Stability of Small Carbon-Nitride Heterofullerenes

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Carbon nitride nanostructures have been produced by the arc-discharge technique and analyzed by mass spectrometry. A series of structured peaks in the region of masses from 480 up to 600 suggests the existence of heterofullerenes $C_{n-x}N_x (40 \leq n \leq 50)$. The structure and stability of these small fullerenes were theoretically investigated by quantum chemical calculations. The obtained heats of formation indicate that C_n molecules stabilize upon nitrogen substitution. Two $C_{n-x}N_x$ cages are quite stable, with heats of formation per atom approaching that of C_{60}. These molecules could be the seeds of onionlike structures seen in CN materials [Phys. Rev. Lett. **87**, 225503 (2001)].

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The theoretical prediction of a superhard carbon-nitride solid of composition C_3N_4 [1] has directed the efforts of many experimental groups to synthesize this compound. The characterization of the carbon-nitride materials produced so far showed that the nitrogen concentration is usually much below the ideal composition 3:4. Furthermore, the binding of C and N tends to be of sp^2 character. While an appropriate synthetic route to obtain the C_3N_4 solid is still unknown, the sp^2-connected CN_x materials motivated the search for nanostructures such as nitrogen-doped nanotubes [2–5] and nano-onions [6].

In a previous work [7] we reported on quantum chemical calculations of carbon-nitride systems. From these calculations we proposed a new molecular cage of chemical formula $C_{24}N_{32}$, which has the required 3:4 composition of the theoretically predicted superhard solid. Besides the intrinsic interest of a new closed molecular form, if synthesized, this molecule could allow the production of C_3N_4, just as diamond can be formed from C_{60} solid [8]. Encouraged by this possibility, a carbon-nitride powder was prepared and analyzed by mass spectrometry as a first attempt to synthesize this molecule [9]. The mass spectra showed one feature at a mass-to-charge ratio (m/z) of 368, suggestive of the doubly ionized $C_{24}N_{32}$, though this result is not conclusive about its existence. A collection of peaks in the m/z range from 480 to 580 called our attention to what could be carbon-nitride heterofullerenes. In the present paper we reconsider this mass spectrum and propose that its features originate from small fullerenes and carbon-nitride heterofullerenes having from 40 to 50 atoms. A recent report by Hultman and collaborators [6] gives further support to these ideas. The study on the stability of several small fullerenes and the nitrogen-substituted molecules is based on quantum chemical calculations.

The synthesis of heterofullerenes, and, in particular, the nitrogen-doped heterofullerenes, has been reported by several authors [10]. The main interest in those reports is the identification C_{60} and C_{70} substituted species.

