

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/238953861>

# Structure of Polynitrogen Clusters Encapsulated in C<sub>60</sub>: A Density Functional Study

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY C · MAY 2010

Impact Factor: 4.77 · DOI: 10.1021/jp908755r

---

CITATIONS

20

READS

90

## 4 AUTHORS:



Hitesh Sharma

Punjab Technical University

33 PUBLICATIONS 144 CITATIONS

[SEE PROFILE](#)



Isha Mudahar

Punjabi University, Patiala

15 PUBLICATIONS 60 CITATIONS

[SEE PROFILE](#)



Keya Dharamvir

Panjab University

127 PUBLICATIONS 499 CITATIONS

[SEE PROFILE](#)



Vijay K Jindal

Panjab University

197 PUBLICATIONS 985 CITATIONS

[SEE PROFILE](#)

# Structure of Polynitrogen Clusters Encapsulated in C<sub>60</sub>: A Density Functional Study

Hitesh Sharma,<sup>†,‡</sup> Isha Garg,<sup>†</sup> Kuya Dharamvir,<sup>†</sup> and V. K. Jindal<sup>\*,†</sup>

Department of Physics, Center of Advanced Studies in Physics, Panjab University, Chandigarh, India 160014, and Department of Applied Sciences, RBIEBT, Saharan, Mohali, Punjab 140104, India

Received: September 10, 2009; Revised Manuscript Received: February 22, 2010

Using density functional theory, we explore the possibility of trapping polynitrogen clusters inside C<sub>60</sub> fullerene cages. We found that a maximum of 13 nitrogen atoms can be encapsulated in a C<sub>60</sub> cage without distorting the C<sub>60</sub> cage significantly. The nitrogen clusters in confinement exhibit unique stable structures in polymeric form, mostly in single- and double-bonded formations. The N<sub>n</sub>@C<sub>60</sub> molecules retain their structure, even at 300 K, for n ≤ 12. The Mulliken charge analysis shows a very small charge transfer in N@C<sub>60</sub>, consistent with the quartet spin state of N. However, for 2 < n < 10, charge transfer takes place from the cage surface to the N<sub>n</sub> compounds, and inverse polarization thereafter.

## I. Introduction

In recent years, interest in polynitrogen or polymeric nitrogen has drawn considerable attention not only because of its theoretical significance but also because of its possible application as a high energy density material (HEDM).<sup>1,2</sup> Polynitrogen molecules are formed by a combination of lower-order bonds, and while decaying into dinitrogen (N<sub>2</sub>) molecules, they release enormous amount of energy and are environmentally safe.

Over the last few decades, there have been consistent efforts to predict new exotic forms of all-nitrogen molecules using various experimental and theoretical techniques.<sup>3–6</sup> The higher members of the nitrogen cluster family (N<sub>n</sub> for n > 3) are unstable in free space and, therefore, present a challenge to their synthesis. In 1999, Christe et al.<sup>7</sup> synthesized successfully a N<sub>5</sub><sup>+</sup> salt N<sup>+</sup>AsF<sup>−</sup>, which is the third readily accessible homonuclear polynitrogen species. Subsequently, the same group reported the stability of N<sub>5</sub><sup>+</sup>SbF<sub>6</sub><sup>−</sup> up to 70 °C and its relative insensitivity to impact.<sup>8</sup> This discovery opened a new dimension to explore neutral polynitrogen compounds and the basis for the first synthesis of stable nitrogen allotropes.

Nitrogen-rich compounds such as nitrogen hydrides (N<sub>n</sub>H<sub>m</sub>) (n > m) could also be used as starting materials to produce N<sub>n</sub> species, since deprotonation of N<sub>4</sub>H<sup>+</sup><sup>9</sup> and dehydrogenation of N<sub>4</sub>H<sub>6</sub> and N<sub>4</sub>H<sub>4</sub><sup>10,11</sup> may lead to the formation of neutral N<sub>4</sub>. Nitrosyl oxide N<sub>4</sub>O, which dissociates to form N<sub>2</sub> + N<sub>2</sub>O with a small activation energy of 28 kJ mol<sup>−1</sup>, has been experimentally observed.<sup>12</sup> Furthermore, it has been suggested that higher N<sub>n</sub> could be synthesized via direct or indirect excitation of electronic states in liquid and solid nitrogen, followed by collision addition of a ground state N and excited N<sub>n−1</sub> or N<sub>n−2</sub>, thereby forming higher N<sub>n</sub> compounds. For example, combining different N<sub>n</sub> moieties such as N<sub>5</sub> and N<sub>3</sub> might lead to the formation of N<sub>8</sub> species.<sup>13</sup>

In 2002, Cacace et al.<sup>14</sup> demonstrated the existence of the tetranitrogen molecule (N<sub>4</sub>) as a metastable species whose lifetime exceeds 1 μs at 298 K. The identification of N<sub>4</sub> represents the first addition in nearly half a century to the family of the polynitrogen molecules. Hammerl and Klapotke<sup>15</sup> explored the possibility of finding experimental evidence for a

pentazole compound with the highest possible nitrogen content, and their theoretical calculations were used to predict the stability of several tetrazolepentazole species. At the most fundamental level, a molecule will exist only if it has high enough energy barrier that keeps it away from dissociation.

This possibility has been explored theoretically. Various novel polynitrogen species have been studied in a variety of forms, such as cyclic, acyclic, or caged conformations. The species investigated include ionic clusters,<sup>16–18</sup> cylinders,<sup>19</sup> cages,<sup>20–23</sup> nanoneedles,<sup>24</sup> and helixes.<sup>25</sup> Isomers of smaller systems (N<sub>7</sub>,<sup>26</sup> N<sub>10</sub>,<sup>27</sup> and N<sub>12</sub><sup>28</sup>) have also been reported theoretically in free space. The majority of these studies have focused on the evaluation of these novel forms of molecular nitrogen. However, Wang et al.<sup>29</sup> has described the possible synthesis route for all-nitrogen systems. Dixon et al.<sup>30</sup> has successfully demonstrated the ability of the theory to predict the stability of such compounds. Despite these efforts, so far, no higher members (n > 4) of a polynitrogen family in free space have been synthesized experimentally. The present difficulties in synthesizing the polynitrogen molecules motivates us to look for new avenues to realize the stability of polynitrogen molecules.

In addition, the new polymeric forms of nitrogen have also been explored under extreme conditions of high pressure and temperature. The application of high pressure to a nitrogen system leads to destruction of covalent bonds and may lead to the formation of an intermediate polymeric network of single- and double-bonded atoms which has been verified experimentally.<sup>31–34</sup> Using ab initio calculations, other forms of polymeric nitrogen, such as black phosphorus (BP),<sup>35</sup> A7,<sup>36</sup> metallic,<sup>37</sup> the simple tetragonal phase,<sup>37</sup> and cubic gauche (CG) form<sup>34</sup> have been proposed at extreme conditions. The CG form has also been observed experimentally.<sup>38</sup> Therefore, the success of ab initio studies<sup>39</sup> in predicting new polymeric phases of nitrogen under extreme conditions motivates us to study polynitrogen in other physical environments, such as in confinement.

More recently, nitrogen has been predicted to exist in polymeric form (N<sub>8</sub>) in confinement of nanostructures; that is, carbon nanotubes. It was proposed that N<sub>8</sub> stabilizes as a chain that is stable up to room temperature.<sup>40</sup> Therefore, apart from extreme conditions of high temperature and pressure, confinement offers an alternate environment for stabilization of

\* Corresponding author. E-mail: jindal@pu.ac.in.

<sup>†</sup> Panjab University.

<sup>‡</sup> RBIEBT.

polynitrogen compounds. Since the environment of  $C_{60}$  has been extensively studied by our group<sup>41–44</sup> as well as others,<sup>45,46</sup> it offers a new possibility for polynitrogen encapsulation. The  $C_{60}$  cage has already been explored for endohedral doping with alkali metals,<sup>47</sup> transitional metals,<sup>48</sup> nonmetals,<sup>49</sup> and noble gases.<sup>50</sup> Among all endohedral complexes, nitrogen-doped  $C_{60}$  is quite interesting and needs further investigation. As per our knowledge,  $N@C_{60}$  is the only endohedral complex that has been explored extensively theoretically<sup>45,46,51,52</sup> as well as experimentally.<sup>53,54</sup> However,  $N_2@C_{60}$  was successfully synthesized using pressure heating,<sup>55</sup> and one isolated study of its stabilization energy has been recently reported.<sup>56</sup> To date, the higher members of the nitrogen family ( $n > 2$ ) have not been explored at endohedral position in  $C_{60}$ . Keeping this in view, further investment of efforts is needed in both experimental and theoretical sides to help in designing new ways for generating  $N_n@C_{60}$  compounds and understand their stability in different environments.

