Electronic, vibrational and magnetic properties of a novel C_{48}N_{12} aza-fullerene

Rui-Hua Xie and Garnett W. Bryant
National Institute of Standards and Technology, Gaithersburg, MD 20899-8423, USA
Vedene H. Smith, Jr.
Department of Chemistry, Queen’s University, Kingston, ON K7L 3N6, Canada
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We study the structural, electronic, vibrational and magnetic properties of a novel C_{48}N_{12} aza-fullerene using density functional theory and restricted Hartree-Fock theory. Optimized geometries and total energy of this fullerene have been calculated. We find that for C_{48}N_{12} the total ground state energy is about -67617 eV, the HOMO-LUMO gap is about 1.9 eV, five strong IR spectral lines are located at the vibrational frequencies, 461.5 cm\(^{-1}\), 568.4 cm\(^{-1}\), 579.3 cm\(^{-1}\), 1236.1 cm\(^{-1}\), 1338.9 cm\(^{-1}\), the Raman scattering activities and depolarization ratios are zero, and 10 NMR spectral signals are predicted. Calculations of diamagnetic shielding factor, static dipole polarizabilities and hyperpolarizabilities of C_{48}N_{12} are performed and discussed. Our results suggest that C_{48}N_{12} may have potential applications as semiconductor components and possible building materials for nanometer electronics, photonic devices and diamagnetic superconductors.

Since the discovery of C_{60} [1], doped fullerenes have attracted a great deal of interest in the research community of physics, chemistry and material engineering due to their remarkable structural, electronic, optical and magnetic properties [2–5]. For example, it has been shown that the doped fullerenes can exhibit large third-order optical nonlinearities and be ideal candidates as photonic devices including all-optical switching, data processing and eye and sensor protection [4]. Another example is alkali-doped C_{60} crystals, which can become superconductors [6,7], for example, at a critical temperature T\(_c\) = 30 K [6]. Besides the alkali metal doping, there is also another type of doping, named substitute doping [2–5], i.e., substituting one or more carbon atoms of fullerenes by other atoms. Over the past 10 years, boron and nitrogen atoms have been successfully used to replace carbon atoms of C_{60} and synthesize many kinds of doped C_{60} molecules, C_{60-}\text{m-nX_{m}Y_{n}} [2–5,8]. A very efficient method of synthesizing C_{59}N has been recently developed by Hummelen et al. [9]. Their method has led to a number of detailed studies of the physical and chemical properties of C_{59}N [3–5], which suggests that the new type of substituted fullerenes may be used as semiconductor components and possible building materials for future nanometer electronics since their band gaps and electronic polarizations can vary with different substitute doping [2–5].

Very recently, C_{60} with more than one nitrogen atom replacing a carbon atom in the cage has been synthesized by Hultman et al. [10]. They reported the existence of a novel C_{48}N_{12} aza-fullerene [10,11], which has one nitrogen atom per pentagon and the symmetry of the S_6 point group. Hence, it would be interesting and significant to investigate and predict the structural, electronic, vibrational and magnetic properties of this new aza-fullerene from the viewpoint of practical applications. This forms the purpose of the present paper. In the following, we report ab initio calculations of the optimized geometric structure, electronic properties, vibrational frequencies, IR spectra, NMR shielding tensors, diamagnetic shielding factor, static dipole polarizabilities and hyperpolarizabilities of the stable C_{48}N_{12} aza-fullerene. Our results suggest that C_{48}N_{12} may have potential applications as semiconductor components and possible building materials for nanometer electronics and diamagnetic superconductors.

\[\text{FIG.1: C}_{48}\text{N}_{12} \text{geometry structure obtained from ab initio B3LYP geometry optimizations with a 6-31G basis set. The center numbers }\{5, 9, 14, 21, 26, 30, 35, 39, 45, 50, 55, 60\} \text{are for nitrogen atoms and the others for carbon atoms.}\]
Full geometry optimization and total energy calculation of \( \text{C}_{48}\text{N}_{12} \) were performed by using the NWChem program [12,13], where we have employed the B3LYP [14] hybrid density functional theory (DFT) method that includes a mixture of Hartree-Fock (exact) exchange, Slater local exchange [15], Becke 88 non-local exchange [16], the VWN III local exchange-correlation functional [17] and the LYP correlation functional [18]. Throughout the split-valence 6-31G basis set is used in our calculations. All results are calculated to machine precision. As will be discussed later, the best total energy calculations with other basis sets differ from the 6-31G basis set results by less than one percent. This should define the accuracy of our calculations.

