Solid State Sciences xxx (2012) 1–7

Contents lists available at SciVerse ScienceDirect

Solid State Sciences

journal homepage: www.elsevier.com/locate/ssscie

The route to highly stable $MeB_xN_yC_z$ molecular wheels. I. The features of preliminary results

I. Boustani [a,*], R. Pandey [b]

[a] Bergische Universität Wuppertal, FB C - Mathematik und Naturwissenschaften, Gaußstraße 20, 42119 Wuppertal, Germany
[b] Michigan Technological University, Department of Physics, Houghton, MI 49931, USA

ARTICLE INFO

Article history:
Received 24 October 2011
Received in revised form
9 March 2012
Accepted 14 March 2012
Available online xxx

Keywords:
Molecular wheels
Titanium boride clusters
Boron wheels

ABSTRACT

By means of *ab initio* quantum chemical methods we have determined the energies and electronic structures of molecular wheels TiB_n, TiB_nN_{10-n}, TiC_nN_{10-n} and TiC_nB_{10-n} (for $n = 0–10$). The ground state energies and the corresponding spin states of each atom, cluster and molecular wheel were calculated first in the framework of Hartree-Fock self-consistent-field (HF-SCF) using minimal and more accurate basis sets STO-3G and 6-31G. Computations at higher level and accuracy are processing in a follow-up study. The most stable wheel system is TiC_nB_{10-n} (for $n = 5–10$). Thereof particularly highly stable is the TiC_5B_5 molecular wheel followed by the TiC_6B_4. At the HF-SCF/6-31G level, however, we have calculated the wheel system MeC_5B_5 considering for Me, the first row of transition metal atoms Me = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn. The molecular wheel MeC_5B_5 favours Sc atom at the centre, but also Ti and Fe are the next favoured atoms.

1. Introduction

Interest in synthesis and exploration of structure and energetics of boron clusters and boron-compounds has both academic and practical aspects. Such structures should have a wide variety of applications. The reason lies simply by the atomic boron which is the only element except carbon that can build molecules of any size by covalently bonding to itself. Due to sp^2 hybridization of the valence electrons, large coordination number and short covalent radius, boron prefers to form strong directional bonds with various elements. Due to its electron deficiency boron makes multi-centre bonds where pair of electrons is shared between two atoms and more [1].

At the molecular level, elemental boron clusters B_n for ($n = 2–8$) were investigated in 1990 by I. Boustani et al. (unpublished results) using a double-ζ basis set with polarization function (DZ + P) in the framework of the Hartree-Fock (HF) self-consistent-field (SCF) theory and configuration interaction (CI), published in part 1991 [2]. The most interesting structure is the so-called molecular wheel B_8, which is composed of a central boron atom surrounded by a regular boron heptagon. The ground state of B_8 molecular wheel is D_{7h} ($^3A_2$). The bondlength of the heptagon is 1.516 Å, and the distance to the central atom is about 1.747 Å. Further pure boron clusters have been extensively explored namely both theoretically [3] and experimentally [4]. Thus boron clusters B_n were found to exhibit planar configurations for $n \leq 14$ and consequently are aromatic. The aromatic (planar) boron clusters possess more circular shapes whereas anti-aromatic ones are elongated. Recent experimental [5] and theoretical [6] studies on boron clusters show that the anionic and neutral B_{19} clusters are the largest two-dimensional aggregates of boron.

On the other hand, small clusters of the neighbouring element carbon C_n, determined for ≤ 10, are linear chains for odd n and closed rings for even n [7]. Carbon clusters C_n for ($6 \leq n \leq 13$) were also investigated Slanina et al. [8]. They found that the carbon clusters C_n for ≤ 10 have also linear chains for odd n and cyclic structures for even n. But however, the carbon clusters C_{11}, C_{12} and C_{13} have cyclic structures. Larger carbon clusters C_n for ($14 \leq n \leq 24$, n even) were investigated by Jones and Seifert [9]. They found that the carbon clusters have chains, rings, graphitic plate, bowl and cage-like structures. They also found that the most stable isomers for the carbon clusters C_{14}, C_{16} and C_{18} have monocyclic ring structures.

Binary compounds of boron and carbon atoms, known as boron carbides, are the most widely investigated compounds. The rhombohedral elemental cell of a single-crystal boron carbide is composed of boron icosahedra residing at each vertex containing three atomic linear chains, like C–B–C or C–C–C, located at the main cell diagonal of the rhombohedron [10]. However, small neutral and charged boron carbide $B_{8-m}C_m$ clusters for $m = 1$ to 3

* Corresponding author. Tel.: +49 202596665.
E-mail addresses: boustani@t-online.de, boustani@uni-wuppertal.de (I. Boustani).

1293-2558/$ – see front matter © 2012 Elsevier Masson SAS. All rights reserved.
doi:10.1016/j.solidstatesciences.2012.03.003

are recently studied by S. S. Park [11] using density functional theory. He investigated eight B_7C^{-1}, twelve B_6C_2, and twelve $B_5C_3^{+1}$ isomers and found that the most stable structures are molecular wheels with a central boron atom. Molecular-dynamics simulation of structural and thermodynamic properties of cubic boron nitride c-BN were studied by Sekkal et al. [12] using well-tested Tersoff potential. They predicted the corresponding various physical quantities including the thermal expansion coefficient and heat capacity. They extended these simulations to study liquid boron nitride at various densities.

Titanium carbide clusters were also studied by Wang et al. [13]. They reported the vibrationally resolved photoelectron spectra of a series of TiC_x^{-1} clusters for $x = 2-5$ and observed that ground state vibrational frequencies and electron affinities are tentatively interpreted to support ring-type structures for these clusters. Furthermore, small clusters of metal boride MeB_n ($n \leq 7$) particularly those of transition metals (Cr to Ni) were investigated by X. Liu et al. [14]. They used first-principles DFT-GGA methods and studied their electronic and magnetic properties. They found that MeB_n clusters with $n \leq 5$ have planar triangular geometries, those with $n = 6$ have wheel forms, while MeB_n clusters with $n = 7$ are three-dimensional. Metal-boron molecular wheels were studied by Pu et al. [15] using also density functional theory. They found that B_9 and B_{10} rings accommodate the first row of transition metals. Microstructure and properties of superhard Ti–B–C–N films deposited on stainless steel substrated by a dc unbalanced magnetron sputtering were studied by I.-W. Park et al. [16]. They found that the hardness of the Ti–B–C–N films increases with the increase of N content up to a maximum value of approximately 45 GPa at 10 at. % N, with a subsequent decrease in hardness at higher N.