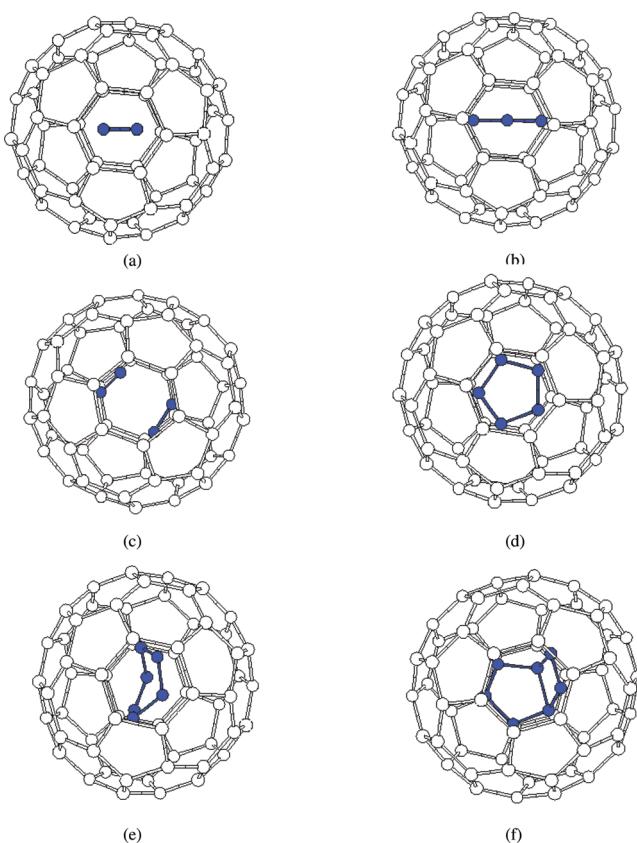
In this paper, we have extended our earlier work on azafullerenes<sup>57</sup> to nitrogen at the endohedral position of the  $C_{60}$  cage. We report the results of our ab initio calculations on  $N_n@C_{60}$  for  $n \leq 16$ , which describes the novel possibility of stabilizing the higher members of all-nitrogen molecules in the confined environment of  $C_{60}$ . We intend to show that  $C_{60}$  can act as an ideal candidate to trap nitrogen in polymeric form. The present study would provide some valuable information for synthesizing more stable all-nitrogen clusters to develop novel materials for the future.

## II. Computational Details and Validation

We have used the Spanish Initiative for Electronic Simulation with thousands of atoms (SIESTA) computational code, which is based on numerical atomic orbital density functional theory method.<sup>58–60</sup> We have used  $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$  ( $4S_{3/2}$ ) configuration of atomic nitrogen corresponding to the spin quartet state, which is consistent with experimental observation.<sup>54</sup> The calculations are carried out using generalized gradient approximation (GGA) that implements Becke gradient exchange correlation functional (BLYP).<sup>61</sup> Core electrons are replaced by nonlocal, norm-conserving pseudopotentials factorized in the Kleinman–Bylander form,<sup>62</sup> whereas valence electrons are described using a linear combination of numerical pseudo atomic orbitals of the Sankey–Niklewski type<sup>63</sup> but generalized for multiple- $\zeta$  and polarization functions. In this work, we have used a split valence, double- $\zeta$  (DZP) basis set with energy shift equal to 100 meV. The real space cutoff grid energy is taken as 200 Ry. Periodic boundary conditions have been considered using a simple cubic shell of 20 Å that is large enough to avoid any significant spurious interactions with periodically repeated images.

We first performed test calculations on the  $C_{60}$  and  $N_2$  molecules. In  $C_{60}$ , we found the  $C=C$  and  $C-C$  bond distances as 1.40 and 1.46 Å, respectively, in agreement with experimental values.<sup>64</sup> The ionization potential and electron affinity were 6.9 and 2.70 eV, respectively, in good agreement with experimental values of  $7.5 \pm 0.01$ <sup>65</sup> and  $2.689 \pm 0.008$ ,<sup>66</sup> respectively. In the  $N_2$  molecule, the  $N-N$  bond distance and ionization potential are 1.12 Å and 15.43 eV, which are in good agreement with experimental values of 1.15 Å and 15.60 eV, respectively.<sup>67</sup> We have successfully described the structural, electronic, and vibrational properties of N-doped heterofullerenes,<sup>57</sup> which validates the applicability of our calculations on carbon- and nitrogen-based systems.

We now proceed with the investigation of nitrogen clusters inside  $C_{60}$ . We started with different initial atomic configurations

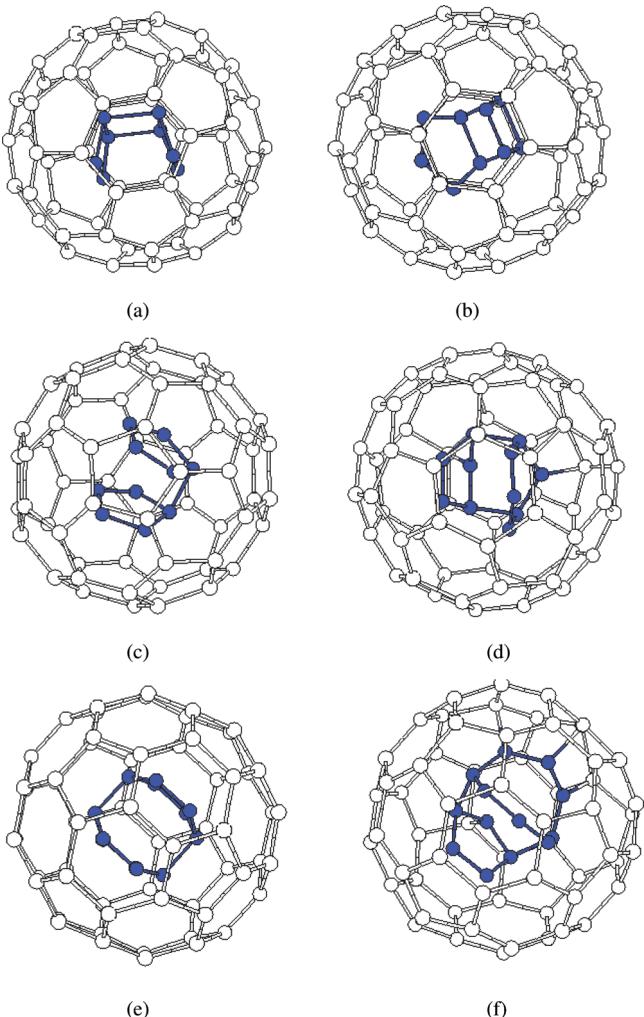


**Figure 1.** Geometries of  $N_n@C_{60}$ : (a)  $N_2$  placed at the center of  $C_{60}$ ; (b)  $N_3$  as a linear chain placed symmetrically; (c)  $N_4$  exists as two independent  $N_2$  molecules placed symmetrically across center; (d, e)  $N_5$  and  $N_6$  exist as a pentagon ring and a nonplanar distorted hexagon with 100% single bond character; and (f)  $N_7$  exists as  $N_5$  and  $N_2$  as separate units; however, its nearly isoenergetic structure is shown.

of  $N_n$  for  $n = 1–16$ . The following considerations were taken into account while starting and determining the final structure for particular configuration: (a) Nitrogen atoms were placed sufficiently away from the walls of  $C_{60}$  so that there is no likelihood to form any  $C-N$  bond. (b) Nitrogen atoms were allowed to form bonds among themselves and make polynitrogen compounds. (c) Each structure was allowed to relax until the forces on each atom converge up to 0.001 eV/Å. (d) The structure with the minimum energy is considered as the final stable polymeric form of nitrogen. (e) All the optimized nitrogen clusters inside  $C_{60}$  were also relaxed in free space at 0 K. (f) The structures of  $N_n@C_{60}$  were also relaxed at room temperature (300 K) to confirm their stability. (g) The spin-polarized calculations were performed on the final stable polymeric  $N_n@C_{60}$  to determine the spin states. (h) Harmonic vibrational frequency analysis on all optimized structures was performed to further ensure their ground state geometries.

