ABSTRACT

This study calculated reactivity parameters of extended graphene (black graphene with D$_{2h}$ symmetry) and boron nitride (h-BN) (white graphene with C$_{2v}$ symmetry), both with dimensions of 1.0 nm$^2$, using the density functional theory (DFT) combined with an HCTH/GGA/DNP methodology. For structural stability, we considered the criterion of obtaining positive eigenvalues in the Hessian matrix. For reactivity parameters (chemical potential, chemical hardness, gap, and electrophilic index), the HOMO and LUMO molecular orbitals were considered. Furthermore, the molecular density of states (DOS) and electrical and electronic properties were reported. The results indicate that white graphene is much more stable, but also more reactive than black graphene. This is due to the values obtained for chemical hardness (1.157 eV and 0.329 eV, respectively), chemical potential (2.39 eV and 3.85 eV, respectively), and gap (2.313 eV and 0.657 eV, respectively). The electrophilic index values indicate that black graphene could adsorb molecules on its surface preferentially through physisorption ($\epsilon = 0.0$ eV), while white graphene could be more suitable for chemisorption given the observed non-zero values ($\epsilon = 0.28$ eV).

KEYWORDS: Graphene, boron nitride, density functional theory, molecular orbitals, reactivity parameters.

PARÁMETROS DE REACTIVIDAD DEL GRAFENO NEGRO VS. GRAFENO BLANCO DE DIMENSIONES DE 1,0 NM$^2$: ESTUDIO QUÍMICO CUÁNTICO COMPUTACIONAL

RESUMEN

Se investigaron los parámetros de reactividad del grafeno extendido (grafeno negro con simetría D$_{2h}$) y el nitruro de boro (h-BN) (grafeno blanco con simetría C$_{2v}$), ambos con dimensiones de 1.0 nm$^2$, usando la teoría del funcional de la densidad (DFT) combinada con la metodología HCTH/GGA/DNP. Para la estabilidad estructural se consideró el crite-
Reactivity parameters of black graphene vs. white graphene with dimensions of 1.0 nm²:
A computational quantum chemistry study

1. INTRODUCTION

In order to understand the potential of nanotechnology, it is important to know that the physical and chemical properties of matter change on a nanometric scale given the dominance of quantum effects. Electrical conductivity, heat, resistance, elasticity, reactivity, and other properties of a material behave differently at different scales; Bodden and Junge (2011). Nanotechnology has had a significant impact on the field of chemistry, and the study of atom nanoclusters is a current topic of interest; Jacobser (2009), Maubert, et al. (2008), Whitesides (2005). Nanoclusters are important both for catalysis and for the development of new materials for various applications. On the nanometric scale, materials like graphene and boron nitride have been theoretically studied using molecular models which allow researchers to characterize these materials and thereby determine their potential applications, for example, their ability to adsorb molecules. The hexagonal structure of two-dimensional graphite, called graphene, was isolated by the group Novoselov et al. (2004), giving rise to a variety of materials with the same hexagonal structure as boron nitride; Novoselov, et al. (2005),...
graphene; Sofo, Chaudhari & Barber (2007), Elias et al. (2009). Recently, researchers were able to use exfoliation and chemical vapor deposition techniques to isolate monolayers of graphite with variable thicknesses, leading to a new type of tridimensional material known as graphene; Dresselhaus (2010), Nagashima, et al (1993). These structures have been confirmed by different experimental techniques, such as optical and atomic force microscopy, among others.