The purpose of this study is to show first that the formation of TiB_n systems, composed of a single transition metal atom like Ti and of boron atoms embedded one by one, favours aromatic two-dimensional (2D) over three-dimensional (3D) structures, as it is the case of planar boron clusters, and leads to molecular wheels. Furthermore it is to show the route of stability of the molecular wheels when boron atoms are replaced by nitrogen then by carbon atoms. Since the metal atom Ti can link and accomodate in a plane maximum 10 boron atoms so that the surrounding binding boron atoms around the central metal atom just building reasonable bonds to each other and also to the centre Ti. Therefore the size of the molecular wheels beside Ti atom is limited by 10 atoms and thus the stability of the $MeB_xN_yC_z$ wheels does not depend more on the size but only on the combination of boron, nitrogen and carbon atoms around the central transition metal atoms. Thereupon, we will study the geometry, electronic structures and cluster stability of the molecular wheels of the TiB_n, TiB_nN_{10-n}, TiC_nN_{10-n} and TiC_nB_{10-n} (for $n = 1-10$) systems as well as MeC_5B_5, for (Me = Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn). The paper is organized as follows: the computational methods will be described then discussion and results and finally summary and conclusions.

2. Computational details

Ab initio quantum chemical methods for solving the many-electron problems in the framework of the Hartree-Fock self-consistent-field (HF-SCF) were applied to determine the ground state energies of the molecular systems. All-electron calculations in the current work were performed using STO-3G and 6-31G basis sets. Computations at higher level of theory with more accurate and extensive functionals, pseudopotentials and basis sets are in process in a follow-up study [17]. The optimization procedure, based on the analytical gradient method, has been carried out for the ground state energies using the restricted and unrestricted Hartree-Fock theory for closed- and open-shell systems, using the minimal basis set STO-3G. The most stable molecular wheel MeC_5B_5 was calculated for the first row of metal atoms at the HF-SCF/6-31G level of theory. In order to determine the stability of the cluster compounds we have calculated the binding energy (E_b) in eV/atom as follows:

$$E_b = \frac{1}{n}\{E(\mathrm{Me}) + xE(\mathrm{B}) + yE(\mathrm{C}) + zE(\mathrm{N}) - E(\mathrm{MeB}_x\mathrm{C}_y\mathrm{N}_z)\} \quad (1)$$

where n is the total number of atoms in the clusters, E(Me) is the energy of atomic transition metal Me = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn, where E(B), E(C), and E(N) are the energies of boron, carbon, and nitrogen atoms, respectively. $E(\mathrm{MeB}_x\mathrm{C}_y\mathrm{N}_z)$ is the energy of the cluster or of the molecular wheel, while x, y and z are the number of compounds in the cluster or wheel. In all calculations we have considered symmetry constraints in the form of a point group symmetry. We have also calculated different spin states for each atom and cluster selecting the corresponding lowest energy to be the ground state energy. These calculations were carried out using the Gaussian 03 [18] and Gamess_UK [19] program packages.

Concerning the calculations at the HF-SCF level of theory and at the basis set STO-3G, we are aware of the limitation of this method as well as the basis set to get a qualitative guidance about the stability of the systems, when adding boron atoms one by one around Ti to obtain the molecular wheel, then replacing boron by nitrogen or carbon atoms to achieve larger stability. However and as mentioned above, we are working in a follow-up paper [17] in which qualitative and quantitative calculations at higher quality basis sets and pseudopotentials as well as much more accurate functionals beyond the HF-SCF to verify and confirm the trend in stability of the system predicted at the HF-SCF/STO-3G level of theory.

3. Results and discussion

Earlier *ab initio* calculations of boron clusters have shown that small clusters favour 2D quasiplanar formations [20,21]. But how do behave these structures as soon as we dope a single transition metal atom into the cluster? The best way to approach the answer is to take a metal atom like Ti adding boron atoms solong until acheaving stable structures. The first route is the planar system TiB_n (for $n = 1–10$) starting by the TiB dimer adding atom by atom building a cyclic ring around Ti. In order to show that the TiB_n clusters favour 2D structures we have determined also some isomers of arbitrary 3D structures mostly pyramids with an apex or central Ti atom. These calculations were carried out at the HF-SCF/STO-3G level of theory considering doublet- and triplet-states for clusters with odd and even n, respectively.

3.1. The 2D TiB_n systems

The linear TiB and the equilateral triangle TiB_2 with Ti as an apex atom have been determined having binding energies of 1.83 and 2.32 eV/atom. The linear TiB molecule of $C_{\infty v}(^2\Sigma_g)$ symmetry and state has a bondlength of 1.84 Å. Concerning TiB_2, the atomic distance between the apex atom Ti and both boron atoms in the triangular trimer is about 2.18 Å, while the bondlength between both boron atoms is about 1.64 Å. The 2D structure TiB_3 cluster is a rectangle in which the Ti atom is connected to three bonding boron atoms forming an arc, as shown in Fig. 1. The calculated E_b of the planar TiB_3 cluster of $C_{2v}(^2B_2)$ symmetry and state is about 2.47 eV/atom. The bondlength between the Ti atom and the middle boron atom is 2.14 Å, while the it is about 2.08 Å to the outer atoms. The atomic distance between the boron atoms is 1.54 Å. The 2D

Please cite this article in press as: I. Boustani, R. Pandey, The route to highly stable $MeB_xN_yC_z$ molecular wheels. I. The features of preliminary results, Solid State Sciences (2012), doi:10.1016/j.solidstatesciences.2012.03.003

