Full Articles

Quantum chemical calculations of N@C_n endofullerenes ($n \leq 60$)

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The geometric parameters and energy characteristics of small endofullerenes N@C_n (n = 20, 24, 30, 32, 40, 50) and N@C_{60} in the quartet ground state were calculated by the B3LYP/6-31G* method. The N atom is located at the center of the carbon cage in all molecules except N@C_{30}, where it is bound to the cage wall. Encapsulation of nitrogen atom has little effect on the fullerene cage geometry for n = 40, 50, and 60. No significant charge transfer from the N *endo*-atom to the cage was revealed for all the N@C_n endofullerenes studied. The calculated spin density on the nitrogen *endo*-atom increases as the size (n) of the carbon cage increases. The relative stabilities of C_n fullerenes and corresponding endofullerenes N@C_n are discussed.

Key words: small fullerenes, endofullerenes, inclusion energy, quantum chemical calculations, density functional theory.

The synthesis and investigation of endofullerenes have been attracting increasing attention of researchers;[1] however, most studies in this field are concerned with endohedral compounds of higher fullerenes C_n ($n \geq 60$). A large number of endohedral compounds with rare gases,[1] metals,[1] and nitrogen and phosphorus atoms[2,3] were obtained and studied. Of particular interest is the N@C_{60} endofullerene, because experiments revealed an unexpectedly large value of the hyperfine coupling (HFC) constant on the *endo*-atom compared to free nitrogen atom.[2] Both experiment and theory (see Refs 2 and 4—7) show that in this molecule the nitrogen atom is located at the center of the fullerene cage and retains its initial electronic configuration (...$2p^3$). Endohedral compounds of small fullerenes C_n ($n < 60$)* with nitrogen have not been synthesized as yet. There is also a few theoretical studies of N@C_n systems. For instance, semiempirical[10,11] and *ab initio* (HF)[11] calculations of the N@C_n systems were carried out. The results of MNDO/AM1 calculations suggested the possibility for endohedral compounds of C_{34} and C_{36} fullerenes (D_{2d}-, D_{3h}- and C_{2v}-isomers of C_{36} were considered) with nitrogen to exist.[10] In the

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* To date, the syntheses of C_{20} [8] and C_{36} [9] were reported.

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$N@C_{34}$ system, the nitrogen endo-atom is covalently bound to the carbon cage, whereas in all the $N@C_{36}$ isomers it is located at the center.[10] PM3 and UHF/3-21G calculations[11] of the D_{2d}- and D_{6h}-isomers of C_{36} fullerene were performed. In the $N@C_{36}$ molecule (D_{6h} symmetry) the N *endo*-atom is situated at the center of the carbon cluster, while in the $N@C_{36}$ system (D_{2d} symmetry) it is displaced from the center toward the cage wall.[11] Noteworthy is that calculations by different methods[10,11] predict different positions of the nitrogen atom within the carbon cage of the D_{2d}-isomer of C_{36} fullerene.

Paramagnetic endofullerene $N@C_{60}$ is of practical interest as possible information carrier for quantum computer.[12,13] Preliminary calculations and experiments suggest feasibility of this idea in the foreseeable future.[12,13] Small endofullerenes $N@C_n$ can also be considered as potential candidates for being used in memory devices for quantum computers.

Earlier,[14] we have reported density functional B3LYP/6-311G* calculations of the geometric parameters and energy characteristics of endohedral rare-gas fullerenes $X@C_n$ (X = He, Ne, Ar; n = 20, 24, 30, 32, 40, 50, 60). In this work, we carried out density functional calculations of carbon polyhedra C_n and endofullerenes $N@C_n$ in order to clear up the possibility of synthesis of small endofullerenes with nitrogen. In connection with the problem of compressed atoms[15] we discuss here the relative stabilities of the endohedral compounds under study and the dependence of their energy characteristics, spin density, and charge on the nitrogen *endo*-atom on the size of the carbon polyhedron.

