INTRODUCTION

DFT (density functional theory) is one of the computational methods which can be used in different systems and it is more useful for some calculations than other methods. It is clear that basis sets are vast various. Primarily discovery of C60 has led to synthesizing higher fullerenes, carbon nanotubes, and other non-carbon nanostructures such as BN nanotubes. Although BN neocons have been known since 1994, we have been able to observe these structures experimentally until recently1-6.

The carbon nanotube (CNT) is a representative nano-material. CNT is a cylindrically shaped carbon material with a nano-metric-level diameter10-20.

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NMR Shielding Tensors and Thermodynamic Investigation of B_{28}N_{28} Nano-cone Structure: A molecule for Fe^{3+} Capturing

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ABSTRACT

M06&B3LYP/3-21G/6-31G/6-31G*/6-311G* density functional theory (DFT) and HF/3-21G/6-31G/6-31G*/6-311G* ab-initio calculations have performed for the structure and stability of B_{28}N_{28} nano-cone. In this work, it was calculated the geometrical structure, and stability to predict NMR and thermodynamics parameters. We have found these kinds of nano-cone are useful for capturing of Fe^{3+} ion

Key words: Fe^{3+} Ion, Density functional theory (DFT), Ab-initio calculation, Geometrical structure, Thermodynamic parameters, Active sites.

INTRODUCTION

Although it is a commonplace material using in pencil leads, its unique structure causes it to present characteristics that had not found with any other materials. CNT can be classified into single-wall CNT, double-wall CNT and multi-wall CNT according to the number of layers of the rolled graphite16-20.

The type attracting most attention is the single-wall CNT, which has a diameter deserving the name of "nanotube" of 0.4 to 2 nanometers. The length is usually in the order of microns, but single-wall CNT...
with a length in the order of centimeters has recently released

CNT can be classified into single-wall CNT, double-wall CNT and multi-wall CNT according to the number of layers of the rolled graphite. The type attracting most attention is the single-wall CNT, which has a diameter deserving the name of “nanotube” of 0.4 to 2 nanometers.

The length is usually in the order of microns, but single-wall CNT with a length about centimeters have recently released. The extremities of the CNT have usually closed with lids of the graphite sheet.

The lids consist of hexagonal crystalline structures (six-membered ring structures) and a total of six pentagonal structures (five-membered ring structures) placed here and there in the hexagonal structure. Two years later single walled nanotubes were reported. SWCNTs have considered as the leading candidate for nano-device applications because of their one-dimensional electronic bond structure, molecular size, and biocompatibility, controllable property of conducting electrical current and reversible response to biological reagents hence SWCNTs make possible bonding to polymers and biological systems such as DNA and carbohydrates.

Boron nitride nanotube (BNNTs) have attracted much interests due to their large gap semi conducting character. Boron nitride (BN) is a structural existing in cubic (diamond-like), hexagonal (graphite-like), and amorphous forms. these compounds have been produced by a variety of methods, such as arc melting, high temperature chemical reaction, carbon nanotube templates, and laser ablating. The most attention has been focused on the development of new methods for the production of nanotube and inorganic fullerene of other materials.

In addition, theoretical calculations have been described the possible existence of small BN clusters. Jensen and Toftlund performed ab initio calculations for B28N28, c-sters in different geometries. Based on density functional calculations it has also been proposed that other nanotube could be synthesized.

Theoretical studies have been performed for fullerene-like B28N28 clusters in which it has been found that a structure built from squares and hexagons is more stable than those built from pentagons and hexagons. This is because in the second case less stable B-B and N-N bonds are formed.

The most stable B28N28 structure is built from six squares and eight hexagons.

In this work, we focused on B28N28 nano-con. Our aim was to obtain the global minimum energy structure. For this structure, we use the hybrid B3LYP exchange-correlation functional within density functional theory. Primary, structure optimization calculated and then Nuclear Magnetic Resonance (NMR) parameters by density Functional Theory (DFT) method calculated on the optimized structure. Isotropic chemical shielding, anisotropic chemical shielding parameters at all of the atoms nuclei are presented in Table 1. And also, Thermodynamic Properties have been considered in Table 2.

We have found that these kinds of Nano-cones are useful for Fe3+ Capturing. In material sciences Boron nitride, which appears in a manifold of crystalline modifications, has been an extremely practical material with hexagonal and cubic boron nitride as most outstanding materials. The BN cluster is a polar molecule and BN nanotubes have an inert chemical structure. We can see that there is a negative charge at nitrogen atom and a positive charge at boron atom, so we can use an electrophilic or nucleophilic reagent as a solution for BN clusters.

BN nanotubes are very suitable for composite materials because these structures have a higher temperature resistance to oxidation than the carbon nanotubes. All the BN nanotubes are semiconductors. The BN nanotubes have the band gaps which can be greater than 2 eV for most tubes also we know that the smallest carbon nanotubes are semiconductors and these structures obtain the properties of graphite when the diameter of these structures increases but BN nanotubes are semiconductors without attention to the diameter. On
the basis of the similarities in characteristics between

the carbon and BN-based (BN=boron nitride) substances,

BN-based nanotubes can be stable and therefore their
electronic structure can be studied. The comparison
between BN nanotubes and carbon nanotubes shows
that BN nanotubes have more interesting
characteristics than the carbon nanotubes60-100.

Recently the boron nitride (BN) nanoscale
cone particles have been discovered and these
structures are made up of conical shells without any
seamless. Most of the studies about nanocones have
been done so far with carbon structures. High-
resolution transmission electron microscopy and
nanobeam electron diffraction made the orientation of
the BN hexagonal rings possible. Recently theoretical
investigations on (BN) n nanocones have gained
more attention in carbon nanotubes when there is not
any experimental result [55-100].

