Density Functional Theory Study on the Encapsulation of a Polymeric Nitrogen N_8 Chain inside Boron Nitride Nanotube

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Abstract. A new nanoscale hybrid material, where a nitrogen chain N_8 is encapsulated inside a boron nitride nanotube, is studied by density Functional theory (DFT). The structure, NBO charges, binding energy and electronic property are calculated at the B3LYP-D3/6-31G(d) level of theory. It is found that the N_8 chain could be stable in the boron nitride nanotube confinement. This work could provide a new sight into synthesizing the nitrogen-based high-energy density materials.

Introduction

For recent years, polynitrogen molecules have been extensively studied as promising candidates for high-energy density materials (HEDMs) because a uniquely large amount of energy is released when they decompose into pure nitrogen molecules N_2 which are environmentally friendly. However, only some of them have been synthesized or detected experimentally due to their low stability in free space, such as N_3, N_4, N_3^-, N_5^- and N_5^+ [1-5]. Over the past decades, various theoretical techniques have been used to predict the various forms of all-nitrogen molecules, such as chained, cyclic, caged and other structures. All-nitrogen molecules (such as N_{10} [6]) have also been researched theoretically in free space. In addition, various novel polynitrogen species have also been explored by theory and experiment under extreme conditions of high temperature and pressure [7-9]. For example, the cubic gauche structure (cg-N), which can be stable at the pressure of 140GPa and the temperature of 2000K, was observed successfully experimentally [9]. Also various theoretical studies have investigated on N_8. For example, Leininger et al. [10] theoretically studied three isomers of N_8 using SCF, MP2, CISD, and CCSD methods with DZP basis sets. Recently, Hirshberg [11]has theoretically predicted a novel metastable molecular crystal at ambient pressure, which is consisting of N_8 molecules. In addition, in 2008 Abou-Rachid et al. [12, 13] theoretically proposed that, the polymeric nitrogen N_8 as a chain could be encapsulated in the carbon nanotubes confinement at ambient pressure and room temperature. In 2014, Wang et al [14]. synthesized successfully N_8^- polynitrogen stabilized on the multi-walled carbon nanotubes by using cyclic voltammetry (CV) at ambient conditions, and the density functional theory (DFT) calculations indicate that the N_8^- anion inside the carbon tubes is a chain structure with C_{2h} symmetry. The possibility of trapping polynitrogen molecules inside hollow nano-materials sparks us to study the stability of polynitrogen clusters in differently confined environments.

Furthermore, as we all known, the electronic properties of boron nitride (BN) unit are similar to the corresponding bicarbon (CC) unit, so boron nitride system becomes the attractive prospective materials for nanotechnological applications. Nowadays boron nitride nanotubes (BNNTs) [15] have been extensively researched theoretically and experimentally. It was interesting to note that the encapsulated molecules inside BNNTs can influence the electronic properties [16]. In the present paper, we investigate the encapsulation of a polymeric nitrogen chain N_8 inside a single wall BNNTs (named as BNNT(6,6)) by density functional theory (DFT), and mainly focus on their stability and electronic properties.

Computational methods

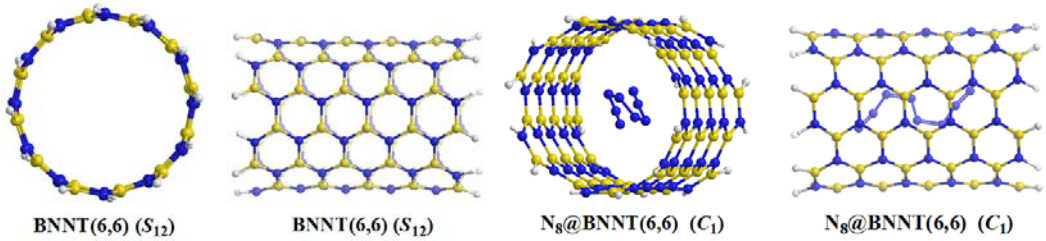
As mentioned in the previous reports [17], the edges of BNNT(6,6) is saturated by hydrogen atoms. In order to keep consistent with the previous convention [18-20], polymeric nitrogen chain N_8 encapsulated inside BNNT(6,6) is named as N_8@BNNT(6,6). The pure BNNT(6,6) and N_8@BNNT(6,6) are optimized at DFT/ B3LYP-D3 [21, 22] level of theory with the basis set of 6-31G(d). The binding energies (BE) were calculated by using the following equation:

$$BE = E_{N_8@BNNT(6,6)} - (E_{BNNT(6,6)} + E_{N_8}) \quad (1)$$

In this equation, $E_{N_8@BNNT(6,6)}$, $E_{BNNT(6,6)}$ and E_{N_8} are the total energy of the N_8@BNNT(6,6) complex, pure BNNT(6,6) and N_8 chain, respectively. The calculated BE were corrected for the basis set superposition error (BSSE) using the counterpoise method suggested by Boys and Bernardi [22]. The natural bond orbitals (NBO) calculations [23, 24] were performed through NBO version 3.1 program[24] as implemented in the Gaussian 09 package [25]. All these calculations were performed by Gaussian 09 program package.

Results and Discussion

Geometric Structure and NBO Charges. Optimized geometries of BNNT(6,6) and N_8@BNNT(6,6) are presented in Fig. 1. The optimized BNNT(6,6) and N_8@BNNT(6,6) have S_{12} symmetry and C_1 symmetry, respectively. The polymeric nitrogen N_8 chain with C_1 symmetry is at the center of BNNT(6,6). The structure of the encapsulated N_8 chain is shown in Fig. 2(a) with bond lengths (in Å) and angles.

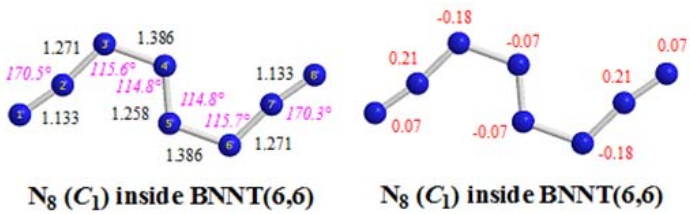


(a) (b)

Fig. 1 Optimized structures of BNNT(6,6) and N_8@BNNT(6,6) at the B3LYP-D/6-31G(d) level of theory viewed from two perspective (their symmetries are shown in the parentheses). The subsequent figures have the same arrangement

The nature charge populations of the encapsulated N_8 chain are analyzed by the NBO program as shown in Figure 2(b). The NBO analysis and the structures indicates that the encapsulated N_8 chain has four bond types: terminal triple bonds (N_1-N_2 and N_7-N_8 with the bond lengths of 133 Å), a double bond (N_4-N_5 with the bond lengths of 1.258 Å), single bonds (N_3-N_4 and N_5-N_6 with the bond lengths of 1.386 Å) and ionic bonds (N_2-N_3 and N_6-N_7 with the bond lengths of 1.271 Å). The ionic bond of N_2-N_3 is because of the charge separation of ~0.2e between N_2 and N_3, and the bond of N_6-N_7 has the similar situation. The results are consist with the previous report by Hirshberg [11].

BSSE Corrected Binding Energies. The calculated binding energies for the N_8@BNNT(6,6) complex is -26.18 kcal·mol^{-1}, indicating that the N_8@BNNT(6,6) complex may be synthesized in experiment. What's more, it shows the polymeric nitrogen N_8 chain could be stable inside the BNNT(6,6).



(a) (b)

Fig. 2 The geometric structures (a) and the nature charge populations (b) of the encapsulated N_8 chain

Electronic Property. Changes in the electronic structure of BNNT(6,6) upon encapsulation of the N_8 chain has been studied by calculating HOMO, LUMO and HOMO-LUMO energy gap. The calculated results are shown in Table 1. The presence of the encapsulated N_8 chain inside BNNT(6,6) significantly modifies the electronic property. The calculated HOMO-LUMO energy gap of BNNT(6,6) after the encapsulation of N_8 chain is decreased from 6.35 eV to 3.09 eV.

Table 1 The calculated energies (in eV) of HOMO, LUMO, HOMO-LUMO Gap (E_{gap}) for BNNT(6,6) and N_8@BNNT(6,6).