## III. Results and Discussion

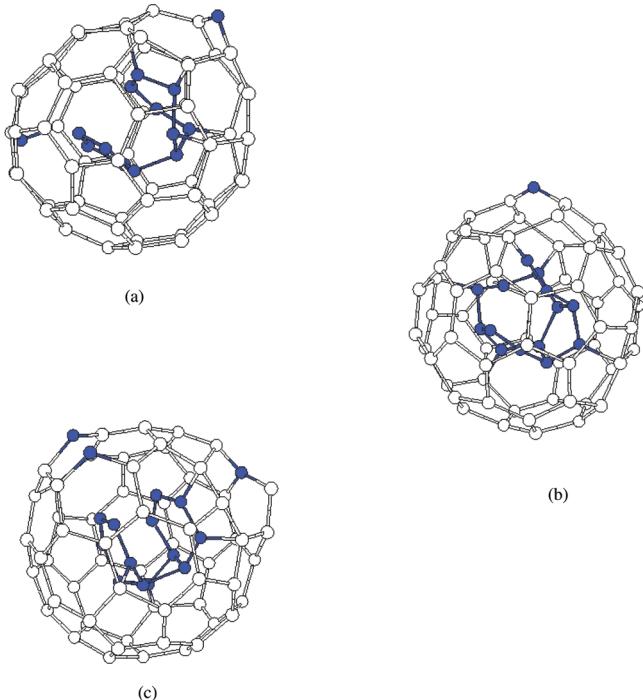
The optimized ground state structures of polynitrogen compounds inside  $C_{60}$  are shown in Figures 1–3. The ground state structures of polynitrogen clusters inside  $C_{60}$  along with their bond lengths and bond angles are shown in Figure 4. We started our calculation with a single nitrogen. The nitrogen was placed at different positions inside  $C_{60}$ , and the SCF total energy isosurface is explored throughout region inside  $C_{60}$ . We found the atomic nitrogen at the center to be a stable structure with small zero point vibrations. Since the atomic nitrogen is highly reactive, if we place nitrogen at a distance of more than 1.50 Å



**Figure 2.** Geometries of N<sub>n</sub>@C<sub>60</sub>: (a) N<sub>8</sub> exists as two planar rings of N<sub>4</sub> placed symmetrically and connected by a weak N–N bond (1.57 Å); (b) N<sub>9</sub> exists as two planar rings of N<sub>4</sub> and N<sub>5</sub> connected by a weak N–N bond (1.48 Å); (c) N<sub>10</sub> exists as two planar and slightly inclined pentagon rings connected by a weak N–N bond (1.50 Å); (d) N<sub>11</sub> exists as an interconnected structure of planar N<sub>5</sub> and nonplanar N<sub>6</sub> placed across the center; (e) N<sub>12</sub> exists as two symmetrically placed, boat-shaped hexagons connected by a N–N bond distance of 1.39 Å; (f) N<sub>13</sub> exists as an interconnected structure of planar N<sub>5</sub> and a heavily distorted N<sub>8</sub>; however, the less interstitial space inside C<sub>60</sub> forces the nitrogen atoms to make bonds with surface carbon atoms. The above structures of polynitrogen molecules in C<sub>60</sub> show nearly 50–60% single-bond character.

from the center of the cage, it has a tendency to form a weak covalent bond on the order of 1.54 Å with two adjacent carbon atoms of a hexagon–hexagon interface of the C<sub>60</sub> inner surface.<sup>68</sup> When two nitrogen atoms are placed inside C<sub>60</sub> at different positions, they form a N<sub>2</sub> molecule that is found to stabilize at the center of the C<sub>60</sub>. The resultant structure is a N<sub>2</sub> molecule with a N≡N bond distance of 1.12 Å, which is the same as in free space.

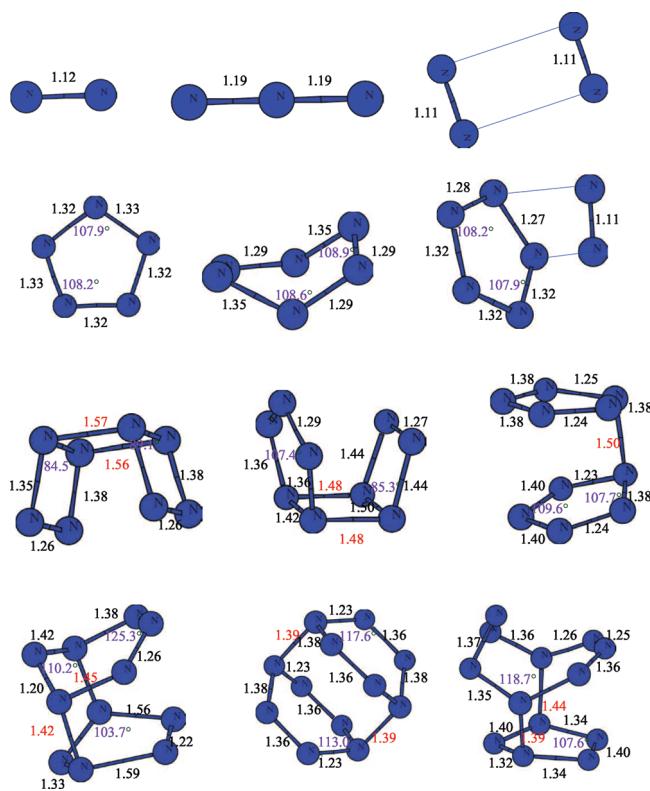
In N<sub>3</sub>@C<sub>60</sub>, N<sub>3</sub> in linear form with D<sub>∞h</sub> symmetry is found to be stable at the center with a N–N bond length of 1.19 Å. However, the triangular structure D<sub>3h</sub> is found to be another stable isomer inside C<sub>60</sub>. Interestingly, most of the initial N<sub>3</sub> configurations including the combination of N<sub>2</sub> and a single N at distance results in an isosceles triangular structure with bond lengths of 1.33 Å and 1.58 Å and bond angles 53.5° and 73.1° respectively. The energy difference between both the structures is on the order of 0.9 eV. N<sub>4</sub> is found to exist as two dimers of



**Figure 3.** (a) N<sub>14</sub>@C<sub>60</sub> exists as a distorted complex with N<sub>12</sub> existing as an interconnected structure of N<sub>5</sub> and N<sub>7</sub>. Two nitrogen atoms undergo chemisorption, resulting in 62 atom cages with the formation of two heptagons on the surface. (b) N<sub>15</sub>@C<sub>60</sub> does not show any pattern in the structure of the polynitrogen molecule. Hexagons and pentagons of C<sub>60</sub> show heavy distortion, with C–C bond distances increasing up to 1.65–1.67 Å, which is the breaking point for the C<sub>60</sub> cage. (c) N<sub>16</sub>@C<sub>60</sub> exists as a polymeric complex with three nitrogen atoms getting substituted at the surface and making a heptagon and octagon, which henceforth leads to the opening of the cage, indicating the threshold limit for nitrogen encapsulation at 0 K. In the above structures, due to less available space, nitrogen tends to make bonds with the surface atoms as well as undergoing chemisorption. These structures are unstable at room temperature.

N<sub>2</sub> with a bond length of 1.11 Å and placed at a distance of 2.26 Å symmetrically across the center of cage. The arrangement of two N<sub>2</sub> molecules on either side of the center of C<sub>60</sub> may be explained on the basis of extra stability of N<sub>2</sub> and its reluctance to form a lower-order bond. The structures with T<sub>d</sub> and D<sub>2h</sub> symmetry are found to be the other stable isomers. However, in the free state, N<sub>4</sub> has been predicted to be stable in C<sub>2h</sub>-T, T<sub>d</sub>, and D<sub>2h</sub> symmetries, respectively.<sup>69</sup> N<sub>5</sub> is found to be stable at center in a perfect pentagon shape having D<sub>5h</sub> symmetry with each bond length of 1.32 Å and a bond angle of 108.0°. We tried various initial configurations of N<sub>5</sub> (including dimers and single atom). It was observed that all the configurations lead to the formation of a pentagon structure, which may be due to the confined environment of the C<sub>60</sub>.

