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Structure, Stability, and NMR Properties of Lower Fullerenes $C_{38}-C_{50}$ and Azafullerene $C_{44}N_6$

Guangyu Sun,[†] Marc C. Nicklaus,*[,†] and Rui-hua Xie[‡]

Laboratory of Medicinal Chemistry, NCI-Frederick, CCR, NCI, NIH, DHHS, 376 Boyles St.,
Frederick, Maryland 21702, and National Institute of Standards and Technology,
Gaithersburg, Maryland 20899

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A systematic survey of the complete set of isomers of fullerenes C_{38}, C_{40}, C_{42}, C_{44}, C_{46}, C_{48}, C_{50} and azafullerene $C_{44}N_6$ is reported. All isomeric structures were optimized using first-principle density functional theory at the B3LYP/6-31G* level. The isomeric structures with the lowest energies are C_{38}:17, C_{40}:38, C_{42}:45, C_{44}:75, C_{44}:89, C_{46}:109, C_{48}:171, and C_{50}:270. The ground-state structure of the azafullerene $C_{44}N_6$ in the framework of C_{50}:270 has D_3 symmetry. The ^{13}C NMR chemical shifts and nucleus-independent chemical shifts (NICS) for the stable isomers of each fullerene are presented.

Introduction

Since the discovery of buckminsterfullerene C_{60},[1,2] the search for other fullerenes has been an active research area, resulting in much success for C_{60} and the higher fullerenes.[3−9] Lower fullerenes (C_n with $n < 60$), on the other hand, have proved elusive from a structural characterization point of view for a long time. Many attempts[10−13] yielded evidence of lower fullerenes, yet milligram or larger scale production and conclusive assignment of molecular structures for lower fullerenes are desirable. An experimental breakthrough in the preparation of lower fullerenes was achieved recently by Xie et al.[14] by means of a modified graphite arc-discharge process.[15] Through the inclusion of trace amounts of CCl_4, these researchers were able to obtain chlorinated fullerene C_{50} in the form of $C_{50}Cl_{10}$. The structure of $C_{50}Cl_{10}$ has been determined unambiguously by a wide range of spectroscopic methods, including MS, NMR, IR, Raman, and UV−vis, as well as theoretical DFT calculations. Other related species have also been shown to exist and await structural characterization.[14] This experimental study demonstrates the possibility of obtaining samples of other lower fullerenes in a similar fashion.

In addition to the synthesis of $C_{50}Cl_{10}$, other progress in lower fullerenes has also been made recently. In the presence of N_2 and He, electric arc discharge from high purity graphite electrodes produced a carbon-nitride material that showed the existence of small carbon-nitride heterofullerenes that are N-substituted C_n ($n = 40-50$) in a mass spectrometry study by Schultz et al.[16] Semiempirical calculations were then performed by these authors on highly symmetric isomers of the small fullerenes in search of candidates of the observed species. On the basis of the theoretical results, the major peaks in the mass spectrum were tentatively assigned to the N-substituted C_{40}, C_{42}, and C_{44}. One obvious limitation of the theoretical study is the selection of highly symmetric fullerene isomers, since, except for C_{60} (I_h) and C_{70} (D_{5h}) whose ground-state structures do have very high symmetries, the stable isomers of most fullerenes have rather low symmetries.[17] To identify the ground-state structure of the lower fullerenes, it is essential to consider all possible isomers.

While higher fullerenes have been the subject of numerous theoretical studies, the structures and stabilities of lower fullerenes C_n ($n < 60$), especially those with $38 \leq n < 60$, have attracted limited research effort. All pentagon-bearing isomers of fullerenes $C_{20}-C_{50}$ have been studied using Hückel theory.[18] The resulting Hückel gaps for these fullerenes specify whether the electronic configuration of an isomer is open-shell or closed-shell. A small number of selected isomers of $C_{38}-C_{50}$ were first studied by tight-binding molecular-dynamics total energy optimization.[19] Selected isomers of C_{40} have been studied using quantum consistent force field for π electrons,[20] Hartree−Fock (HF) approximation,[21] and density functional theory (DFT) at the B3LYP/6-31G* level,[22] before a full survey of all the C_{40} isomers was conducted at the HF/6-31G* level of theory.[23] Selected isomers of C_{50} have been studied at DFT[22,24] and HF[25] theory levels. Recently, a set of 27 C_{48} isomers have been studied by DFT.[26] Mostly because of the lack of computing resources, these earlier studies have considered only a small number of selected isomers, except for C_{40} for which high level results are available. Therefore, the ground-state structures of most of the lower fullerenes $C_{38}-C_{50}$ have not been found until now.

