Full Articles

Chemical bond inside a fullerene cage: is it possible?

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The geometries, electronic structures, and hyperfine coupling constants of azafullerene $C_{59}N$ (a π-electron radical) and its derivatives, $C_{59}NH$ and endofullerene $H@C_{59}N$, were calculated at the B3LYP level of the density functional theory. Analysis of calculated potential energy profiles along trajectories of the motion of encapsulated hydrogen atom from the center of the fullerene sphere toward different atoms of $C_{59}N$ revealed formation of a chemical bond between the H atom and a carbon atom that is involved in the 6,6-bond with the N atom and bears the most part of the π-electron spin density. The C—H *endo*-bond length is 1.12 Å, the bond dissociation energy being equal to 26.4 kcal mol^{-1}. The C—H *exo*-bond involving the same carbon atom is 0.02 Å shorter than the *endo*-bond, the bond dissociation energy being much higher (78.4 kcal mol^{-1}).

Key words: azafullerene, density functional theory, isotropic hyperfine coupling constant

A feature of endohedral complexes of C_{60} fullerene with nonmetals is chemical inertness of the fullerene cage to encapsulated atom. The lifetimes of $N@C_{60}$ and $P@C_{60}$ are known to be of the order of a few hours and the electronic and spin states of the encapsulated atoms are nearly identical to those of free atoms.[1—4] Chemical stability of the inner surface of fullerene cage is in marked contrast with high reactivity of the outer surface that can easily be chemically modified in radical and molecular reactions.

The reason for different reactivities of the inner and outer surfaces of the fullerene cage is that formation of an *endo*-bond requires a large energy expenditure for distortion of the bond lengths and bond angles in the fullerene cage compared to structural distortions accompanying the formation of an *exo*-bond. To estimate this energy difference, we performed quantum-chemical calculations of azafullerene $C_{59}N$ (**1**), which is known to be a π-electron radical,[5] and endofullerene $H@C_{59}N$ (**2**). Our goal was to calculate the potential energy profiles along the reaction trajectories corresponding to motion of a hydrogen atom from the center of the $C_{59}N$ sphere toward different azafullerene atoms. In other words, the aim of this study was to test a feasibility of chemical bond formation between two radicals, an H atom and $C_{59}N$, inside the fullerene cage. For comparison, we also calculated the potential energy profiles for the case where hydrogen atom approaches the atoms of $C_{59}N$ cage from the outside.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 51—54, January, 2005.

Calculation Procedure

The equilibrium structures of the $C_{59}N$ (doublet) and $H@C_{59}N$ (singlet) systems were optimized using the density functional theory with the three-parameter exchange-correlation functional B3LYP and the 6-31G* basis set[6] using the GAUSSIAN-98 program.[6,7] From the standpoint of accuracy and computational efficiency the B3LYP/6-31G* approximation is appropriate for calculations of similar systems.[8,9] This approximation was also employed for calculating (i) potential energy profiles along the trajectory of motion of a hydrogen atom from the center toward different atoms of the $C_{59}N$ cage in the $H+C_{59}N$ system with rigid $C_{59}N$ cage geometry and (ii) isotropic hyperfine coupling constant (HFC) for the optimized structure of radical **1**.

Results and Discussion

Structure and spin densities. The structure of the $C_{59}N$ cage (Fig. 1, *a*) remains nearly undistorted upon encapsulation of a hydrogen atom, *i.e.*, formation of an endofullerene $H@C_{59}N$. The main structural parameters of systems **1** and **2** (Table 1) nearly coincide; the bond lengths and bond angles differ by at most 1%, the difference for the C(2)—N bond being somewhat larger, 1.7%. The parameters of $C_{59}N$ obtained in this work are comparable with the published data.[10]

The calculated and experimentally measured HFC constants for radical **1** are listed in Table 2. Our calculations reproduce the experimental data somewhat better compared to earlier calculations,[11] though in both cases the discrepancies between the theory and the experiment for positions C(2), N, and C(3) is rather large.

