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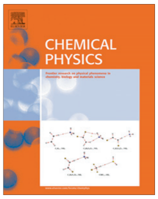

Non bonded interaction between B_nN_n (stator) and $BN^{(-,0,+)}B$ (rotor) systems: A quantum rotation in IR region

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ABSTRACT

The electromagnetic non-bonded interactions of $BN^{(-,0,+)}B$ molecule as a quantum rotor inside several of B_nN_n molecular rings as a stator has been investigated by using EPR-II and EPR-III basis sets. Optimized structures, relative stability and hyperfine spectroscopic parameters, have been calculated.

In this study, we have shown that the B_nN_n–BNB systems can be works as a nano rotor–stator molecular motor for the biological systems.

Although in our previous works, we have discussed (Monajjemi et al. (2010) [20] and Monajjemi and Boggs (2013) [18]) of the stability and electromagnetic properties of some kind of B_nN_n rings, using of these systems as a detector are much more significant and have investigated in this work.

The study for the B_nN_n–$BN^{(-,0,+)}B$ systems and then for Adenine–Thymine and Guanine–Cytosine base pairs coupled with $BN^{(-,0,+)}B$ inside the B_nN_n ($n = 8, 12, 15, 16, 18, 20, 24$) have been investigated. Three quantized rotational frequencies in cationic, radical, and anionic forms have been calculated and all frequencies appeared in the IR rotational region.

1. Introduction

Recently there are a few reports concerning of some advances of molecular motor fabrication in biological applications, such as F1-ATPase motors [1]. Although the investigations of these kind motors have been started in a new phenomenon of macromolecules in biological systems, there is no report concerning the nano-molecular motor in small scales.

Due to excellent thermal and chemical stability, boron nitride has a great potential in nanotechnology. The thermal conductivity of BN is among the highest of all electric insulators. Little is known on the electronic structure and electromagnetic behavior of boron nitride in non-bonded interactions.

Boron nitride has an isoelectric feature and exists in various crystalline forms, including hexagonal and cubic forms. The hexagonal form corresponding to graphite is the most stable and softest one and is employed as the lubricant and an additive to cosmetic products [2–4].

By considering the similarity between B–N and C–C units, a lot of effort has been devoted to BN fullerene-like materials in recent years, which have excellent properties such as heat resistance, insulation and structural stability [5,6].

Several studies have been made on BN nanomaterial such as BN nanotubes, BN nano-capsules, and BN clusters since they have excellent properties such as heat resistance in air and insulation, and these nano-particles are expected to be useful as electronic devices, high heat resistance semiconductors, and insulator lubricants [7,8].

From the experimental standard formation enthalpy, the energies of hybridized $sp^2$and sp^3B–N bonds are known to be stronger in comparison with those of B–B and N–N bonds, namely, 4.00, 2.32, and 2.11 eV, respectively [9].

Along with the experimental efforts, extensive theoretical studies have also been carried out on BN fullerenes to understand their relative stability and size dependence of the properties [10,11].

Several investigations have dealt with the possibility of inorganic analogues of the fullerene cages that would be constructed entirely of BN pairs [12–15].

We have investigated the B_nN_n cages, tubes, with perfect BNBN alternation and a non-bonded systems of B_nN_n rings including BNB axis, should be stable with respect to other possible structures due to the lowering of their strain energy and aromatic destabilization [16–20].

Furthermore, it was predicted some particular octahedral cages ($x = 12$, 16, and 28) to be energetically more favorable than others and the experimental confirmation of these theoretical results was presented [21,22]. Also, many other experimental syntheses of boron nitrides reconfirmed the octahedral model [23].

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The major focus of the present study is the investigation of electrostatic interactions within the BNB–B_nN_n ($n = 8, 12, 15, 16, 18, 20, 24$) systems. For further investigation of these kind interactions, the quantum mechanical atomic charges caused by the asymmetric distribution of electrons in chemical bonds play an important role in simulations of intermolecular forces and condensed phase properties and they are often used for a qualitative understanding of the structural aspects and mutual electrostatic interaction of two molecules [24].

Recently, an increasing number of studies on atomic charges have been performed [25–28]. Moreover, nuclear quadrupole resonance (NQR) parameters have been known as the proper tool for the description of the electrostatic interaction and charge transfer properties of B_nN_n–BNB system [29–31].

In this study, to accomplish the evaluation of partial atomic charges we have used Chelp G quantum chemical ECP method for various anion, cation, and radical types of $BN^{(-,0,+)}B$ ion inside the B_nN_n rings.

The main goal was to make a systematic exploration of the structure pattern of these boron nitrogen cage structures, i.e., presuming the B_nN_n rings as a quantum mechanical rotating system holding a specific rotation axis as BNB, we planned to simulate BH_2NBH_2 ($BN^{(-,0,+)}B$) and $NH_2BHNBHNH_2$ inside the B_nN_n rings in accordance with an quantized nano-rotor–stator molecular motor arising of various quantized parameters in a given biomolecule.

Indeed, a comprehensive picture of the electronic structure of these magnetically unusual nano-particles motivated us to imagine such a nano-system as like as a quantized mechanic rotating system.

This system would induced an electromagnetic field through electrostatic interaction of $BN^{(-,0,+)}\mathbf{B}$ to the B_nN_n rings and also has a capability of detecting the quantized parameters of the system considered as well as other bimolecular systems which can be coupled with that.