Both the decorated[14,27] and nitrogen-substituted fullerenes[28−30] have potential in many types of applications such as molecular electronics and nonlinear optics. Yet the search for such materials is slowed by the lack of understanding of even the parent pristine fullerenes. To meet the challenge raised by the recent experimental studies on lower fullerenes, we report here on a systematic survey of the isomers of fullerenes $C_{38}-C_{50}$ and a N-substituted C_{50}. We use the hybrid functional B3LYP in the density functional theory formalism and the medium-sized basis set 6-31G* to calculate the structure and relative energy for all the isomeric fullerene structures containing only pentagons and hexagons. The energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is used as an indicator for the kinetic stability of the fullerene isomers. The stable isomers of the

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* Corresponding author. E-mail: mn1@helix.nih.gov.
[†] NCI-Frederick.
[‡] NIST.

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fullerenes $C_{38}-C_{50}$ are thus predicted. For the fullerenes C_{40}, C_{48}, and C_{50} that have been previously analyzed using comparable theoretical levels, our results agree well with those previous studies. We report, for the stable isomers of each fullerene, the calculated NMR chemical shifts and nucleus-independent chemical shifts (NICS) at the cage center, which provide an important basis for possible future experimental characterization and theoretical investigation.

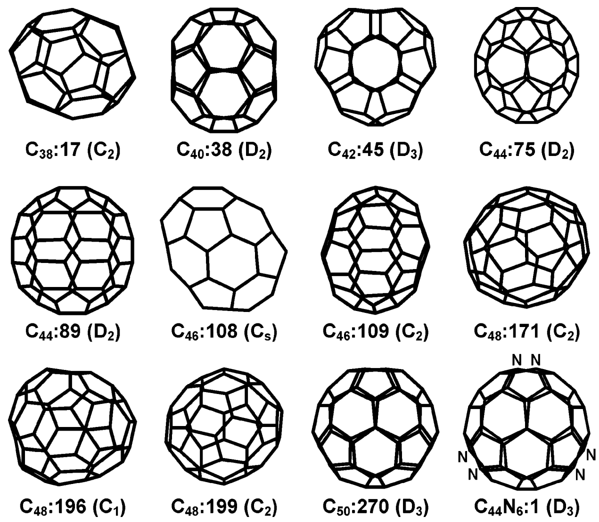
Computational Methods

The fullerene structures consisting of 12 pentagons and various numbers of hexagons have been enumerated and tabulated by Fowler and Manolopoulos.[18] We considered all isomers with nonvanishing Hückel HOMO−LUMO gaps as listed in ref 18, since a zero HOMO−LUMO gap indicates an open-shell electronic configuration. Such an open-shell electronic configuration not only poses a great challenge to achievement of convergence in theoretical calculations but also indicates the lack of stability of the particular isomer at the elevated temperature that is present in the electric arc environment. All isomers of fullerenes C_{38}, C_{40}, and C_{42} were included since their numbers are relatively small. For fullerenes $C_{44}-C_{50}$, we studied the isomers that have only isolated pentagons and pentagons fused with one or two other pentagons while excluding those isomers having pentagons fused with three or more other pentagons. This restriction is justified on the basis of an earlier study on C_{40},[23] which showed that pentagon adjacency correlates very well with stability in that fused pentagons increase the energy. The isolated pentagon rule (IPR) for higher fullerenes is also based on the same principle.[18] In total, the number of fullerene isomers studied here is 330.

The structures of a N-substituted C_{50}, $C_{44}N_6$, within the framework of C_{50}:270 (D_3), were also considered. Assuming the C_3 rotation axis is intact in the substituted fullerene, the six nitrogen atoms were divided into two sets and each set was placed at different positions of C_{50}:270. This arrangement resulted in 64 possible structures. Please note that this scheme is not meant to be an exhaustive search, in fact, it explores only a very limited structural space.

