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Evaluation of Physical Properties of $B_{16}N_{16}$ and $B_{16}N_{16}$-X(X=Cu, Cu^{+}, Cu^{++})

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ABSTRACT

To investigate the electromagnetic interaction of molecules inside the nanotubes, first, the structure of nanotubes $B_{16}N_{16}$ was optimized with hybrid density functional theory (B3LYP) using the EPR-II basis set, then Cu, Cu^{+}, Cu^{++} were located in nanotube and we studied the total energy, band gap energy, electrical potential, changes of band gap energy in terms of total energy and dipole moment in the $B_{16}N_{16}$-X(X= Cu, Cu^{+}, Cu^{++}) systems. Also, to investigate the electromagnetic interaction of molecules inside the nanotubes, we studied the nuclear magnetic resonance properties (NMR) and shielding parameters between nanotubes.

Keywords: Electrical potential, Physical Chemistry, NMR

INTRODUCTION

Boron nitride (BN) is one of the most interesting III–V compounds due to its unique properties, such as low density, high thermal conductivity, excellent mechanical strength wear resistance, stability at high temperatures, and possibility of easy doping with silicon (n-type) and beryllium (p-type). Thus, the material appears as a good alternative for carbon-related materials in several applications [1-3]. CNTs are either metals or semiconductors depending on their chirality, while BNNTs are always semiconductors [4, 5] with the gap (~5.5eV) practically independent of the nanotube chirality and its diameter [5]. The electronic structures of boron nitride (BN) nanotubes under a transverse discussed by Chunyi Zhi *et al.*[6], for instance, applying electric field [7-9] or chemical methods, like doping [10, 11], introducing defects [12,13]. Physical methods could directly reduce the band gap of BNNTs, while chemical methods were found to tune the band gap by introducing localized energy levels inside the gap [6] and perpendicular electric field were investigated with theory (DFT) calculations [14]. Various methods have been developed to tune the electronic structure of BNNTs is nicely.

COMPUTATIONAL METHODS:

The geometry of nanotubes $B_{16}N_{16}$ has been optimized by Beck's hybrid three-parameter exchange functional and the nonlocal correlation functional of the Lee, Yang, and Parr (B3LYP) method [15, 16] with the EPR-II basis sets of Baron[16].

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The Gaussian quantum chemistry package was used for all calculations [17].In order to analyze the $B_{16}N_{16}$- X (X=Cu, Cu^{+}, Cu^{++}) systems, we have carried out calculations on Hartree–Fock (HF) wave function with lanl$_2$dz basis set .The first, we have optimized a (4, 4) armchair nanotube $B_{16}N_{16}$ and then Cu, Cu^{+}, Cu^{++} were located in nanotube.

RESULTS AND DISCUSSION

Energy

The total energy of molecule, including all forms of kinetic motion (translation, vibration, and rotation) and all forms of potential energy (electrostatic interaction between changes, magnetic interactions between spinning charges, and potential energy of bonds), determines the reactivity and stability of a molecule. So, to investigate the structural stability, we first optimized the structure of nanotubes $B_{16}N_{16}$ and then copper and copper cations were located in nanotube and total Energy calculated for everyone, that are presented in Table 1. According to Table 1, can be understood that, when Cu^{2+} cation is located in nanotube, structure has the lowest energy and the more stability. As can be seen in the diagram in Figure 3, when copper and copper cations placed inside the nanotube structures, energy levels are extremely low. It has been understood that probably putting copper cations inside the nanotube, caused the system's structural.

The LUMO-HOMO (band gap) is a gap between the LUMO (the lowest unoccupied molecular orbital) and HOMO (the highest occupied BN molecular orbital) nanotubes have a wide band gap (E) of~5.5ev and non-magnetism independent of the tube diameters .The large LUMO-HOMO gap is often regarded as a molecule stability condition [18].

Table 1. Energy of band gap (ev), total energy for $B_{16}N_{16}$-X(X= Cu, Cu^{+}, Cu^{++}) 3.2 Band gap energy of the Systems.

