

Spin propagation through the C–C and C–H bonds

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The signs of spin density on the carbon atoms and protons attached to them in nitroxides (nitroxyl radicals) with fixed geometry strictly alternate demonstrating unambiguously that spin propagation along the carbon chains of saturated C–C bonds occurs by a mechanism of spin polarization. Spin densities, both calculated and measured by NMR spectroscopy, exhibit convincing agreement both in signs and magnitudes.

Electric current along the saturated C–C bonds is known to attenuate almost exponentially with the number of bonds; its measuring becomes accessible at the level of a single molecule.¹ Electric conductivity of chemical bonds is directly relevant to the molecular electronics; spin conductivity is important in terms of molecular spintronics. Another problem stimulating interest in the spin propagation is the design of purely organic ferromagnetic materials based on organic spin molecules such as nitroxides.² The goal of this work was to calculate spin densities in saturated nitroxides, to control their validity by experimental data and to formulate a mechanism of electron spin propagation along the C–C and C–H bonds. We have chosen nitroxides as a model system, for which hyperfine coupling constants (HFCs) measured by NMR spectroscopy were summarized⁷ and referred to the fixed conformations of radicals.^{8–13}

The distribution of spin density in any spin molecule is inhomogeneous in both magnitude and sign: in some points of the molecule, spin density is negative, *i.e.*, partial local spin at these points is aligned opposite to the total electron spin of the molecule. The magnitudes of spin densities $\rho(0)$ are usually determined by hyperfine coupling constants a measured by EPR spectroscopy according to the well-known equation³

$$a = (8\pi/3)\gamma_e\gamma_n\rho(0). \quad (1)$$

Here, γ_e and γ_n are magnetic parameters for the electron and nucleus, respectively. However, the most reliable means to measure simultaneously both the sign and magnitude of spin density is NMR spectroscopy. The NMR lines of spin molecules are shifted with respect to those of the corresponding diamagnetic, spinless molecules by magnitudes^{4,5}

$$\Delta H = -a(\gamma_e/\gamma_n)(\gamma_e H_0/kT). \quad (2)$$

Here H_0 is the magnetic field strength. Usually, $\rho(0)$ is determined according to the equation

$$\rho(0) = a/a_0 \quad (3)$$

by comparing experimentally found a with the parameter a_0 calculated as if unpaired electron is wholly occupying the ns orbital of an atom concerned. The magnitudes a_0 were tabulated;⁶ particularly, a_0 is 1420 MHz for the hydrogen atom and it is 3110 MHz for the ¹³C nucleus.

The summary of calculated spin densities[†] is given in Table 1S (see Online Supplementary Materials). Note that the different computational models result in the quite close magnitudes.

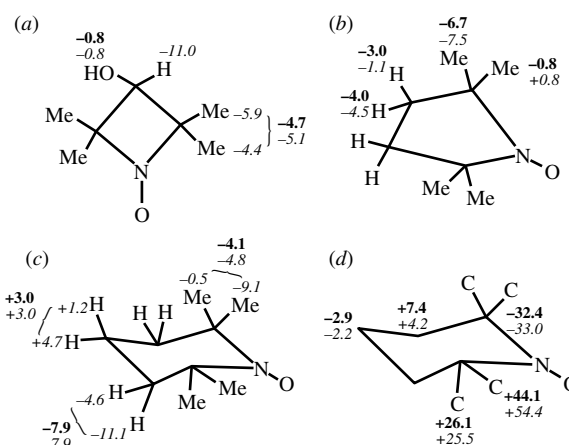


Figure 1 Spin densities in four-, five- and six-membered rings.

Chemical structures of nitroxides are shown in Figures 1 and 2; calculated spin densities are indicated by figures at the certain positions; experimental magnitudes are marked bold, calculated ones are italics. All spin densities are given in the units of (a/a_0) multiplied by 10^4 ; for instance, 4.7 means 4.7×10^{-4} of the absolute spin density. Nitrogen atom in nitroxides is considered to be in the α -position, the distant carbon atoms are in the β , γ , δ and ϵ positions, respectively.

