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Time-Dependent Density Functional Theoretical Study of the Absorption Properties of BN-Substituted C_{60} Fullerenes

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Time-dependent density functional theoretical calculations using the B3LYP functional and 6-31G* basis set for a series of BN-substituted C_{60} fullerenes reveal that, unlike C_{60}, these molecules would absorb in the visible region and that the optical and electronic properties of fullerenes can be fine-tuned with proper BN substitution.

Introduction

The discovery of fullerene as an allotrope of carbon accelerated the research in the field of atomic clusters.[1] Fullerenes of various sizes and shapes have been reported subsequently. Interestingly, fullerenes undergo various types of reactions, with the result of a new branch of chemistry called fullerene chemistry emerging.[2] Clusters of boron (B_n) and nitrogen (N_n) have also been reported by different groups.[3,4] So far, homonuclear clusters of boron and nitrogen have not received much attraction. However, mixed BN clusters of various sizes and shapes have been studied extensively both by theory and experiment.[5−9] The structural similarities of BN sheets to that of graphite layers naturally led to the discovery of BN analogues of fullerenes and carbon nanotubes. In 1995, Chopra et al. reported the first successful synthesis of boron nitride nanotubes from BN sheets using a plasma discharge.[10] Later, BN cages of various sizes and shapes were made by different methods.[11,12] These compounds are expected to have potential applications in various fields and have therefore provided an impetus to a lot of theoretical and experimental studies. While fullerene cages are invariably "closed" by pentagons, the B, N cages and tubes are closed by square or hexagonal rings.[13] This is understandable because the pentagonal rings will result in the formation of homonuclear B−B or N−N bonds. Studies have shown that, compared to the heteronuclear B−N bonds, formation of homonuclear B−B and N−N bonds makes the system unstable.[14,15] Therefore, an exact BN analogue of fullerene $B_{30}N_{30}$ is unlikely.

Attempts have also been made to dope fullerenes with heteroatoms for making materials having novel properties. B, N substitution in a fullerene can result in interesting properties, without seriously altering the structure of the cage.[16−18] While doping by boron makes an electron-deficient system, doping by nitrogen makes it electron rich. Such systems are expected to act as p-type and n-type semiconductors, respectively. However, simultaneous substitution of boron and nitrogen (in the 1:1 ratio) makes the system isoelectronic to the parent fullerene, and the resultant species are generally known as CBN balls. Nakamura et al.[19] have reported the synthesis of a single BN-substituted C_{60} molecule by laser vaporization of BC_2N graphite. BNC_{58} has been investigated theoretically by many groups, and the structure with a BN bond between two hexagons is predicted to be the most stable, when compared to those having the BN in a pentagon−hexagon bond or structures where B and N atoms are disconnected.[20−21] This can be explained by the formation of a dative bond between boron and nitrogen atoms in the heterofullerene. The structure, stability, and electronic properties of more BN-substituted fullerenes have been studied by many groups, and some rules regarding the position of heteroatoms have emerged.[22−25] According to these rules, after the first substitution in the hexagon−hexagon bond, further substitution continues in the same ring until it is completely substituted. This is known as the "hexagon filling" rule. Kar et al.[25] theoretically studied the successive BN substitution in fullerenes using MNDO and DFT (B3LYP)/3-21G levels of theory without imposing any symmetry constraints. They have reported that after covering one hexagon of the cage structure, the substitution progresses in one direction, covering other hexagons one by one and finally connecting the BN units at the starting point.

Despite all of the studies mentioned above on BN-substituted heterofullerenes, nothing is known about their optical properties. In this Letter, we report the results of a detailed time-dependent density functional theoretical study (TDDFT) of the optical absorption properties of a few BN-substituted C_{60} fullerenes.

