Full Articles

Spin density distribution in paramagnetic azafullerene

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Hyperfine coupling (HFC) constants for ^{14}N and ^{13}C nuclei in azafullerene $C_{59}N$ (**1**) were calculated. The HFC constants for the ^{1}H and ^{13}C nuclei in the $^{\bullet}CH_3$ radical were calculated as functions of the pyramidal distortion of the angles at the carbon atom. Using this angular dependence, the spin density distribution of the unpaired π-electron in **1** was determined. The spin density of the unpaired π-electron in **1** is mainly localized around the nitrogen atom.

Key words: azafullerene, hyperfine coupling constant, spin density, quantum-chemical calculations.

Among a variety of fullerenes, only one, namely, azafullerene $C_{59}N$ (**1**, Fig. 1) possesses paramagnetic properties. Replacement of a carbon atom in C_{60} molecule by a nitrogen atom creates a "vacancy" (an unpaired π-electron occupying the lowest unoccupied MO) at the neighboring atom C(2). In the solid phase and in solution

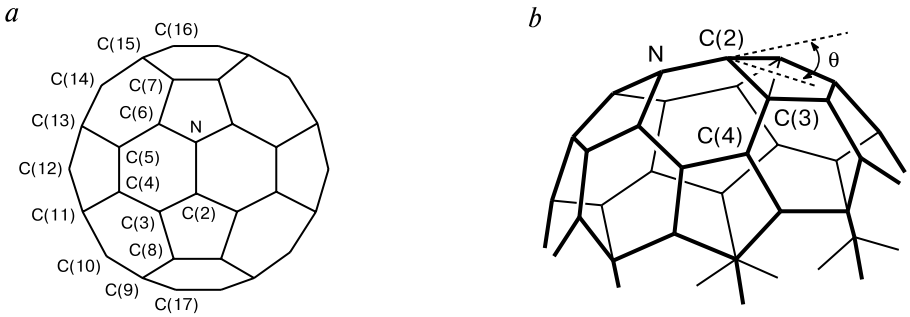

Fig. 1. $C_{59}N$ molecule (*a*) and deviation of C(2) atom from the plane characterized by the angle θ (*b*). The atomic numbering scheme is the same as that used in Ref. 4.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2372—2374, November, 2004.
1066-5285/04/5311-2475

Table 1. Calculated and experimental hyperfine coupling constants $a(^{14}N)$ and $a(^{13}C)$ and π-electron spin density, ρ^{π}, on atoms of azafullerene $C_{59}N$

Atom	a/G				ρ^{π}	
	Calculations			Experiment[4]	Calculations	
	DFT		PAW		III	IV
	I	II				
N	4.1	8.7	3.3	3.6	—	0.08
C(2)	17.9	22.9	13.8	11.8	0.15	0.30
C(3)	−6.5	−8.0	−4.0	(−)5.2	(−)0.07	−0.08
C(4)	6.8	8.8	5.5	4.8	0.06	0.14

Note: I — obtained in this work; II — data taken from Ref. 4; PAW denotes the results obtained using the projected augmented wave method;[5] III — calculated using relation (1) and experimental data taken from Ref. 4; and IV — obtained in this work from B3LYP/6-31G* calculations.

azafullerene exists as a dimer, $(C_{59}N)_2$,[1] which undergoes a reversible dissociation being heated or photolyzed both in solution[2] and in the solid phase.[3]

The ESR spectrum of **1** in solid solutions of $C_{59}N$ in C_{60} was studied in detail.[4] Table 1 lists the experimental isotropic hyperfine coupling (HFC) constants and the HFC constants obtained from earlier DFT[4] and projected augmented wave (PAW)[5] calculations.

Comparison of the calculated and experimental HFC constants demonstrates a common trend in their distribution over nuclear sites (carbon and nitrogen atoms); however, quantitative agreement between experiment and theory is not always satisfactory (the best results were obtained in Ref. 5 and in this work).

The unpaired π-electron delocalized over the π-system of the $C_{59}N$ fullerene sphere is distributed nonuniformly. To estimate the "pure" π-electron spin density on C atoms rather than the s-orbital contribution responsible for the isotropic HFC constant, one should establish a quantitative relation between the π-electron spin density and the isotropic HFC constant. For planar π-radicals (*e.g.*, $^{\bullet}CH_3$), this relation is well known[6]

$$a(^{13}C) = Q\rho^{\pi}, \qquad (1)$$

where ρ^{π} is the π-electron density on the C atom and Q = 45 G. A feature of non-planar radicals including $C_{59}N$ is the "umbrella" effect characterized by (i) deviation of the C atom containing the unpaired electron from the plane and (ii) partial change in the hybridization of this C atom, which becomes intermediate between sp^2 and sp^3. This results in an increase in the HFC constant $a(^{13}C)$ and in the parameter Q (the isotropic HFC constant normalized to $\rho^{\pi} = 1$).

We calculated the deviation of the C(2) atom from the plane as function of the angle θ (see Fig. 1, *b*) starting from the B3LYP/6-31G*-optimized[7] geometry of $C_{59}N$ and found that θ = 30.5°. To determine ρ^{π} from Eqn (1) using experimental $a(^{13}C)$ values, one should know the parameter Q at θ = 30.5°.