Calculation Procedure

Density functional calculations were carried with the B3LYP three-parameter exchange-correlation functional (see Ref. 16) using the GAUSSIAN-98 program[17] and conventional 3-21G and 6-31G* split-valence basis sets.[16] Full optimization of the geometries and energy characteristics was performed at the B3LYP/6-31G* level of DFT (this method allows one to obtain a correct description of the parameters of related systems[14,18,19] including the vibrational frequencies). The calculated vibrational frequencies characterize the optimized structures as energy minima (number of negative eigenvalues of the Hessian at a given point $N_{\text{imag}} = 0$) or saddle points ($N_{\text{imag}} \geq 1$). The energies of formation of products of the reactions $N + C_n \rightarrow N@C_n$ in the quartet ground state (inclusion energies, E_{inc}) were calculated with allowance for the basis set superposition error (BSSE). The BSSE was estimated using conventional counterpoise technique.[20] The B3LYP/3-21G approximation was used for calculating the potential energy surfaces (PES) along the trajectories of the motion of the N atom from the center of the C_n fullerene toward the carbon cage wall (calculations were performed with the geometric parameters obtained at the B3LYP/6-31G* level).

Results and Discussion

Geometric parameters. As earlier,[14] in this work we considered the most stable isomers of the fullerenes C_{20} (C_i symmetry), C_{24} (D_{6d} symmetry), C_{30}-3 (C_{2v} symmetry), C_{32}-6 (D_3 symmetry), C_{40}-38 (D_2 symmetry), C_{50}-271 (D_{5h} symmetry), and C_{60} (I_h symmetry) and the corresponding endofullerenes, $N@C_n$, in the quartet ground state. The symmetry of isomers and their numbering schemes are consistent with the accepted classification.[21] The compounds studied are shown in Fig. 1 and their geometric parameters are listed in Table 1. These fullerene isomers were chosen based on the total energy (E_{total}) minimum according to the results of the DFT and semiempirical MNDO, AM1, and PM3 calculations (see Ref. 19). The bandgap between the higher occupied and lower unoccupied molecular orbitals (HOMO and LUMO, respectively) of the isomers was also taken into account.[14] In all calculations of the $N@C_n$ systems the nitrogen *endo*-atom was placed at the center of the C_n molecule. The *endo*-atom retained its position after full optimization of the endofullerene geometries in all cases except $N@C_{30}$ where it forms an internal covalent bond with the fullerene carbon cage, see Fig. 1).

The results of B3LYP/6-31G* calculations of the most stable fullerenes and the corresponding endohedral compounds are listed in Table 1. For each system we show the

