

Vibrational Dynamics of B₃N₃ Substituted C₆₀ Fullerene

Ambrish Kumar Srivastava^{1,a)} Sarvesh Kumar Pandey^{2,b)}, Abhishek Kumar¹ and Neeraj Misra^{1,c)}

¹Department of Physics, University of Lucknow, University Road, Lucknow-226007, Uttar Pradesh, India

²Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur-208016, Uttar Pradesh, India

Corresponding authors: ambrishphysics@gmail.com ; neerajmisra11@gmail.com

Abstract. Introduction of heteroatoms into C₆₀ fullerene leads to enhance its physical and chemical properties in one way or other. In this paper, we have studied C₆₀ fullerene in which one of C₆ hexagons is replaced by B₃N₃. The resulting heterofullerene B₃N₃C₅₄ closely mimics the structure of C₆₀. The vibrational spectrum of B₃N₃C₅₄ has been calculated and compared with that of C₆₀. The substitution results in a number of additions peaks including the strongest peak due to BN stretching.

INTRODUCTION

Heterofullerenes possess distinguished physical and chemical properties which enable them to be promising materials for some unique applications [1-3]. In particular, BN substituted C₆₀ cages have been studied several times [4-8]. Esfarjani *et al.* [4] have studied the band structure and chemical bonding in BNC₅₈ heterofullerenes and its electronic spectra are studied by Chen *et al.* [5]. Pattanayak *et al.* have performed a systematic study on C_{60-2x}(BN)_x (x = 1-7) hybrid fullerene [6] and extended their study up to C₁₂B₂₄N₂₄ subsequently [7]. More recently, Anafcheh *et al.* [8] have performed NMR calculations on C_{60-2x}(BN)_x (x = 1, 2, 3, 6, 9, 12, 15, 18, 21 and 24) using density functional theory (DFT). Since polar BN bond is similar to covalent CC bond in many aspects [9], BN substituted C₆₀ fullerenes are structurally analogous to pure C₆₀. Vibrational spectra provide the signature of structure of a molecular system. Therefore, it seems interesting to analyze the vibrational spectra of BN modified C₆₀ and compare it with pure C₆₀. In this paper, we report the vibrational properties of B₃N₃ substituted C₆₀ i.e. B₃N₃C₅₄ and compare with those of C₆₀.

COMPUTATIONAL METHODS

The study was performed using DFT method as implemented in Gaussian 09 program [10]. The structures were optimized without any symmetry constraint at B3LYP/6-31G(d) level.

Vibrational frequency calculations and natural population analysis (NPA) have been carried out within same computational scheme. Molecular structures and vibrational spectra were visualized by Avogadro1.1 software.

RESULTS AND DISCUSSION

The equilibrium structure of $B_3N_3C_{56}$ along with C_{60} is displayed in FIG. 1. One can note that the structure of $B_3N_3C_{54}$ closely resembles that of C_{60} in which one of C_6 hexagon is replaced by B_3N_3 . We have analyzed the free C_6 and B_3N_3 hexagons also shown in FIG. 1, and noticed that they are almost similar in structure. Both possess equalized bond lengths, 1.358 Å for B–N and 1.327 Å for C–C. This fact is consistent with the structural similarity of benzene to borazine [9]. In TABLE 1, we have collected the bond lengths of hexagon-hexagon and hexagon-pentagon in $B_3N_3C_{54}$ and C_{60} . Evidently, the B–N bond lengths increase to 1.437 Å and 1.478 Å in hexagon-hexagon and hexagon-pentagon edges which indicate that B–N bonds of the substituted fullerene are weaker than those of free B_3N_3 . Furthermore, the difference of B–N and C–C bond lengths is significantly increased. This may be expected due to redistribution of charges on B and N atoms in $B_3N_3C_{54}$.

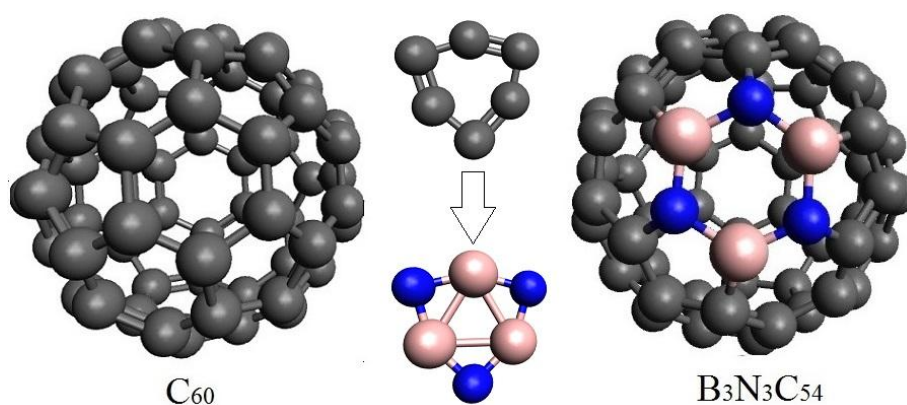


FIGURE 1. Equilibrium structures of C_{60} and $B_3N_3C_{54}$ at B3LYP/6-31G(d) level of theory.

