

Satellite lines in the EPR spectra of nitroxide radicals: experimental data and DFT calculations

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The ^{13}C coupling constants in the β - and γ -positions of stable nitroxide radicals were obtained by the simulation of EPR spectra and quantum-chemical calculations.

Stable nitroxide radicals are of interest as spin probes for studying the structures of various matrices, the kinetics and mechanisms of reactions in chemical and biological systems, *etc.*^{1–4} These radicals give an opportunity to compare the results of quantum-chemical calculations with experimental data.^{1,5}

For the successful application of nitroxides as spin probes, it is necessary to know peculiarities of their EPR spectra, which consist of three lines due to the hyperfine interaction of an unpaired electron with the ^{14}N nucleus. However, the spectra recorded in liquid solutions at a high temperature often include additional low-intensity lines (satellites) as a result of the hyperfine interaction of the magnetic moment of an unpaired electron with the magnetic moments of ^{13}C and ^{15}N nuclei.

The hyperfine structure (HFS) constants on ^{13}C nuclei suggest a spreading of spin density, which is mainly localized on the π -orbitals of nitrogen and oxygen atoms in the molecule. The experimental determination of HFS constants on ^{13}C is quite rare research. For example, such data were obtained by NMR spectroscopy for di-*tert*-butyl nitroxide and 2,2,6,6-tetramethylpiperidin-1-oxyl.^{6,7} The aim of this work was to compare the calculated ^{13}C coupling constants with the experimental data for three stable structurally different nitroxide radicals 1–3 (Figure 1).[†]

The quantum-chemical computations were performed using the ORCA software package. The B3LYP/N07D computational model was used for geometry optimization. Previously, this model was tested with 2,2,6,6-tetramethylpiperidin-1-oxyl, 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl and 3-carbamoyl-2,2,5,5-tetramethylpyrrolidin-1-oxyl. The optimized bond lengths and angles differed from the values found by X-ray single crystal diffraction analysis⁸ by no more than 10^{-3} nm and 0.5° , respectively. For calculating HFS constants, we used the B3LYP functional and

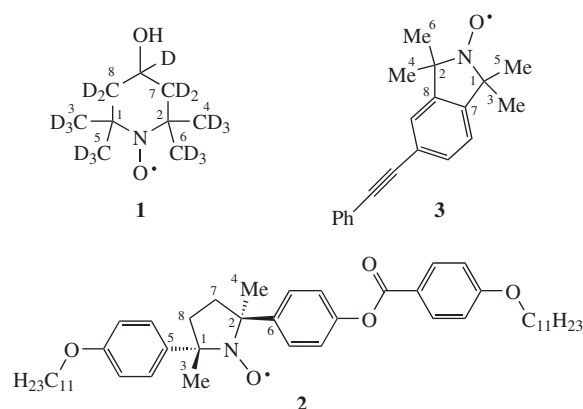


Figure 1 Structures of the test radicals. The carbon atoms, for which the splitting constants are discussed, are marked by numbers: 1, 2 (β -C), 3–8 (γ -C).

N07D, EPR-II, EPR-III, cc-pVTZ basis sets. The computation was performed according to the COSMO continuum model (toluene, $\epsilon = 2.3879$).

Figure 2 shows fragments of the EPR spectra of radicals 1–3. It was found in additional experiments that the number of satellites in a spectrum does not depend on the solvent.

The satellites marked by three stars can be attributed to ^{15}N hyperfine splitting ($I = 0.5$; g -factor, -0.5663784 ; nature content $\sim 0.4\%$). The value of this splitting is greater than the splitting on ^{14}N ($I = 1$; g -factor, 0.4037607 ; nature content $\sim 99.6\%$) by a factor of 1.4. Such satellites were described in detail elsewhere.¹⁰ In the spectra of radicals 2 and 3, these lines are masked by wide basic lines because of the unresolved splitting on hydrogen nuclei, but they are well distinguishable in the spectrum of deuterated radical 1. The satellites marked by one and two stars are related to splitting on ^{13}C nuclei.^{11–13} The natural content of ^{13}C ($I = 0.5$) comes to 1.1%. If unpaired electron density is distributed among several carbon atoms, the molecules containing the ^{13}C nuclei in different positions contribute to the integral intensity of satellites.