The structures of the 330 isomers of fullerenes $C_{38}-C_{50}$ and the 64 isomers of $C_{44}N_6$ were optimized with DFT using the hybrid functional B3LYP[31,32] and the medium-size basis set 6-31G*.[33] The calculated total electronic energy is reported without further modification. Energies are also reported for the optimized geometries using the smaller basis sets STO-3G[34] and 3-21G.[33] We have used this approach previously to study higher fullerenes and obtained satisfactory results in identifying their ground-state structures.[35−39] The energy gap between HOMO and LUMO is used as an indicator for the kinetic stability of the fullerene isomers.[40] Since there has been evidence for severe underestimation of the DFT-calculated HOMO−LUMO gap for fullerene C_{80}:1,[17] we also report the HOMO−LUMO gap calculated at the HF/6-31+G* level at the DFT optimized geometry.

For the stable isomers with relative energies of less than 25 kcal/mol at the highest theory level, the isotropic shielding constants were calculated using the gauge-independent atomic orbital (GIAO) method[41] and were converted to chemical shifts using the experimental chemical shift (143.15 ppm) of C_{60}.[42] Accurate NMR chemical shifts obtained in this way have been used to successfully identify the observed isomers of higher fullerenes.[37,39,43−45] The nucleus-independent chemical shifts (NICS) are a good criterion for aromaticity in conjugated molecules.[46,47] Here, we calculate the NICS at the cage center for the stable isomers using GIAO−HF/6-31+G* at the DFT optimized geometry. All calculations were performed using Gaussian 03 program package.[48]



C_{38}:17 (C_2) C_{40}:38 (D_2) C_{42}:45 (D_3) C_{44}:75 (D_2)

C_{44}:89 (D_2) C_{46}:108 (C_s) C_{46}:109 (C_2) C_{48}:171 (C_2)

C_{48}:196 (C_1) C_{48}:199 (C_2) C_{50}:270 (D_3) $C_{44}N_6$:1 (D_3)

Figure 1. Structures of the stable isomers of fullerenes $C_{38}-C_{50}$ and azafullerene $C_{44}N_6$.

Results and Discussion

Using the calculated total electronic energy as the criteria, we have determined the ground-state structures of fullerenes $C_{38}-C_{50}$. Figure 1 shows the stable isomers of these fullerenes that have relative energies of less than 4 kcal/mol with respect to that of the most stable isomer of each fullerene. The calculated relative energies are listed in Table 1 for the isomers of fullerene $C_{38}-C_{50}$ that have relative energies of less than 25 kcal/mol at the highest level of theory. The relative energies calculated by the smaller basis sets, STO-3G and 3-21G, agree very well with those obtained with the larger 6-31G* basis set. However, the larger basis set is required to obtain a good geometry which is needed for accurate prediction of NMR chemical shifts[49] and NICS.[46,47]

Energy. The cagelike structure of fullerene dictates that all carbon atoms have pyramidal configuration instead of the planar configuration optimal for sp^2-hybridized carbon. This structural distortion leads to high strain energies in fullerene molecules. The smaller the fullerene, the higher this energy. This trend can be clearly seen in Figure 2, which shows the calculated energy per atom for fullerenes $C_{38}-C_{50}$ relative to that of C_{60}. For each of the fullerenes $C_{38}-C_{42}$, there is a single isomer much more stable than all the others, partly because of the relatively small number of their possible isomers. On the other hand, fullerenes $C_{44}-C_{50}$ all possess several isomers with low energies.

HOMO−LUMO Gap. The HOMO−LUMO gaps of fullerenes calculated at the DFT B3LYP/6-31G* level have proved to be useful in determining their stabilities. In general, gaps larger than 1.3 eV indicate high stability while gaps lower than 1.3 eV may indicate low stability. Most of the observed isomers of higher fullerenes $C_{60}-C_{90}$ follow this trend. One known exception is fullerene C_{80}:1. The fullerene C_{80}:1 is predicted to have a spectral range of ^{13}C NMR chemical shifts of 94.39−159.59 ppm at the B3LYP/6-31G* level,[36] in contrast with the experimental range of 128.9−163.9 ppm.[50] On the other hand, the spectral range of ^{13}C NMR chemical shifts is calculated at the HF level as 123.59−152.87 ppm,[17] which compares well with experimental value. Thus, the small B3LYP gap (0.99 eV) has been suggested as the cause of this large discrepancy, since