Considering the above mentioned, BN
nanotubes are very important and interesting for new
research and can open a huge spectrum in the field
of theoretical and experimental research. In the fig.1
structure of B28N28 is shown and this particular
nanocone configuration has been proposed in this
research.

Computational Method

The Gaussian 98 program was run to obtain
the best prediction of this particular structure. Also all
Ab-Initio and DFT (density functional theory)
calculations were done with the Gaussian 98
program. Frequency analyses were carried out to
show that the optimized structures are true minima or
transition states on the potential energy surfaces of a
specific structure without imaginary frequencies.

In this work, geometry optimizations in the
gas phase for B28N28 were performed at density
functional theory (DFT) level with B3LYP and Ab-Initio
with HF (hartree fock) methods in different basis sets
at the temperature of 298.15K. The parameters were
calculated for B28N28 in the gas phase in different
methods and basis sets include thermodynamic and
NMR parameters. The chemical shielding shows the
phenomenon which is dependent on the secondary
magnetic field which is built by the induced movements
of the electrons which encompass the nuclei. The
chemical shielding is built by a three-by-three matrix
which is biodegraded into a single scalar term, three
antisymmetric pseudo vector components, and five
components which correspond to a symmetric tensor.
It can be observed the single scalar and the five
symmetric tensor elements in the normal NMR spectra
of the solids.

The chemical shielding tensor includes the
chemical shift isotropy (CSI) and chemical shift
anisotropy (CSA) and the anisotropy (\(\Delta\sigma\)) of the
tensor, the shielding tensor asymmetry parameter (\(\eta\))
and chemical shift (\(\delta\)) are calculated.

The thermodynamic parameters that were
calculated in this research are Gibbs free energy,
enthalpy, internal energy (It is clear that the sum of
zero point energy (ZPE) and thermal energy is internal
energy.) and entropy then these reports were
compared with each other in order to obtain the best
results. These results were reported in tables.

RESULTS AND DISCUSSION

The results are listed in tables 1-3, and the
figures are explained in figs 1-4. The geometry
optimization for B28N28 nano-cone has been done with
HF and B3LYP methods at different basis sets such
as 4-31G, 6-31G, 6-31G* and 6-311G*. Then
thermodynamic properties were calculated for this
structure in gas phase at 298.15K in the same
methods and basis sets. A comparison of Gibbs free
energy (G), Enthalpy (H), Entropy (S) and Internal
energy (E) in different methods and basis sets are
shown in table 2. As shown in table 2, the maximum
values for Gibbs free-energy (G)
, Enthalpy (H)
and Internal energy (E) were calculated when 6-311G*
basis set had been applied at B3LYP method.

According to the results that are shown in
table2, the largest values have been obtained in
B3LYP method.

Considering the optimized structure, the
NMR shielding tensors were calculated then these
parameters were used to show active sites in this
structure. The results of \(\sigma_{\text{iso}}\), \(\sigma_{\text{aniso}}\), \(\delta\), \(\eta\) and \(\cdot\) for this
nanocone in the same methods and basis sets are
shown in table 3. Finally the charts of \(\sigma_{\text{iso}}\), \(\sigma_{\text{aniso}}\), \(\delta\) and
\(\eta\) for the atoms of B28N28 in the 4-31G, 6-31G, 6-31G*,
6-311G* level of theory and B3LYP and HF
methods. We can obtain the interesting results from the NMR charts. Comparison of these charts ($\sigma_{iso}$, $\sigma_{aniso}$, $\delta$, and $\eta$) shows that some of peaks in these charts are similar to each other. If these peaks are reviewed, we can understand which similar atoms are situated in the same peaks of different charts. The comparison of these peaks shows that three atoms are exactly repeated in $\sigma_{iso}$, $\sigma_{aniso}$, $\delta$ and $\eta$ charts. These three atoms are the active sites in this structure in $B_{28}N_{28}$.

In general, the chart of electronic charge in different methods and basis sets is similar to the charts of NMR parameters. Nitrogen atoms have more electrons than Boron atoms. Therefore, the location of negative electronic charge is on Nitrogen atoms and

Table 1: HOMO and LUMO and Gap energy of 3 N28B28 Nanocone

<table>
<thead>
<tr>
<th>Methods</th>
<th>Basis set</th>
<th>Relative E(kcal/mol)</th>
<th>$-G$(kcal/mol) Relative</th>
<th>$H$(kcal/mol) Relative</th>
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<tr>
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<tr>
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Table 2: Thermodynamic properties in different methods and basis sets, for B28N28 without and including Fe$^{3+}$ at 298.15K in gas phase

<table>
<thead>
<tr>
<th>Methods</th>
<th>Basis set</th>
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<th>$-G$(kcal/mol) Relative</th>
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</table>
Fig 1: The optimized structures of 3 Nano Cone including Fe$^{3+}$ ion capturing

Fig. 2: Shaded Surface map with projection for electron density of 3 nano-cone of B28N28

Fig. 3: Color map of 3 28N28 shows the most density in top of each nano-cone

Fig. 4: The line of contour map

Fig. 5: Relief map shows the situation of 3 nano-cones versus distance
positive electronic charge is situated on Boron atoms. It is clear that Nitrogen atoms will be active sites in this structure.

CONCLUSION

In summary, the stability of $B_{28}N_{28}$ was investigated. It is found that the amount of Gibbs free energy ($G$), Enthalpy ($H$) and internal Energy ($E$) obtained in B3LYP/6-311G* level in the gas phase (298.15K) are the largest amount and also optimization of $B_{28}N_{28}$ nano-cone at the B3LYP/6-311G* is suitable for this structure. The NMR data and the thermodynamics results indicate that this kind of nano-cone is suitable for capturing Fe$^{3+}$ ion.

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