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Prediction of Extended Aromaticity for a Novel $C_{48}N_{12}$ Azafullerene Structure

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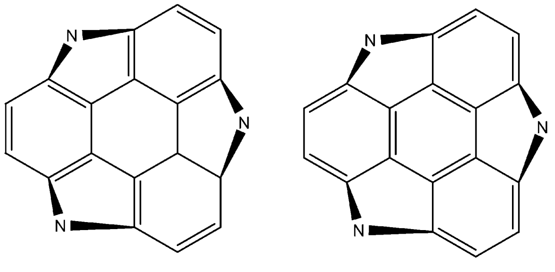
Using magnetron sputtering, it was recently demonstrated that a new fullerene-like material consisting of cross-linked nano-onions of carbon and nitrogen could be grown on a substrate to yield thin solid films.[1] With the aid of electron microscopy and energy-loss spectroscopic analysis, the core shell was identified to correspond to a $C_{48}N_{12}$ composition. Nanoindentation tests showed evidence of a highly elastic material, combined with an appreciable resilience: hardness is 7 GPa and the Young's modulus is 37 GPa. These properties render the nanostructured material ideal for wear-protective applications and provide an opportunity toward the synthesis of nitrogen-substituted fullerene-analogues with novel structural, electronic, and conducting properties. Earlier, the synthesis of solid $(C_{59}N)_2$,[2] and the formation of molecular species of the type $C_{60-2n}N_{2n}$ has also been reported.[3]

Concurrent with the experimental finding, a structure having S_6 point group symmetry and in which the nitrogen atoms were distributed as one atom per pentagon was proposed to be the exceptionally stable form for the new dodecaaza[60]fullerene molecule.[4] The reported structure reveals a minimum separation of two carbon atoms between the nitrogen atoms. This separation enhances the overall stability by avoiding the repulsive nitrogen−nitrogen interactions and results in an overall structure that contains only two all-carbon hexagons. In contrast, we report the existence of a novel $C_{48}N_{12}$ structure that is 13.1 kcal/mol energetically more stable than the previously reported one and for which the extended local aromaticity of eight all-carbon hexagonal rings is the driving force toward the maximum stability.

The structure includes two triphenylene-type units (the cup and cap), each connected to three nitrogen atoms, as in Figure 1. Each unit provides an extended region of cyclic electron delocalization that enhances the overall stability of the $C_{48}N_{12}$ molecule through added contributions from resonance energy. Since the resonance energies of fused systems increase as the number of principal canonical forms increases,[5] triphenylene has eight canonical forms of the structure (a) in Figure 1. The molecular unit, therefore, behaves as if the 18 π electrons are distributed in such manner so as to give each of the outer rings a benzene-like sextet.[6] This effect accounts for the unusual stability of triphenylene, demonstrated in its lack of solubility in concentrated sulfuric acid and its low reactivity.[7]

The remaining six nitrogen atoms are distributed around the equator of the buckyball so that each nitrogen atom is separated from its neighboring nitrogen atom in the cup or cap unit by one carbon atom. As we will show, this closer nitrogen−nitrogen repulsive interaction is outweighed and compensated for by the stabilizing contribution of the local aromatictity in the two units. Figure 2 displays a front view of this isomer, indicating the full positioning of nitrogen atoms.



(a) (b)

Figure 1. Extended local aromaticity of a triphenylene-type structure constituting the cup and cap units of $C_{48}N_{12}$. There are eight canonical forms of a and only one form of b.

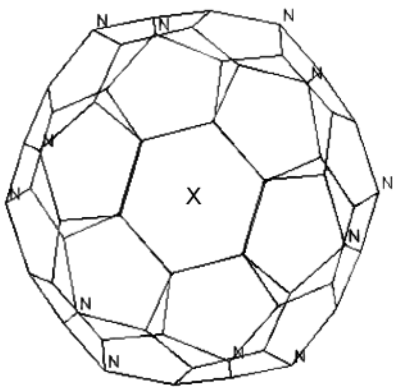


Figure 2. Front view of the S_6 symmetry $C_{48}N_{12}$ structure showing the positioning of all nitrogen atoms. Seven all-carbon hexagons are clearly visible, while the eighth is superimposed on the central ring. X indicates the C_6 symmetry axis through the plane of the paper.