Table 1. Structural parameters of $C_{59}N$ and $H@C_{59}N$

Parameter	$C_{59}N$	$H@C_{59}N$
Bond	d/Å	
C(2)—N	1.408	1.384
C(6)—N	1.424	1.422
C(2)—C(3)	1.434	1.432
C(2)—H	—	3.507
Angle	ω/deg	
C(3)—C(2)—C(3)	108.7	109.8
C(3)—C(2)—N	120.1	121.7

Table 2. Calculated and measured constants $a(^{14}N)$ and $a(^{13}C)$ (in mT) of hyperfine coupling with atoms of $C_{59}N$

HFC	Atom	Calculations*		Experiment[11]
		I	II [11]	
$a(^{14}N)$	N	0.41	0.87	0.36
$a(^{13}C)$	C(2)	1.79	2.29	1.18
	C(3)	−0.65	−0.80	(−)0.52
	C(4)	0.68	0.88	0.48

* This work (I) and data taken from Ref. 11 (II).

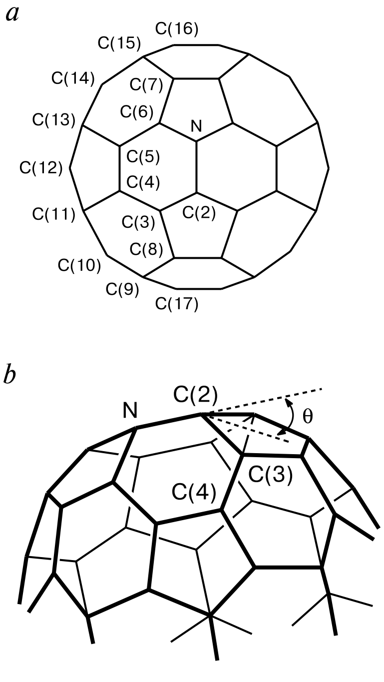

Fig. 1. Molecule $C_{59}N$ (*a*) and deviation of C(2) atom from the plane, characterized by the angle θ (*b*). The atomic numbering scheme is the same as that used in Ref. 11.

In the $C_{59}N$ radical the unpaired π-electron is delocalized over the π-system; however, from experimental and calculated HFC constants[11] it follows that most part of the spin density is localized on the carbon atom C(2); here, $a(^{13}C) = 1.18$ mT. To evaluate the net π-electron spin density on the C(2) atom, we calculated the "umbrella" effect in the $^{\bullet}CH_3$ radical and the dependence of the constant $a(^{13}C)$ on the deviation from the plane.[12] Deviation of the C(2) atom from the plane, which is measured by the angle θ (see Fig. 1, *b*), equals 30.5°; the constant $a(^{13}C)$ calculated for methyl radical with $\theta = 30.5°$ equals 7.9 mT. The estimate of "pure" π-electron spin density on the atom C(2) was obtained as follows: $1.18 : 7.9 = 0.15$. Similarly, the π-electron spin density on the atoms C(3) and C(4) was respectively estimated at −0.07 (−0.52 : 7.9) and 0.06 (0.48 : 7.9) using the same θ and $a(^{13}C)$ values (see Table 2). Negative spin density on the atom C(3) is created by spin polarization of π-bonds; on the contrary, positive spin densities on the atoms C(2) and C(4) are due to spin delocalization.

Reaction trajectories. The potential energy profiles were calculated by varying the distance between the center of the $C_{59}N$ cage and an H atom moving along the lines defined by the vectors connecting the center of $C_{59}N$ and the N, C(2), *etc.*, atoms (see Fig. 2). Calculations were carried out using specified bond length and bond

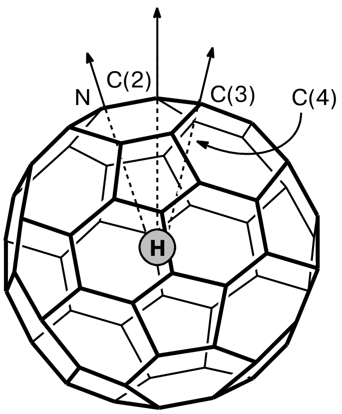

Fig. 2. Trajectories of motion of hydrogen atom from the center of $C_{59}N$ sphere toward the N, C(2), and C(3) fullerene cage atoms.