When BNB is coupled with two points of the $B_nN_n$rings, different radical, cationic, and anionic forms of BNB are expected to appear because of the potential energy difference or voltage caused by the BNB. So, investigation of the electrostatic interaction of $BN^{(-,0,+)}\mathbf{B}$ with its surrounding ring evaluating variations of different physicochemical properties such as dipole and quadrupole moments as well as natural bond orbital (NBO) and NQR parameters of the $BN^{(-,0,+)}\mathbf{B{-}B_nN_n}$ is of great interest.

In order to test the radical, cationic, and anionic forms of the system's stability we have calculated the barrier energies as well as basis set super position error (BSSE) values in transitions and rotation of BNB at specific distances and rotational angles. Also in each case the structural stability as well as conductivity of the system through calculating the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) band gap have been done [32,33].

In addition, analysis of the total atomic charges, electron spin density, and isotropic Fermi coupling constants provided valuable information on the interaction characteristics. The NBO analysis has also been investigated to study the intermolecular orbital interactions in the complexes [34–37].

2. Computational method

The geometry of the B_nN_n ($n = 8, 12, 15, 16, 18, 20, 24$) systems and $BN^{(-,0,+)}\mathbf{B}$ has been optimized by Becke's hybrid three-parameter exchange functional and the nonlocal correlation functional of the Lee, Yang, and Parr (B3LYP) method with the EPR-III and EPR-II basis sets of Barone [38,39]. The Gaussian quantum chemistry package was used for all calculations [40].

The optimization was done along with a frequency calculation to verify that the geometry was a real minimum without any imaginary frequency.

The BSSE is a consequence of the finite basis set approximation used in the calculations. The description of the intra-molecular energy of both individual molecules, namely $BN^{(-,0,+)}\mathbf{B}$ and the B_nN_n ring is wanted within the nano system as compared with the calculations performed for the free separate molecules.

Since the basis orbitals of the partner molecule are also available, the most commonly used cure for BSSE is to perform "counter poise" CP corrections defined by Boys and Bernar [41]. In this approach, we can determine the interaction energy by computing the energy of the free $BN^{(-,0,+)}\mathbf{B}$ and B_nN_n individually for every geometrical arrangement of the system. So, in this study the BSSE corrections were applied during the optimizations and the interaction energies were evaluated.

In addition, we have obtained dipole moments as the coefficients of a series expansion of a potential due to continuous or discrete sources such as an electric charge distribution. If we consider a molecule consisting of N particles with charges $e\,(Z_i)$, the particle i has spherical polar coordinates $r_i,\ \theta_i$, and ϕ_i.

The electrostatic dipole operator is:

$$Q_i^j = \sum_{i=1}^{N} eZ_iR_l^m(r_i), \tag{1}$$

where $R_l^m(r_i)$ is a regular solid harmonic function [42–44].

The HOMO corresponds to a combination of lone pair orbitals on the N atoms as well as the LUMO, which is characterized by large contributions from vacant p orbitals on B atoms with some admixture of N-based orbitals having been calculated [45]. The terms in the effective Hamiltonian are obtained after integration over electronic spatial coordinates; each term contains angular momentum operators and molecular parameters [46].

The spin–spin magnetic hyperfine Hamiltonian as a part of the molecular Hamiltonian can be presented as:

$$H_{hf}^{ss} = \frac{\mu_0}{4\pi} g_s\mu_B\mu_N \sum_{i,\alpha} g_\alpha \left\{ 3\frac{(\vec{S}_i\vec{r}_{i\alpha})(\vec{I}_\alpha\vec{r}_{i\alpha})}{r_{i\alpha}^5} - \frac{(\vec{S}_i\vec{I}_\alpha)}{r_{i\alpha}^3} + \frac{8\pi}{3} \times (\vec{S}_i\vec{I}_\alpha).\delta^{(3)}\vec{r}_{i\alpha} \right\}, \tag{2}$$

where "g_s" is the free electron's g-factor and "μ_B" is the Bohr magneton. g_α and "μ_N" are nuclear g-factor and nuclear magneton respectively, $\vec{S}_i$ is 'the spins' of the electron "i" and $\vec{I}_\alpha$ is the nucleus "α", meanwhile $\vec{r}_{i\alpha}$ represents the distance between an electron and nucleus.

This operator acts both in the state space of the electrons and in the state space of the nuclei. The anisotropic dipole–dipole interaction between the electronic and nuclear spin magnetic moments are represented by the first and the second part of the considered equation.

The last term is isotropic Fermi's contact term, arises from the magnetic field inside the nucleus, created by its magnetic moment. Isotropic Fermi contact constant is defined by:

$$b_F = \frac{2\mu_0}{3h} g_s g_N \mu_B \mu_N |\Psi(0)|^2. \tag{3}$$

Thus, the basic quantities that determine the HF interaction at the N_{th} nucleus are those in brackets and $|\Psi(0)|^2$. Ab-initio calculated isotropic constant directly depend unto the Fermi contact spin-density function per unpaired electron at a nucleus [45]:

$$b_F = \frac{2\mu_0}{3h} g_s g_N \mu_B \mu_N p^s(N). \tag{4}$$

The natural bond orbital (NBO), analysis has also been applied to study the intermolecular orbital interactions in the complexes [47,48]. The isotropic Fermi coupling which depends on the direct transfer of electron spin to the "s" orbital has been calculated.