	HOMO	LUMO	E_{gap}
BNNT(6,6)	-6.45	-6.45	6.35
N_8@BNNT(6,6)	-0.10	-3.36	3.09

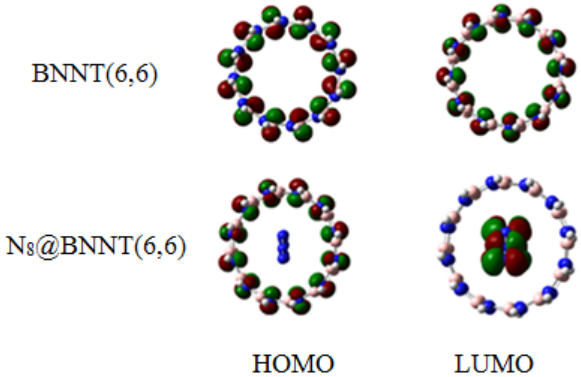


Fig. 3 The frontier molecular orbitals (HOMO and LUMO) of BNNT(6,6) and N_8@BNNT(6,6)

The frontier molecular orbitals (HOMO and LUMO) of BNNT(6,6) and N_8@BNNT(6,6) are shown in Fig. 3. In the pure BNNT(6,6), the electron density for the HOMO and LUMO mainly concentrate in the boron nitride naonotube. For N_8@BNNT(6,6), the electron density of HOMO still concentrate in the BNNT(6,6), similar to the pure BNNT(6,6). However, different from the pure BNNT(6,6), the electron density of LOMO mainly concentrate in the encapsulated N_8. Therefore the encapsulation of the polymetric nitrogen N_8 chain could influence the electronic property of BNNT(6,6).

Summary

In order to search a new possible way to stabilize the polynitrogen materials as high energy density materials, we proposed a high energetic nanomaterial, where a polymeric nitrogen chain N_8 is encapsulated inside a boron nitride nanotube (BNNT(6,6)), which is named as N_8@BNNT(6,6). We have studied the structure, NBO charges, binding energy and electronic property of N_8@BNNT(6,6) at the B3LYP-D/6-31G(d) level of theory. The binding energy of -26.18 kcal·mol^{-1} indicates the N_8@BNNT(6,6) can be synthesized in experiment. The NBO nature charges and the structure of the encapsulated N_8 chain indicate that it has four bond types: two terminal triple bonds, one double bond, two single bonds and two ionic bonds. The electronic properties study of the N_8@BNNT(6,6) complex shows that the encapsulated N_8 chain significantly influences the electronic structure of the BNNT(6,6).

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References

[1] T. Curtius. The Azide Ion, Berichte Dtsch Chem Ges. Vol. 23 (1890) p. 3023-3033.

[2] B. A. Thrush. The Detection of Free Radicals in the High Intensity Photolysis of Hydrogen Azide, Proceedings of the Royal Society of London Series A, Mathematical and Physical Sciences. Vol. 235 (1956) No. 1200, p. 143-147.

[3] Karl O. Christe, William W. Wilson, Jeffrey A. Sheehy, et al. N_5^+: A Novel Homoleptic Polynitrogen Ion as a High Energy Density Material. Angew. Chem. Int. Ed. Vol. 38 (1999) No. 13/14, p. 2004-2009.

[4] Ashwani Vij, James G. Pavlovich, William W. Wilson, et al. Experimental Detection of the Pentaazacyclopentadienide (Pentazolate) Anion, Cyclo-N_5^-. Angew. Chem. Int. Ed. Vol. 41 (2002) No. 16, p. 3051-3054.

[5] F. Cacace, G. de Petris, A. Troiani. Experimental Detection of Tetranitrogen. Science. Vol. 295 (2002) p. 480-481.

[6] Li Jie Wang, Marek Z. Zgierski. Super-high Energy-rich Nitrogen Cluster N_{60}. Chemical Physics Letters. Vol. 376 (2003) p. 698-703.

[7] A. K. McMahan, R. LeSar. Pressure Dissociation of Solid Nitrogen under 1 Mbar. Physical Review B. Vol. 54 (1985) No. 17, p. 1929-1932.

[8] M. M. G. Alemany, José Luís Martins. Density-functional Study of Nonmolecular Phases of Nitrogen: Metastable Phases at Low Pressure. Physical Review B. Vol. 68 (2003) p. 024110.

