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Ammonia adsorption on the $C_{30}B_{15}N_{15}$ heterofullerene: DFT study of nuclear magnetic shielding and electric field gradient tensors of N and B nuclei

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Ammonia adsorption on the external surface of $C_{30}B_{15}N_{15}$ heterofullerene was studied using density functional calculations. Three models of the ammonia-attached $C_{30}B_{15}N_{15}$ together with the perfect model were optimized at the B3LYP/6-31G* level. The optimization process reveals that dramatic influences occurred for the geometrical structure of $C_{30}B_{15}N_{15}$ after ammonia adsorption; the B atom relaxes outwardly and consequently the heterofullerene distorts from the spherical form in the adsorption sites. The chemical shielding (CS) tensors and nuclear quadrupole coupling constants of B and N nuclei were calculated at the B3LYP/6-311G** level. Our calculations reveal that the B atom is chemically bonded to NH_3 molecule. The B atom in the NH_3-attached form has the largest chemical shielding isotropic (CSI) value among the other boron nuclei. The C_Q parameters of B nuclei at the interaction sites are significantly decreased after ammonia adsorption.

1. Introduction

Carbon exists in several forms in nature and one of the carbon allotropes is fullerene. Fullerene was discovered in 1985 as an unexpected matter during the vaporization of graphite by laser irradiation. The 1996 Nobel Prize in chemistry was because of this discovery. ^{60}C is the most important member of the family of fullerenes [1]. In this molecule, 60 carbon atoms (with sp^2 hybridizations) are placed at the vertices of a *truncated icosahedron* (I_h) with 12 pentagons and 20 hexagons so that none of the pentagons are in contact with each other [2] and this is the so-called isolated pentagon rule (IPR). In the production of the fullerene carbon cages, several attempts have been made to obtain heteroatom doped analogs [3]. Structurally, several different doping possibilities occur, including the endohedral doping (dopant is inside the fullerene shell), the substitutional doping (dopant is included in the fullerene shell) and the exohedral doping (dopant is outside or between the fullerene shells) [4]. The substitutionally doped structures may also be called as heterofullerenes and were designed by Smalley and coworkers [5–7]. Heterofullerenes are fullerene molecules in which one or more carbon atoms are replaced by heteroatoms through the on-ball doping [2]. Doping of carbon cages with boron and nitrogen atoms appears a promising way to modify the physical and chemical properties of fullerenes [3,4,8]. Since the $(BN)_n$ clusters are currently of much interest for their great stability [3,9–11], the inclusion of both nitrogen and boron dopants is the best candidate for the formation of heterofullerenes with general formula $C_{60-2n}B_nN_n$. The BN doped ^{60}C contains the same number of electrons as ^{60}C and therefore both compounds are isoelectronic [3,8]. Boron–nitrogen heterofullerenes have been investigated by the semi-empirical and the density functional theory (DFT) calculations; the structure, electronic spectra, spectroscopic properties, stability and prediction of the nucleus independent chemical shift (NICS) of some isomers of $C_{48}B_6N_6$ were described by the DFT calculations [3,8] and the structural and electronic properties of $C_{30}B_{15}N_{15}$ at the first time examined by performing the semi-empirical and DFT calculations [4]. The calculation of nuclear magnetic resonance (NMR) [12] and nuclear quadrupole resonance (NQR) [12,13] parameters using DFT methods has become a major and powerful technique in investigation of molecular structure [14]. The nuclear magnetic chemical shielding tensors (CS) at the sites with the fractional nuclear spin numbers, e.g. B-11 and N-15, and the electric field gradient (EFG) tensors for the nuclei with the spin angular momentums greater than one-half ($I > 1/2$), e.g. B-11 and N-14, are very sensitive to electronic density and are easily perturbed; hence, they can provide very valuable information about physical environment and especially electrostatic environment around the nuclei [15].

In this study, we report the results of density functional calculations that indicate the changes in N and B nuclear magnetic shielding and electric field gradient tensors of $C_{30}B_{15}N_{15}$ on exposure to NH_3 molecule at the three possible adsorption sites.

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2. Computational details

In the present work, the adsorption behavior of an ammonia molecule on the three possible adsorption sites of $C_{30}B_{15}N_{15}$ heterofullerene is taken for consideration and comparison. The initial geometry of ^{60}C was taken and 15 carbon atoms were replaced by nitrogen atoms and other 15 carbon atoms were replaced by boron atoms [4]. First, each of the four structures, including perfect and NH_3-attached $C_{30}B_{15}N_{15}$ heterofullerenes at the three possible adsorption sites, was allowed to fully relax during the geometrical optimization process using the B3LYP-DFT method [16] and 6-31G* basis set. Additional calculations are also performed by the B3LYP method with 6-311G** standard basis set in the optimized structures to evaluate the NMR and NQR parameters of N-15 and B-11 nuclei. The gage-including atomic orbital (GIAO) method [17] was applied to calculate the nuclear magnetic shielding and the electric field gradient. The quantum chemical calculated CS tensors in the principal axes system (PAS) ($\sigma_{33} > \sigma_{22} > \sigma_{11}$) were used for converting to measurable NMR parameters, chemical shielding isotropic (CSI) and chemical shielding anisotropic (CSA), using Eqs. (1) and (2) [14,15,18]:

$$\text{CSI (ppm)} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3 \tag{1}$$

$$\text{CSA (ppm)} = \sigma_{33} - (\sigma_{11} + \sigma_{22})/2 \tag{2}$$

The isotropic value, i.e., the center of gravity, is the average value of principal components and the anisotropic value describes the largest separation from the center of gravity (see Fig. 1 for more details). Eq. (3) [13,19] was employed to convert the EFG tensors of B-11 and N-14 nuclei to the quadrupole coupling constants (C_Q). C_Q refers to the interaction energy between the electric quadrupole moment (*eQ*) and the EFG tensors at the site of quadrupole nucleus. The *Q* values reported by Pyykkö [20] are used in Eq. (3); $Q(^{11}B) = 40.59$ mb and $Q(^{14}N) = 20.44$ mb [21].

$$C_Q\ (\text{MHz}) = e^2 Q q_{zz}/h \tag{3}$$

All calculations were performed by the Gaussian 03 [22] package of programs.