TABLE 1: Relative Energy, HOMO−LUMO Gap, and NICS Values of Lower Fullerenes C_{38}−C_{50}, Calculated with DFT at the B3LYP/6-31G* Level[a]

	# of isomers[b]	stable isomers[c]	symm	rel. energy	$\Delta E_{\mathrm{LUMO-HOMO}}$	NICS[d]
C_{38}	16/17	17	C_2	0.00	1.78	−7.3
C_{40}	37/40	0[e]	D_{4h}	24.42	1.29	7.2
		26	C_1	23.77	1.47	−21.6
		29	C_2	21.58	1.20	−5.3
		31	C_s	16.08	1.65	1.5
		38	D_2	0.00	2.00	2.3
		39	D_{5d}	10.91	2.14	1.3
C_{42}	45/45	33	C_1	23.28	1.57	−3.2
		45	D_3	0.00	2.00	−6.4
C_{44}	22/89	69	C_1	19.16	1.61	−7.2
		72	D_{3h}	7.98	2.14	−26.0
		75	D_2	0.00	1.85	−7.7
		89	D_2	0.61	1.88	−7.3
C_{46}	32/116	86	C_1	20.49	1.59	−17.9
		88	C_1	19.22	1.72	−29.7
		90	C_1	24.69	1.38	−22.9
		99	C_s	7.47	1.58	−31.9
		101	C_1	22.06	1.58	−32.4
		103	C_1	5.84	1.42	−20.8
		107	C_s	5.89	2.01	−18.8
		108	C_s	1.86	1.75	−14.2
		109	C_2	0.00	1.59	−11.4
		110	C_1	23.99	1.36	−22.2
		114	C_1	6.22	1.35	−17.1
		116	C_2	7.44	1.28	−24.7
C_{48}	69/199	138	C_{2v}	12.69	1.78	−37.8
		139	C_1	11.20	1.72	−36.7
		149	C_1	15.15	1.36	−21.8
		150	C_1	23.29	1.27	−20.3
		160	C_2	21.95	2.01	−33.0
		161	C_2	24.86	2.11	−28.5
		162	C_1	21.97	1.72	−38.6
		163	C_2	13.58	2.10	−31.7
		165	C_1	15.57	1.63	−36.2
		168	C_s	20.09	1.82	−27.5
		169	D_2	18.56	1.65	−28.0
		171	C_2	0.00	1.56	−39.3
		192	C_2	22.26	1.50	−36.3
		196	C_1	3.02	1.30	−29.7
		197	C_s	5.27	1.63	−19.4
		199	C_2	2.71	1.16	−26.5
C_{50}	109/271	260	C_2	22.71	1.50	−23.3
		262	C_s	24.82	1.63	−16.3
		263	C_2	10.56	2.09	−46.4
		264	C_s	18.11	1.61	−45.4
		266	C_s	8.14	1.77	−43.8
		270	D_3	0.00	2.27	−46.7
		271	D_{5h}	5.94	1.28	−39.6
C_{60}		1	I_h	0.00	2.76	−10.9

[a] Relative energy in kcal/mol, HOMO−LUMO gap in eV, and NICS in ppm. [b] Number of isomers studied/total number of possible isomers. [c] Isomers having relative energies lower than 25 kcal/mol are listed. Numbering of isomers follows Fowler and Manolopoulos.[19] [d] GIAO−HF/6−31+G*//B3LYP/6−31G*. [e] This is the only isomer studied here that contains two four−membered rings.

a HOMO−LUMO gap of 4.56 eV is calculated at the HF level.[17] Since the DFT gap of C_{80}:1 is much smaller than that of all other observed fullerene isomers, the DFT value has been deemed erroneous for the purpose of NMR chemical shift prediction. To ascertain that the HOMO−LUMO gaps calculated for the lower fullerenes do not show this problem (in particular for the stable isomers for which we predict the NMR chemical shifts), we have also calculated the HOMO−LUMO gaps for the stable isomers at the HF level of theory.