2. Computational Method

All of the calculations reported in this Letter were carried out using the Gaussian suite of programs.[26] Preliminary investigations were carried out using the AM1 method. Geometries of all systems were fully optimized using density functional theory with B3LYP parametrization and the 6-31G* basis set. The highest possible symmetry was imposed in all calculations unless specified otherwise. Frequency calculations at the same level of theory were carried out for all of the systems reported in this Letter, and real frequencies were obtained, confirming that all of them were minimum energy structures

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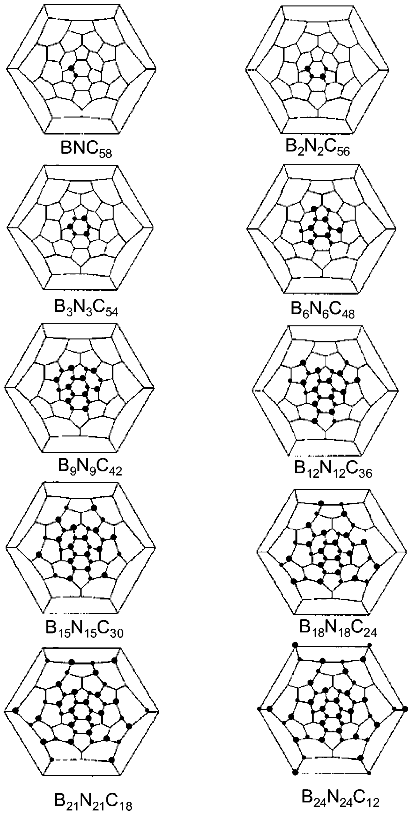

Figure 1. Schlegel diagram showing the substitution pattern in a C_{60} fullerene. Small filled circles represent boron atoms, and the relatively larger filled circles represent nitrogen atoms.

on the potential energy landscape. These optimized minimum energy structures were used for TDDFT calculations using the B3LYP functional and 6-31G* basis set to study the absorption properties.

3. Results and Discussion

For the sake of clarity, the substitution patterns considered in the present study are illustrated by Schlegel diagrams, as shown in Figure 1. For example, the substitution of carbon atoms of one of the hexagon−hexagon bonds in the C_{60} fullerene by boron and nitrogen atoms will lead to the formation of BNC_{58} with C_s symmetry. Substitution of carbon atoms continues in the same hexagonal ring until it is saturated with boron and nitrogen atoms. Complete BN substitution of one of the hexagonal rings will make a C_3-symmetric heterofullerene ($B_3N_3C_{54}$). Further BN substitutions are carried out by keeping the C_3 symmetry in the system. Thus, three BN units are added in each step, and this substitution spreads in all directions of the previously substituted hexagonal ring. The carbon atoms connecting the pentagons that are in-plane with the C_3 axis are left unsubstituted in each step. This eliminates the possibility of unstable BCN balls having homonuclear B−B and N−N bonds. This pattern of substitution continues until the formation of $B_{24}N_{24}C_{12}$ with C_i symmetry.

The formation of a C_{60} fullerene is an endothermic process. Calculated heats of formation by the AM1 method for fullerenes and BN-substituted fullerenes are plotted in Figure 2. It is clear that the heat of formation value decreases algebraically with an increase in the number of BN units. As a result, the formation of fullerenes with a large number of BN units becomes exothermic.

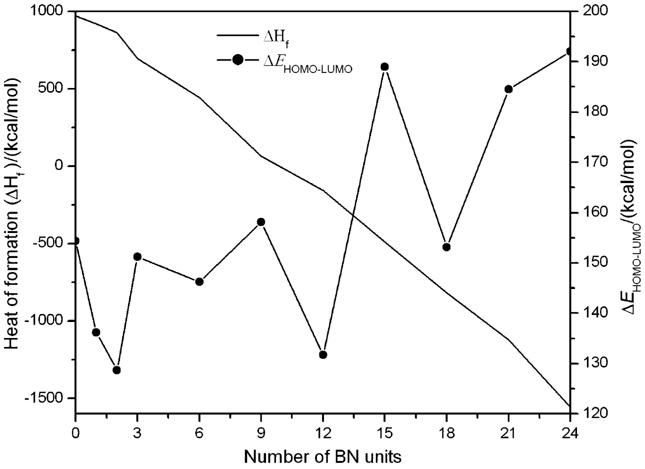

Figure 2. Standard heat of formation and HOMO−LUMO energy gap for BN-substituted C_{60} fullerenes.