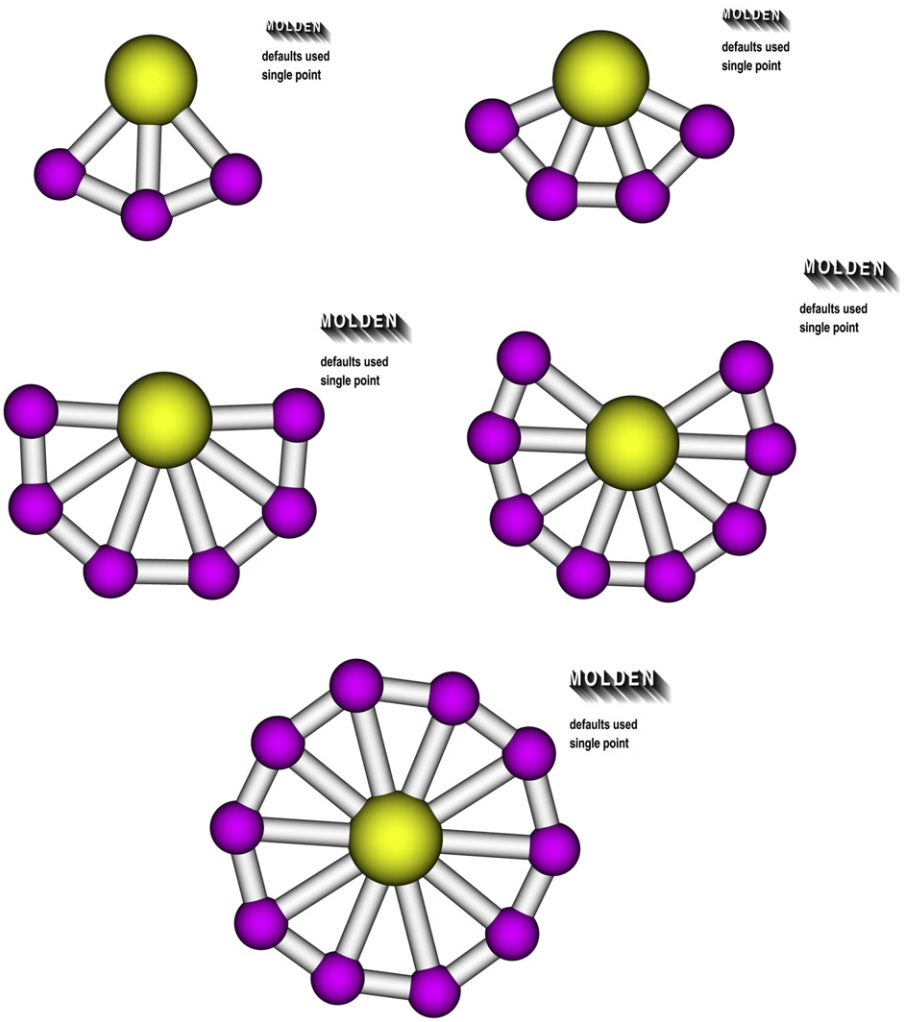

Fig. 1. 2D structures TiB_3, TiB_4, TiB_6, TiB_8 and TiB_{10}.

structure of the TiB_4 cluster is developed from the planar TiB_3 cluster, as shown in Fig. 1. The E_b of TiB_4 determined in $C_{2v}(^3A_1)$ symmetry and state is about 2.88 eV/atom. The distances in planar TiB_4 between Ti atom and the arc of four boron atoms are 2.25 Å to the middle atoms, while 2.07 Å to the outer atoms. The atomic distanace between the middle boron atoms is 1.50 Å, while the distance to the outer atoms is 1.53 Å. The planar structure of TiB_5 of $C_{2v}(^2B_2)$ symmetry and state with an E_b of 3.23 eV/atom is a further development of TiB_4. The average bond distance from Ti atom to the central arc of boron atoms is 2.15 Å, while the average bondlength between the boron atoms is about 1.53 Å.

The same tendency of stability by the clusters with even n can be ascertained by the 2D clusters TiB_6 and TiB_8, as shown in Fig. 1. The stability of clusters TiB_6 of $C_{2v}(^3A_1)$ and TiB_8 of $C_{2v}(^3B_2)$ symmetry and state is determined to 3.17 and 3.41 eV/atom, respectively. Regarding the planar TiB_6 structure, the bondlength between the Ti atom to the middle boron atoms of the arc is about 2.29 Å, while the distance to next two atoms is 2.27 Å, then to outer atom is 2.08 Å. The atomic distance between the middle boron atoms is about 1.48 Å, while it is 1.50 and 1.52 Å to the next and over next boron atoms. The average bondlength between Ti atom in TiB_8 and the the eight boron atoms is about 2.08 Å, while the average atomic distance between the boron atoms is about 1.59 Å.

The stability of the planar TiB_7 and TiB_9 clusters of odd boron atoms, both of C_{2v} symmetry, obtained from planar TiB_6 and TiB_8 clusters by adding further boron atom to each one, is 3.27 and 3.42 eV/atom, respectively. The average atomic distance between Ti atom and the arc of boron atoms for TiB_7 of $C_{2v}(^2A_1)$ is about 2.20 Å and the average bondlength between boron atoms is about 1.58 Å. The TiB_9 cluster optimized in $C_{2v}(^2B_2)$ symmetry and state approachs a wheel structure with an average radial distance of 2.22 Å, while the average distance between the peripheral boron atoms is about 1.52 Å. The final 2D structure TiB_{10} is a wheel with a D_{10h} symmetry calculated in $D_{2h}(^3B_{3g})$ symmetry and state as shown in Fig. 1. The calculated E_b of the 2D TiB_{10} structure is about 3.69 eV/atom. The atomic distance between the Ti atom and the cyclic boron atoms is about 2.39 Å, while the bondlength of the decagon is about 1.48 Å.

3.2. The 3D TiB_n systems

The 3D structure of the TiB_3 cluster is a trigonal pyramid of $C_{3v}(^4A_1)$ symmetry and state in which Ti is the apex atom, is shown in Fig. 2. The calculated E_b of the trigonal pyramid TiB_3 cluster is about 2.05 eV/atom. The distance between the triangle boron atoms and the apex Ti atom is about 1.85 Å, while the bondlength of the triangle boron atoms is 1.56 Å. The binding energy of the

Please cite this article in press as: I. Boustani, R. Pandey, The route to highly stable $MeB_xN_yC_z$ molecular wheels. I. The features of preliminary results, Solid State Sciences (2012), doi:10.1016/j.solidstatesciences.2012.03.003