Usually, the carbon-nitride material produced is dissolved in toluene to extract the aza-fullerene. However, many aza-fullerenes could be insoluble in this solvent. In order to avoid this limitation we adopted a different approach consisting in the analysis of the material without any treatment, i.e., as deposited. The graphite powder samples containing nitrogen were produced in similar conditions to those used in fullerene formation, i.e., in a conventional bell jar where one of the two high purity graphite electrodes is vaporized by an arc discharge between them. The base pressure of the chamber was $\sim 10^{-4}$ Pa. In fullerene production, the nucleation is promoted by He [11]. Differently, in order to incorporate nitrogen, the reaction is quenched by a suitable atmosphere of N_2 and He at 100–200 mb. The N_2 partial pressure of 50% was observed to be a good compromise between nitrogen incorporation and nanocage formation [5,12]. The residual soot on the chamber was collected and analyzed *ex situ* by mass spectrometry. The mass spectra of the soot were obtained using a mass spectrometer, model VG *Autospec* GC-MS (Gas Chromatography Mass Spectrometer) containing three deflection field sectors (electric/magnetic/electric), resistive heating (up to 600 °C) and a photomultiplier type detector. The ionization process is by electron impact (12670 eV). A small quartz tube containing tiny amounts of the material is introduced in a vacuum lock-locked chamber and transferred to the analysis chamber after reaching the high vacuum conditions required by the system. Electron impact ionizes the evaporated material obtained by gradually heating up the quartz tube containing the soot and the mass spectra simultaneously registered. This procedure eliminates volatile material (including atmospheric moisture) containing lower m/z ratio species. Therefore, the material of interest containing m/z ratios characteristic of larger molecular species begins to evaporate at higher temperatures (400 °C and above in the present experiment). Figure 1 displays the typical mass spectrum obtained at temperatures ≈ 400 °C. The most intense peak is at $m/z = 368$, as commented above.
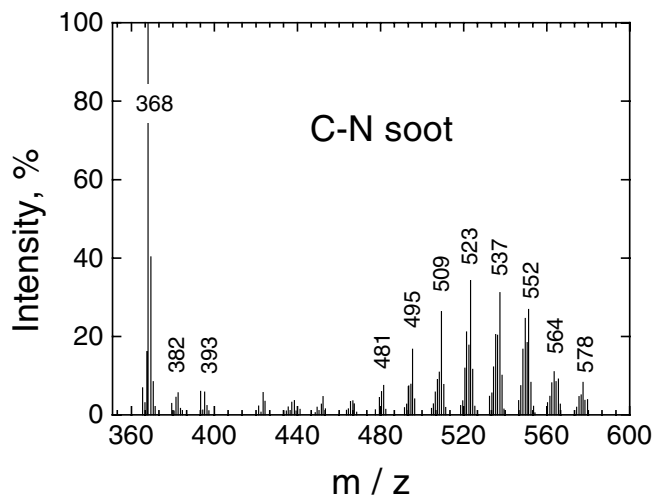
FIG. 1. Typical mass spectrum of carbon-nitride powder obtained by arc discharge under He/N_2 atmosphere.

Starting in $m/z = 481$ and up to 537, the peaks are sequentially obtained by adding the mass of one nitrogen atom. The sequence starting at $m/z = 552$ is obtained adding to the 537 specie the masses of a nitrogen and a proton, the latter probably stemming from residual water in the deposition chamber. The smaller side peaks around the dominant ones correspond to nitrogen substitution of carbon atoms (mass differences of two units). Because of the N_2 partial pressure adopted in the soot preparation and the temperature at which these species were evaporated from the soot, multiply ionized species having m/z ~500 are not expected. Therefore, these features are probably due to closed molecular clusters. Spectra from several samples (not shown) hardly show structures above 650. Assuming that these features originate from small fullerenes and heterofullerenes, we selected the most symmetrical forms with an appropriate number of atoms in order to theoretically study their stability.

Fullerenes are formed by pentagons and hexagons, since smaller bond angles would make the structure too unstable. Therefore, we looked for the possible structures containing only pentagons and hexagons and a convenient number of atoms. In addition, we focused on the most symmetrical structures, since they are more likely to be stable. The composition that generates the most symmetrical spheroid is the one containing 12 pentagons and 20 hexagons, found in the C_{60}. In this structure, the pentagons are all isolated from each other (surrounded by hexagons). For smaller structures than C_{60}, there is the need of bringing the pentagons together, since we can reduce the number of hexagons, but never the number of pentagons. Then we built closed molecular structures in which all the possibilities of associating 2, 3, or 4 pentagons were explored. These groups are surrounded by hexagons and combined to form the smaller fullerenes containing 40 to 50 atoms. The only exception to this rule is one C_{40} structure having squares, pentagons, and hexa-

gons [13], which was considered due to its high symmetry. The conformations of 14 molecular cages, including C_{60} for comparison, were optimized within the semiempirical Hamiltonian parametric method 3 (PM3) [14] contained in GAMESS package [15]. PM3 is a very reliable method to predict molecular geometries and heats of formation of organic systems, which are related to the present ones. It is also a very fast computational method when compared to *ab initio* techniques. Its choice is justified by the number of molecular structures to be optimized (~ 280 molecules including the N-substituted species).