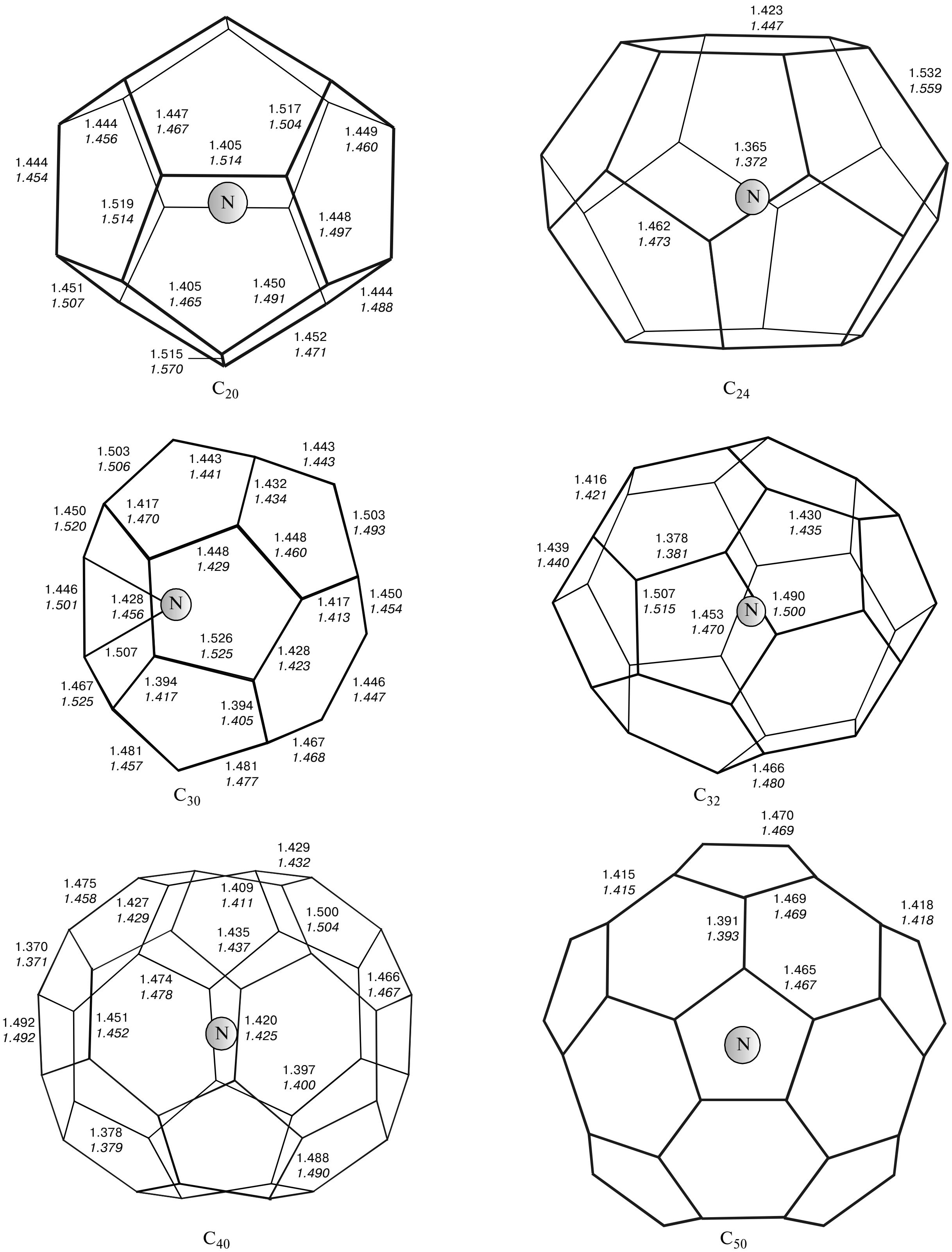
Table 1. Geometric parameters of the C_n fullerenes and corresponding $N@C_n$ endofullerenes obtained from B3LYP/6-31G* calculations

Molecule (symmetry)	Bond length	R^a	R_{av}	ΔR^b
	Å			
C_{20} (C_i)	1.404—1.519	1.943—2.084	2.035	—
$N@C_{20}$	1.454—1.571	1.969—2.190	2.083	0.048
C_{24} (D_{6d})	1.365—1.533	2.168—2.332	2.250	—
$N@C_{24}$	1.372—1.559	2.217—2.345	2.281	0.031
C_{30}-3 (C_{2v})	1.359—1.526	—	—	—
$N@C_{30}{}^c$	1.391—1.525	—	—	—
C_{32}-6 (D_3)	1.378—1.507	2.437—2.810	2.594	—
$N@C_{32}$	1.381—1.515	2.469—2.801	2.606	0.012
C_{40}-38 (D_2)	1.370—1.500	2.756—3.056	2.903	—
$N@C_{40}$	1.370—1.504	2.766—3.055	2.908	0.005
C_{50}-271 (D_{5h})	1.391—1.470	2.956—3.445	3.244	—
$N@C_{50}$	1.393—1.470	2.966—3.443	3.246	0.002
C_{60} (I_h)	1.3955—1.454	3.5412	—	—
$N@C_{60}$	1.3953—1.4541	3.5508	—	0.01

[a] Range of radii for aspherical fullerenes.

[b] Difference between the average radii of $N@C_n$ and corresponding fullerene C_n.