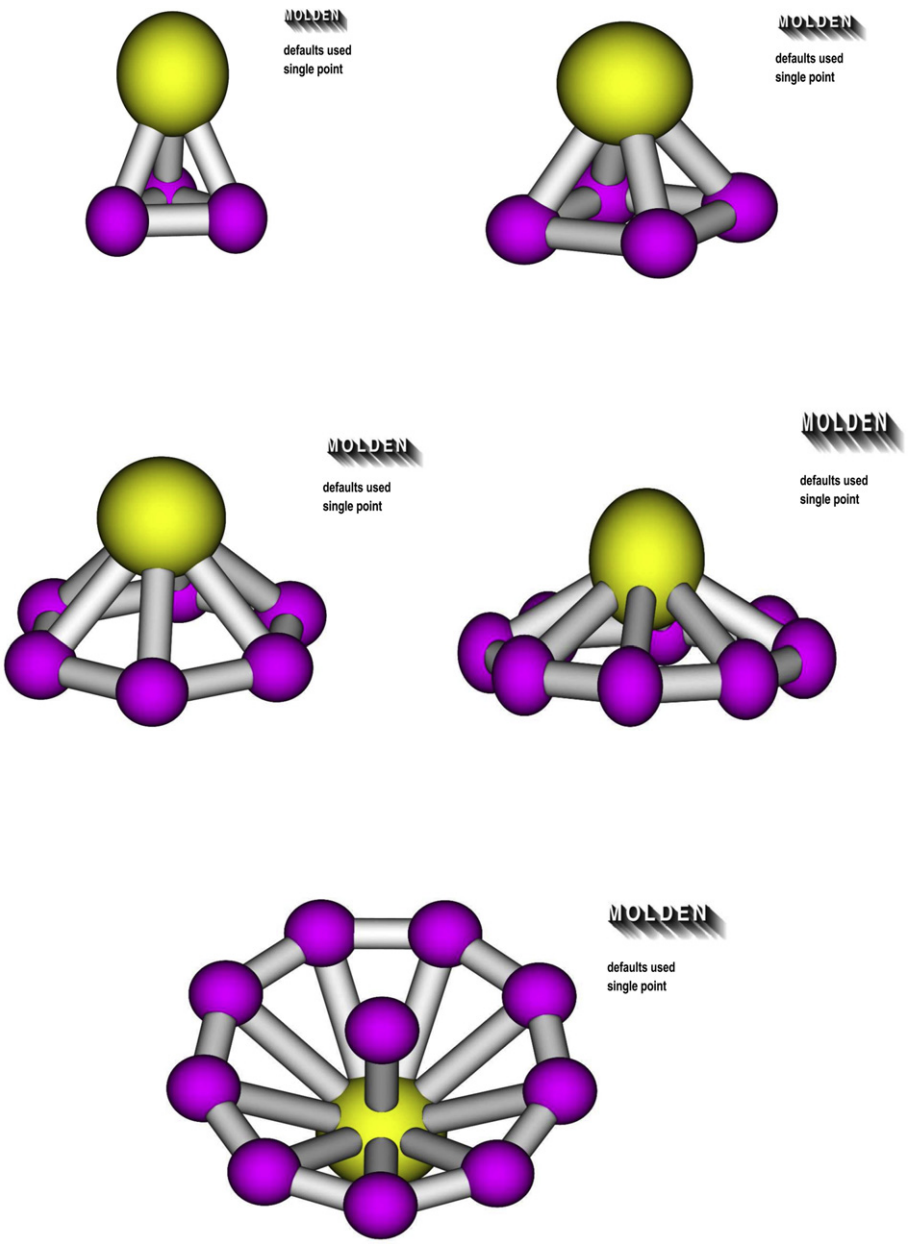

Fig. 2. 3D structures TiB_3, TiB_4, TiB_6, TiB_8 and TiB_{10}.

tetragonal pyramid TiB_4 of $C_{4v}(^3A_1)$ symmetry and state, as presented in Fig. 2, is about 2.42 eV/atom. The apex Ti atom departs to the boron square about 2.46 Å, while the bondlength of the square is about 1.56 Å. The E_b of the pentagonal pyramid TiB_5 of $C_{5v}(^2A_1)$ symmetry and state is about 3.11 eV/atom. The atomic distance between the apex Ti and the five fold boron atoms is 2.23 Å, while the bondlength of the pentagon is about 1.52 Å.

The 3D structures, the hexagonal pyramid TiB_6 of $C_{6v}(^3A_1)$ symmetry and state and the octagonal pyramid TiB_8 with $C_{8v}(^3B_1)$ symmetry and state, as presented in Fig. 2, are less stable than the 2D structures, where their binding energies are assigned to 3.07 and 3.30 eV/atom, respectively. For the TiB_6 cluster, the atomic distance between the apex Ti and the hexagon is 2.29 Å, while the bondlength of the hexagon is about 1.53 Å. For the TiB_8 cluster, the atomic distance between the apex Ti and the octagon is 1.94 Å, while the bondlength of the octagon is about 1.49 Å. The heptagonal pyramid TiB_7 with an E_b of 3.25 eV/atom is slightly less stable than the planar one. The atomic distance of the apex Ti atom to the heptagon is about 2.19 Å and the bondlength of the heptagon is about 1.51 Å.

The 3D TiB_9 cluster of C_{8v} symmetry, calculated in $C_{2v}(^2B_2)$ symmetry and state, is an octagonal umbrella or satellite dish in form of an octagon in which Ti atom is located at the centre and bonded to boron atom localized at the focus. The corresponding E_b is about 3.32 eV and thus less stable than the planar one. The atomic distance from the Ti atom to the octagon is 2.34 Å and to the boron atom at the focus is 2.01 Å, while the bondlength of the octagon is about 1.49 Å. Finally we determined the 3D structure of TiB_{10} cluster of C_{9v} symmetry, calculated in $C_s(^3A'')$ symmetry and state. It is a nonagonal umbrella or satellite dish with Ti at the centre of the nonagon bonded to boron atom at the focus, as can be seen in Fig. 2. The calculated E_b is about 3.56 eV and thus is less stable than the planar one. The atomic distance between the Ti atom and the cyclic boron atoms is about 2.36 Å, and the distance to

Please cite this article in press as: I. Boustani, R. Pandey, The route to highly stable $MeB_xN_yC_z$ molecular wheels. I. The features of preliminary results, Solid State Sciences (2012), doi:10.1016/j.solidstatesciences.2012.03.003

the boron atom lying at the focus is 2.03 Å, while the bondlength of the nonagon is about 1.48 Å.