The optimized geometric structure of \( \text{C}_{48}\text{N}_{12} \) is presented in Fig.1. As shown by Hultman et al. [10], the \textit{ab initio} calculations show that there is only one nitrogen atom per pentagon and two nitrogen atoms preferentially sit together in one hexagon. The symmetry of the stable isomer of \( \text{C}_{48}\text{N}_{12} \) is the \( \text{S}_6 \) point group [11]. The radial distance \( R_i \) from the \( i \)-th atom to the center (i.e., the origin) of \( \text{C}_{48}\text{N}_{12} \) is listed in Table I. We find that there are 10 different radii, which suggest that \( \text{C}_{48}\text{N}_{12} \) is an ellipsoid structure, different from \( \text{C}_{60} \) where each carbon atom has equal radial distance from the center.

\[
\text{Table I: Calculated net Mulliken charges } Q_i \quad (q = 1.602 \times 10^{-19}), \text{ electrostatic potential } V_i \quad (v = 2.7209 \times 10^4), \text{ electron density } \rho_i \quad (\eta = 1.08 \times 10^{12}) \text{ and radial distance } R_i \text{ at the atom center number } n_i \text{ in } \text{C}_{48}\text{N}_{12} \text{ by using B3LYP hybrid DFT method with a split-valence 6-31G basis set.}
\]

| \(n_i\) | Atom | \(Q_i/q\) | \(V_i/v\) | \(\rho_i/\eta\) |
|------|------|-----------|----------|----------|
| \{ 8, 20, 22, 44, 46, 56\} | C | 0.3495 | 0.262 | -14.6663 | 117.999 |
| \{ 10, 17, 25, 41, 49, 59\} | C | 0.3508 | 0.255 | -14.6674 | 118.029 |
| \{ 4, 15, 27, 34, 40, 54\} | C | 0.3541 | 0.249 | -14.6679 | 118.027 |
| \{ 1, 13, 16, 31, 38, 51\} | C | 0.3535 | 0.215 | -14.6686 | 118.058 |
| \{ 7, 19, 23, 43, 47, 57\} | C | 0.3448 | 0.210 | -14.6631 | 118.004 |
| \{ 6, 18, 24, 42, 48, 58\} | C | 0.3470 | 0.199 | -14.6694 | 117.992 |
| \{ 2, 12, 29, 32, 37, 52\} | C | 0.3545 | 0.002 | -14.7041 | 118.109 |
| \{ 3, 11, 28, 33, 36, 53\} | C | 0.3549 | -0.017 | -14.7026 | 118.103 |
| \{ 5, 14, 30, 35, 39, 55\} | N | 0.3595 | -0.669 | -18.2639 | 191.331 |
| \{ 9, 21, 26, 45, 50, 60\} | N | 0.3531 | -0.705 | -18.2547 | 191.325 |
| Carbon atoms in \( \text{C}_{60} \) | C | 0.3535 | 0 | -14.7146 | 118.181 |

The net Mulliken charges of carbon and nitrogen atoms in \( \text{C}_{48}\text{N}_{12} \) are listed in Table I. It is found that there are two types of nitrogen atoms in the structure. The net Mulliken charges on the two types of nitrogen atoms are \(-0.67\) \( q \) and \(-0.71\) \( q \). The carbon atoms separate into two groups, one-fourth of the carbon atoms having net Mulliken charges in the range of \(-0.02\) \( q \) to \( 0.01\) \( q \) and the remaining three-fourth in the range of \( 0.19\) \( q \) to \( 0.27\) \( q \). Although the Mulliken analysis cannot estimate the atomic charges quantitatively, their signs can be estimated [19]. From these results, we find that the doped nitrogen atom exists as an electron acceptor whose net Mulliken charge is negative, and \( 7/8 \) of the carbon atoms as electron donors whose net Mulliken charges are positive. We should mention that we also performed calculations of net Mulliken charges of carbon and boron atoms in \( \text{C}_{48}\text{B}_{12} \). It is found that the doped boron atom exists as an electron donor and carbon atom as an electron acceptor (more detailed results for \( \text{C}_{48}\text{B}_{12} \) will be reported in another paper [20]), which is consistent with the experimental result [8]. Therefore, \( \text{C}_{48}\text{N}_{12} \) and \( \text{C}_{48}\text{B}_{12} \) have opposite electronic polarizations, while \( \text{C}_{60} \) is isotropic. In the case of doping into silicon, we know that the doped phosphorous (the V family in the periodic table) exists as a donor, while the doped boron (the III family) exists as an electron acceptor. Thus, the results for \( \text{C}_{48}\text{N}_{12} \) and \( \text{C}_{48}\text{B}_{12} \) differ greatly from that for silicon. We propose that \( \text{C}_{48}\text{N}_{12} \) and \( \text{C}_{48}\text{B}_{12} \) may be important components of semiconductors with opposite electronic polarizations.