For n ≥ 6, different combinations of N, N<sub>2</sub>, N<sub>3</sub>, and higher polynitrogens were considered as separate substitutional identities in C<sub>60</sub>. We found an interesting pattern in the arrangement of the nitrogen atoms in polynitrogen compounds, which are very stable and are placed symmetrically across the center. The other observed isomeric structures, although stable, are found distinctly less stable by an energy difference of ~0.5–2.0 eV. The minimum energy configuration structure of N<sub>6</sub> comes out to be a boat-shaped cyclic ring with bond lengths on the order of 1.28–1.35 Å and bond angles of 108.8° and 122.5°. In the free state, N<sub>6</sub> is found to be stable in the hexaazadewarbenzene structure with C<sub>2v</sub> symmetry, which is also one of the stable isomers in confinement.<sup>70</sup>



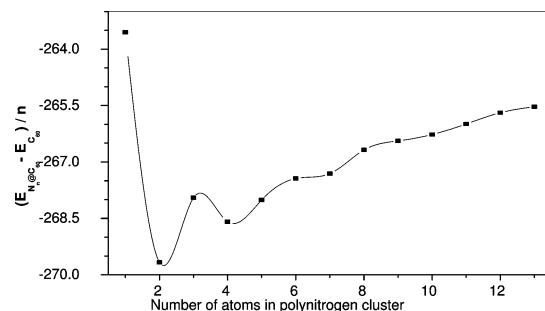
**Figure 4.** Geometries of polynitrogen clusters for  $n = 2\text{--}13$  inside a  $\text{C}_{60}$  cage along with the bond lengths (in black), connecting bonds (red), and bond angles (purple).

**TABLE 1: Bond Distances (in Å) for Polynitrogen Molecules Inside  $\text{C}_{60}$ <sup>a</sup>**

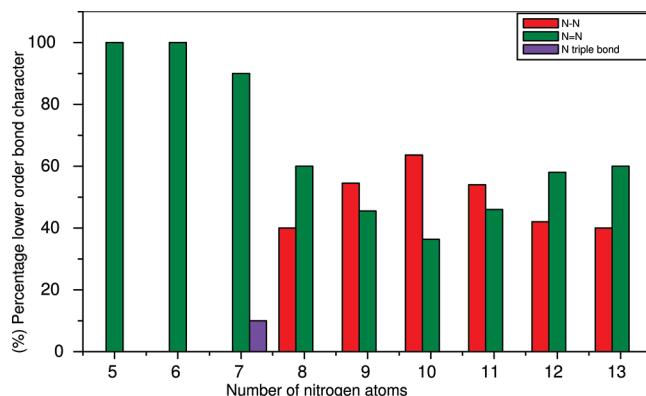
$\text{N}_n@\text{C}_{60}$	N—N	N= N	N≡ N	$E_{\text{N}_n@\text{C}_{60}}$ (eV)	$E_{\text{N}_n}$ (eV)
N@C <sub>60</sub>				-9490.2	-263.55
N <sub>2</sub> @C <sub>60</sub>			1.12	-9766.0	-539.35
N <sub>3</sub> @C <sub>60</sub>			1.18	-10030.5	-803.85
N <sub>4</sub> @C <sub>60</sub>			1.11	-10301.0	-1074.35
N <sub>5</sub> @C <sub>60</sub>	1.31–1.33			-10566.7	-1340.05
N <sub>6</sub> @C <sub>60</sub>	1.28–1.35			-10931.3	-1704.65
N <sub>7</sub> @C <sub>60</sub>	1.28–1.32	1.11		-11097.8	-1871.15
N <sub>8</sub> @C <sub>60</sub>	1.45–1.56	1.26–1.38		-11360.1	-2133.45
N <sub>9</sub> @C <sub>60</sub>	1.42–1.48	1.27–1.38		-11624.6	-2397.95
N <sub>10</sub> @C <sub>60</sub>	1.51	1.23–1.38		-11889.4	-2662.75
N <sub>11</sub> @C <sub>60</sub>	1.45–1.59	1.26–1.38		-12152.6	-2925.95
N <sub>12</sub> @C <sub>60</sub>	1.40	1.23–1.38		-12414.9	-3188.25
N <sub>13</sub> @C <sub>60</sub>	1.38–1.44	1.24–1.34		-12678.6	-3451.95

<sup>a</sup> The total energy ( $E_{\text{N}_n@\text{C}_{60}}$ ) of  $\text{N}_n@\text{C}_{60}$  complexes and nitrogen complex energy  $E_{\text{N}_n} = (E_{\text{total}} - E_{\text{C}_{60}})$  in electronvolts are tabulated. Total energies of  $\text{C}_{60}$  molecule and  $\text{N}_2$  are taken as -9226.65 and -538.84 eV, respectively.

$\text{N}_7$  is found to exist as an assembly of a pentagon with bond lengths 1.28–1.32 Å and a dimer having a bond length 1.11 Å as two separate units. The presence of  $\text{N}_5$  as an independent identity is responsible for lowering the energy of  $\text{N}_7@\text{C}_{60}$ , indicating its extra stability. However, one closed structure involving  $\text{N}_5$  and  $\text{N}_2$  does exist as a close energy isomer, as shown in Figure 1.  $\text{N}_8$  is found to exist in two planar rings having distinct bond lengths of 1.27, 1.38, 1.45, and 1.38 Å, which are connected together with a weak N—N bond of 1.57 Å.  $\text{N}_9$  exhibits a stable structure with  $\text{N}_5$  and  $\text{N}_4$  planar rings connected together with a bond of 1.48 Å. The bond lengths for both rings are in the range 1.27–1.50 Å.  $\text{N}_{10}$  forms a structure with two planar symmetrical pentagon rings on either side of center of the  $\text{C}_{60}$  ( $D_{5h}$  symmetry) connected to each other



**Figure 5.** The variation of total energy of  $\text{N}_n$  complexes inside a  $\text{C}_{60}$  cage per nitrogen atom vs number of atoms in a polynitrogen cluster.



**Figure 6.** The percentage of lower-order bond character of polynitrogen compounds encapsulated in a fullerene cage.

with a single bond of 1.50 Å. The  $\text{N}_{11}$  polynitrogen compound is also stable in a ring structure with one planar pentagon and one nonplanar hexagon connected by bond distances of 1.42 and 1.45 Å, respectively.  $\text{N}_{12}$  stabilizes itself symmetrically into two nonplanar, boat-shaped hexagons connected by a N—N bond of 1.39 Å.

For  $n > 12$ , the polynitrogen compounds do not show any symmetry in distribution of the nitrogen atoms due to the availability of less space. They make complex yet stable structures.  $\text{N}_{13}$  is found to exhibit a geometry with one planar pentagon connected to a nonplanar closed  $\text{N}_8$  ring with significant distortion on the  $\text{C}_{60}$  cage.  $\text{N}_{14}$  and  $\text{N}_{15}$  compounds make a distorted endohedral complex, with nitrogen undergoing chemisorption at the surface, breaking the surface C—C and C=C bonds and making a C—N bond of 1.36 Å. This leads to the formation of a heptagon in the cage, which results in a very large distortion, and the maximum and minimum diameters are 7.60 and 7.30 Å, respectively. At  $n = 16$ , the chemisorption of three nitrogen atoms results in the opening of the  $\text{C}_{60}$  cage.

