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

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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 (unpublished results) using a double-ζ basis set with polarization function (DZ + P) in the framework of the Hartree-Fock (HF) self-consistent-field (SCF) theory and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

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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:

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

where n is the total number of atoms in the clusters, $E(\mathrm{Me})$ is the energy of atomic transition metal Me = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn, where $E(\mathrm{B})$, $E(\mathrm{C})$, and $E(\mathrm{N})$ 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 Games_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