Nanotube	Energy of band gap (eV)	E(Hartree)
$B_{16}N_{16}$	5.680778	-1274.8223375
$B_{16}Cu_1N_{16}$(2)	8.036952	-1461.656329
$B_{16}Cu_1N_{16}$(1+)	9.374902	-1461.4336655
$B_{16}Cu_1N_{16}$(2+,2)	10.05245	-1460.9510909

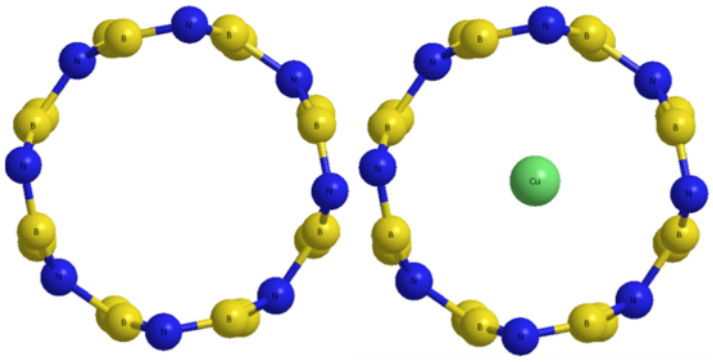

Fig. 1. $B_{16}N_{16}$ nanotube and $B_{16}N_{16}$-X(X=Cu, Cu+, Cu++) system.

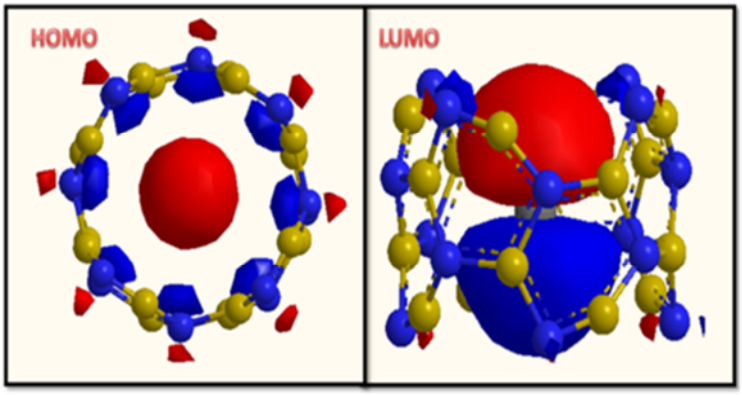

Fig. 2. HOMO and LUMO for $B_{16}N_{16}$-Cu^{2+}.

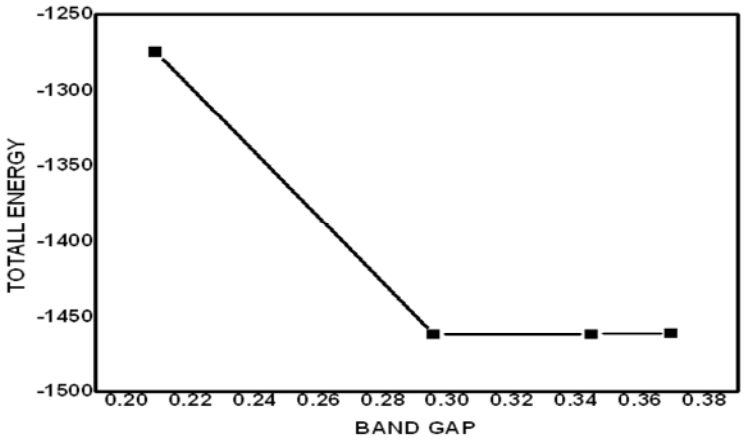

Fig. 3. Total energy versus the band gap energy.

The data given in the table shows the band gap energy increased by placing copper and copper ions inside the nanotube. Also, with increasing positive charge on the copper, energy band gap increases. The large LUMO-HOMO gap is often regarded as a molecule stability condition [19]. Therefore, the following trend could be observed for stability:

$B_{16}N_{16}$- Cu $^{2+}$> $B_{16}N_{16}$- Cu^{+}> $B_{16}N_{16}$-Cu> $B_{16}N_{16}$

HOMO-LUMO band gaps were between 5.68-10.05 eV. As can be seen in figure 3, band gaps of the system are inversely related with energy.

Analysis of Chemical Shift and Chemical Shielding in NMR

In NMR spectroscopy, the chemical shift δ is one of the most often observed parameters in NMR which encodes information about the chemical and electronic environment of a nucleus via a shift (hence the term chemical shift) in resonant frequency from the reference frequency. This local field shields the nucleus from the external field, resulting in a shift in the observed frequency. The isotropic values, σ_{iso}, are the average values of the principal components, and correspond to the center of gravity of the line shape. Changes of isotropic values, σ_{iso} versus muliken charge are calculated for all nanotubes versus muliken charge.