In Fig. 2 are displayed the calculated heats of formation per atom ($\Delta H_f/n$) of all the C_n molecular cages. The heats of formation are positive since these molecules are less stable than graphite. The stability parameter $\Delta H_f/n$ decreases as the number of atoms increases, as expected. Further calculation showed that the most stable compounds were also stable against fragmentation. The carbon-nitride molecules were built from the optimized conformations, with appropriate substitution of a given number of carbon atoms by nitrogen. Later, a new geometry optimization is performed. For the substitutions, some criteria should be adopted. First, adjacent atoms should not be substituted, since N_2 molecule is a much more stable configuration for the nitrogen atom than the inclusion in the fullerene structure. The substitution of an even number of atoms is also preferable because a closed shell system is formed. It is still possible to substitute an odd number of atoms, but the resulting open shell system would greatly increase the molecule's reactivity.

To organize the process of substitution, the geometries of the fullerenes were analyzed and the possible types of substitutions were identified. Basically, the substitutions
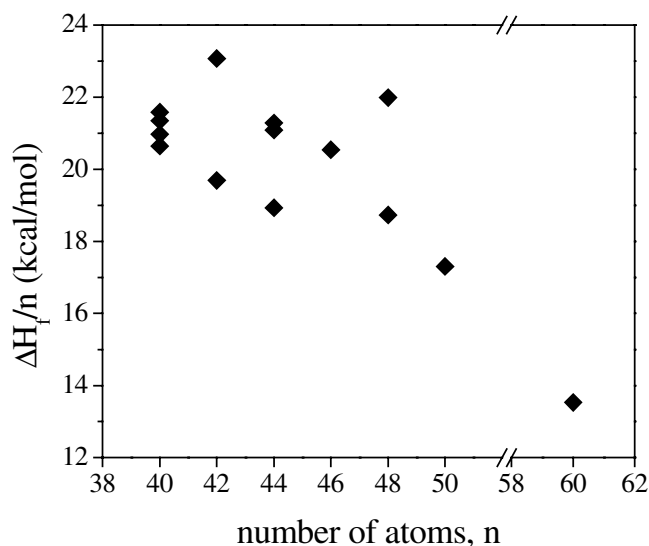

FIG. 2. Calculated PM3 heats of formation per atom ($\Delta H_f/n$) of fullerenes C_n.

can be divided according to the number of pentagons in which the substituted atom is inserted and according to the type of the group of pentagons. More symmetrical (therefore more interesting) molecules usually have only one type of disposition of pentagons. Still, in a given group of pentagons there can be different types of substitutions in which the atom is part of the same number of pentagons. The different types of substitution can be combined, as long as there are no adjacent substitutions. After determining all possible groups of substitutions, the corresponding carbon-nitride molecules were built, always with an even number of N atoms and trying to maintain the highest possible symmetry. Combinations among many groups were made, until the maximum number of nitrogen atoms was reached. One exception appeared, the isomer of C_{42} having three groups of four sequentially arranged pentagons: the substitution of nine carbons by nitrogens gave the most symmetrical structure and was also calculated.

Figure 3 displays the heat of formation per atom $(\Delta H_f/n)$ for all the $C_{n-x}N_x$ molecules, distributed by molecular mass. The sequence of N-substituted C_{60} molecules up to $C_{48}N_{12}$ is also shown for comparison. It is clear from this figure that in all molecules the presence of nitrogen stabilizes the structures. This is expected since the typical bond angles and bond lengths of the C-N bonds, together with the more pyramidal arrangement of bonds around the nitrogen atom, decrease the stress introduced by the curvature of the molecular cages, especially in the pentagonal rings. This effect is more pronounced in the small fullerenes than in C_{60}. The number of nitrogens that make the molecules most stable is eight for C_{40}, nine for C_{42}, between six and eight for C_{44} and C_{48}, ten for C_{46}, and six for C_{50}. Among the many

molecules with a heat of formation per atom that strongly suggests stability, one deserves special attention: the $C_{33}N_9$, which is much more stable than the other molecules around its mass. This molecule has a mass of 522, very close to the highest peak in the experimental mass spectrum shown in Fig. 1.

