21 Q. B. Yan, Q. R. Zheng and G. Su, Phys. Rev. B, 2008, 77, 224106.
- 22 A. Y. Liu, R. R. Zope and M. R. Pederson, *Phys. Rev. B*, 2008, **78**, 155422.
- 23 N. G. Szwacki, Nanoscale Res. Lett., 2008, 3, 80.
- 24 Q. B. Yan, X. L. Sheng, Q. R. Zheng, L. Zhang and G. Su, *Phys. Rev. B*, 2008, **78**, 201401R.
- 25 R. R. Zope, T. Baruah, K. C. Lau, A. Y. Liu, M. R. Pederson and B. I. Dunlap, *Phys. Rev. B*, 2009, **79**, 161403R.
- 26 J. Zhao, L. Wang, F. Li and Z. Chen, J. Phys. Chem. A, 2010, 114, 9969.
- 27 P. Jin, C. Hao, Z. Gao, S. Zhang and Z. Chen, J. Phys. Chem. A, 2009, 113, 11613.
- 28 N. G. Szwacki, A. Sadrzadeh and B. I. Yakobson, *Phys. Rev. Lett.*, 2007, 98, 166804.
- 29 D. Yu. Zubarev and A. I. Boldyrev, Phys. Chem. Chem. Phys., 2008, 10, 5207.
- 30 A. P. Sergeeva, D. Yu. Zubarev, H.-J. Zhai, A. I. Boldyrev and L. S. Wang, J. Am. Chem. Soc., 2008, 130, 7244.
- 31 W. Huang, A. P. Sergeeva, H.-J. Zhai, B. B. Averkiev, L. S. Wang and A. I. Boldyrev, *Nat. Chem.*, 2010, 2, 202.
- 32 D. Yu. Zubarev and A. I. Boldyrev, J. Org. Chem., 2008, 73, 9251.
- 33 D. Yu. Zubarev and A. I. Boldyrev, J. Phys. Chem., 2009, 13, 866.
- 34 J. P. Foster and F. Weinhold, J. Am. Chem. Soc., 1980, 102, 7211.
- 35 F. Weinhold and C. Landis, Valency and Bonding. A Natural Bond Orbital Donor-Acceptor Perspective, Cambridge University Press, Cambridge, UK, 2005.
- 36 A. P. Sergeeva and A. I. Boldyrev, Comments Inorg. Chem., 2010, 31, 2.
- 37 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, 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, Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, P. J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, GAUSSIAN 03, (Revision D.01), Gaussian, Inc., Wallingford, CT, 2004.
- 38 U. Varetto, *Molekel 5.4.0.8*, Swiss National Supercomputing Centre, Manno (Switzerland).
- 39 P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. R. v. E. Hommes, J. Am. Chem. Soc., 1996, 118, 6317.
- 40 A. N. Alexandrova, A. I. Boldyrev, H.-J. Zhai and L. S. Wang, *Coord. Chem. Rev.*, 2006, 250, 2811.
- 41 B. Kiran, S. Bulusu, H. J. Zhai, S. Yoo, X. C. Zeng and L. S. Wang, Proc. Natl. Acad. Sci. U. S. A., 2005, 102, 961.
- 42 H. J. Zhai, B. Kiran, J. Li and L. S. Wang, *Nat. Mater.*, 2003, **2**, 827.

ged. ork performed in China was jointly