The optimized C-C and C-N bond lengths in \( \text{C}_{48}\text{N}_{12} \) are listed in Table II. We find that there are six different C-N bond lengths and nine different C-C bond lengths, which are in agreement with the calculations of Staafström et al. [11]. The calculated C-C bond lengths in \( \text{C}_{60} \) are also shown in Table II. It is seen that \( \text{C}_{60} \) has only two kinds of bond lengths, i.e., one single C-C bond with \( 0.14445\) nm and one double bond with \( 0.13944\) nm, which are in good agreement with the results measured by neutron scattering (0.145 nm and 0.1391 nm) [21] or nuclear magnetic resonance (0.146 nm and 0.140 nm) [22]. It is obvious that most of C-C bond lengths in \( \text{C}_{48}\text{N}_{12} \), due to the electronic polarizations, are different from those in \( \text{C}_{60} \).

The distribution of bond angles (C-C-C, C-N-C, C-C-N) in \( \text{C}_{48}\text{N}_{12} \) is shown in Fig.2. The C-C-C and C-N-C (and C-C-N) bond angles separate into three groups: one in the range of \( 107^\circ \) to \( 109^\circ \), one in the range of \( 116^\circ \) to \( 119^\circ \) and the other one in the range of \( 119.5^\circ \) to \( 122^\circ \). In contrast, there are only two kinds of bond angles, \( 108^\circ \) and \( 120^\circ \), in \( \text{C}_{60} \). Hence, only few bond angles in \( \text{C}_{48}\text{N}_{12} \)
are similar to those of C\textsubscript{60}.

**Table II:** Calculated bond lengths in C\textsubscript{48}N\textsubscript{12} by using B3LYP hybrid DFT method with a split-valence 6-31G basis set.

| Bond   | Center Number | Bond Length [nm] |
|--------|---------------|------------------|
| C-C    | (3, 4) (11, 15) (27, 28) | 0.13971          |
|        | (33, 34) (36, 40) (53, 54) |                 |
| C-C    | (6, 10) (17, 18) (24, 25) | 0.14004          |
|        | (58, 59) (41, 42) (48, 49) |                 |
| C-C    | (7, 8) (19, 20) (22, 23) | 0.14068          |
|        | (43, 44) (46, 47) (56, 57) |                 |
| C-C    | (1, 2) (12, 13) (16, 29) | 0.14125          |
|        | (31, 32) (37, 38) (51, 52) |                 |
| C-C    | (6, 7) (18, 19) (23, 24) | 0.14217          |
|        | (42, 43) (47, 48) (57, 58) |                 |
| C-C    | (3, 10) (11, 59) (17, 33) | 0.14346          |
|        | (25, 36) (28, 49) (41, 53) |                 |
| C-C    | (4, 46) (8, 15) (20, 40) | 0.14354          |
|        | (22, 54) (27, 44) (34, 56) |                 |
| C-C    | (2, 3) (11, 12) (28, 29) | 0.14488          |
|        | (32, 33) (36, 37) (52, 53) |                 |
| N-C    | (7, 60) (9, 47) (19, 26) | 0.14189          |
|        | (21, 57) (23, 45) (43, 50) |                 |
| N-C    | (8, 9) (20, 21) (22, 26) | 0.14149          |
|        | (44, 45) (46, 50) (56, 60) |                 |
| N-C    | (9, 10) (17, 21) (25, 26) | 0.14226          |
|        | (41, 45) (49, 50) (59, 60) |                 |
| N-C    | (4, 5) (14, 15) (27, 30) | 0.14286          |
|        | (39, 40) (34, 35) (54, 55) |                 |
| N-C    | (1, 5) (13, 14) (16, 30) | 0.14315          |
|        | (31, 35) (38, 39) (51, 55) |                 |
| N-C    | (5, 42) (6, 35) (14, 48) | 0.14317          |
|        | (18, 55) (24, 30) (39, 58) |                 |
| C-C carbon in C\textsubscript{60} | | 0.13944          |
| C-C carbon in C\textsubscript{60} | | 0.14445          |