Notice that variations on the heats of formation in the C_{60} series are small and approximately linear as the number of N atoms increases, in agreement with the more accurate *ab initio* results reported in Ref. [6]. The exception is the most symmetric $C_{48}N_{12}$ molecule, which presented the largest stabilization energy. As the PM3 technique has been parametrized to reproduce heats of formation and molecular conformations with great accuracy, we believe it is correctly accounting for the influence of symmetry in the molecular stability.

The structures of the most stable $C_{33}N_9$ and $C_{44}N_9$ molecules are shown in Fig. 4. Both structures have C_3 symmetry. The average diameters of these molecules are
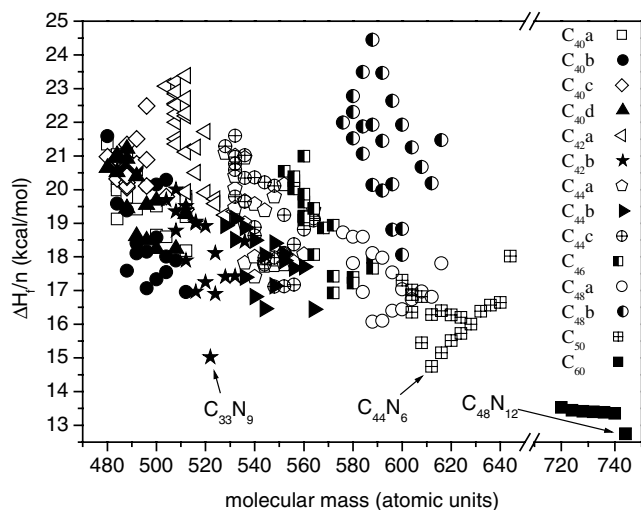

(a)

(b)

FIG. 3. Heats of formation per atom $(\Delta H_f/n)$ of substituted fullerenes $C_{n-x}N_x$ from PM3 calculations, as a function of the molecular mass. The labels *a*, *b*, *c*, and *d* stand for the various isomers of each structure.
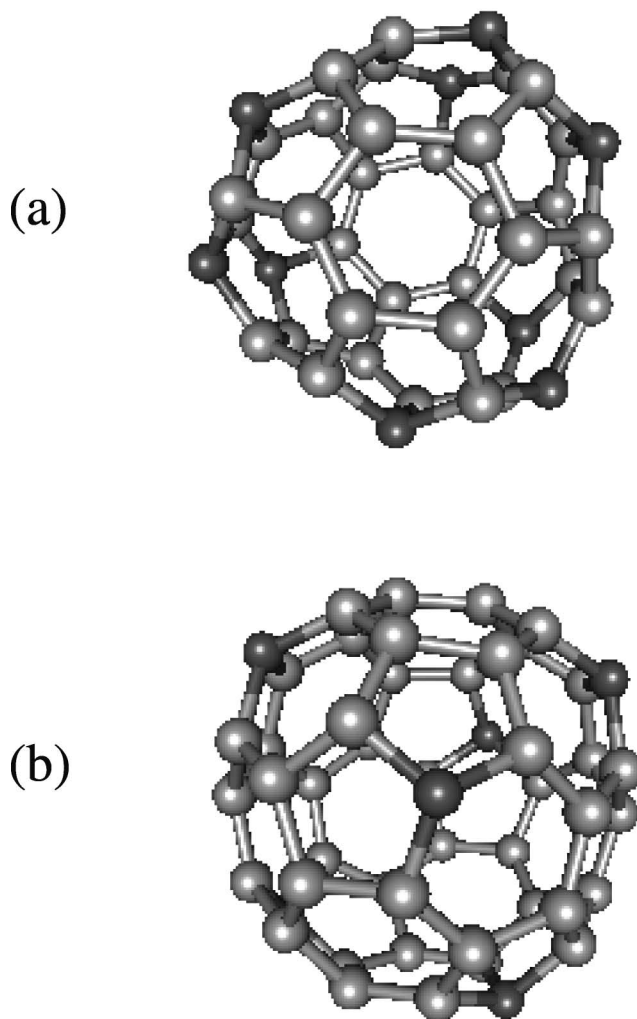
FIG. 4. Structures of (a) $C_{33}N_4$ and (b) $C_{44}N_6$. Light and dark gray spheres represent carbon and nitrogen, respectively.