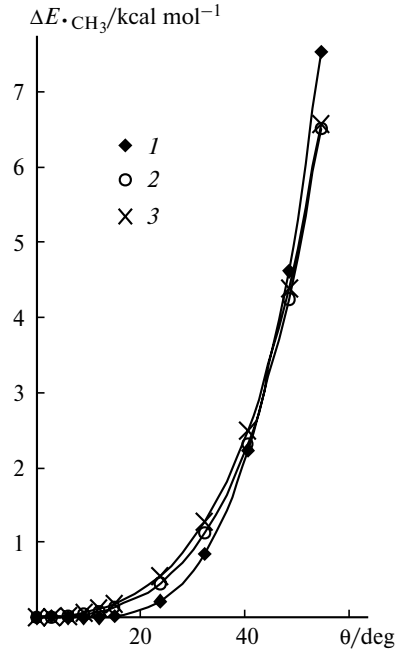

Fig. 2. Changes in energy (ΔE) of $^{\bullet}CH_3$ radical plotted *vs.* angle θ. Enegy calculations were performed by the INDO (*1*), UHF/6-311G** (*2*), and UMP2/6-311G** (*3*) methods.

To this end, we calculated the energy and the HFC constants for $^{\bullet}CH_3$ radical as functions of the angle θ. Changes in the energy of the $^{\bullet}CH_3$ radical relative to the energy of the most stable planar structure are shown in Fig. 2. Note that at small and moderate structural distortions all methods give nearly coinciding results.

The HFC constants $a(^{13}C)$ and a(H) plotted *vs.* angle θ are shown in Fig. 3. In systems similar to those under study the absolute value of the HFC constant a(H) decreases[8,9] because the contribution of positive spin density in the 1s-orbital on proton increases, thus compensating the negative spin density created in the planar radical due to spin polarization of the π-electron of the C—H bond.[6] The HFC constant $a(^{13}C)$ increases as θ increases (*i.e.*, as the "umbrella" turns inside out). At θ = 30.5°, $a(^{13}C)$ equals 79 G (at $\rho^{\pi} = 1$). Now, substituting the $a(^{13}C)$ values into Eqn (1) with Q = 79 G, we can obtain "pure" π-electron spin densities on carbon atoms in **1** (see Table 1, column III).

Comparison of these ρ^{π} values with the results of calculations (see Table 1, column IV) reveals considerable differences between them (nearly twofold differences for the C(2) and C(4) atoms). The ρ^{π} values listed in column IV should be considered as reliable. The reason for discrepancies is that the semiempirical relationship (1) is

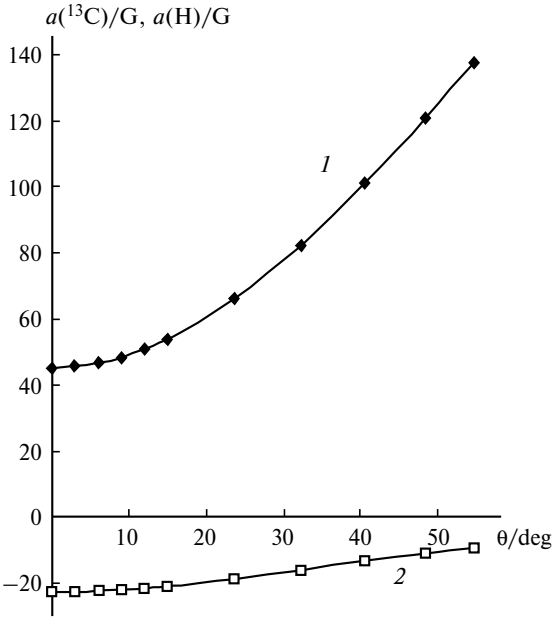

Fig. 3. Hyperfine coupling constants $a(^{13}C)$ (*a*) and *a*(H) (*b*) for radical $^{\bullet}CH_3$ plotted *vs*. angle θ. Calculated by the INDO method.

too rough to allow for nonlocal contributions of adjacent atoms to the spin polarization. A much more accurate value of the parameter Q in Eqn (1) can be obtained if we use the experimental value $a(^{13}C) = 11.8$ G and a ρ^{π} value of 0.30 calculated for the C(2) atom. Then, $Q \approx 40$ G.

Clearly, at least half the spin density of the unpaired electron of fullerene radical $C_{59}N$ is localized on carbon atoms near the nitrogen atom, which can be considered as a specific kind of a spin trap.

Calculation Procedure

The HFC constants for $C_{59}N$ (see Table 1) were calculated using the DFT approach with the three-parameter exchange-correlation potential B3LYP with the 6-31G* basis set,[10] and the GAUSSIAN-98 program suite.[11]

For $^{\bullet}CH_3$, energy calculations were carried out by the *ab initio* methods in the 6-311G** basis set using the unrestricted Hartree—Fock method and with inclusion of electron correlation in the framework of the UMP2 procedure, and by the semiempirical INDO method.[12] The HFC constants were calculated by the INDO method. All C—H bond lengths in all structures of the $^{\bullet}CH_3$ radical were assumed to have a standard value of 1.09 Å.

This work was carried out with the financial support from the Chemistry and Materials Science Branch 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. 01-07-90072).

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Received May 19, 2004;
in revised form August 31, 2004