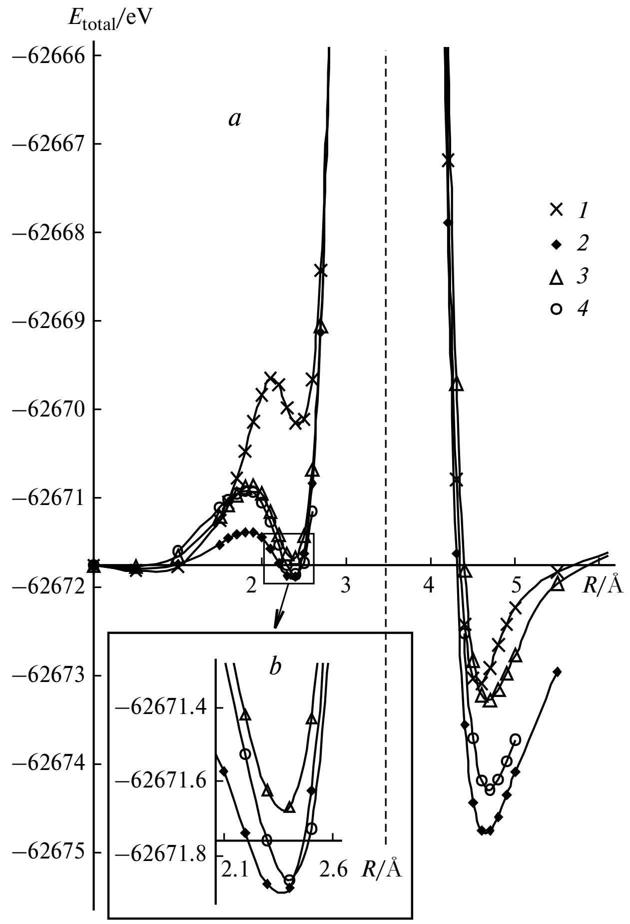

Fig. 3. *a*) Potential energy profiles along the H—N (*1*), H—C(2) (*2*), H—C(3) (*3*), and H—C(4) (*4*) trajectories: $R = 0$ corresponds to hydrogen atom located at the center of $C_{59}N$ sphere; the vertical dashed line at $R = 3.5$ Å denotes positions of fullerene cage atoms. The range $0 \le R < 3.5$ Å corresponds to inner trajectories passing inside the fullerene cage while at $R > 3.5$ Å, trajectories pass outside the fullerene cage. *b*) Fragments of the potential energy profiles in the range $2.1 \le R \le 2.6$ Å (magnified).

angle values in radical **1** optimized at the B3LYP/6-31G* level. The distance R between the center of the $C_{59}N$ sphere and the atom H was varied in the range $0 \le R \le 6.0$ Å.

The calculated potential energy profiles along reaction trajectories (see Fig. 2) are shown in Fig. 3. They can be divided into two groups, namely, the profiles characterizing the motion of the hydrogen atom from the center of fullerene cage toward the N, C(2), C(3), and C(4) atoms and the profiles corresponding to the motion of a distant hydrogen atom from the outside toward the same atoms along the same trajectories.

The energy profiles of the "inner" trajectories correspond to full repulsion; however, local energy minima corresponding to weak bonding between the H atom and the N, C(2), C(3), and C(4) atoms appear in the vicinity of these atoms of the fullerene cage. For two trajectories, H—N and H—C(3), the bonding energy (depth of local minimum) is too low to overcome repulsion, but the H—C(2) trajectory at a distance of 2.4 Å from the center of the fullerene cage exhibits a bonding energy of 3 kcal mol^{-1} (in absolute value) relative to the energy of the hydrogen atom located at the center of $C_{59}N$ taken as zero. In this case, the energy of chemical bonding is higher than the repulsion energy and an *endo*-bond C—H can be formed. The H—C(2) *endo*-bond length is 1.1 Å, being typical of ordinary C—H bonds. Note that as the hydrogen atom approaches the atom C(2), repulsion again dominates the chemical bonding (see Fig. 3).