**FIG.2:** *ab initio* B3LYP/6-31G DFT calculation of C-C-C (open circles) and C-N-C (or C-C-N) (filled circles) bond angles in C\textsubscript{48}N\textsubscript{12}. The center numbers are labeled in Fig.1.

**Table III:** Total energy calculations of C\textsubscript{48}N\textsubscript{12} aza-fullerene and C\textsubscript{60} by using B3LYP hybrid DFT method with a split-valence 6-31G basis set.

|                      | C\textsubscript{60} | C\textsubscript{48}N\textsubscript{12} |
|----------------------|----------------------|---------------------------------------|
| total DFT energy (eV)| -62192.890           | -67617.316                            |
| one electron energy (eV)| -537319.738         | -577022.480                           |
| Coulomb energy (eV)  | 256457.119           | 274997.383                            |
| exchange-correlation energy (eV) | -8887.049     | -9361.705                             |
| nuclear repulsion energy (eV) | 227556.778   | 243769.848                            |
| LUMO (eV)            | -3.382               | -2.707                                |
| HOMO (eV)            | -6.216               | -4.633                                |
| binding energy (eV/atom) | 8.676              | 8.188                                 |
| first ionization energy (eV) | 7.548              | 5.993                                 |

The results of total energy calculations of C\textsubscript{48}N\textsubscript{12} aza-fullerene are summarized in Table III. For comparison, the results of C\textsubscript{60} are also listed in Table III. Their DFT orbital energies with the orbital symmetries are shown in Fig.3. Because of the valency of the doped nitrogen atoms, the electronic properties of C\textsubscript{48}N\textsubscript{12} are greatly different from C\textsubscript{60}. Since the icosahedral symmetry of C\textsubscript{60} is lost by the substituted doping, each energy level in C\textsubscript{48}N\textsubscript{12} splits. In detail, we find that the ground state energy of C\textsubscript{48}N\textsubscript{12} is -67617.316 eV, which is 5423 eV lower than that of C\textsubscript{60}. For C\textsubscript{60}, the gap obtained from the on-set of the occupied fivefold-degenerate \( b_1 \) energy level (i.e., HOMO) and the threefold-degenerate \( t_{1g} \) level (i.e., LUMO) is 2.834 eV, which is in agreement with the experiment [26]. For C\textsubscript{48}N\textsubscript{12}, the HOMO is a doubly degenerate level of \( a_g \) symmetry and the LUMO is a single level of \( a_u \) symmetry, and the corresponding LUMO-HOMO gap is 1.926 eV, which is 0.908 eV smaller than that of C\textsubscript{60}. These results indicate the possibility that C\textsubscript{48}N\textsubscript{12} can be the components of semiconductors with small band gaps. Since C\textsubscript{48}N\textsubscript{12} is isoelectronic with C\textsubscript{60}, it corresponds to a complete filling of the \( t_{1u} \) and \( t_{1g} \) levels of C\textsubscript{60} [10]. From Fig.3, it is seen that the HOMO of C\textsubscript{48}N\textsubscript{12} appears at about 1.583 eV above that of C\textsubscript{60}. This difference in the HOMO levels is in agreement with the calculation of Stafstr"{o}m et al. [11] and corresponds to the difference between the first ionization energies of C\textsubscript{48}N\textsubscript{12} and C\textsubscript{60}. These results suggested that the aza-fullerene C\textsubscript{48}N\textsubscript{12} is a very good electron donor [11]. The binding energies (i.e., the difference in the total energies of the whole system and the fragments) are also listed in Table III. We find that the binding energy for C\textsubscript{48}N\textsubscript{12} is 8.188 eV per atom, which is about 0.5 eV smaller than that (=8.676 eV per atom) of C\textsubscript{60}. Hence, as synthesized by Hultman et al. [10], C\textsubscript{48}N\textsubscript{12} would be a stable aza-fullerene.