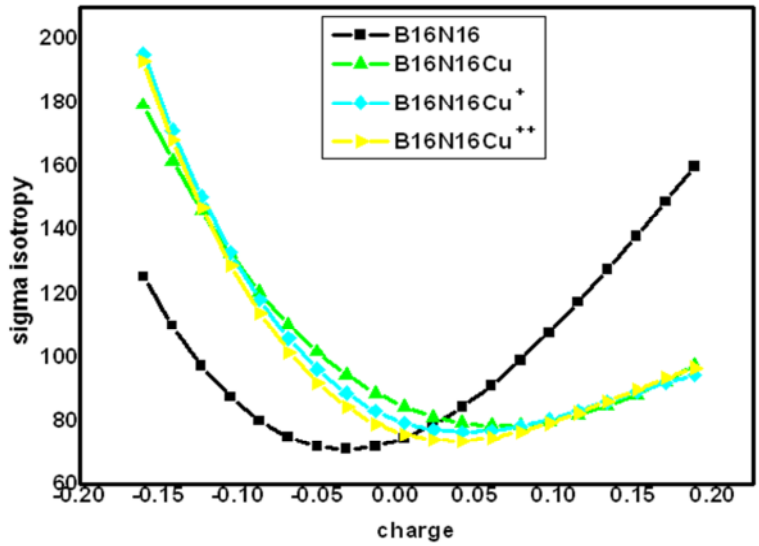

Fig. 4. Compares isotropic values, σ_{iso} in $B_{16}N_{16}$-X(X=Cu, Cu^{+}, Cu^{++}) versus muliken charge.

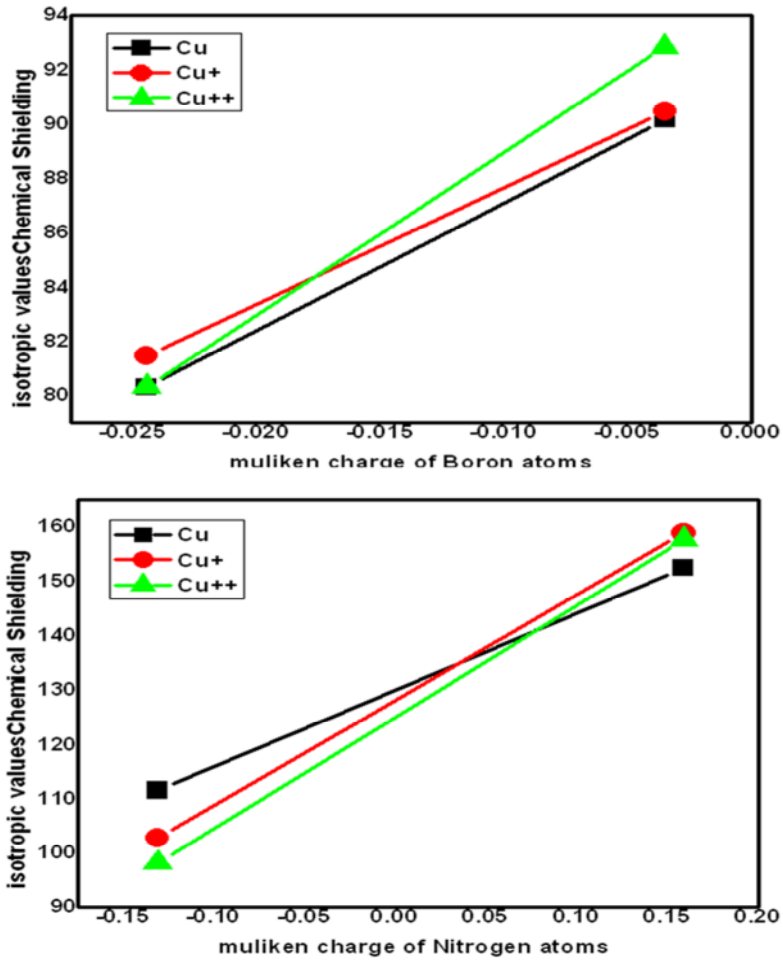

Fig. 5. Compares isotropic values, σ_{iso} in $B_{16}N_{16}$-X(X=Cu, Cu^{+}, Cu^{++}) versus charge of Boron (top)of ,Nitrogen(bottom).

For all type of curves, a cubic polynomial fit are quite appropriate**.** Isotropic values σ_{iso} is reported for boron and nitrogen atoms in the blank nanotube as the reference Table 2 and also for boron and nitrogen atoms in the nanotube $B_{16}N_{16}$-X(X=Cu, Cu^{+}, Cu^{++}) .Then, chemical shift of atoms is calculated in three structure, $B_{16}N_{16}$-X(X=Cu, Cu^{+}, Cu^{++}).