Due to the fact that the all 2D structures of TiB_n are energetically favoured over the 3D pyramides, we have considered the planar clusters and presented their stability in Fig. 3, as a function of cluster size or the number of boron atoms. It can be asserted that the function E_b of the system TiB_n for ($n = 1$–10) increases with increasing the number of boron atoms, represented by the stars. In addition, we have selcted some 2D and 3D structures of TiB_n for ($n = 3, 4, 6, 8$ and 10) and presented in Figs. 1 and 2, respectively. In addition, we have listed the stability of the 2D and 3D structures and the corresponding point group symmetry and spin states in Table 1.

3.3. The TiB_nN_{10-n} system

After obtaining the titanium boron molecular wheel, we have started to dope this wheel with nitrogen atoms by replacing boron by nitrogen atoms one by one calculating the E_b at each step of doping and keeping the original geometry of TiB_n. The binding energies E_b are listed in Table 2. As can be seen in Fig. 3, we have recorded the E_b of this TiB_nN_{10-n} system as a function of the number of nitrogen atoms n for ($n = 10$ to 0). For $n = 10$ we still have the system TiB_{10}. For $n = 9$ means the first doping occurs by replacing the first nitrogen with boron atom to get TiB_9N_1 with an E_b of 4.19 eV/atom. The next value $n = 8$ means TiB_8N_2 and the corresponding binding energy is about 4.42 eV/atom. The E_b values increase with increasing the number of nitrogen atoms until arriving the maximum of this function labelled by $n = 5$ achieving an E_b of 5.01 eV/atom. Afterwards the E_b function of TiB_nN_{10-n} decreases down to 2.70 eV/atom with increasing the number of nitrogen atoms until TiN_{10}. The substitution of nitrogen atoms occurs first alternately, like b–n–b–n, until $n = 5$ obtaining symmetrical wheel TiB_5N_5, afterwards the residual boron atoms will be replaced by nitrogen one by one. The E_b function of the TiB_nN_{10-n} system is assigned by red squares.

3.4. The TiC_nN_{10-n} system

We proceed in the same manner doping now the TiN_{10} system with carbon atoms. Starting by $n = 1$ and replacing one nitrogen by a carbon atom we receive the molecular wheel TiC_1N_9 with an E_b of 2.91 eV/atom. The next step is assigned by substituting the next nitrogen atom by carbon getting for $n = 2$ the wheel TiC_2N_8. The corresponding E_b is about 3.31 eV/atom. However, The calculated E_b values of this system are also listed in Table 2. Further steps are continued by replacing nitrogen by carbon atoms one by one in clockwise direction obtaining for $n = 10$ the cluster TiC_{10} with an E_b of 5.80 eV/atom. The substitution of nitrogen by carbon atoms occurs first alternately, like c–n–c–n, until $n = 5$ obtaining the symmetrical wheel TiC_5N_5. Afterwards for $n \geq 6$ the residual nitrogen atoms are replaced by carbon one by one. It is to observe that the E_b function of the TiC_nN_{10-n} system, as shown in Fig. 3 and assigned by a green triangle down, increases upwards with increasing the number of carbon atoms n.

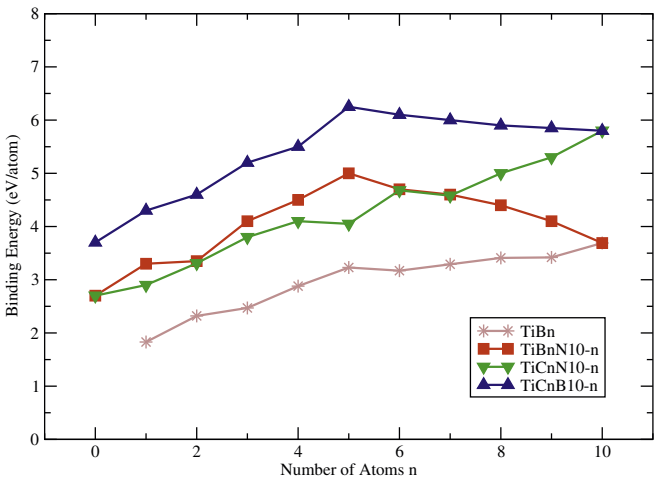

Fig. 3. Stability of clusters and molecular wheels.

Table 1
Dimension, Structure, Symmetry(State), E_b binding energy, determined at the HF-SCF/STO-3G level of theory.

Dimension	Structure	Symmetry(State)	E_b (eV/atom)
2D Clusters	TiB-Linear	$C_{\infty v}(^2\Sigma_g)$	1.83
	TiB_2-Planar	$C_{2v}(^2B_2)$	2.32
	TiB_3-Planar	$C_{2v}(^2B_2)$	2.47
	TiB_4-Planar	$C_{2v}(^3B_2)$	2.88
	TiB_5-Planar	$C_{2v}(^2B_2)$	3.23
	TiB_6-Planar	$C_{2v}(^3A_1)$	3.17
	TiB_7-Planar	$C_{2v}(^2A_1)$	3.29
	TiB_8-Planar	$C_{2v}(^3B_2)$	3.41
	TiB_9-Planar	$C_{2v}(^2B_2)$	3.42
	TiB_{10}-Wheel	$D_{2h}(^3B_{3g})$	3.69
3D Clusters	TiB_3-Trigonal Pyramid	$C_{3v}(^4A_1)$	2.05
	TiB_4-Tetragonal Pyramid	$C_{4v}(^3A_1)$	2.42
	TiB_5 Pentagonal Pyramid	$C_{5v}(+A')$	3.07
	TiB_6-Hexagonal Pyramid	$C_{6v}(^3A_1)$	3.11
	TiB_7-Heptagonal Pyramid	$C_{7v}(^2A_1)$	3.25
	TiB_8-Octagonal Pyramid	$C_{8v}(^3B_1)$	3.30
	TiB_9-Octagonal Umbrella	$C_{2v}(^2B_2)$	3.37
	TiB_{10}-Nonagonal Umbrella	$C_s(^3A'')$	3.56

3.5. The TiC_nB_{10-n} system

The substitution of carbon with boron atoms up to $n = 5$ occurs first alternately receiving the wheel system TiC_5B_5, with the corresponding E_b listed in Table 2. Afterwards the residual carbon atoms will be replaced by boron atoms approaching the TiB_{10} system once again. As can be seen in Fig. 3, the E_b function increases with increasing the number of boron atoms up to $n = 5$. Thereafter it drops towards the E_b value of 3.69 eV/atom of the wheel TiB_{10}. A distinguishable maximum in Fig. 3 can be observed by $n = 5$ corresponding to the largest E_b value of 6.25 eV/atom for the symmetrical molecular wheel TiC_5B_5. The next stable wheel is the TiC_6B_4 with an E_b of 6.10 eV/atom, calculated at the HF-SCF/STO-3G

Table 2
The E_b/atom (eV) of TiB_nN_{10-n}, TiC_nB_{10-n} ($n = 10$ to 0) & TiC_nN_{10-n} ($n = 0$–10) molecular wheels, calculated at the HF–SCF/STO-3G level.