In contrast to the "inner" trajectories, the "outer" trajectories correspond to attraction (see Fig. 3). Their energy profiles exhibit minima at R(H—N) = 4.6 Å and R(H—C(3)) = 4.7 Å, the bonding energies being ~30 and ~35 kcal mol^{-1}, respectively. The "H—C(2)" trajectory is characterized by the strongest bonding that corresponds to formation of a chemical bond H—C(2) with R(H—C(2)) = 4.6 Å. The *exo*-bond length is 1.1 Å and the bond dissociation energy is ~70 kcal mol^{-1}, being somewhat lower than the energy of the C—H bond in the Me group of toluene (~85 kcal mol^{-1}). As should be expected, as the H atom comes closer to the fullerene cage atoms from the outside, repulsion becomes increasingly stronger.

Corrected energy diagram. As mentioned above, the potential energy profiles along the reaction trajectories of the motion of the H atom were calculated with the rigid fullerene cage geometry. To refine the energies and geometric parameters of the H—C(2) *endo*- and *exo*-bonds, we performed quantum-chemical calculations of corresponding systems with geometry optimization (Table 3). By counting the energies of other molecular systems relative to the energy of noninteracting reagents taken as zero

Table 3. H—C(2) bond energies and bond lengths for optimized geometry

Molecule	d(H—C(2))/Å	E_{total}/a.u.
$C_{59}N$	—	−2302.79137
Noninteracting reagents: $C_{59}N$, H	—	−2303.29164
$H@C_{59}N$	—	−2303.26437
$C_{59}NH$	1.097*	−2303.41658*
	1.120**	−2303.33378**

* *Exo*-bond.

** *Endo*-bond.

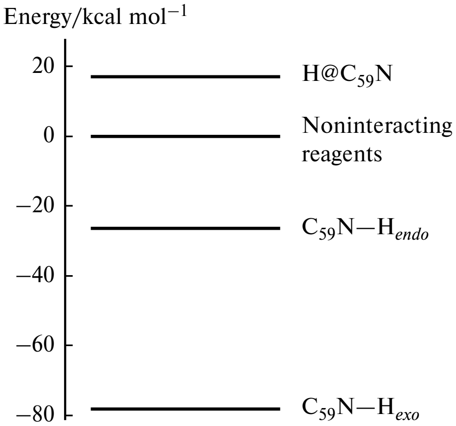

Fig. 4. Energy diagram of the $C_{59}N—H$ system. The total energy of noninteracting reagents is taken as zero: 17.1 ($H@C_{59}N$), 0 (noninteracting reagents: $C_{59}N$ + remote H), −26.4 ($C_{59}N—H_{endo}$), and −78.4 ($C_{59}N—H_{exo}$) kcal mol^{-1}.

it is possible to represent the data listed in Table 3 as a diagram (Fig. 4).

Location of the hydrogen atom at the center of $C_{59}N$ sphere increases the energy of the system $H@C_{59}N$ by 17.1 kcal mol^{-1}. The energy of the $C_{59}NH$ molecule with the H—C(2) *endo*-bond 1.12 Å long decreases by 26.4 kcal mol^{-1}, thus unambiguously suggesting formation of the H—C(2) chemical bond characterized by a dissociation energy of 26.4 kcal mol^{-1} inside the fullerene cage. The energy of the $C_{59}NH$ molecule with the H—C(2) *exo*-bond decreases even more, *viz.*, by 78.4 kcal mol^{-1}. This means that the energy of the H—C(2) *exo*-bond is three times larger than the energy of the corresponding *endo*-bond.

Thus, theoretical analysis of the reaction trajectories of the hydrogen atom placed inside of the $C_{59}N$ sphere revealed chemical bonding between the H atom and the C(2) cage atom bearing the most part of positive π-electron spin density. The *endo*-bonding energy is about 26.4 kcal mol^{-1} and the *endo*-bond length is 1.12 Å. The structure with the H—C(2) *endo*-bond is by 17.1 + 26.4 = 43.5 kcal mol^{-1} more energetically favorable than the $H@C_{59}N$ structure with the hydrogen atom located at the center.

This work was carried out with the financial support from the Division of Chemistry and Materials Science of the Russian Academy of Sciences and the Russian Federation Ministry of Education and Science (in the framework of the Program for Support of Leading Scientific Schools under Grant NSh-1221.2003.3). GAUSSIAN-98 calculations were carried out with the financial support from the Russian Foundation for Basic Research (Project No. 04-07-90220).

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Received September 20, 2004;
in revised form December 3, 2004