For better comparison and evaluation, the graphs of the boron and nitrogen atoms are plotted separately in figure 5. Boron and nitrogen atoms in the nanotube in terms of electrical charge are divided into two categories. The atoms are located at the edge of the nanotube, charge them less than other atoms, because these atoms have dangling bond (dangling bond a chemical bond associated with an atom in the surface layer of a solid that does not join the atom with a second atom but extends in the direction of the solid's exterior). In Figure 5(top) can be seen that in the boron atoms with low charge value -0.0035 isotropic values σ_{iso} for Cu^{++} cation is the most but in the boron atoms with high

charge value -0.0244, isotropic values σ_{iso} for Cu+ cation is the most. In Figure 6(bottom), can be seen that in the nitrogen atoms with negative charge value -0.131 isotropic values σ_{iso} for Cu is the most and is reduced by increasing the positive charge on Cu, but in the nitrogen atoms with positive charge value 0.158936, isotropic values σ_{iso} Cu has the lowest.

Also, isotropic values σ_{iso} of atoms and Chemical Shift of atoms in $B_{16}N_{16}$-(Cu, Cu^{+}, Cu^{++}) are reported in table 3.

Electrical Potential

First,we calculated the potential difference between the central cations with atoms of nitrogen and boron nanotube body. We plotted as a graph the potential difference in terms of quantities such as dipole moment and quadrupole moment and the atomic number and the total energy and the energy gap. It can be seen in figure 5,The potential difference decreased with increase in atomic number of central ions from Sc^{2+} to Cu^{2+} ,and But for Zn^{2+} cation increases.

As can be seen in table 2, the potential difference between boron and nitrogen atoms of nanotube from the copper atom is greater than copper cations. Dipole moment of the system is increased by increasing the positive charge. A Mulliken atomic charge of the central metal in $B_{16}N_{16}$- Cu has negative value -0.396 but $B_{16}N_{16}$- Cu^{+} and $B_{16}N_{16}$- Cu^{++} have positive values.

CONCLUSIONS

According to calculations for the total energy, can be understood that when Cu^{2+} cation is located in $B_{16}N_{16}$-nano tube, structure has the lowest energy and the more stability. In NMR spectroscopy calculation, chemical shift of atom in three structure, $B_{16}N_{16}$-X (X=Cu, Cu^{+}, Cu^{++}) are shown in figure 5.With increasing dipole moment, electrical potential difference between boron and nitrogen atoms of the central copper atom is reduced.

Table 2. Electrostatic Properties of the System.

SYSTEM	Difference Of potential B from Cu	Difference Of potential N from Cu	Dipole moment Debye	Charge on metal of center
$B_{16}N_{16}$- Cu	15.12085	8.05225	0.0968	**0.396-**
$B_{16}N_{16}$- Cu^{+}	15.01918	7.951025	1.1461	**0.480**
$B_{16}N_{16}$- Cu^{++}	15.0212	7.95648	1.8210	**0.464**

Table 3. Isotropic value and chemical shift for $B_{16}N_{16}$-X(X=Cu, Cu^{+}, Cu^{++}).

#	atom	Isotropic Value of atom in B16N16-Cu	Chemical Shift of Atom in B16N16-Cu	Isotropic Value of atom in B16N16-Cu+	Chemical Shift of Atom in B16N16-Cu^{+}	Isotropic Value of atom in B16N16-Cu^{++}	Chemical Shift of Atom in B16N16-Cu^{++}	Isotropic Value of B16N16 (Reference)
1	B	80.3309	8.9215	81.4696	10.0602	80.3528	8.9434	71.4094
3	B	90.177	16.6981	90.4732	16.9943	92.8627	19.3838	73.4789
5	B	80.3141	8.9048	81.4346	10.0253	82.7303	11.321	71.4093
7	B	90.1927	16.7138	90.3437	16.8648	93.2484	19.7695	73.4789
9	B	80.3549	8.9456	81.4797	10.0704	80.3608	8.9515	71.4093
11	B	90.2025	16.7236	90.3549	16.876	92.8962	19.4173	73.4789
13	B	80.3713	8.962	81.4973	10.088	82.7843	11.375	71.4093
15	B	90.185	16.7061	90.3274	16.8485	93.2271	19.7482	73.4789
17	B	90.1777	16.8331	90.2954	16.9508	88.1689	14.8243	73.3446
19	B	80.315	8.8397	81.5337	10.0584	82.5773	11.102	71.4753
21	B	90.1823	16.8377	90.3329	16.9883	91.0214	17.6768	73.3446
23	B	80.3328	8.8575	81.456	9.9807	83.691	12.2157	71.4753
25	B	90.201	16.8564	90.3548	17.0102	88.1687	14.8241	73.3446
27	B	80.3729	8.8976	81.4994	10.0241	82.5777	11.1024	71.4753
29	B	90.1954	16.8508	90.3444	16.9998	90.9995	17.6549	73.3446
31	B	80.3539	8.8786	81.4791	10.0038	83.5753	12.1	71.4753
2	N	111.635	9.2137	102.7517	0.3304	98.2488	-4.1725	102.4213
4	N	152.5263	9.8219	158.9131	16.2087	157.8339	15.1295	142.7044
6	N	111.5468	9.1255	102.7675	0.3462	98.4396	-3.9817	102.4213
8	N	152.1822	9.4778	158.6308	15.9264	165.1979	22.4935	142.7044
10	N	111.2545	8.8332	102.4613	0.04	98.2136	-4.2077	102.4213
12	N	152.1788	9.4744	158.6365	15.9321	157.9279	15.2235	142.7044
14	N	111.3433	8.922	102.5154	0.0941	98.3449	-4.0764	102.4213
16	N	152.5236	9.8192	158.8198	16.1154	165.2365	22.5321	142.7044
18	N	152.598	9.8403	158.9348	16.1771	145.8268	3.0691	142.7577
20	N	111.6495	9.1402	102.8622	0.3529	52.1198	-50.3895	102.5093
22	N	152.3539	9.5962	158.7397	15.982	138.6169	-4.1408	142.7577
24	N	111.3873	8.878	102.6151	0.1058	-431.384	-533.893	102.5093
26	N	152.1088	9.3511	158.5872	15.8295	146.3477	3.59	142.7577
28	N	111.2401	8.7308	102.424	-0.0853	53.1739	-49.3354	102.5093
30	N	152.3484	9.5907	158.7401	15.9824	138.7349	-4.0228	142.7577
32	N	111.5092	8.9999	102.6642	0.1549	-431.802	-534.311	102.5093