TiB_nN_{10-n}	E_b	TiC_nN_{10-n}	E_b	TiC_nB_{10-n}	E_b
$TiB_{10}N_0$[a]	3.69	TiC_0N_{10}[b]	2.70	$TiC_{10}B_0$[c]	5.80
TiB_9N_1	4.19	TiC_1N_9	2.91	TiC_9B_1	5.85
TiB_8N_2	4.42	TiC_2N_8	3.31	TiC_8B_2	5.91
TiB_7N_3	4.61	TiC_3N_7	3.82	TiC_7B_3	6.01
TiB_6N_4	4.79	TiC_4N_6	4.10	TiC_6B_4	6.10
TiB_5N_5	5.01	TiC_5N_5	4.05	TiC_5B_5	6.25
TiB_4N_6	4.52	TiC_6N_4	4.68	TiC_4B_6	5.50
TiB_3N_7	4.11	TiC_7N_3	4.58	TiC_3B_7	5.20
TiB_2N_8	3.35	TiC_8N_3	5.01	TiC_2B_8	4.62
TiB_1N_9	3.30	TiC_9N_1	5.30	TiC_1B_9	4.33
TiB_0N_{10}[b]	2.70	$TiC_{10}N_0$[c]	5.80	TiC_0B_{10}[a]	3.69

[a] $TiB_{10}N_0$ and TiC_0B_{10} means TiB_{10}.
[b] TiB_0N_{10} and TiC_0N_{10} means TiN_{10}.
[c] $TiC_{10}N_0$ and $TiC_{10}B_0$ means TiC_{10}.

Please cite this article in press as: I. Boustani, R. Pandey, The route to highly stable $MeB_xN_yC_z$ molecular wheels. I. The features of preliminary results, Solid State Sciences (2012), doi:10.1016/j.solidstatesciences.2012.03.003

level of theory, as the case of whole substitutions in the TiC_nB_{10-n} system. Both molecular wheels TiC_5B_5 and TiC_6B_4 are represented in Fig. 4. The distribution of the E_b function of the TiC_nB_{10-n} system is assigned in Fig. 3 by a blue triangle up. However, further computations beyond the HF-SCF level show that the sequence of the stability of both wheels TiC_5B_5 and TiC_6B_4 is reversed when considering the functionals B3LYP and 6-31G basis set [17].

3.6. The MeC_5B_5 system

In order to understand the nature of chemical bonds of metal atoms with boron and carbon wheels we have computed the wheel system MeC_5B_5 considering for Me the first row of transition metal atoms Me = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn. Of course higher spin multiplicity could mean lower ground state energy of individual metal atoms. However, we have optimized each structure at the HF-SCF/6-31G level of theory, and calculated the ground state energies at different spin states for each metal atom. We selected the lowest energy and determined the corresponding binding

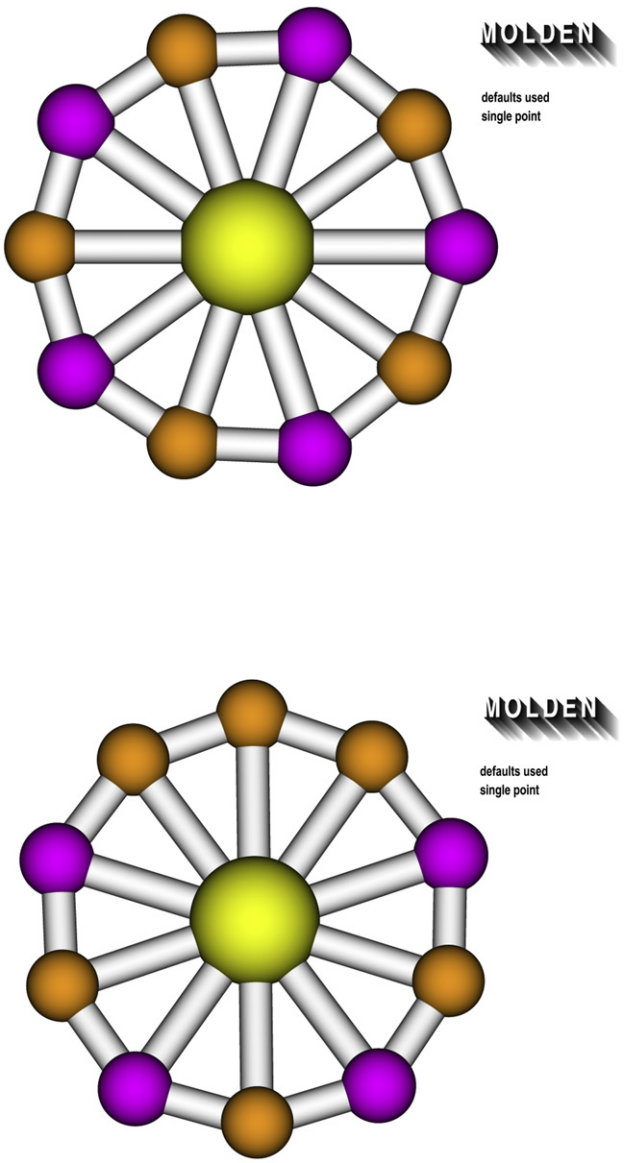

Fig. 4. Molecular wheels of TiC_5B_5 and TiC_6B_4.

Table 3
The molecular wheels MeC_5B_5, where Me is the first row of transition metal atoms calculated at the HF-SCF/6-31G level of theory, symmetry and spin state, binding energy E_b/atom (eV), and bondlength R (Å).