In addition, to have an idea of the stabilization of polynitrogen clusters formed inside the  $\text{C}_{60}$  cage, we have calculated the total energy,  $E_{\text{N}_n@\text{C}_{60}}$ , of the polynitrogen complex (tabulated in Table 1). We have also listed the energy of the nitrogen complex ( $E_{\text{N}_n}$ ) alone by defining it as

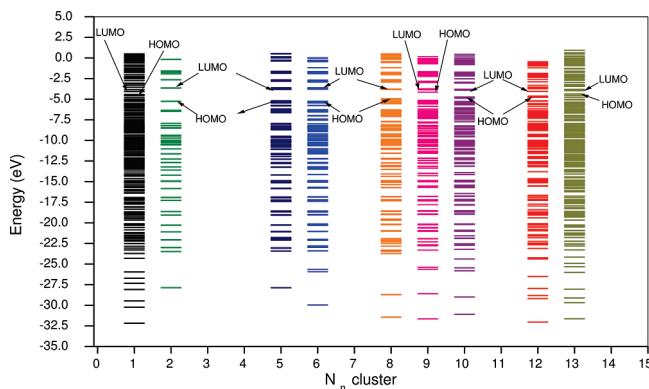
$$E_{\text{N}_n} = E_{\text{N}_n@\text{C}_{60}} - E_{\text{C}_{60}} \quad (1)$$

in Table 1. This energy per nitrogen atom as a function of the size of the polynitrogen cluster is plotted in Figure 5. It seems there is a systematic increase in nitrogen energy inside the  $\text{N}_n@\text{C}_{60}$  complexes, and there is a variation of  $\approx 5$  eV per N atom from the smallest cluster to the largest cluster inside  $\text{C}_{60}$ . Thus, bigger clusters tend to release energy on lowering the cluster size by each successive N atom by  $\approx 5$  eV.

**TABLE 2: HOMO, LUMO, HOMO–LUMO Gap ( $E_{\text{gap}}$ ), Spin Multiplicities ( $M$ ), and Net Charge ( $Q_n$ ) on the C<sub>60</sub> Cage for N<sub>*n*</sub>@C<sub>60</sub> Complexes<sup>a</sup>**

N <sub><i>n</i></sub> @C <sub>60</sub>	HOMO (eV)	LUMO (eV)	$E_{\text{gap}}$ (eV)	$M = (2s + 1)$	$Q_n$
N@C <sub>60</sub> (N at center)	-4.55	-3.68	0.87	4 [4(expt)]	
N@C <sub>60</sub> (N at the surface bonded)	-4.82	-4.54	0.29	2	+0.03
N <sub>2</sub> @C <sub>60</sub>	-5.26	-3.65	1.61	1	-0.05
N <sub>3</sub> @C <sub>60</sub>	-5.12	-3.74	1.45	2	+0.25
N <sub>4</sub> @C <sub>60</sub>	-5.21	-3.75	1.46	1	-0.02
N <sub>5</sub> @C <sub>60</sub>	-5.20	-3.81	1.39	2	+0.57
N <sub>6</sub> @C <sub>60</sub>	-5.26	-3.79	1.47	1	+0.05
N <sub>7</sub> @C <sub>60</sub>	-5.14	-3.85	1.29	2	+0.49
N <sub>8</sub> @C <sub>60</sub>	-4.94	-3.83	1.11	1	+0.20
N <sub>9</sub> @C <sub>60</sub>	-5.14	-4.14	1.00	2	+0.18
N <sub>10</sub> @C <sub>60</sub>	-4.73	-3.91	0.82	1	+0.31
N <sub>11</sub> @C <sub>60</sub>	-4.59	-3.97	0.62	2	-0.15
N <sub>12</sub> @C <sub>60</sub>	-4.64	-4.06	0.58	1	0.00
N <sub>13</sub> @C <sub>60</sub>	-4.37	-3.37	1.00	4	-0.48

<sup>a</sup> Charge loss/gain is denoted by positive/negative sign, respectively.



**Figure 7.** The Kohn–Sham energy eigen values for N<sub>*n*</sub> clusters (*n* = 1, 2, 5, 6, 8, 9, 10, 12, 13).

We have calculated the bond character in the polynitrogen clusters and identified all the distances as the following: the bond distance  $\geq 1.35 \text{ \AA}$  as N–N, distance  $\geq 1.25 \text{ \AA}$  as N=N, and in the range of 1.12–1.24 Å as the N≡N bond, although it is not easy to distinguish between the N–N and N=N bond character. As we can observe from Figure 6, most of the polynitrogen clusters stabilize in a mixture of N–N and N=N bond character. Only for *n* = 7, because of the splitting of N<sub>7</sub> into N<sub>5</sub> and N<sub>2</sub>, there is a formation of one triple bond.

The encapsulated polynitrogen clusters result in a distortion of the icosahedral symmetry of the C<sub>60</sub>, thereby altering the electronic properties of N<sub>*n*</sub>@C<sub>60</sub> significantly. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) gap are calculated from Kohn–Sham eigen values. The HOMO and LUMO levels and the HOMO–LUMO gap are tabulated in Table 2. The gap varies as a function of the number of nitrogen atoms, which shows a gradual decrease with higher values for *n* = 2, 4, 6, 8, 10. To visualize this, we have plotted the Kohn–Sham energy levels for N<sub>*n*</sub>@C<sub>60</sub> complexes in Figure 7. In addition, the electronic densities of states (EDOS) for the structures are shown in Figures 8 and 9, which shows a substantial difference between EDOS near the fermi level as a function of encapsulated cluster size. For odd *n*, the EDOS is significant at fermi level, whereas there is no EDOS at fermi level for even *n*. The innermost states are found to vary from -23.60 eV for C<sub>60</sub> to -25.23 eV for N@C<sub>60</sub>, -27.86 eV for N<sub>2</sub>@C<sub>60</sub>, -31.44 eV for N<sub>8</sub>@C<sub>60</sub>, and -32.03 eV for N<sub>12</sub>@C<sub>60</sub>.

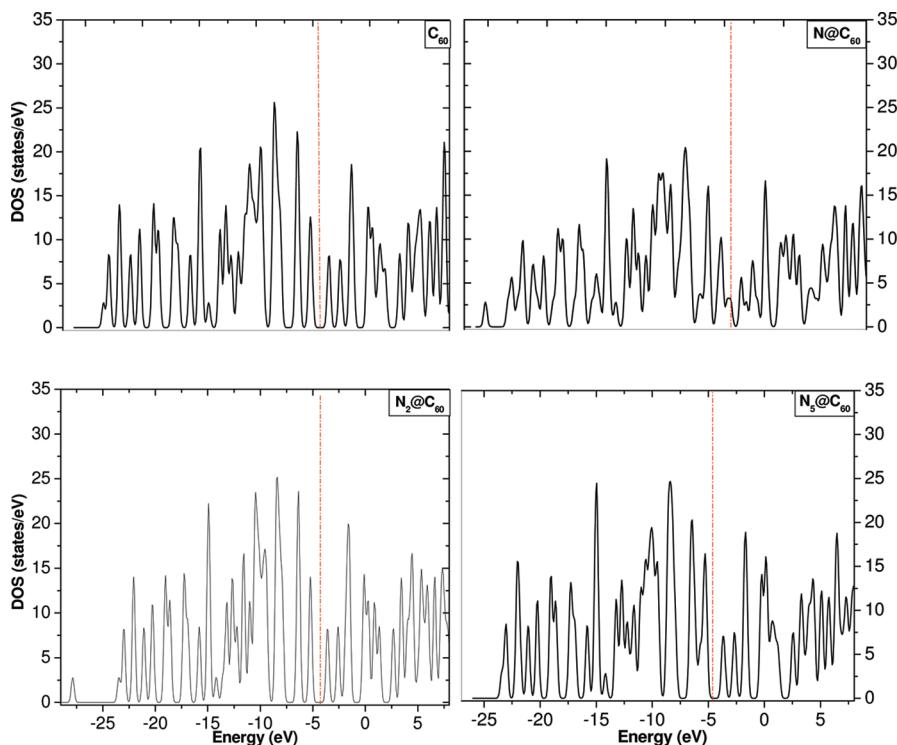
We carried out spin-polarized calculations on all the optimized geometries. Multiplicities defined as  $(2s + 1)$ , where *s* is the

spin of the system, are calculated from the difference of spin up and spin down electrons ( $Q(\uparrow) - Q(\downarrow)$ ) and are tabulated in Table 2.