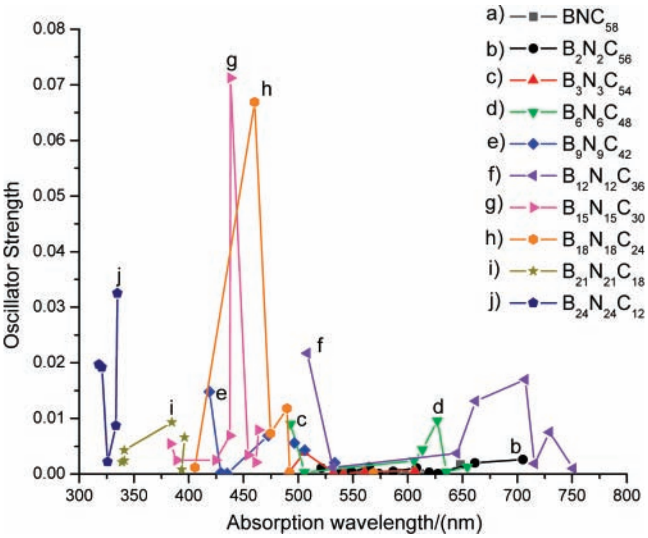

Figure 3. Calculated electronic absorption properties of BN-substituted C_{60} fullerenes.

The energy gap ($\Delta E_{\mathrm{HOMO-LUMO}}$) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the C_{60} fullerene and its BN-substituted analogues obtained from DFT calculations are also plotted in Figure 2. A careful analysis of the graph suggests that the HOMO−LUMO energy gap depends critically on the number of BN units and their position. Compared to C_{60}, the energy gap is less for the first few BN substitutions ($n = 1-3$). There is a sharp rise in the energy gap for fullerenes having completely BN-substituted hexagonal rings. The value of $\Delta E_{\mathrm{HOMO-LUMO}}$ follows an irregular pattern, and finally, the energy gap increases with an increase in BN substitution. Kar et al.[24] had reported a similar irregular pattern in the value of $\Delta E_{\mathrm{HOMO-LUMO}}$ in their studies of BN substitution along one direction. As the spreading of BN units occurs in a distorted icosahedron, avoiding B−B and N−N bonds, a regular pattern in the HOMO−LUMO energy gap is not expected. Plots of frontier orbitals (HOMO and LUMO) given in the Supporting Information show the lack of regularity in the energy gap upon substitution. However, the results do show that the electronic properties of fullerenes can be fine-tuned with appropriate BN substitution.

The degeneracy of the highest occupied and lowest unoccupied molecular orbitals of C_{60} results in a set of close-lying low-energy excited states. Electronic transitions between these states and the ground state are symmetry forbidden. The allowed transitions occur in the ultraviolet region. However, due to the vibronic coupling, the fullerene shows some weak absorption in the visible region. Thus, the absorption properties of BN-substituted fullerenes become important both from fundamental and application points of view. The calculated absorption wavelengths and corresponding oscillator strengths of various BN-substituted fullerenes are plotted in Figure 3.

Unlike $C_{60,}$ the transitions between the ground electronic state and the low-lying excited states are not forbidden in BN-substituted fullerenes. In a majority of cases, absorption occurs in the visible region. However, the oscillator strength is negligible for the first few BN-substituted fullerenes, and it becomes considerable when at least one hexagonal ring is saturated with boron and nitrogen. Absorption becomes prominent with an increase in the number of BN units. From the figure, it can be seen that absorption is particularly strong for $B_{15}N_{15}C_{30}$ and $B_{18}N_{18}C_{24}$. A further increase in the number of BN units shifts the absorption maximum to ultraviolet region, as observed in the case of BN sheets and BN nanotubes.[27]

As was explained earlier in the text, because of the constraint (avoiding B−B and N−N bonds) in the substitution pattern and the distorted icosahedral geometry, a regular pattern is not expected in the reported absorption maxima and the corresponding oscillator strengths for these BN-substituted fullerenes. It is worth pointing out that there is a good correlation between the dipole moment and the oscillator strength in most of the cases.

4. Summary

TDDFT calculations for a series of BN-substituted fullerenes suggest that the optical and hence the electronic properties of fullerenes can be fine-tuned by B, N substitution in the cage. It is predicted that some of the BCN fullerenes will absorb in the visible region with considerable oscillator strength.

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Supporting Information Available: Frontier molecular orbitals (HOMO and LUMO) of the BN-substituted fullerenes. This material is available free of charge via the Internet at http://pubs.acs.org.

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