[c] The nitrogen atom is displaced from the center of fullerene and forms a 6/6 bond with the C_{30} carbon cage (see Fig. 1).



C_{20} C_{24} C_{30} C_{32} C_{40} C_{50}

Fig. 1. Geometric parameters of the most stable isomers of fullerenes C_n and corresponding endofullerenes N@C_n (shown in italic) obtained from B3LYP/6-31G* calculations. Presented are only the lengths of inequivalent bonds (in Å). For the N@C_{30} endofullerene we present the optimized structure with the N atom chemically bound to the carbon cage.

range of the lengths of inequivalent carbon—carbon bonds and the average values of the radii of the C_n carbon cage and N@C_n endofullerene obtained after optimization. For aspherical fullerenes, we report the range of changes in their radii. The results obtained can be considered reliable, as follows from comparison of our data with the results of B3LYP/6-31G** calculations[22] and with the X-ray diffraction data for the 6/6- and 6/5-bond lengths in C_{60}.[23] Indeed, our calculations respectively gave values of 1.396 and 1.454 Å (*cf.* 1.395 and 1.453 Å from Ref. 22 and experimental[23] values of 1.388(9) and 1.432(5) Å).

The optimized geometric parameters of the fullerenes C_n and endofullerenes N@C_n are similar for n = 40, 50, and 60 (see Fig. 1 and Table 1). Encapsulation of nitrogen atom causes somewhat larger changes in the N@C_{32} fullerene cage geometry (0.003—0.008 Å) and even more pronounced bonds elongation in the N@C_{24} (by 0.007—0.026 Å) and N@C_{20} (by 0.05—0.07 Å) molecules.

Energy parameters and vibrational frequencies. To assess the possibility of synthesis of small endofullerenes with nitrogen, it is interesting to calculate the inclusion energies (E_{inc}) of endofullerene in the reaction $\text{N} + \text{C}_n \rightarrow \text{N@C}_n$. The inclusion energies, E_{total}, of endofullerenes calculated in the B3LYP/6-31G* approximation as $E_{\text{inc}} = E_{\text{total}}(\text{N@C}_n) - E_{\text{total}}(\text{C}_n) - E_{\text{total}}(\text{N})$, the corresponding zero-point vibrational energies, and the lowest vibrational frequencies are listed in Table 2. One can see that the energies E_{inc} decrease as the size of the carbon cluster C_n increases. The E_{inc} values for N@C_{40} and N@C_{50} are lower than for the experimentally detected[24] dodecahedrane endohedral complex He@$C_{20}H_{20}$ (38.0 kcal mol^{-1}, calculated[25] in the same approximation). The E_{inc} values for N@C_{20}, N@C_{24}, and N@C_{32} are much higher than for He@$C_{20}H_{20}$, so the formation of these three systems requires an extremely large energy expenditure and is unlikely.

Calculations predict real vibrational frequencies for the N@C_{32} endofullerene and imaginary ones for N@C_{20} and N@C_{24} (3 and 2 frequencies, respectively); therefore, the structures with the N atom at the center of the C_{20} and C_{24} fullerenes correspond to the saddle points. For the endofullerenes N@C_{40} and N@C_{50} with the atom N at the center, we carried out B3LYP/3-21G calculations of the PES along the trajectories of the motion of the N atom from the center toward the wall of the carbon cage C_n. We considered the trajectories passing through the centers of inequivalent pentagonal and hexagonal faces of the fullerene polyhedron and further away from the C_n molecule (Fig. 2). As the *endo*-atom moves away from the center of C_n, its potential energy monotonically increases and reaches a maximum value at the center of the pentagonal or hexagonal face of the fullerene polyhedron and then decreases on further motion along the trajectory outside the fullerene cage (see Fig. 2). Location of the N atom at the center of the C_n fullerene corresponds to a rather deep (~25 eV, calculations with the 3-21G basis set) minimum in the PES and is energetically more favorable than any other position. Thus, the calculated vibrational frequencies of the endofullerenes N@C_{32}, N@C_{40}, and N@C_{50} suggest the possibility of synthesis of these com-