For explaining the different numbers of satellites in the spectra of the nitroxides, we performed the DFT computation of isotropic HFS constants on carbon nuclei using the B3LYP functional and several basis sets including the N07D special basis¹⁴ for the calculation of magnetic characteristics (Table 1). The calculated values exceed 1 G only for carbon atoms in the β - and γ -positions (Figure 1, 1–6). Note that the HFS constants for γ - ^{13}C in the 7- and 8-position are considerably lower than those for γ - ^{13}C in the 3- to 6-positions. The HFS constants can be considerably different for γ - ^{13}C in axial and equatorial methyl substituents. Table 1 indicates that, in the case of radical 3, the absolute values

[†] Radical 1 was purchased from Aldrich and radicals 2 and 3 were kindly provided by Professor R. Tamura (Kyoto University, Japan) and Professor S. Bottle (Queensland University, Australia), respectively. The radicals were used without additional purification and toluene (solvent) was purified by distillation.

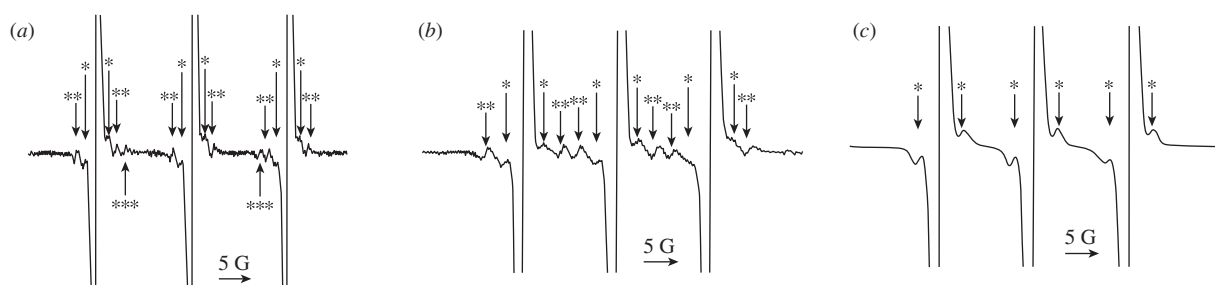
The solutions of the radicals in toluene (concentration, $\sim 1 \times 10^{-3}$ mol dm^{-3} ; volume, ~ 0.07 ml) were placed in quartz ampoules (inner diameter, ~ 3 mm) and degassed by three times repeated freezing (77 K)–pumping (10^{-2} Torr)–heating (298 K) cycles.

The EPR spectra were recorded at 298 K using a Varian-E3 spectrometer. For the calibration of a magnetic field scale, the sample of MgO with an admixture of Mn^{2+} ions was used.

Computer simulation of the spectra was performed by the software developed by our research team (author – A. Kh. Vorobiev, Moscow State University, Russia). The open source code program can be found here: <http://www.chem.msu.ru/eng/lab/chemkin/ODF3/>.

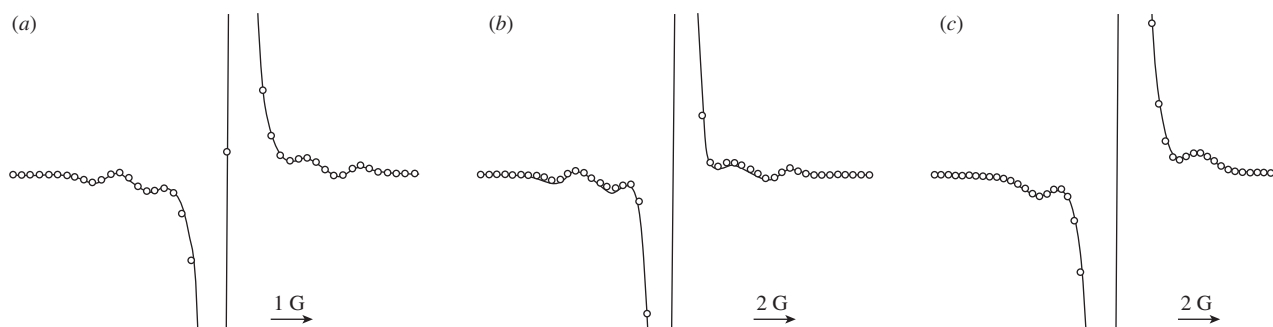
Table 1 The absolute values of isotropic HFS constants (G) for ^{13}C nuclei obtained by quantum-chemical calculations (B3LYP).