Similar to the previously reported structure,[4] this nitrogen distribution results in each pentagon having only one nitrogen atom. The molecular structure belongs to the S_6 full point group, where the C_6 rotational axis runs through the center of the central hexagon in the cup and cap units. According to the IUPAC numbering system for [60-I_h] fullerene, this molecular structure is denoted (8,13,18,-23,26,29,32,35,38,40,45,50)-dodecaaza[60-S_6]fullerene.[8]

We performed quantum mechanical calculations at the density functional B3LYP[9,10]/6-31G* level of theory on the structure of Figure 2 (referred to as isomer 1) and 12 out of possible 19 S_6 symmetry isomers, including the previously reported structure (referred to as isomer 2).[4] Optimization within the S_6 and C_i symmetry constraints of these structures confirmed isomer 1 as the lowest-energy conformation with total energy of −2485.697203 au. Isomer 2 proved to have the second-lowest energy of −2485.676370 au, in accordance with the result of Stafström et al.[11] Isomer 1 reported herein is, therefore, 13.1 kcal/mol energetically more stable, and should be the ground-state equilibrium structure of the $C_{48}N_{12}$ molecule. We also calculate the HUMO−

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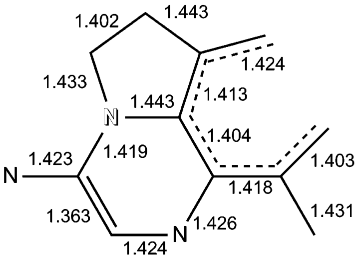

Figure 3. B3LYP/6-31G* optimized bond distances (in Å) of the repeating unit in $C_{48}N_{12}$. N (in shadow) represents one of the nitrogen atoms in Figure 1.

LUMO gap to be 2.74 eV for isomer 1, which is contrasted with a 1.77 eV separation for isomer 2. Therefore, it is predicted that solid materials of $C_{48}N_{12}$ should be insulators.

The enhanced stability of isomer 1 over that of isomer 2 can be understood on the basis of augmented resonance energy contributions. It was shown that resonance energies can be estimated accurately by counting resonance structures via the relationship RE = 1.185 ln SC, where RE is the resonance energy and SC is the number of resonance structures.[12] For triphenylene in Figure 1, having nine structures, the resonance energy is 60 kcal/mol, which is in good agreement with SCF calculated value of 61 kcal/mol,[13] whereas isomer 2 has only two benzene-like rings, each having two resonance structures, resulting in a resonance energy contribution of 19 kcal/mol.[13] This enhanced contribution easily compensates for the nitrogen−nitrogen repulsion that has been increased due to a reduction from a two- to a one-carbon atom minimum separation in isomer 1.

For isomer 1, we identify a repeated unit of collected atoms whose optimized bond distances are shown in Figure 3. Only one C−C double bond (1.363 Å) and one C−C single bond in the pentagon (1.443 Å) are unmistakably present in the unit. The delocalization of electronic clouds in the hexagonal ring is demonstrated by similar C−C bond length in the 1.403−1.424 Å range. Two different types of nitrogen atoms are present, but while differing by the C−N bond length of 1.443 and 1.424 Å, both types have very similar net Mulliken charges of $-0.59|q_e|$ and $-0.60|q_e|$, as was the case for isomer 2.[4] In contrast, however, two-thirds of seven types of carbon atoms have net charges in the range of $+0.18$ to $+0.44|q_e|$, while the remaining one-third exhibit a similar distribution of charges in the range of -0.01 to $-0.02|q_e|$.

A second derivative calculation (Hessian) has proved isomer 1 to be a minimum structure (all modes are positive) on the energy surface of the $C_{48}N_{12}$ molecule. Due to the large number of modes (a total of 174), we report three active infrared bands based on their intensity to be compared with future experimental identification (see Table 1). The strongest band with intensity of 243 km/mol is determined for the highest frequency mode at 1669 cm^{-1}. Two strong bands with frequencies of 1426 and 1309 cm^{-1} have relative intensities of 109 and 157 km/mol, respectively. Five modes with relative intensity in the range of 50−100 km/mol are termed moderate. A complete list of the harmonic vibrational frequencies and IR intensities is available from the corresponding author.

Table 1. Selected Infrared-Active Bands of $C_{48}N_{12}$

band	frequency (cm^{-1})
very strong	1669
strong	1309, 1426
moderate	560, 1293, 1327, 1394, 1423

Finally, the exciting synthesis of $C_{48}N_{12}$ opens up the opportunity of examining the stabilities and energetics of others isomers. Of particular interest, isomers with nitrogen−nitrogen bonded congregates can be considered as high-energy density forms of this molecule. The extended composition of carbon could, for example, stabilize benzene-like rings of nitrogen, a leap toward the realization of high-symmetry forms of polynitrogen.[14] Such opportune investigations, along with simulations on the solid-state properties of isomer 1 are currently in progress and will be the subject of future publications.

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