MeC_5B_5	Sym./State	E_b	R_{MeC}	R_{MeB}	R_{BC}
ScC_5B_5	$D_{5h}(^3A_1')$	3.75	2.34	2.31	1.44
TiC_5B_5	$D_{5h}(^4A_1')$	3.70	2.28	2.33	1.43
[a]VC_5B_5	$C_{2v}(^5B_1)$	3.22	2.26	2.32	1.41
[a]CrC_5B_5	$C_{2v}(^2B_1)$	3.15	2.26	3.34	1.42
MnC_5B_5	$D_{5h}(^1A_1')$	3.80	2.24	2.30	1.41
FeC_5B_5	$D_{5h}(^8A_1')$	3.70	2.34	2.29	1.43
[a]CoC_5B_5	$C_{2v}(^3A_2)$	3.10	2.28	2.31	1.42
NiC_5B_5	$D_{5h}(^8A_1')$	3.11	2.44	2.27	1.46
CuC_5B_5	$D_{5h}(^1A_1')$	3.01	2.41	2.21	1.44
[a]ZnC_5B_5	$C_{2v}(^4A_2)$	3.35	2.36	2.29	1.44

[a] These wheels have D_{5h} symmetry but calculated in C_{2v} one.

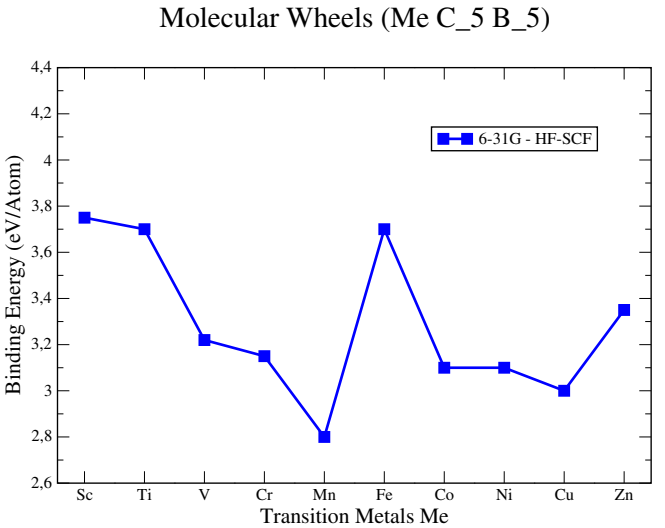

Fig. 5. Stability of molecular wheel MeC_5B_5.

energy, symmetry, spin state and bondlengths between the central and peripheral atoms as well as between carbon and boron atoms, all are listed in Table 3. The calculated E_b, as defined in eq (1), is plotted in Fig. 5 as a function of the metal atoms. As shown in Fig. 5, the molecular wheel MeC_5B_5 favours Sc atom at the centre, but also Ti or Fe are the next favoured transition metal atoms. The spin multiplicity considered in the MeC_5B_5 wheels for the Sc, Ti and Fe atoms was triplet, quadruplet and octuplet, respectively. In Fig. 5, the E_b function of the system MeC_5B_5, determined at the HF-SCF/6-31G level, is represented by blue squares. However, further computations of MeC_5B_5 and MeC_6B_4 in a follow-up study [17] are running at higher level of theory to verify the final stability of these structures.

4. Summary and conclusions

Based on the fact that small boron clusters B_n ($n \leq 19$) have planar or quasiplanar structures, we have doped boron clusters with transition metal atoms and enquired whether the planarity would keep consistent. Therefore we have investigated 2D and 3D structures of TiB_n for ($n \leq 10$) using simple STO-3G basis set at the HF-SCF level of theory. The 2D TiB_n structures where shoosen to be flat where Ti is at the focus and the boron atoms located at one side forming arcs and growing up to cycles or precisely to molecular wheels. The 3D structures of TiB_n where shoosen to be pyramids

Please cite this article in press as: I. Boustani, R. Pandey, The route to highly stable $MeB_xN_yC_z$ molecular wheels. I. The features of preliminary results, Solid State Sciences (2012), doi:10.1016/j.solidstatesciences.2012.03.003

where Ti is always as an apex atom. The obtianed structure of the wheel of TiB_{10} was fixed, then boron atoms where replaced by nitrogen then by carbon one by one. The metal atom in the most stable molecular wheel of TiB_5C_5 was then replaced by all atoms of the first row of transition metals.

We have developed 2D TiB_n system starting by two atomic molecule TiB adding boron atoms as long as the cycle closes gaining a wheel. Because of similarity, we present in Fig. 1 selected 2D TiB_n clusters for $n = 3$, 4, 6, 8 and 10. We have also determined 3D clusters of TiB_n in form of pyramids to show that the 3D pyramidal structures are energetically less favoured. Due to similarity, we present in Fig. 2 selected 3D TiB_n clusters for $n = 3$, 4, 6, 8 and 10. The E_b of 2D and 3D structures are listed in Table 1. The E_b of the 2D TiB_n system is presented in Fig. 3 as a function of cluster size. As can be seen, it increases with increasing the number of boron atoms n arriving the maximal value 3.69 eV/atom for $n = 10$. Furthermore, we have doped the TiB_n system with nitrogen atoms by substituting boron first alternately then completely with nitrogen atoms receiving the TiB_nN_{10-n} system. For $n = 10$ we have the original system TiB_n, but for $n = 9$ we dope the first nitrogen atom obtaining TiB_9N_1 and improving its stability. Further doping with nitrogen atoms improves the stability upwards until fivefold substitutions of boron with nitrogen atoms alternately we reach with 5.0 eV/atom the maximum of the E_b for the TiB_5N_5 wheel. Replacing the residual boron atoms by nitrogen up to TiN_{10} the stability diminishes down to a value of 2.7 eV/atom.

We follow the same procedure in the TiB_nN_{10-n} system by keeping the nitrogen atoms and substituting boron by carbon atoms to produce the TiC_nN_{10-n} system. We embrace the issue whether carbon can rebuild and re-establish the lost stability. The substitution of nitrogen by carbon atoms follows first alternately then completely causing progression in stability up to an E_b value of 5.8 eV/atom for the TiC_{10} wheel. However, further substitution of carbon with boron into the system TiC_nB_{10-n} leads to increment the stability achieving by $n = 5$ another maximum of stability of 6.26 eV/atom, obtaining the wheel TiC_5B_5. Afterwards the stability decreases so far until the carbon atoms are completely replaced by boron returning back to the wheel TiB_{10}, obtained by the first route, with the original E_b value 3.69 eV/atom. After structural optimization of TiC_5B_5, we found that the distance between Ti and carbon atoms is shorter as to boron atoms. Thus, the atomic distance between the centre Ti and peripheral atoms B and C is respectively 2.27 and 2.21 Å, while the bondlength of B–C is about 1.38 Å. As mentioned above, we will see in the follow-up paper [17] that at the B3LYP functionals and 6-31G basis set the TiC_6B_4 wheel is with 0.04 eV/atom slightly more stable than the TiC_5B_5.