Since graphene was isolated, important properties and applications have been found for it, including its hardness, flexibility, optics, and its ability to absorb gaseous molecules; Schedin, et al. (2007), Lee, et al. (2008), Nair, et al. (2008). Since it was the first completely bidimensional type of material at the molecular level, graphene is considered to be a structural model for computational simulation studies related to graphite, fullerenes, and carbon nanotubes. Given its physical, chemical, and mechanical properties, such as hardness, high melting point, low dielectric constant, and large energy gap (6.0 eV), boron nitride is one of the most interesting compounds formed by atoms from groups II and IV of the periodic table; Arya & D’Amico (2002). Boron nitride forms different phases which are analogous to those of carbon. The hexagonal phase of boron nitride (h-BN) is similar to graphite, and the cubic phase of boron nitride (c-BN) is similar to diamond; Teghil, Marotta, & Di Palma (1998). Depending on the phase, different properties can be found. For example, boron nitride in the hexagonal phase forms sp² hybridization and is therefore a very useful material for lubricants compared to graphite; Xiaopeng, H. & Meiyan Y. (2002). h-BN is electrically insulating due to the lack of relocation of π bonds; Reisse & Weissmantel (1999). This material has a hardness of approximately 15 GPa and is also widely used for field emission devices, optoelectronic devices, and high-powered semi-conductors; Miyake & Wang (2005). Meanwhile, cubic boron nitride (c-BN) shows sp³ hybridization, which allows it to have diverse properties such as high resistance to wear, resistance to oxidation, and a low coefficient of friction. It is also considered to be the second-hardest material after diamond with a hardness of 70GPa; Deng & Chen (2006). This material is a good candidate for coating tools that have been exposed to high-wear environments such as cutting tools. This hard coating depends highly on the thickness of the film. He & Li (2005). The research group that carried out this research has been interested in studying materials at the nanometric level with possible applications in different fields. Therefore, this study aims to use computational chemistry methods to examine the reactivity parameters of extended graphene and hexagonal boron nitride with dimensions of 1.0 nm².

2. MATERIALS AND METHODS (COMPUTATIONAL DETAILS)

This study used the density functional theory (DFT) Kohn, Becke & Parr (1996), Jones & Gunnarsson (1989), and Kohn (1999), developed by Walter Kohn in the 1960s, and the DMOL-3 code (version 4.3) made available by Accelrys Inc.; Delley (1990). The method was combined with the HCTH functional at the LDA level developed by Hamprecht, et al. (1998), which includes correction for the correlation gradient, and the polarized atomic base (including a p orbital for hydrogen and a d orbital for carbon, nitrogen, and boron) at the all-electron level for treatment of the core (DNP); Delley (1990) and Delley (2000). Multiplicity=1 (singlet) and charge=0 (neutral) were used for all structures. HOMOs (highest occupied molecular orbitals) and LUMOs (lowest unoccupied molecular orbitals) were considered to obtain reactivity parameters. Chemical hardness was represented as: \( n = (\text{LUMO}-\text{HOMO})/2 \) Becke (1993). Chemical potential was represented as \( \mu = (\text{LUMO}+\text{HOMO})/2 \) Perdew, Burke & Wang (1992). The electrophilic index was represented as \( \epsilon = n^2/2u \) (considered as a parameter of electronic transference); Hehre, Dichfied & Pople (1972). The energy difference between the HOMO and LUMO is the gap energy; Fujita, et al. (1996). The convergence thresholds used with DFT/GGA/HCTH for energy variation, maximum force, and maximum atomic displacement between the optimization cycles were: 1×10⁻⁵ Hartree, 0.002 Hartree/Å and 0.005 Å, respectively. The maximum change allowed for any Cartesian coordinate was 0.3 Å. The criterion of having positive vibration frequencies was followed to find the minimum structure stability; Foresman & Frisch (1996).
3. RESULTS

As a preliminary step to studying the potential applications of graphene and h-BN, DFT calculations were used to theoretically describe the structural and reactivity properties of these materials using chemical and vibrational descriptors. According to the structural results obtained, we observed that both B-N, C-C, and C-H bonds and B-N-B and C-C-C angles are within the typical range of values for these atoms (see Table 1). In addition, analysis of the optimized geometries Hessian matrix shows that the structure has a global minimum on the potential energy surface (real vibration frequencies) due to the absence of negative values on the Hessian matrix, with 198 vibration modes for the two materials. Figures 2a and 2b of the HOMO molecular orbitals show contributions of only 2py from carbon for 1.0 nm² and 2pz for the nitrogen in 1.0 nm² h-BN (Table 2).