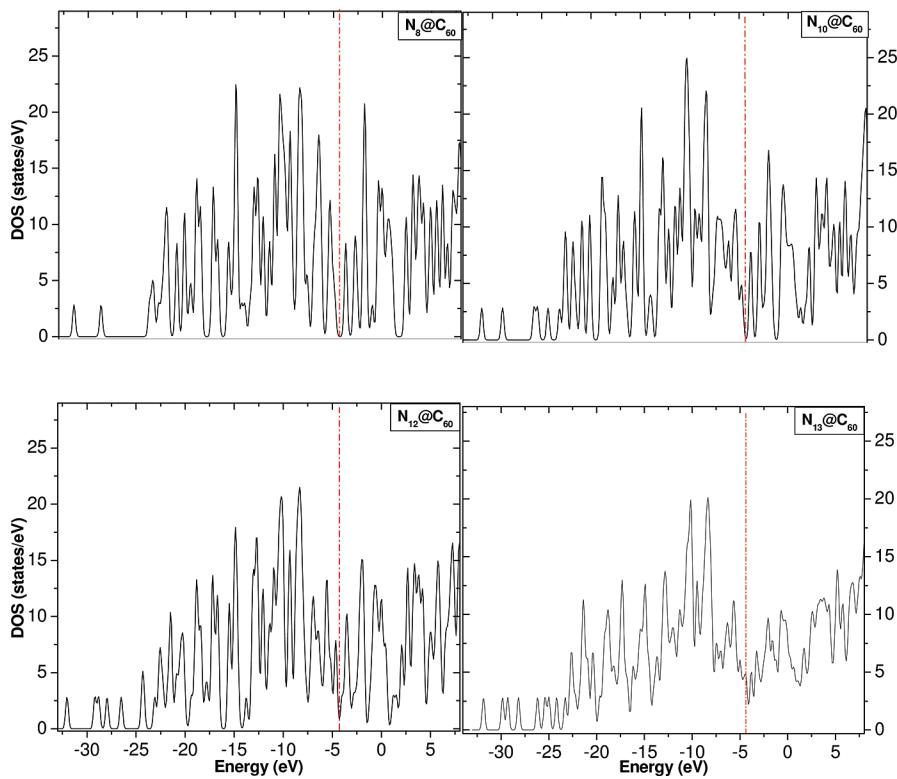
For N@C<sub>60</sub>, we found a spin quartet state when the N atom is placed at the center of the C<sub>60</sub> cage; that is, the N atom retains its atomic nature, which is consistent with the experimental ESR or EPR spectra of N@C<sub>60</sub>.<sup>45,51,53</sup> However, when the N atom moves toward the surface and makes a covalent bond with the cage, it shows a spin doublet state consistent with experimental results.<sup>68</sup> All the structures with even numbers of nitrogen atoms show spin doublet states (*s* = 1/2), whereas when odd numbers of nitrogen atoms are present, they show a spin singlet (*s* = 0) state, except for *n* = 13, which shows a spin quartet state (*s* = 3/2).

The net charge on the polynitrogen compounds and the fullerene cage atoms are investigated by Mulliken charge analysis, tabulated in Table 2. We mention here that charge transfers in SIESTA are dependent on the choice of basis set. Therefore, we carried out test calculations using SZ (single- $\zeta$ ), DZ (double- $\zeta$ ), and DZP (double- $\zeta$  with polarization) (with an energy shift ranging from 50 to 250 meV) basis sets on N@C<sub>60</sub>. It was observed that using SZ basis N shows a small charge loss of 0.04 electrons to the C<sub>60</sub> cage, whereas when using the DZ and DZP basis, N shows a small charge gain from the cage. The magnitude of charge transfer is found to be higher when DZ is used, as compared to that using DZP. Within the DZP basis set, as we increase the energy shift, the Mulliken charge on N tends to increase marginally from 0.027 (energy shift 50 meV) to 0.040 (250 meV). Our work on azafullerenes using the DZP basis set produced reliable charge transfers in C<sub>60-n</sub>N<sub>*n*</sub>,<sup>57</sup> and it reproduced the experimental parameters of C<sub>60</sub> and N<sub>2</sub> very accurately.

For N@C<sub>60</sub>, the small charge transfer of 0.04 electrons from the cage to N at the center is found to be consistent with a spin quartet state, as obtained using spin-polarized calculations. However, there are conflicting claims regarding charge transfers in N@C<sub>60</sub> using various ab initio calculations. Kobayashi et al.<sup>71</sup> using the 6-31G(d) basis set and B3LYP functional has reported a slightly larger spin density at N in N@C<sub>60</sub> than in N@C<sub>70</sub>, which is consistent with observed hyperfine coupling constants. Lu et al.<sup>72</sup> using a user-defined basis set (considering 2s and 2p for C and N) and carrying discrete variational local density functional calculations, had reported a charge transfer of 0.11 from the C<sub>60</sub> cage to the N atom at the center. In addition, Mauser et al.,<sup>68</sup> using a semiempirical method and DFT(B3LYP)



**Figure 8.** Electronic densities of states (DOS) for  $C_{60}$ ,  $N@C_{60}$ ,  $N_2@C_{60}$ , and  $N_5@C_{60}$ .



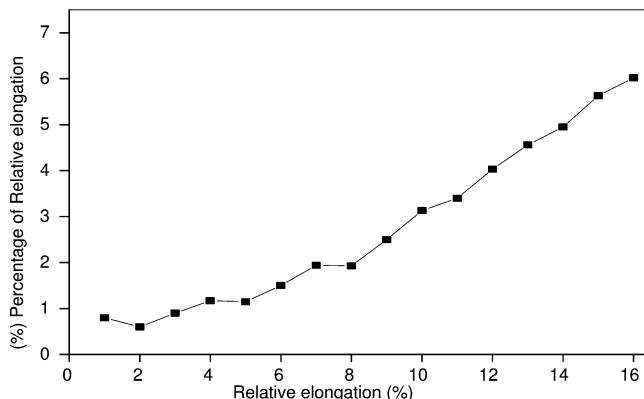
**Figure 9.** Electronic densities of states (DOS) for  $N_8@C_{60}$ ,  $N_{10}@C_{60}$ ,  $N_{12}@C_{60}$ , and  $N_{13}@C_{60}$ .

and Greer<sup>73</sup> using a spin-unrestricted DFT have predicted no charge transfer between the N and  $C_{60}$ .

For  $n = 2$ –10, we found a charge transfer from the cage to  $N_n$ , which may be explained on the basis of the higher values of electronegativity and ionization potential for N than for C atoms. The Mulliken charge calculation suggests an electron charge transfer ranging between 0.05 and 0.57 from carbon atoms to the polynitrogen compounds inside up to  $n = 10$ , except for  $N_2$  which shows an inverse nature. For  $n > 10$ , a

charge transfer of 0.05–0.48 electrons takes place from the nitrogen to the carbon atoms of fullerene. This reversal can be attributed to the reduced space availability and overlapping of orbitals, which may be further responsible for destabilizing the polynitrogen compounds beyond  $n = 13$ . As per our information, to date, there are no references for comparison to any theoretical work on polynitrogen clusters in the  $C_{60}$ .

From the structural analysis of all the  $N_n@C_{60}$  structures and their isomers, it may be concluded that N atoms have preferential



**Figure 10.** The percentage relative elongation of polynitrogen compounds as a function of the number of nitrogen atoms.

sites for stabilization inside fullerenes. Moreover, due to confinement, the nitrogen atoms are forced to form lower-order bonds. We found that the threshold size of polynitrogen compounds to exist inside as a stable molecule is N<sub>13</sub>. Any further addition of nitrogen inside leads to the formation of a C–N bond and a heptagon involving a nitrogen atom on the surface.

The structural distortion expressed in terms of elongation, defined as  $\varepsilon = R/(R_0 - 1)$ , where  $R$  and  $R_0$  are the average radii of expanded and pure C<sub>60</sub>, is shown in Figure 10. The percentage elongation shows a linear increase with the number of nitrogen atoms up to N<sub>15</sub>, except for N<sub>2</sub>, which shows a small contraction in the C<sub>60</sub> cage. The maximum threshold elongation is ~6% for N<sub>15</sub>. Indeed, this elongation leads to estimation of extra pressure. Successive addition of nitrogen atoms exerts this extra pressure from within when their number is increased beyond 2 until the stability limit of C<sub>60</sub> is reached. In addition, the stability of each structure is verified by displacing the nitrogen atoms up to 0.5 Å. Observing the result, we find that after relaxing the structure, it regains its optimized form. Moreover, harmonic vibrational frequency analysis is carried out on all the ground state structures, and the absence of any imaginary frequency value further verifies the true energy minima.