All systems studied above where carried out considering the transition metal atom Ti. Now arises the question: could another atom of the first row of transition metals induce better stability!. Therefore we have established further computations at the HF-SCF/6-31G level to determine the MeC_5B_5 system for Me = Sc to Zn. These calculations are presented in Fig. 5 showing that Sc atom at the centre exhibits the highest binding energy, followed by Ti then by Fe atoms. In the second part of this work [17] we will ascertain that the wheel TiC_6B_4 at the B3LYP/6-31G level is energetically favoured over the ScC_5B_5 one.

We conclude that we have developed a new path of molecular wheels and determined how to increase the stability of molecular structures by substituting boron by nitrogen and carbon. However, the behaviour of the binding energy in increasing and droping seems to depend on the ratio and sequence of the involved boron, nitrogen and carbon atoms around the central titanium atom. Consequently, a further study at at higher quality basis sets and functionals is in progress [17] to verify these points mentioned above. We have established that metal boride clusters favour 2D structures forming molecular wheels similar to those cyclic rings of the boron wheel B_8 [3], to carbon rings [9] or to boron carbide wheels [11]. In addition, the α-, and β-spin HOMO-LUMO gaps of TiB_{10} are 0.330 and 0.253 Hartree, respectively. Slightly larger HOMO-LUMO gaps of α- and β-spin were found for the TiC_5B_5 wheel to be 0.363 and 0.263 Hartree, respectively. These HOMO-LUMO gaps values 0.90 and 0.27 eV of α- and β-spin of TiC_5B_5 versus those of TiB_{10} are a clear evidence for the stabilization character of carbon atoms involved into the wheel.

According to the Mulliken analysis, the electron charge transfer in the most stable molecular wheel TiC_5B_5 at the HF-SCF/STO-3G level of theory occurs slightly from titanium and boron to carbon atoms. The extent of electron charge of titanium and the average of five boron atoms is respectively 0.854 and 0.136 e, while the average of the charge transfer to the five carbon atoms is likely −0.306 e. In contrast, the electron transfer in TiB_{10} occurs with 0.450 e from the Ti atom to the each of the ten boron atoms to achieve a charge of −0.045 e, approving the true electron deficient character of boron. The variation of the stability of the molecular wheels over the transition metal as central atoms, as represented in Fig. 5, gives no insight about the reason. However, in our follow-up study we will try to verify the role and number of d-electrons and their contributions in bonding and character as well as the correlation between the p- and d-electrons. Calculations on molecular wheel systems $MeB_xC_yN_z$, for different combinations of nonzero x, y and z, are still missing. Also some electronic properties like vibrational frequencies, bond order analysis, and aromaticity in connection with the π-orbitals are desirable.

References

[1] R.N. Grimes, J. Chem. Educ. 81 (2004) 657.
[2] V. Bonačić-Kouteck, P. Fantucci, J. Kouteck, Chem. Rev. 91 (1991) 1053.
[3] I. Boustani, Phys. Rev. B 55 (1997) 16426.
[4] H.J. Zhai, B. Kiran, J.L. Li, L.S. Wang, Nat. Mater. 2 (2003) 827.
[5] W. Huang, A.P. Sergeeva, H.-J. Zhai, B.B. Averkiev, L.-S. Wang, A.L. Boldyrev, Nat. Chem. 2 (2010) 202.
[6] I. Boustani, Z. Zhu, D. Tomanek, Phys. Rev. B 83 (2011) 193405.
[7] M. Menon, K.R. Subbaswamy, M. Sawtarie, Phys. Rev. B 48 (1993) 8398.
[8] Z. Slanina, S.-L. Lee, M. Smigel, J. Kurtz, L. Adamowicz, Mat. Res. Symp. Proc. 359 (1995) 163.
[9] R.O. Jones, G. Seifert, Phys. Rev. Lett. 79 (1997) 443.
[10] H. Werheit, A. Leithe-Jasper, T. Tanaka, H.W. Rotter, K.A. Schwetz, J. Solid State Chem. 177 (2004) 575.
[11] S.S. Park, Bull. Korean Chem. Soc. 26 (2005) 63.
[12] W. Sekkal, B. Bouhafs, H. Aourag, M. Certier, J. Phys. Condens. Matter 10 (1998) 4975.
[13] X.-B. Wang, C.-F. Ding, L.-S. Wang, J. Phys. Chem. A 101 (1997) 7699.
[14] X. Liu, G.-F. Zhao, L.-J. Guo, Q. Jing, Y.-H. Luo, Phys. Rev. A 75 (2007) 063201.
[15] Z. Pu, K. Ito, P. v. R. Schleyer, Q.-S. Li, Inorg. Chem. 48 (2009) 10679.
[16] I.-W. Park, K.H. Kim, A.O. Kunrath, D. Zhong, J.J. Moore, A.A. Voevodin, E.A. Levashov, J. Vac. Sci. Technol. B 23 (2005) 588.
[17] A. Güthler, M. B. D. Andaloussi, R. Pandey, I. Boustani, in preparation .
[18] Gaussian 03, Revision C.02, 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, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, 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, J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
[19] GAMESS-UK is a package of ab initio programs. See: http://www.cfs.dl.ac.uk/gamess-uk/index.shtml M.F. Guest, I.J. Bush, H.J.J. van Dam, P. Sherwood, J.M.H. Thomas, J.H. van Lenthe, R.W.A. Havenith, J. Kendrick, The GAMESS-UK electronic structure package: algorithms, developments and applications, Mol. Phys. 103 (2005) 719–747.
[20] T.B. Tai, D.J. Grant, M.T. Nguyen, D.A. Dixon, J. Phys. Chem. A 114 (2010) 944.
[21] A.N. Alexandrova, A.I. Boldyrev, H.-J. Zhai, L.S. Wang, Coord. Chem. Rev. 250 2811 (2006).

Please cite this article in press as: I. Boustani, R. Pandey, The route to highly stable $MeB_xN_yC_z$ molecular wheels. I. The features of preliminary results, Solid State Sciences (2012), doi:10.1016/j.solidstatesciences.2012.03.003