3. Results and discussion

3.1. Considered models and geometries

To demonstrate the three possible adsorption sites on a $C_{30}B_{15}N_{15}$ heterofullerene, we used the labeled and numbered ^{60}C Schlegel diagram in Fig. 2 to describe the relevant structural parameters. In this figure, the boron adsorption sites are defined with bold scripts and the other boron sites were not studied, because they were similar to the three considered sites in position and neighboring atoms so that the boron atoms of 34, 35, 36, 38 and 39 are in similar position to the B.37 (site I) and also the boron atoms of 53, 55, 56, 59 and 60 are in similar position to the B.54 (site II) and finally, the boron atoms of 52 and 57 are in similar position to the B.58 (site III). The optimized geometrical properties of the considered structures are exhibited in Tables 1–3. In these tables, interatomic distances and bond angles at the adsorption sites are listed for the NH_3-attached $C_{30}B_{15}N_{15}$ heterofullerenes and also for the perfect model for comparison. It must be noted that the changes in geometries are significant just for those atoms placed in the nearest neighborhood of adsorption sites and studying other atoms is not important.

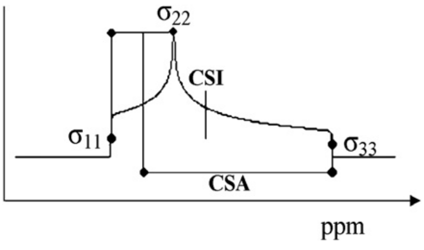

Fig. 1. Schematic diagram of the theoretical NMR powder pattern spectrum.

In comparison with the perfect model, the B atom relaxes outwardly and consequently the heterofullerene distorts from the spherical form in the adsorption sites. The distance between the B atom at the adsorption site and its first neighbor (N or C atom) increases after the adsorption. For example at adsorption site I, the distances between the B.37 atom and the C.3, N.40 and N.42 atoms increase from 1.52, 1.44 and 1.47 Å to 1.59, 1.51 and 1.55 Å, respectively. On the other hand, at adsorption site II, the distances between the B.54 atom and the C.4, N.44, and N.45 atoms increase from 1.55, 1.44 and 1.46 Å to 1.62, 1.51 and 1.54 Å, respectively, and at adsorption site III, the distances between the B.58 atom and the C.14, N.46, and N.47 atoms increase from 1.53, 1.47 and 1.46 Å to 1.60, 1.53 and 1.55 Å, respectively. The distances between the same B atoms in sites I, II and III and nitrogen atom of the ammonia molecule are 1.678, 1.674 and 1.674 Å, respectively. Consequently, changes in bond angles at the adsorption sites are expected. For instance, at adsorption site I, the bond angles of B.37–N.42–B.38, B.37–N.40–C.5 and B.37–N.42–C.1 increase from 118°, 118° and 105° to 121°, 120° and 109°, respectively, and so forth. Similar changes are observed for the other adsorption sites. The changes in the structural parameters during adsorption (structural deformations) are due to the fact that the B atom (in the adsorption site) with four non-equivalent chemical bonds makes a distorted tetrahedron.

3.2. ^{11}B NMR and ^{15}N NMR parameters

The CS tensors at the sites of ^{11}B and ^{15}N nuclei are calculated in each of the four optimized structures of the perfect model and NH_3-attached forms of the considered $C_{30}B_{15}N_{15}$ heterofullerene, then the results are converted to the CSI and CSA parameters (Tables 4 and 5) using Eqs. (1) and (2). It is noted that the N.61 nucleus is from ammonia. A quick look at the results reveals that various ^{11}B nuclei exist with almost dissimilar CSI and CSA parameters, which means they have dissimilar electrostatic properties. The B.37 and B.38 have the smallest CSI, 37 ppm, among all the ^{11}B nuclei of the perfect model but the B.57 has the largest CSI (before adsorption). These results reveal that the electronic densities at the B.37 and B.38 are less than the other ^{11}B nuclei; also the electronic density at the B.57 is the maximum. Since NH_3 molecule is chemically bonded to $C_{30}B_{15}N_{15}$ heterofullerene and a new B – N bond is formed between $C_{30}B_{15}N_{15}$ heterofullerene and N atom of NH_3 molecule in the NH_3-attached $C_{30}B_{15}N_{15}$ heterofullerene, the CS tensors at the adsorption sites (B.37, B.54 and B.58) are perturbed. The average B – N bond length is 1.45 Å in the perfect model whereas the bond length between the boron atom in $C_{30}B_{15}N_{15}$ heterofullerene and N atom of NH_3 molecule is about 1.67 Å at the adsorption site. In comparison with the perfect model, the B atom at the adsorption site is significantly influenced by NH_3 molecule. Therefore, the CSI parameters of B.37, B.54 and B.58 nuclei are significantly increased in the NH_3-attached forms and shifted to upper fields (about 45 ppm). This is caused by lone pair of electrons transformation from nitrogen to empty orbital of boron. The anisotropy values for B.37, B.54 and B.58 nuclei decreased in the NH_3-attached forms. However, the effect is more significant for the B.54 and B.58 nuclei. These results indicate that the electronic charge distributions around the B.37, B.54 and B.58 nuclei become more symmetric as a result of the NH_3 adsorption.