As listed in Table 1, all stable C_{38}−C_{50} isomers have gaps larger than 1.20 eV, which is substantially larger than in the problematic case of C_{80}:1. We plot in Figure 3 the gaps calculated at the HF/6-31+G* level versus the DFT values for the C_{38}−C_{50} isomers with relative energies of less than 25 kcal/mol. In general, the larger the DFT gaps, the larger the HF values. The linear correlation between the HF and DFT gaps is best described by $\Delta E_g(\mathrm{HF}) = 1.3129 \times \Delta E_g(\mathrm{DFT}) + 3.1934$ on the basis of least-squares fitting. For small DFT gaps, a wide range of HF gaps is seen. For instance, for DFT gaps close to 1.3 eV, the HF gaps rang from 4.2 to 5.5 eV. For the DFT gaps larger than 1.8 eV, the HF gaps have more uniform values. Three fullerene isomers seem to be outliers relative to the general trend: C_{44}:72, C_{50}:263, and C_{50}:270. However, none is so to the extent that they would indicate that the DFT gaps is erroneously low.

Structure and Stability of Each Fullerene Family. We studied seven pristine fullerene families C_n ($n = 38$, 40, 42, 44, 46, 48, and 50) and one heterofullerene $C_{44}N_6$. Below, we discuss in detail the stable isomers of each of these fullerene families.

Fullerene C_{38} has 17 possible isomers.[18] Isomer **2** (D_{3h}.) has open-shell electronic configuration and is not included in our study. Of the 16 isomers studied, isomer **17** has much lower energy than the rest, which all have relative energies higher than 25 kcal/mol at the B3LYP/6-31G* level. The DFT predicted HOMO−LUMO gap of isomer **17** is 1.78 eV, a large value by DFT standards, while the HF predicted gap is 5.69 eV. Therefore, both relative energy and HOMO−LUMO gap indicate that isomer **17** is stable. The 12 pentagons in isomer **17** form one linear chain with the 10 pentagons in the middle of the chain fused with two other pentagons and the two terminal ones fused with one other pentagon. Isomers **1**, **3−15** all have at least one pentagon fused with three or more other pentagons and are predicted to have higher relative energies (data not shown). Isomer **14** has one pentagon that is fused with three other pentagons and is predicted to have the lowest energy (26.6 kcal/mol) among these isomers. All the 12 pentagons in isomer **16** are fused with two other pentagons, leading to a relative energy of 29.9 kcal/mol.

Among the 37 isomers of C_{40} having closed-shell electronic configuration, isomer **38** has the lowest energy and a large HOMO−LUMO gap. Other isomers that have energies lower than 25 kcal/mol are **38** < **39** < **31** < **29** < **26**. This is in full agreement with earlier SCF and DFT results for fullerene C_{40} by Albertazzi et al.[23] In addition to the IPR isomers, we have also included an C_{40} isomer (**0**) having two four-membered rings, as suggested by Salcedo and Sansores.[21] At the B3LYP/6-31G* level of theory, this isomer has a relative energy of 24.4 kcal/mol. On the basis of the moderate relative energy of isomer **0**, there might exist isomers for other lower fullerenes that contain four-membered rings and have moderate stabilities.

All 45 isomers of fullerene C_{42} were studied here. Isomer **45** (D_3) has the lowest energy and a large HOMO−LUMO gap