For the LUMO orbital (Figures 3a and 3b), an atomic orbital contribution of 2pz from the boron in 1.0 nm² and 2py from the carbon in 1.0 nm² were observed. Figures 2a and 3a show that when the graphene moves from the HOMO to the LUMO, there is a phase change in the wave function, which can be observed in the change of color on the right side of Figure 3a with regards to Figure 2a. In h-BN there is charge displacement since the charge distribution changes from the nitrogen atoms (HOMO) to the boron atoms (LUMO), and the charge density disappears from the center, increasing around the edges on the boron, that is, there is surface polarization. As was mentioned in the methodology section, these orbitals were used to ascertain the chemical reactivity of the systems. According to the results of the reactivity parameters (Table 4), these indicate that graphene shows a lower degree of reactivity than h-BN (according to chemical potential). This result does not agree with those reported by Chigo & Juárez, (2008). Likewise, graphene shows a lower resistance to electronic redistributions (according to chemical hardness) than does h-BN. In addition, graphene behaves as a semi-conductor (Graph 1a. DOS for graphene), and h-BN behaves as an insulator. (Graph 1b. DOS for h-BN).

The low numerical value of the electrophilic index (ԑ) indicates that graphene could be more stable when it accepts an additional electronic charge, with preference for the physisorption process (ԑ=0,0 eV), while h-BN may prefer chemisorption given that values other than zero were observed (ԑ=0,28 eV). Finally, there is a greater degree of covalence in graphene than in boron nitride, as is indicated by the dipole moment value.
Table 2. HOMO molecular orbitals for 1.0 nm² graphene and 1.0 nm² h-BN obtained using the DFT/GGA/HCTH/DNP methodology.

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>Dipole moment (Debye)</th>
<th>Chemical potential (µ) (eV)</th>
<th>Chemical hardness (n) (eV)</th>
<th>Electrophilic index (ε) (eV)</th>
<th>Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 nm² graphene (D₆h symmetry)</td>
<td>0.0</td>
<td>-3.85</td>
<td>0.329</td>
<td>-0.01</td>
<td>-0.657</td>
</tr>
<tr>
<td>1.0 nm² h-BN (C₂v symmetry)</td>
<td>0.22</td>
<td>-2.39</td>
<td>1.157</td>
<td>-0.28</td>
<td>-2.313</td>
</tr>
</tbody>
</table>

Figure 2a. HOMO molecular orbital of 1.0 nm² graphene with atomic distribution by 2py carbon atomic orbitals.  
Figure 2b. HOMO molecular orbital of 1.0 nm² h-BN whose atomic contribution is due to 2pz nitrogen orbitals.

Table 3. LUMO molecular orbitals for 1.0 nm² graphene and 1.0 nm² h-BN obtained using DFT/GGA/HCTH/DNP methodology.

Figure 3a. LUMO molecular orbital of 1.0 nm² graphene with atomic contribution from 2py carbon atomic orbitals.  
Figure 3b. LUMO molecular orbital of 1.0 nm² h-BN with atomic contribution from 2pz boron atomic orbitals.

Table 4. Chemical reactivity parameters calculated using HOMO and LUMO values and dipole moment for 1.0 nm² graphene and 1.0 nm² h-BN obtained using DFT/GGA/HCTH/DNP methodology.
4. CONCLUSIONS

Computational molecular simulation was used in this study to provide results that are in agreement with those reported in the literature; Novoselov, et al. (2004) & Schedin, et al. (2007) regarding the existence of extended graphene and boron nitride under conditions of temperature and pressure. Said systems show semi-conductor electronic behavior for black graphene, and for boron nitride (white graphene) insulating electronic behavior was observed, but with greater chemical reactivity and a lower covalence than black graphene (indicated by dipole moment). Finally, we conclude that black graphene shows greater difficulty regarding the process of chemisorption than does h-NB, according to the numerical values for chemical reactivity parameters. This study is useful to better understand the process of atom and molecule adsorption on the surface of these materials, as well as to predict new structures.
REFERENCES