5.8 and 6.4 Å, respectively, to be compared with those of C_{60} and $C_{48}N_{12}$, which are 7.1 and 7.2 Å. These diameters are close to the ones observed experimentally in the core of some nano-onions reported in Ref. [6].

The absorption spectra of the most stable carbon-nitride heterofullerenes were simulated (not shown) through the semiempirical ZINDO/S-CI technique [16]. While the pure fullerenes show almost no activity in the visible region of the spectrum, the carbon-nitride species present a very rich absorption spectrum, which is indicative of high chemical reactivity. This is also consistent with the highly cross linked structure of the carbon-nitride nano-onions reported by Hultman and co-workers [6]. However, as these species form closed molecular structures, probably their bonds are weak, as in the $C_{59}N$ dimer [10]. One last test on $C_{33}N_9$ is the stability against fragmentation, or the heat of reaction of $C_{33}N_9 \rightarrow \frac{1}{2}(C_{32}N_8 + C_{34}N_{10})$, which gives $\Delta H = 86.8$ kcal/mol. This enthalpy is very large, indicating that this molecule has a quite stable structure, even considering that both molecules used in the calculation are also very stable.

Because these molecular cages are predicted to be reactive, we cannot exclude the possibility that some of them bring groups such as -CN or other species attached. Protons are surely incorporated since several peaks in the mass spectrum have odd mass numbers. However the mass differences between consecutive peaks are always 2 (between the side peaks) or 14 (between major peaks). While the first difference is consistent with the exchange of carbon by nitrogen, the second one is equivalent to one nitrogen mass, or seven carbons replaced by nitrogens. We notice that these small fullerenes get most stable when substituted by six to eight nitrogen atoms. Hence, excluding attached groups other than protons, we could tentatively assign the structures around each major peak to C_{40} (481 and 495), C_{42} (509 and 523), C_{44} (537 and 552), and the last two could come from C_{46} and C_{48}. Although N-substituted C_{50} compounds, and of course those from C_{60}, are the most stable, they do not appear in the mass spectrum probably due the low temperature used for the soot evaporation and due to kinetic aspects of the synthesis. It has been reported by other authors [12] that nitrogen gas in the arc discharge drastically lowers the C_{60} formation. Yet, other reports [5,6] revealed a tendency of nitrogen to induce the formation of pentagons when incorporated into sp^2 carbon materials, thus favoring the formation of the pentagon-rich structures of the small fullerenes.

In summary, we reported on carbon-nitride production and analysis by mass spectrometry. The mass spectra strongly suggest the formation of carbon-nitride small heterofullerenes having from 40 to 50 atoms. The structures of these molecules were theoretically investigated by semiempirical quantum chemical calculations. The results show that the substitution of carbon by nitrogen atoms stabilizes smaller fullerenes. The most stable molecule obtained from these calculations is a compound of the C_{42} family which has a molecular mass of 522 a.u., in close correspondence to the highest peak in the mass spectra of carbon-nitride powder. The carbon-nitride molecular cages are predicted to be reactive species. The average diameters of the most stable species are of the order of magnitude of those seen in nano-onions.

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