Table 2. Energy characteristics and the lowest vibrational frequencies[a] obtained from B3LYP/6-31G* calculations

Molecule[b] (symmetry)	$-E_{\text{total}}$ (au)	ZPE /kcal mol^{-1}	ω1 /cm^{-1}	E_{inc}	E_{inc} + BSSE	$-Q_{\text{N}}$	S_{N}
				kcal mol^{-1}			
C_{20} (C_i)	761.43007	70.96	78.7	—	—	—	—
N@C_{20}	815.66018	66.50	–752.9i	221.37	193.94	0.35	1.17
C_{24} (D_{6d})	913.82255	86.66	276.3	—	—	—	—
N@C_{24}	968.17580	82.88	–842.2i	144.10	141.85	0.43	2.60
C_{30}-3	1142.53440	111.48	326.2	—	—	—	—
N@C_{30}	1197.04649	112.21	333.8	44.42	9.7	0.32	1.09
C_{32}-6	1218.80905	121.46	370.6	—	—	—	—
N@C_{32}	1273.30766	121.84	357.7	52.88	55.73	0.20	2.78
C_{40}-38	1523.69814	152.93	303.2	—	—	—	—
N@C_{40}	1578.25214	153.59	224.0	18.12	21.76	0.08	2.87
C_{50}-271	1904.89019	193.65	278.2	—	—	—	—
N@C_{50}	1959.46352	194.07	122.1	5.99	9.22	0.03	2.93
C_{60} (I_h)[c]	2286.12710	—	—	—	—	—	—
N@C_{60}[c]	2340.70845	—	—	0.77	—	0.001	2.97

[a] Listed are the total energies of the molecule (E_{total}), zero-point vibrational energies (ZPE), the lowest real (or imaginary) frequencies (ω1), the energies of formation of N@C_n in the reaction $\text{N} + \text{C}_n \rightarrow \text{N@C}_n$ without (E_{inc}) and with inclusion of correction for the basis set superposition error (E_{inc} + BSSE), the charges Q_{N} (in terms of Mulliken population analysis), and the spin density S_{N} on the nitrogen *endo*-atom.

[b] Listed are the symmetry or numbering scheme of isomers according to Ref. 21.

[c] Insignificant contributions of the ZPE and BSSE for C_{60} and N@C_{60} were not calculated.