The interaction energy of a nucleus of magnetic moment $\mu$ with a weak external magnetic field $\mathbf{B}$ is given by $E = -\mu \cdot \mathbf{B}(1 - \sigma)$, where $\sigma$ is the diamagnetic shielding factor (DSF) [24,25] arising from induced magnetic fields at the nucleus. In Fig.4, we present the calculated DSF $\sigma$ of carbon and nitrogen atoms in C$_{48}$N$_{12}$ by using the NWChem program [12,13] with the B3LYP hybrid DFT method and the split-valence 6-31G basis set. In comparison with the calculated results of C$_{60}$ by using the Gaussian 98 program [13,23] with B3LYP/6-31G hybrid DFT method. For C$_{48}$N$_{12}$, there are 3n-6 = 174 vibrational modes for n=60 (the number of atoms). The corresponding vibrational frequencies at 298.15 K and 1 atmosphere of pressure are shown in Fig.5, which also presents the IR intensity at each vibrational frequency. Since experimental IR spectroscopic data do not directly indicate the specific type of nuclear motion producing each IR peak, we do not give here the normal mode information for each vibrational frequency and the displacements of the nuclei corresponding to the normal mode. From Fig.5, we find that C$_{48}$N$_{12}$ has five strong IR lines with the intensities 8.44 x 10^{-4} cm^{-1}, 6.81 x 10^{-4} cm^{-1}, 5.93 x 10^{-4} cm^{-1}, 5.15 x 10^{-4} cm^{-1}, and 4.2 x 10^{-4} cm^{-1}, being located at the vibrational frequencies 461.5 cm^{-1}, 1236.1 cm^{-1}, 1338.4 cm^{-1}, 579.3 cm^{-1}, and 568.4 cm^{-1}, respectively. The vibrational frequencies, 461.5 cm^{-1}, 1236.1 cm^{-1}, 1338.4 cm^{-1}, and 568.4 cm^{-1}, correspond to two degenerate normal modes. Also, it is found that the zero-point energy correction to the total electronic energy is about 10.1 eV, and the thermal corrections to the total electronic energy, enthalpy, Gibbs free energy are 10.7 eV, 10.8 eV and 9.0 eV, respectively. By contrast, the calculated result for C$_{60}$ is shown in the inset in Fig.5, where we observe four strong IR spectral lines with the intensities 2.76 x 10^{-4} cm^{-1}, 8.2 x 10^{-4} cm^{-1}, 1.0 x 10^{-4} cm^{-1}, and 1.72 x 10^{-4} cm^{-1} at the vibrational frequencies 553.0 cm^{-1}, 586.5 cm^{-1}, 1208.5 cm^{-1} and 1479.3 cm^{-1}, respectively, which are in good agreement with the experimental (528 cm^{-1}, 577 cm^{-1}, 1183 cm^{-1} and 1429 cm^{-1}) measured by Krätschmer et al. [27].
of the polarizabilities there is no difference between z and x (or y) components. Obviously, because the electron distribution for C\textsubscript{48}N\textsubscript{12} is isotropic in the x, y and z directions, it is known that the molecular vibration must be accompanied by a change in the polarizability of the molecule in order for a molecular vibration to be Raman active [30]. Although the polarizability ellipsoid may have higher symmetry than the molecule, all the symmetry elements possessed by the molecule will also be possessed by the ellipsoid [30]. Hence, if the polarizability ellipsoid is changed in size, shape, or orientation as a result of vibrational motion, a Raman spectrum will result [30]. In our case, the calculated Raman scattering activities and depolarization ratios for C\textsubscript{48}N\textsubscript{12} are zero. Thus, its vibration is not Raman active, which implies that the polarizability of the molecule does not change in a molecular vibration, and a measurement of its depolarization ratio cannot provide a means of distinguishing totally symmetrical vibrations from the rest.

The first-order hyperpolarizability \( \beta \) [31] of C\textsubscript{48}N\textsubscript{12} is also calculated and found to be zero, the same as that of C\textsubscript{60}. This is actually expected since they display inversion symmetries. Consequently, this aza-fullerene C\textsubscript{48}N\textsubscript{12} cannot produce the second-order nonlinear optical (NLO) interactions. Based on the available studies of the third-order optical nonlinearities of C\textsubscript{59}N and C\textsubscript{58}N\textsubscript{2} [4], we expect that C\textsubscript{48}N\textsubscript{12} may exhibit large second-order hyperpolarizability \( \gamma \) because of its large electronic polarizations and small HOMO-LUMO gap. This suggests that C\textsubscript{48}N\textsubscript{12} may be one of the molecules, for which we are looking to build third-order NLO materials for photonic applications.