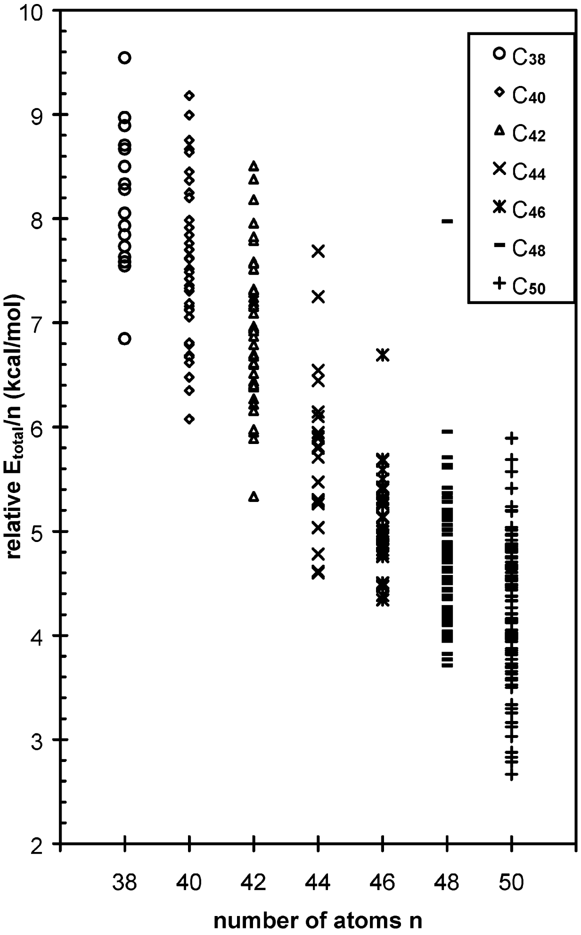


Figure 2. Per atom total energy for fullerenes $C_{38}-C_{50}$ relative to that of C_{60} calculated at the B3LYP/6-31G* level of theory.

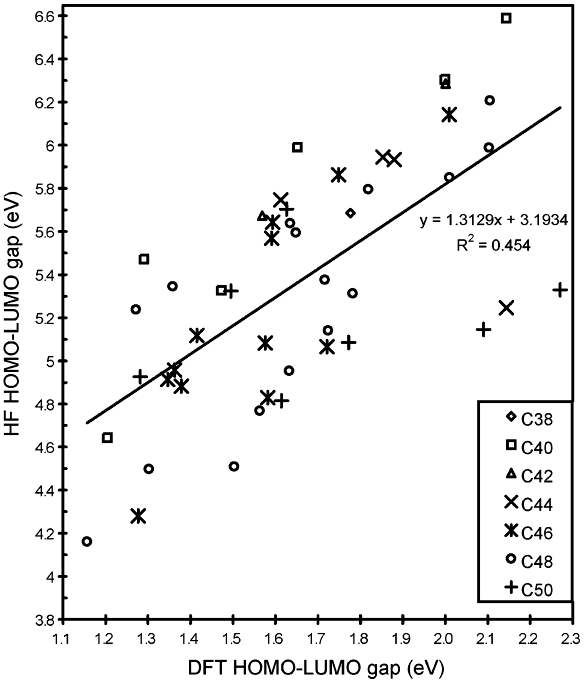


Figure 3. Correlation between the DFT and HF calculated HOMO−LUMO gaps of fullerenes $C_{38}-C_{50}$. DFT values obtained at the B3LYP/6-31G* level and HF values at the HF/6-31+G* level for isomers having relative energies less than 25 kcal/mol.

(2.00 eV) and thus is the ground-state structure. Its 12 pentagons form three copies of a four-pentagon-long linear chain. Isomer **33** is the second most stable isomer with a relative energy of 23.28 kcal/mol. All other isomers have much higher energies.

Starting with fullerene C_{44}, we excluded, in addition to the isomers having vanishing HOMO−LUMO gaps, the isomers with pentagons that are adjacent to three or more other pentagons.[18] As a result, 22 out of the 89 possible C_{44} isomers (**67**−**81**, **83**−**89**) were considered here. Isomers **75** and **89** are essentially isoenergetic, with isomer **75** slightly favored by 0.6 kcal/mol. Both isomers **75** and **89** have four pentagons, each fused with two other pentagons, and eight pentagons, each fused with one other pentagon. Isomers **72** and **69** follow with relative energies of 7.98 and 19.16 kcal/mol, respectively. Thus, the order of stability of the four stable isomers is **75** ∼ **89** < **72** < **69**. These four isomers also have large HOMO−LUMO gaps. All other isomers have much higher energies.

Out of the 116 isomers of fullerene C_{46}, we studied 32 isomers, **84**−**116** (except **94**). A total of 12 isomers have energies lower than 25 kcal/mol at the B3LYP/6-31G* level. The ground-state structure is isomer **109**, which has the lowest energy and a large HOMO−LUMO gap (1.59 eV). Six other isomers have relative energies of less than 10 kcal/mol, and their stability order is **109** < **108** < **103** ∼ **107** < **114** < **116** ∼ **99**. The band gaps for these isomers range from 1.28 eV for isomer **116** to 2.01 eV for **107**.

Among the 69 C_{48} isomers studied here (**130**−**199**, except **189**), 16 have energies lower than 25 kcal/mol. Isomer **171** is the ground-state structure. Four other isomers have energies lower than 10 kcal/mol and their stabilities are **171** < **199** ∼ **196** < **197**. Our results are in full agreement with a recent DFT study on selected isomers of C_{48}.[26] The HOMO−LUMO gaps of isomers **171**, **196**, and **197** calculated by DFT are large, but the gap of isomer **199** is small (1.16 eV). Further HF calculation yielded a HOMO−LUMO gap of 4.16 eV for isomer **199**, confirming its small gap nature.