TABLE 1. Main bond lengths (in Å) of $B_3N_3C_{54}$ and C_{60} at B3LYP/6-31G(d) level of theory.

System (Bond Length)	Hexagon-Hexagon	Hexagon-Pentagon
C_{60} (C–C)	1.395	1.453
$B_3N_3C_{54}$ (B–N)	1.437	1.478
(B–C)	1.526	1.526
(N–C)	1.434	1.434

The vibrational frequency calculations performed on $B_3N_3C_{54}$ heterofullerene reveal all real and positive values. This suggests that $B_3N_3C_{54}$ belongs to at least some local minimum in the potential energy surface. The calculated vibrational infrared (IR) spectra of $B_3N_3C_{54}$ and C_{60} are depicted in FIG. 2. For N -polyatomic systems, there are $3N-6$ normal modes of vibration. Due to

extremely high symmetry of C_{60} (I_h point group), however, there are only four characteristic modes possessing appreciable intensity. The mode with the highest intensity is assigned at the lowest wavenumber, 537 cm^{-1} . The CC stretching modes of C_{60} are assigned in the higher wavenumber region, 1460 and 1214 cm^{-1} . The substitution of B_3N_3 into C_{60} leads to destruction of the sharpness of peaks in the IR spectrum due to C_1 point group. As seen in FIG. 2, a number of additional modes as well as mixing of various modes appear due to BN, BC and NC stretchings. For instance, the BN stretching modes appear at 1394 cm^{-1} . This mode possesses the strongest intensity due to charge transfer from B to N atoms. Note that the BN stretching mode was calculated at 1372 cm^{-1} in $B_2N_2C_2H_6$ heterocyclic ring [11]. Furthermore, CC stretching modes of $B_3N_3C_{54}$ are shifted toward higher wavenumber region as compared to C_{60} . For example, the modes calculated at 1606 and 1586 cm^{-1} are assigned to CC stretchings with weak intensities. However, CC stretching and lower wavenumber mode of $B_3N_3C_{54}$ corresponding to C_{60} are obtained at 1468 cm^{-1} (medium) and 539 cm^{-1} (weak). Finally, it should be noted that the wavenumbers mentioned here are unscaled and therefore, a proper scaling is needed to order to compare them with the experimental values.

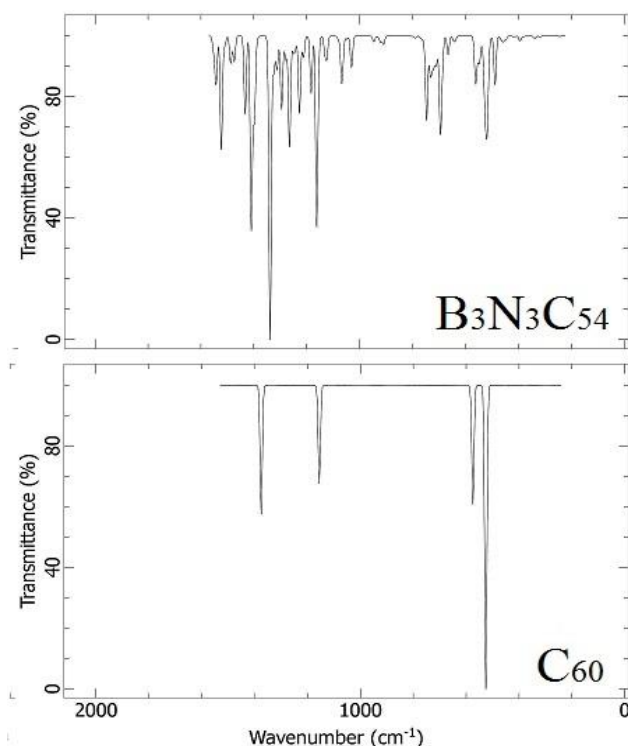


FIGURE 2. Calculated IR spectra at B3LYP/6-31G(d) level of theory.

CONCLUSION

Using density functional theory based calculations; we have studied the substitution of B_3N_3 hexagon into C_{60} fullerene. We noticed that the structure of $B_3N_3C_{54}$ closely resembles that of C_{60} . However, polar B–N bonds are weaker than that of covalent C–C bonds. The strongest peak in vibrational spectrum of $B_3N_3C_{54}$ is due to BN stretching and CC stretching modes are shifted to higher wavenumber region.

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