Modern high-field, multipulse NMR spectroscopy has proven to be an exceptionally powerful technique in characterizing molecular systems and structures. Here we calculate the NMR shielding tensor of carbon and nitrogen atoms in C\textsubscript{48}N\textsubscript{12} aza-fullerene. Since no current functionals include a magnetic field dependence, the DFT methods do not provide systematically better NMR CS results than Hartree-Fock theory [23]. Hence, we compute the NMR shielding tensor of C\textsubscript{48}N\textsubscript{12} with the gauge-including atomic orbital (GIAO) method [32] by using Gaussian 98 program [23] in the level of restricted Hartree-Fock (RHF) theory with the split-valence 6-31G basis set. Table V summarizes the results for the isotropic and anisotropic absolute shielding constants of the carbon and nitrogen atoms in C\textsubscript{48}N\textsubscript{12}. The isotropic shielding constant \( \Delta_{\text{iso}} \) is defined as \( \Delta_{\text{iso}} = (\Delta_{xx} + \Delta_{yy} + \Delta_{zz})/3 \) [33], where \( \Delta_{ij} \) (\( i,j = x,y,z \)) is the component of the shielding tensor. The anisotropic shielding constant \( \Delta_{\text{aniso}} \), an indication of the quality of the shielding tensor, is defined as \( \Delta_{\text{aniso}} = \Delta_3 - (\Delta_1 + \Delta_2)/2 \) [33], where \( \Delta_1 < \Delta_2 < \Delta_3 \) are the eigenvalues of the symmerized shielding tensor. It is seen that the NMR shielding constants separate into eight groups for carbon atom and two groups for nitrogen atoms. Hence, we predict that there are 10 groups of spectral signals in the NMR

\[ \text{Table IV: Static dipole polarizabilities } \alpha \text{ (1 au } = 0.5292 \times 10^{-30} \text{ m}^3) \text{ of C}_{48}\text{N}_{12} \text{ and C}_{60} \text{ by using B3LYP hybrid DFT method with a split-valence 6-31G basis set.} \]

| Fullerene | \( \alpha_{xx} \) | \( \alpha_{xy} \) | \( \alpha_{yz} \) | \( \alpha_{xz} \) | \( \alpha_{yz} \) | \( \alpha_{zz} \) |
|-----------|----------------|----------------|----------------|----------------|----------------|----------------|
| C\textsubscript{60}   | 460.84 0.00   | 460.84 0.00   | 460.84 0.00   | 460.84 0.00   | 460.84 0.00   |
| C\textsubscript{48}N\textsubscript{12} | 442.55 0.00   | 442.54 0.00   | 442.54 0.00   | 445.88         |

The static dipole polarizability measures the ability of the valence electrons to find an equilibrium configuration which screens a static external field [28]. Hence, molecules with many delocalized valence electrons should display large values of static dipole polarizabilities. In Table IV, we list the calculated static dipole polarizabilities of C\textsubscript{48}N\textsubscript{12}. For comparison, the results of C\textsubscript{60} are also listed in Table IV. Obviously, large values of static dipole polarizabilities are found for both C\textsubscript{48}N\textsubscript{12} and C\textsubscript{60}. Actually, this is expected since the sp structure for carbon chains is rich of \( \pi \) bonds delocalized along the entire body of the system [28]. Our calculated polarizabilities for C\textsubscript{60} are in agreement with those of Fowler et al. [29]. From Table IV, we notice that only \( \alpha_{xx} \), \( \alpha_{yy} \) and \( \alpha_{zz} \) are different from zero, i.e., there exist three mutually perpendicular directions in the molecule for which the induced dipole moments are parallel to the electric field. The locus of points formed by plotting \( 1/\sqrt{\alpha} \) in any direction from the origin yields a surface called the polarizability ellipsoid [30] whose axes are x, y, and z. Obviously, because the electron distribution for C\textsubscript{60}, as discussed before, is isotropic in the x, y and z directions, there is no difference between z and x (or y) components of the polarizabilities \( \alpha \) and the polarizability ellipsoid becomes a sphere. However, this difference for C\textsubscript{48}N\textsubscript{12} is pronounced because of the electron polarization caused by the electron acceptor, N atom. The polarizability of C\textsubscript{48}N\textsubscript{12} is the same in both x and y directions. Thus, the polarizability ellipsoid in C\textsubscript{48}N\textsubscript{12} becomes a rotational ellipsoid with two equal axes x and y.
spectroscopy of C$_{48}$N$_{12}$. In contrast, the calculated absolute isotropic and anisotropic NMR shielding constants for C$_{60}$ are 54.10 ppm and 180.09 ppm, respectively, and there is only one NMR spectral signal. In order to compare the predicted values of C$_{60}$ to experimental results, we also list the calculated NMR shielding constants of carbon atoms in tetramethylsilane (TMS). We find that the isotropic NMR shielding constant of carbon atoms in C$_{60}$, relative to that in TMS, is 146.7 ppm, which are in good agreement with the experimental result (=142.7 ppm) of C$_{60}$ [34].