A total of 109 isomers of C_{50} (**163**−**271**) are studied here, among which seven have energies lower than 25 kcal/mol at the B3LYP/6-31G* level. The isomers with significant stability are **270** < **271** < **266** < **263**. The most stable isomer **270** has D_3 symmetry. Its 12 pentagons form six pairs of pentagons fused together. Isomer **271** is the second most stable isomer but has a small gap of 1.28 eV. Our results are in full agreement with those for the isomers that were studied by Lu et al.[24] While the pristine form of C_{50} has yet to be observed, its modified form, the chlorinated isomer **271** ($C_{50}Cl_{10}$), has been obtained in recent experiments in amounts large enough for spectroscopic characterization,[14] indicating that halogen addition may be employed to obtain modified versions of other lower fullerenes.

A recent MS experiment[16] has shown that nitrogen can be incorporated in lower fullerenes to form N-substituted heterofullerenes. On the basis of semiempirical PM3 calculations, it was suggested that heterofullerene $C_{44}N_6$ is among the most stable heterofullerenes. We have carried out a systematic survey following the scheme[16] used earlier: six nitrogen dopants are divided into two groups with three each, and each group is placed at various sites within the structural frame of C_{50}:270. Three stable structures of $C_{44}N_6$ are shown in Figure 4, together with their symmetry, relative energy, and HOMO−LUMO gap. A D_3 isomer of $C_{44}N_6$ (**1**) is the ground-state structure with a HOMO−LUMO gap of 2.70 eV. The earlier reported C_3 structure (**2**) is 6.8 kcal/mol higher in energy with a large gap of 2.85 eV. Another D_3 isomer (**3**) is 9.6 kcal/mol less stable than the ground-state isomer.

The three stable $C_{44}N_6$ isomers share two structural features. In C_{50}:270, the 12 pentagons are paired to form six instances

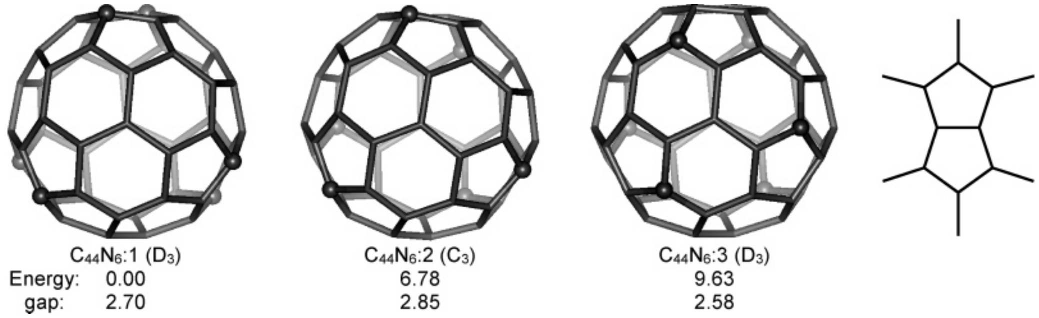


Figure 4. Stable structures of $C_{44}N_6$ in the framework of C_{50}:270. The N atoms are shown as spheres.

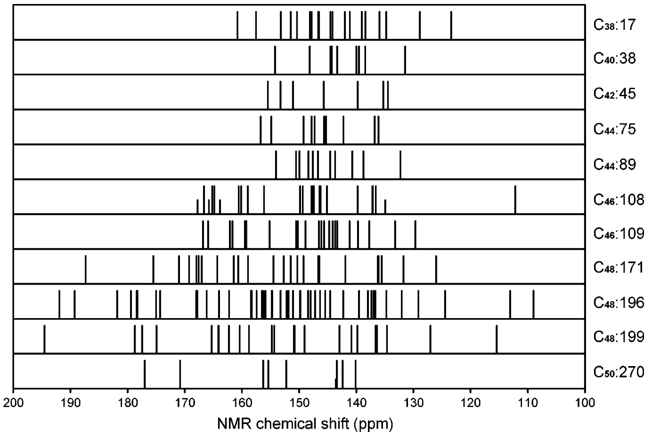


Figure 5. Predicted NMR spectra for the stable isomers of fullerenes $C_{38}-C_{50}$.

of the same motif with two pentagons fused to each other, shown also in Figure 4. We found that the atoms forming the 5/5 bond between the two fused pentagons within this motif are the most prone to N-substitution. In isomer **1** (D_3), the atoms closer to the equator in the 5/5 bond are N-substituted, while in isomer **3** (D_3) the N-substituted atoms are those away from the equator. Combining one-half of isomer **1** and one-half of isomer **3** yields isomer **2** (C_3).