We performed constant-temperature, constant-volume molecular dynamics for N<sub>n</sub>@C<sub>60</sub> at a temperature of 300 K with a time period 10 ps and interval of 1 fs. It was observed that for  $n \leq 12$ , the polynitrogen structures remain intact and do not show any significant deviation from their structures at 0 K, which demonstrates the stability of the polymeric nitrogen structures. For  $n \geq 13$ , however, the C<sub>60</sub> cage opens up due to formation of C–N bonds as a result of thermal vibrations. Interestingly, apart from the addition of N atoms beyond N<sub>13</sub> resulting in destabilization of the cage, our calculations further suggest that the presence of a single water molecule or a few O and H atoms inside the cage results in destabilization of N<sub>n</sub>@C<sub>60</sub> for  $n = 5–8$ . However, more calculations are required to fully understand the nature of cage breaking for  $n < 12$ .

The experimental synthesis of these novel hybrid systems would be a challenging task due to the explosive nature of nitrogen-rich compounds. However, in the literature, various methods have been reported to try to incorporate nitrogen inside CNTs, such as magnetron sputtering,<sup>74</sup> laser ablation,<sup>75,76</sup> pyrolysis of mixtures of organometallic and nitrogen-containing organic compounds,<sup>77,78</sup> and chemical vapor deposition (CVD) of nitrogen-containing hydrocarbons over heterogeneous iron, cobalt, or nickel catalysts.<sup>79,80</sup> From the above-mentioned

methods, it was confirmed that it is rather difficult to obtain uniform NCNT (nitrogen-containing CNT) with a high nitrogen concentration, that is, above 20%, with conventional techniques such as CVD. For a non-CVD synthesis of CNTs, N-rich energetic compounds, such as 3,6-diazido-1,2,4,5-tetrazine and 4,4,6,6-tetraazido-2,2-azo-1,3,5-triazine compounds, can be used.<sup>81</sup> Depending on the different heating processes,<sup>55,82</sup> the thermal decomposition of these compounds can yield N-rich nanolayered, nanoclustered, and nanodendritic carbon nitrides.

#### IV. Conclusions

The polynitrogen compounds formed inside C<sub>60</sub> are found to be quite stable in confinement. The energy difference of the optimized ground state geometries to the isomeric states is found to be significant, thereby indicating a clear choice of ground state structures. The spin states of N<sub>n</sub>@C<sub>60</sub> are found to be quartet for  $n = 1$  and  $n = 13$ , doublet for other odd  $n$ , and singlet for even  $n$ . The reversal of polarization and the space available inside C<sub>60</sub> may be responsible for determining the amount of nitrogen encapsulation inside a fullerene. Therefore, the C<sub>60</sub> cage could provide an ideal environment for stabilizing other reactive species that are otherwise less stable in free space. The maximum number of nitrogen atoms that can be encapsulated inside C<sub>60</sub> is 13, which can form a stable structure at 0 K. The endohedral molecules N<sub>n</sub>@C<sub>60</sub> for  $n \leq 12$  are found to retain their structure at room temperature. It is significant to observe that larger clusters inside the C<sub>60</sub> cage raise the energy of the cluster, indicating the possibility of releasing energy by going to much more stable configurations in lower clusters.

**Acknowledgment.** The authors are thankful to the SIESTA group for providing their computational code and greatly acknowledge the computational support provided by Prof. D. G. Kanhere, University of Pune, Pune. Isha Garg is thankful to the University Grants Commission, New Delhi for providing financial support.

#### References and Notes

- Klapotke, T. M. *Structure and Bonding-High Energy Density Materials*; Springer: New York, 2007, 125.
- Haskins, P. J.; Fellows, J.; Cook, M. D.; Wood, A. *Molecular Level Studies of Polynitrogen Explosives Proceedings 12th International Detonation Symposium*, San Diego, California, August 11–16, 2002.
- Boates, B.; Bonev, S. A. *Phys. Rev. Lett.* **2009**, *102*, 015701-4.
- Mukherjee, G. D.; Boehler, R. *Phys. Rev. Lett.* **2007**, *99*, 225701-4.
- Trojan, I. A.; Eremets, M. I.; Medvedev, S. A.; Gavriliuk, A. G.; Prakapenka, V. B. *Appl. Phys. Lett.* **2008**, *93*, 0919071-3.
- Zahariev, F.; Dudiy, S. V.; Hooper, J.; Zhang, F.; Woo, T. K. *Phys. Rev. Lett.* **2006**, *97*, 1555031-4.
- Christe, K. O.; Wilson, W. W.; Sheehy, J. A.; Boatz, J. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2004–9.
- Vij, A.; Wilson, W. W.; Vij, V.; Tham, F. S.; Sheehy, J. A.; Christe, K. O. *J. Am. Chem. Soc.* **2001**, *123*, 6308–13.
- Shi, L. W.; Chen, B.; Zhou, J.-H.; Zhang, T.; Kang, Q.; Chen, M.-B. *J. Phys. Chem. A* **2008**, *112* (46), 11724–30.
- Leininger, M.; Van Huis, T. J.; Schaefer, F. H. *J. Phys. Chem. A* **1997**, *101*, 4460–4.
- Ball, W. D. *J. Phys. Chem. A* **2001**, *105* (2), 465–70.
- Schulz, A.; Tornieporth-Oetting, I. C.; Klapotke, M. T. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1610–12.
- Nguyen, M. T.; Ha, T. K. *Chem. Ber.* **1996**, *129*, 1157–9.
- Cacace, F.; de Petris, G.; Troiani, A. *Science* **2002**, *295*, 480–1.
- Hammerl, A.; Klapotke, T. M. *Inorg. Chem.* **2002**, *41*, 906–12.
- Li, P. C.; Guan, J.; Li, S.; Quian, S. L.; Wen, G. X. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1116–22.
- Cheng, L.; Li, Q.; Xu, W.; Zhan, S. *J. Mol. Model.* **2003**, *9*, 99–107.
- Liu, Y. D.; Yiu, P. G.; Guan, J.; Li, Q. S. *J. Mol. Struct. (THEOCHEM)* **2002**, *588*, 37–43.