Nucleus	Radical 1				Radical 2			Radical 3		
	N07D	EPR II	EPR III	cc-pVTZ	N07D	EPR II	cc-pVTZ	N07D	EPR II	cc-pVTZ
C1	4.1	3.9	3.7	3.2	6.3	6.2	5.2	6.3	6.6	5.5
C2	4.1	3.9	3.7	3.2	6.4	6.2	5.2	6.3	6.6	5.5
C3	6.5	6.4	6.4	5.8	10.2	10.5	9.7	7.3	6.5	6.0
C4	6.5	6.4	6.4	5.8	7.7	7.6	7.1	7.3	6.5	6.0
C5	2.9	2.8	2.8	2.6	4.0	4.1	3.9	7.3	6.5	6.0
C6	2.9	2.8	2.8	2.6	6.9	8.1	7.5	7.3	6.5	6.0
C7	0.6	0.6	0.6	0.5	0.2	0.2	0.2	0.2	0.3	0.3
C8	0.6	0.6	0.6	0.5	1.0	1.0	0.9	0.2	0.3	0.3

**Figure 2** Fragments of the EPR spectra of radicals (a) 1, (b) 2 and (c) 3 in toluene at 298 K.

of HFS constants for all carbon atoms adjacent to the NO group are close to one another. In this case, only one kind of satellites can be observed in the EPR spectrum. Oppositely, in the cases of radicals **1** and **2**, the absolute values of HFS constants for ^{13}C nuclei in the β - and γ -positions are significantly different; this can lead to the appearance of several groups of additional lines in EPR spectra.

For a comparison of the calculated HFS constants with the experimental ones, we performed a computer simulation of the central components of the experimental EPR spectra (Figure 3). Note that, in the simulation, the satellites were described as individual spectral components, while they can be the superposition of several lines with different splitting. For example, in radical **1**, one pair of satellites is a result of the superposition of lines with the same HFS constants (splitting on nuclei 3 and 4); thus, these satellites can be considered as individual components. At the same time, another pair of satellites arises because of the superposition of lines with close but not the same HFS constants (splitting on nuclei 1, 2, 5 and 6). These satellites can be described as individual components of the spectrum only approximately. An attempt to simulate the EPR spectra taking into account all probable satellites was related to the variation of a large number of correlated parameters, and it did not give unambiguous results. Thus, it was possible to compare the experimental data with the results of quantum calculations only qualitatively. The differences between splitting constants calculated using different basis sets were found within the limits of experimental errors.

**Figure 3** Computer simulation of the central spectral lines of radicals (a) 1, (b) 2 and (c) 3 in toluene at 298 K. Lines and circles refer to the experimental spectra and the results of simulation, respectively.**Table 2** Hyperfine splitting constants and contributions to integral intensity of the spectral line for satellites attributed to the ^{13}C nucleus.

Satellite ^a	Radical 1	Radical 2	Radical 3
a_1	3.6 G (2.6%)	4.4 G (6.3%)	6.0 G (4.1%)
a_2	6.5 G (1.3%)	10.8 G (1.1%)	—

^aSatellites marked by one star (a_1) and by two stars (a_2) in Figure 2.

Table 2 summarizes the experimental HFS constants and the contributions of satellites to the integral intensity of a spectral line. Since the natural content of ^{13}C is $\sim 1.1\%$, such a contribution can be calculated as $(1.1N)\%$, where N is the number of ^{13}C nuclei that contribute to this satellite. In the case of radical **3**, the experimental HFS constant is close to the calculated constant averaged over carbon atoms 1–6. Difference between the integral contribution and the expected value ($\sim 6.6\%$) is probably related to the above errors of spectrum simulation.

In the case of radical **1**, an HFS constant (lines marked by two stars in Figure 2) is equal to the value calculated for C3 and C4. Another constant (marked by one star) is very close to the value averaged over C1, C2, C5 and C6. The total integral contribution of all satellites comes to 3.9% instead of an expected value of 6.6%, but the ratio of contributions of two kinds of satellites is 1/2 as expected.

The results obtained for radical **2** are more difficult to interpret. Qualitatively, the results of quantum calculations correspond to

the experiment. According to the calculation, the HFS constant for the carbon atom C3 differs significantly from the others and lies in a range of 9.7–10.5 G depending on basis set. According to the numerical analysis of the experimental EPR spectrum, one pair of satellites is characterized by a hyperfine splitting of 10.8 G, the integral intensity of these satellites is 1.1%. Consequently, this pair of lines is a result of the interaction of an unpaired electron with one ^{13}C atom. The integral contribution of another pair of satellites is 6.3% (expected value, 5.5%). The experimental HFS constant for these satellites (4.4 G) is considerably lower than the HFS constant averaged over the carbon atoms C1, C2, C4, C5 and C6 (6.2 G). It might be supposed that in the case of the radical with sufficiently asymmetric surrounding of the paramagnetic N–O fragment the quantum calculations cannot give so precise values of splitting constants as in the cases of symmetric radicals.

Thus, multiple satellites in the spectra of nitroxide radicals mainly result from the interaction of an unpaired electron with ^{13}C nuclei. The HFS constants for ^{13}C nuclei can be calculated by quantum chemistry methods.

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