![Table V: Restricted Hartree-Fock calculations of the isotropic $\Delta_{\text{iso}}$ and anisotropic $\Delta_{\text{aniso}}$ absolute shielding constants of the carbon and nitrogen atoms with a split-valence 6-31G basis set in the GIAO method for C$_{48}$N$_{12}$ aza-fullerene, C$_{60}$ and tetramethylsilane (TMS).](image)

| Center Number Atom | $\Delta_{\text{iso}}$ | $\Delta_{\text{aniso}}$ |
|--------------------|------------------|------------------|
| {1, 13, 16, 31, 38, 51} C | 44.0 | 173.0 |
| {4, 15, 27, 34, 40, 54} C | 57.9 | 154.9 |
| {7, 19, 23, 43, 47, 57} C | 59.4 | 152.2 |
| {10, 17, 25, 41, 49, 59} C | 59.5 | 133.5 |
| {2, 12, 29, 32, 37, 52} C | 67.9 | 169.2 |
| {8, 20, 22, 44, 46, 56} C | 70.7 | 150.8 |
| {3, 11, 28, 33, 36, 53} C | 76.6 | 141.2 |
| {6, 18, 24, 42, 48, 58} C | 78.2 | 110.5 |
| {9, 21, 26, 45, 50, 60} N | 95.3 | 202.6 |
| {5, 14, 30, 35, 39, 55} | 114.4 | 171.5 |
| all carbons in C$_{60}$ C | 54.1 | 180.1 |
| all carbons in TMS C | 200.8 | 21.4 |

In this work, we only focus on the split-valence 6-31G basis set and discuss only the frequency analysis at 298.15 K and 1 atmosphere of pressure. Detailed frequency calculations and thermochemical analysis at different temperatures and pressures, the basis set effects including minimal basis sets STO-3G and polarized basis sets 6-31G* [23], and other theoretical methods, for example, MP2 [23] and CSGT method [33], will be discussed in a full paper [35]. For example, the total electronic energies of C$_{48}$N$_{12}$ with respect to basis sets STO-3G, 3-21G, 6-31G and 6-31G* are -66795.835 eV, -67263.725 eV, -67617.316 eV and -67637.659 eV, respectively, which shows that improving the basis set from STO-3G to 6-31G* gives a significantly better total energy and the use of polarization functions is not especially important for total energy calculations, i.e., 6-31G basis set can give a good estimate of the total energy of C$_{48}$N$_{12}$.

In summary, we have performed ab initio calculation of optimized geometries, electronic properties, diamagnetic shielding factor, vibrational frequencies, IR spectrum, NMR shielding tensor, dipole polarizabilities and hyperpolarizabilities of the novel C$_{48}$N$_{12}$ aza-fullerene. Some calculated results of C$_{48}$N$_{12}$ are compared with those of C$_{60}$ at the level of the same theory. It is found that this novel aza-fullerene has some remarkable features which are different from and can compete with C$_{60}$. This aza-fullerene may have potential applications as semiconductor components and possible building materials for nanometer electronics, photonic devices and diamagnetic superconductors since their band gaps are small, diamagnetic shielding factor in carbon atom can be enhanced and electronic polarizations vary largely due to the doping effect.

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