- (19) Zhou, H.; Wong, N.-B.; Zhou, G.; Tian, A. *J. Phys. Chem. A* **2006**, *110*, 7441–6.
- (20) Zhou, H.; Wong, N.-B.; Zhou, G.; Tian, A. *J. Phys. Chem. A* **2006**, *110*, 3845–52.
- (21) Zhou, G.; Pu, X.-M.; Wong, N.-B.; Tian, A.; Zhou, H. *J. Phys. Chem. A* **2006**, *110*, 4107–14.
- (22) Wang, L. J.; Zgierski, M. Z. *Chem. Phys. Lett.* **2003**, *376*, 698–03.
- (23) Strout, D. L. *J. Phys. Chem. A* **2005**, *109*, 1478–80.
- (24) Wang, J. L.; Lushington, G. H.; Mezey, P. G. *J. Chem. Inf. Model.* **2006**, *46*, 1965–71.
- (25) Wang, L.; Mezey, P. G. *J. Phys. Chem. A* **2005**, *109*, 3241–3.
- (26) Zhao, J. F.; Li, Q. S. *Chem. Phys. Lett.* **2003**, *368*, 12–19.
- (27) Wang, L. J.; Mezey, P. G.; Zgierski, M. Z. *Chem. Phys. Lett.* **2004**, *391*, 338–43.
- (28) Li, Q. S.; Zhao, J. F. *J. Phys. Chem. A* **2002**, *106*, 5367–72.
- (29) Wang, L. J.; Warburton, P.; Mezey, P. G. *J. Phys. Chem. A* **2002**, *106*, 2748–52.
- (30) Dixon, D. A.; Feller, D.; Christe, K. O.; Wilson, W. W.; Vij, A.; Vij, V.; Vij, H.; Jenkins, D. B.; Olson, R. M.; Gordon, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 834–43.
- (31) Reichlin, R.; Schiferl, D.; Martin, S.; Vanderborgh, C.; Mills, R. L. *Phys. Rev. Lett.* **1985**, *55*, 1464–7.
- (32) Bini, R.; Ulivi, L.; Kreutz, J.; Jodl, H. L. *J. Chem. Phys.* **2000**, *112*, 8522–9.
- (33) Olijnyk, H.; Jephcoat, A. P. *Phys. Rev. Lett.* **1999**, *83*, 332–5.
- (34) Mitas, L.; Martin, R. M. *Phys. Rev. Lett.* **1994**, *72*, 2438–41.
- (35) Mailhiot, C.; Yang, L. H.; McMahan, A. K. *Phys. Rev. B* **1992**, *46*, 14419–35.
- (36) Lewis, S. P.; Cohen, M. L. *Phys. Rev. B* **1992**, *46*, 11117–20.
- (37) Martin, R. M.; Needs, R. J. *Phys. Rev. B* **1986**, *34*, 5082–92.
- (38) Eremets, M. I.; Gavriliuk, A. G.; Trojan, I. A.; Dzivenko, D. A.; Boehler, R. *Nat. Mater.* **2004**, *3*, 558–63.
- (39) Mattson, W. D.; Sanchez-Portal, D.; Chiesa, S.; Martin, R. M. *Phys. Rev. Lett.* **2004**, *93*, 125501–4.
- (40) Abou-Rachid, H.; Hu, A.; Timosheskii, V.; Song, Y.; Lussier, L. S. *Phys. Rev. Lett.* **2008**, *100*, 196401–4.
- (41) Bajwa, N.; Ingale, A.; Avasthi, D. K.; Ravi, K.; Tripathi, A.; Dharamvir, K.; Jindal, V. K. *J. Appl. Phys.* **2008**, *104*, 054306–13.
- (42) Kaur, N.; Gupta, S.; Dharamvir, K.; Jindal, V. K. *Carbon* **2008**, *46*, 349–58.
- (43) Kaur, N.; Dharamvir, K.; Jindal, V. K. *Chem. Phys.* **2008**, *344*, 176–84.
- (44) Kaur, N.; Gupta, S.; Dharamvir, K.; Jindal, V. K. Proceedings of the 26th International Symposium on Shock Waves ISSW26, Gottingen, Germany, Springer-Verlag: New York, July 15–20, 2007.
- (45) Waiblinger, M.; Lips, K.; Harneit, W.; Weidinger, A. *Phys. Rev. B* **2001**, *63*, 045421–5.
- (46) Weiden, N.; Goedde, B.; Kass, H.; Dinse, K.-P. *Phys. Rev. Lett.* **2000**, *85*, 1544–7.
- (47) Hebard, A. F.; Rosseinsky, M. J.; Haddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. T. M.; Ramirez, A. P.; Kortan, A. R. *Nature* **1991**, *350*, 600–1.
- (48) Bethune, D. S.; Johnson, R. D.; Salem, J. R.; de Vries, M. S.; Yannoni, C. S. *Nature* **1993**, *366*, 123–8.
- (49) Sanville, E.; Bel Bruno, J. J. *J. Phys. Chem. B* **2003**, *107*, 8884–9.
- (50) Ciosowski, J.; Nanayakkara, A. *Phys. Rev. Lett.* **1992**, *69*, 2871–3.
- (51) Dietel, E.; Hirsch, A.; Pietzak, B.; Waiblinger, M.; Lips, K.; Weidinger, A.; Gruss, A.; Dinse, K.-P. *J. Am. Chem. Soc.* **1999**, *121*, 2432–7.
- (52) Murphy, T. A.; Pawlik, T.; Weidinger, A.; Hohne, M.; Alcalá, R.; Spaeth, J.-M. *Phys. Rev. Lett.* **1996**, *77*, 1075–8.
- (53) Dinse, K.-P. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5442–7.
- (54) Knapp, C.; Dinse, K.-P.; Pietzak, B.; Waiblinger, M.; Weidinger, A. *Chem. Phys. Lett.* **1997**, *272*, 433–7.
- (55) Peres, T.; Cao, B.; Cui, W.; Khong, A., Jr.; Cross, J. R.; Saunders, M.; Lifshitz, C. *Int. J. Mass Spectrometry* **2001**, *210/211*, 241–7.
- (56) Slanina, Z.; Pulay, P.; Nagase, S. *J. Chem. Theory Comput.* **2006**, *2*, 782–5.
- (57) Sharma, H.; Garg, I.; Dharamvir, K.; Jindal, V. K. *J. Phys. Chem. A* **2009**, *113*, 9002–13.
- (58) Ordejon, P.; Artacho, E.; Soler, J. M. *Phys. Rev. B (Rapid Commun.)* **1996**, *53*, R10441–4.
- (59) Soler, J. M.; Artacho, E.; Gale, J. D.; Garcia, A.; Junquera, J.; Ordejon, P.; Sanchez-Portal, D. *J. Phys.: Condens. Matter* **2002**, *14*, 2745–79.
- (60) Junquera, J.; Paz, O.; Sanchez-Portal, D.; Artacho, E. *Phys. Rev. B* **2001**, *64*, 235111–19.
- (61) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–9.
- (62) Kleinman, L.; Bylander, D. M. *Phys. Rev. Lett.* **1982**, *48*, 1425–8.
- (63) Sankey, O. F.; Niklewski, D. J. *Phys. Rev. B* **1989**, *40*, 3979–95.
- (64) Johnson, R. D.; Meijer, G.; Bethune, D. S. *J. Am. Chem. Soc.* **1990**, *112*, 8983–4.
- (65) Hertel, I. V.; Steger, H.; deVries, J.; Weisser, B.; Menzel, C.; Kamke, B.; Kamke, W. *Phys. Rev. Lett.* **1992**, *68*, 784–7.
- (66) Lichtenberger, D. L.; Jatcko, M. E.; Nebesny, K. W.; Ray, C. D.; Huffman, D. R.; Lamb, L. D. *Chem. Phys. Lett.* **1991**, *176*, 203–8.
- (67) Utterback, N. G.; Miller, G. H. *Phys. Rev.* **1996**, *124*, 1477–81.
- (68) Mauser, H.; Nicolaas, J. R.; van Hommes, E.; Clark, T.; Hirsch, A.; Pietzak, B.; Weidinger, A.; Dunsch, L. *Angew. Chem., Int. Ed.* **1997**, *36*, 2835–8.
- (69) Nguyen, M. T. *Chem. Rev.* **2003**, *244*, 93–113.
- (70) Tobita, M.; Bartlett, R. J. *J. Phys. Chem.* **2001**, *105*, 4107–13.
- (71) Kobayashi, K.; Nagase, S.; Dinse, K.-P. *Chem. Phys. Lett.* **2003**, *377*, 93–8.
- (72) Lu, J.; Zhang, X.; Zhao, X. *Chem. Phys. Lett.* **1999**, *312*, 85–90.
- (73) Greer, J. C. *Chem. Phys. Lett.* **2000**, *326*, 567–72, 767–774.
- (74) Suenaga, K.; Johansson, M. P.; Hellgren, N.; Broitman, E.; Wallenberg, L. R.; Collie, C.; Sundgren, J.-E.; Hultman, L. *Chem. Phys. Lett.* **1999**, *300*, 695–700.
- (75) Hellgren, N.; Johansson, M. P.; Broitman, E.; Hultman, L.; Sundgren, J. E. *Phys. Rev. B* **1999**, *59* (7), 5162–9.
- (76) Le Normand, F.; Hommet, J.; Szorenyi, T.; Fuchs, C.; Fogarassy, E. *Phys. Rev. B* **2001**, *64*, 2354161–15.
- (77) Choi, H. C.; Park, J.; Kim, B. J. *J. Phys. Chem. B* **2005**, *109*, 4333–40.
- (78) Glerup, M.; Castignolles, M.; Holzinger, M.; Hug, G.; Loiseau, A.; Bernier, P. *Chem. Commun.* **2003**, 2542–3.
- (79) van Dommelen, S.; Romero-Izquierdo, A.; Brydson, R.; de Jong, K. P.; Bitter, J. H. *Carbon* **2008**, *46*, 138–148.
- (80) Tang, C.; Bando, Y.; Goldberg, D.; Xu, F. *Carbon* **2004**, *42*, 2625–33.
- (81) Ye, C.; Gao, H.; Boatz, J. A.; Drake, G. W.; Twamley, B.; Shreeve, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7262–65.
- (82) Huynh, M. H.; Hisky, M. A.; Archuleta, J. G.; Roemer, E. L.; Gilardi, R. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 737–39.

JP908755R