NMR Chemical Shifts. ^{13}C NMR spectroscopy is a powerful technique to determine the molecular structure of the observed fullerenes.[3] At the same time, theoretical NMR chemical shifts calculated at sufficiently high level of theory can significantly facilitate this process, as shown in the case of many higher fullerenes.[17] All experimentally observed fullerenes have shown chemical shifts within the range of 120−170 ppm for the sp^2 carbons. In Figure 5, we present the predicted NMR spectra for the stable isomers of fullerenes $C_{38}-C_{50}$. Among the 11 stable isomers of $C_{38}-C_{50}$, six (C_{38}:17, C_{40}:38, C_{42}:45, C_{44}:75, C_{44}:89, and C_{46}:109) have all predicted chemical shifts within this range, whereas the other five (C_{46}:108, C_{48}:171, C_{48}:196, C_{48}:199, and C_{50}:270) have some chemical shifts that are either too low or too high.

Aromaticity. Whether a molecule is aromatic is well reflected by its NICS value: The lower the NICS, the more aromatic is the molecule.[46] For a planar cyclic compound, the NICS at the ring center shows the aromaticity, with NICS varying from −9.7 ppm for benzene to −3.2 ppm for cyclopentadiene.[46] For molecules having nonplanar structures such as fullerenes, NICS provide a convenient way to assess their electron distribution. For instance, the NICS at the cage center of C_{60} is −10.9 ppm calculated at the GIAO−HF/6-31+G*//B3LYP/6-31G* level. The NICS for fullerenes $C_{38}-C_{50}$ calculated by GIAO−HF/6-31+G* at the B3LYP/6-31G* optimized geometries are listed in Table 1. In general, the larger the molecular size for $C_{38}-C_{50}$, the more negative the NICS value, that is, the more aromatic their nature. For the ground-state isomers of fullerenes $C_{38}-C_{50}$, the NICS varies from a slightly positive value of 2.3 ppm for C_{40}:38 to a large negative value of −46.7 ppm for C_{50}:270.

Conclusions

Motivated by the recent experimental successes in production and characterization of lower fullerenes,[14,16] we have studied the structures and stabilities of all the isomers of lower fullerenes $C_{38}-C_{50}$ using theoretical studies at the DFT level. We have determined the ground-state structure of each of the studied fullerene species by total electronic energy calculation. Each of the fullerenes $C_{38}-C_{42}$ has one single most stable structure: C_{38}:17, C_{40}:38, and C_{42}:45. Fullerenes $C_{44}-C_{50}$ have multiple isomers having similarly large stabilities. The isomers with relative energies of less than 4 kcal/mol, listed in the order of their stability within each fullerene family, are C_{44}:75, C_{44}:89; C_{46}:109, C_{46}:108; C_{48}:171, C_{48}:199, C_{48}:196; C_{50}:270. The ground-state structure of azafullerene $C_{44}N_6$ has D_3 symmetry. The calculated ^{13}C NMR chemical shifts for the stable isomers of fullerenes $C_{38}-C_{46}$ fell within the range typical for observed species whereas those for fullerenes C_{48} and C_{50} showed values above or below the normal range. The predicted NICS values indicate that the aromaticity increases with the molecular size for fullerenes $C_{38}-C_{50}$. With the successful production of $C_{50}Cl_{10}$ having opened a way of obtaining derivatives of other small fullerenes, we hope that the results presented here of our systematic survey of fullerenes $C_{38}-C_{50}$ will assist in the structure determination and further theoretical exploration of such compounds.

Supporting Information Available: The ^{13}C NMR chemical shifts and the optimized structures for all the stable isomers of fullerenes $C_{38}-C_{50}$ are listed in Tables S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org.

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