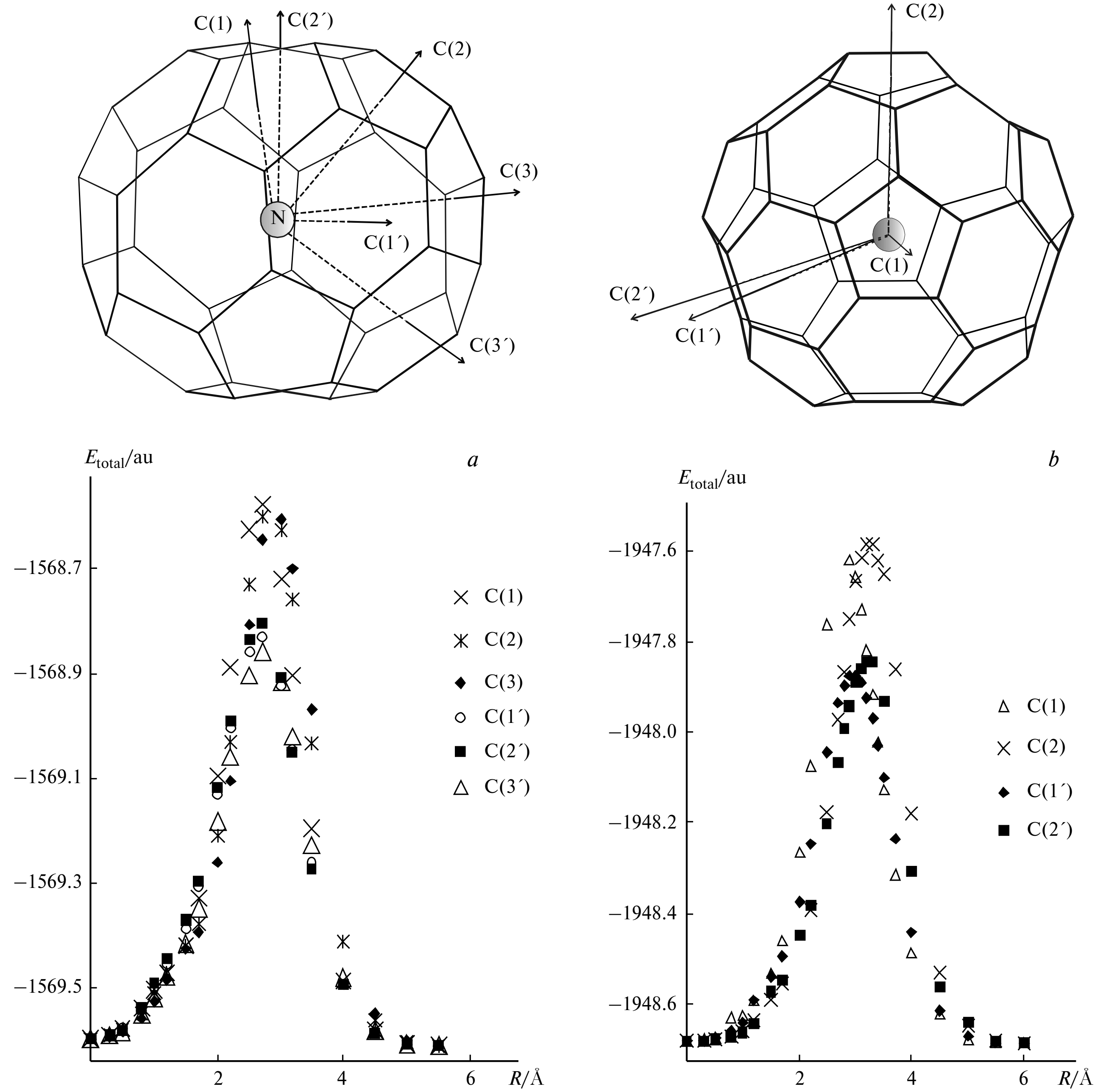


Fig. 2. PES profiles along straight-line trajectories of the motion of the N atom from the center of C_n fullerene toward the carbon cage wall according to B3LYP/3-21G calculations: $n = 40$ (*a*) and 50 (*b*). Shown are the trajectories passing through the centers of inequivalent pentagonal (C(1), C(2), C(3)) and hexagonal (C(1´), C(2´), C(3´)) faces of the fullerene polyhedron.

pounds; however, it is possible to synthesize only the last two of them with allowance for the inclusion energies. The inclusion energy obtained for N@C_{32} is rather high (52.88 kcal mol^{-1}); therefore, the synthesis of this endofullerene seems unlikely.

Spin density and charge on the nitrogen *endo*-atom. Table 2 lists the charges (according to Mulliken population analysis) and spin densities on the nitrogen *endo*-atom. No significant charge transfer between the *endo*-atom and fullerene occurs in all endofullerenes N@C_n. Except for the N@C_{20}, N@C_{24}, and N@C_{32} systems (all are hardly probable to exist), the charges on the nitrogen *endo*-atom are so small that they give almost no indication of a chemical bond.

The spin density on the central atom N in N@C_{40} and N@C_{50} is 2.87 and 2.93, respectively (*cf.* 2.97 for N@C_{60}, calculated in the same approximation), which is consistent with the quartet spin states of these molecules.

Thus, density functional calculations of endohedral compounds of small fullerenes with nitrogen suggest the possibility of existence of the N@C_{40} and N@C_{50} endofullerenes with the N atom in the quartet state, located at the center of the carbon cluster. Under appropriate experimental conditions it is possible to synthesize these molecules whose geometric parameters and energy characteristics are listed in Tables 1 and 2.

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