[9] Mikhaili I. Eremets, Alexander G. Gavriliuk, Ivan A. Trojan, et al. Single-bonded Cubic Form of nitrogen. Nature Materials. Vol. 3 (2004) p. 558-563.

[10] Matthew L. Leininger, C. David Sherrill, Henry F. III Schaefer. N_8: Structure Analogous to Pentalene, and other High Energy Density Minima. J. Phys. Chem. Vol. 99 (1995) No. 8, p. 2324-2328.

[11] Barak Hirshberg, R.Benny Gerber, Anna I. Krylov. Calculations Predict A Stable Molecular Crystal of N_8. Nature Chemistry. Vol. 6 (2014) p. 52-56.

[12] Hakima Abou-Rachid, Anguang Hu, David Arato, et al. Novel Nanoscale High Energetic Materials: Nanostructured Polymeric and Polynitrogen. International Journal of Energetic Materials and Chemical Propulsion. Vol. 7 (2008) No. 5, p.359-371.

[13] Hakima Abou-Rachid, Anguang Hu, Vladimir Timoshevskii, et al. Nanoscale High Energetic Materials: A Polymeric Nitrogen Chain N_8 Confined inside a Carbon Nanotube. Physical Review Letter. Vol. 100 (2008) p. 196401.

[14] Zhiyi Wu, El Benchafia, Zafar Iqbal, et al. N_8^- Polynitrogen Stabilized on Multi-wall Carbon Nanotubes for Oxygen-reduction Reactions at Ambient Conditions. Angewandte Chemie International Edition. Vol. 53 (2014) No. 46, p. 12555-12559.

[15] Angel Rubio, Jennifer L. Corkill, Marvin L. Cohen. Theory of Graphitic Boron Nitride Nanotubes. Physical Review B. Vol. 49 (1994) p. 5081-5084.

[16] Su-Fang Wang, Jian-Min Zhang, Ke-Wei Xu. Structure, Electronic and Magnetic Properties of Fe Nanowires Encapsulated in Boron Nitride Nanotubes. Physica B: Condensed Matter. Vol. 405 (2010) No.4, p. 1035-1039.

[17] Hakkim Vovusha, Suparna Sanyal, Biplab Sanyal. Interaction of Nucleobases and Aromatic Amino Acids with Graphene Oxide and Graphene Flakes. The Journal of Physical Chemistry Letters. Vol. 4 (2013) p. 3710-3718.

[18] Hitesh Sharma, Isha Garg, Keya Dharamvir, et al. Structure of Polynitrogen Clusters Encapsulated in C_{60}: A Density Functional Study. The Journal of Physical Chemistry C. Vol. 114 (2010) p. 9153-9160.

[19] Wei Ji, V. Timoshevskii, H. Guo, et al. Thermal Stability and Formation Barrier of A High-Energetic Material N_8 Polymer Nitrogen Encapsulated in (5,5) Carbon Nanotube. Applied

Physics Letters. Vol. 95 (2009) p. 021904.
[20] V. Timoshevskii, W. Ji, H. Abou-Rachid, L.-S. Lussier, H. Guo, Polymeric nitrogen in a graphene matrix: An ab initio study, Phys. Rev. B, 80 (2009) 115409.
[21] Stefan Grimme, Jens Antony, Stephan Ehrlich, et al. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correctio (DFT-D) for the 94 Elements H-Pu. The Journal of Chemical Physics. Vol. 132 (2010) p. 154104.
[22] Stefan Grimme, Stephan Ehrlich, Lars Goerigk. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. Journal of Computational Chemistry. Vol. 32 (2011) No. 8, p. 1456-1465.
[23] S.F. Boys, F. Bernardi. The Calculation of Small Molecular Interaction by the Difference of Separate Total Energies. Some Procedures with Reduced Erros. Molecular Physics. Vol. 19 (1970) No. 4, p. 553-566
[24] E.D. Glendening, A.E. Reed, J.E. Carpenter, et al. NBO, version 3.1. University of Wisconsin: Madison, WI.
[25] M.J. Frisch, G.W. Trucks, G. W. Schlegel, et. al. Gaussian 09, revision D. 01. Gaussian, Inc., Wallingford, C T, (2013).