REFERENCES

[1] D. Golberg, Y. Bando, M.Mitome, (2002) Physica B 323, 60.

[2] R. Zedlitz, M. Heintze, M.B. Schubert, (1996) J. Non-Cryst. Solids198, 403

[3] A.Zettl, (1996) Adv. Mate 5,443.

[4] X. Blase, A. Rubio, S. G. Louie, and M. L. Cohen, (1994) Euro-physics Letters 28.

[5] J-C. Charlier, A. De Vita, X. Blase, and R. Car, (1997) Science 275.

[6] Chunyi Zhi, Yoshio Bando, Chengchun Tang, Dmitri Golberg (2010). Materials Science and Engineering R 70 92.

[7] S.L. Hu, Z.Y. Li, X.C. Zeng, J.L. Yang, (2008).Journal of Physical Chemistry C 112 8424.

[8] C.H. Park, S.G. Louie, (2008). Nano Letters 8 2200.

[9] H.P. Lan, L.H. Ye, S.A. Zhang, L.M. Peng, (2009). Applied Physics Letters 94 183110.

[10] M. S. Si and D. S. Xue, (2006).Europhys. Lett 76 (4), pp. 664–669.

[11] G.Y. Gou, B.C. Pan, L. Shi, (2009) .Journal of the American Chemical Society 131 4839.

[12] C. Attaccalite,1 M. Bockstedte,2,3 A. Marini,4,5,3 A. Rubio,3,6 and L. Wirtz7, (2011).PHYSICAL REVIEW B **83**, 144115

[13] E. A. Meyer, R. K. Castellano, and F. Diederich, Angew. (2003) .Chem. Int. Ed. Engl 42, 1210.

[14] Claudio Attaccalite, 1, Ludger Wirtz1, 2, Andrea Marini3, and Angel Rubio, (2007) .phys. stat. sol. (b) 244, No. 11, 4288–4292

[15] 2. W. Saenger, (1984). Principles of Nucleic Acid Structure, Springer, New York.

[16] M. F. Brana, M. Cacho, A. Gradillas, B. Pascual-Teresa, and A. Ramos, Curr. (2001) .Pharma. Design, 7 1745 Intercalators as Anticancer Drugs.

[17] M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann,

[18] R. E., Jr.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin,

[19] K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi,

[20] R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.;

[21] Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.;

[22] Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz,

[23] J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.;

[24] Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham,

[25] M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill,

[26] P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez,

[27] C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revisionA.7; Gaussian, Inc.: Pittsburgh, PA, (1998).

[28] Seifert, G.; Fowler, R. W.; Mitchell, D.; Porezag, D.; Frauenheim, Th. (1997), *Chem. Phys. Lett. .268*, 352–358.

[29] (39) Rubio, A.; Corkill, J. L.; Cohen, M. L (1994). *Phys. Re*V. *B*, *49*, 5081.

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