For four-membered ring, spin densities on the protons attached to the γ -C atoms are shown in Figure 1(a); they are negative, both calculated and experimental.

For five-membered ring, both calculated and experimental spin densities on the protons for the four-methyl substituted five-membered ring are presented in Figure 1(b). Similar to the

[†] DFT calculations of spin densities were performed by means of the ORCA software package. For each radical, the geometry optimization was carried out whereupon the magnetic parameters were calculated. The computational model B3LYP/6-31g(d,p) was used for geometry optimization. The optimized geometries of the radicals and the Cartesian coordinates of the atoms are given in Online Supplementary Materials. For calculation of HFC constants, the widely used B3LYP and PBE0 functionals and two basis sets N07D¹⁴ and TZVP¹⁵ were employed. Earlier, it was shown¹⁶ that, in the case of nitroxide radicals, the spin densities calculated using the basis N07D insignificantly differ from those calculated in the EPRII and EPRIII bases. Computation was performed according to the COSMO¹⁶ continuum model (toluene, ϵ 2.387¹⁷).

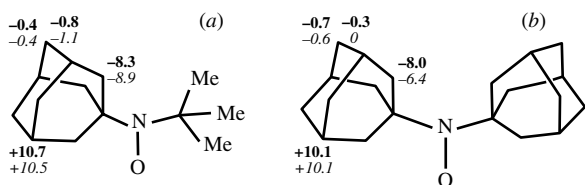


Figure 2 Spin densities in adamantane rings.

four-membered ring, in this case, spin densities are also negative on the protons attached to the γ -C atoms both in axial and equatorial positions with a dominating contribution of axial protons. There is a good agreement between experimental and calculated magnitudes; the only exclusion is a difference in spin densities on the equatorial Me protons (-0.8 and $+0.8$, respectively), but it is hardly important because these densities are small and by an order of magnitude lower than those on the axial Me protons. Note that, in this case, the functional PBE0 results in a negative spin density.

For six-membered ring, the calculations were performed only for the radical in a stable chair form. Like four- and five-membered rings, spin densities on the protons at the γ -C atoms in the six-membered ring are negative [Figure 1(c)] with the dominating contribution of axial protons. Oppositely, on the protons at δ -C atom, spin densities are positive.

Spin densities on the carbon atoms are given in Figure 1(d). On the β -C atoms, they are negative (-32.4), on the γ -C atoms they are positive ($+44.1$, $+26.1$, and $+7.4$), but on the δ -C atoms they are again negative and small (-2.9). The above spin densities were calculated using tabulated magnitudes of the Fermi constants; they signify spin populations of s -orbitals. Moreover, the signs of spin density on the p -orbitals are shown to be identical to those on the s -orbitals for each carbon atom.

Note that the signs of spin densities on the all carbon atoms are opposite to those on the protons attached to them. The calculated and experimental spin densities are in quite good agreement.

Spin density distribution in the adamantane rings (Figure 2) is generally in a perfect agreement with that in the four-, five-, and six-membered rings.

Spin density alternates: on the proton at γ -C atoms, it is negative (-8.3); on the δ -protons, it is positive ($+10.7$), and it is again negative (-0.8 and -0.4) on the ϵ -protons. The results are very similar for the nitroxides with one and two adamantyl groups. A good agreement between calculated and experimental spin densities are clearly expressed.

General properties characterizing spin propagation along the saturated chemical bonds may be formulated as follows. Spin densities on the carbon atoms exhibit sign alternation: $\rho(0)$ is negative on β -C atoms (with respect to positive spin density on the nitrogen α -atom), positive on the γ -C atoms and again negative on the δ -C atoms. Spin densities on the protons attached to the carbon atoms are opposite to those on the carbon atoms: they are negative if protons are attached to the γ -C atoms and positive if they are attached to the δ -C atoms.

The alternation between positive and negative spin densities was discussed for about 50 years. However, the conclusion on the alternation was not rigorous; in particular, for the aliphatic chain $\text{CH}_2(\text{CH}_2)_n\text{CH}_3$ with unpaired π -electron located on the terminal CH_2 radical fragment, spin density was shown to be positive on the protons in β , γ and δ positions with attenuating magnitude along the chain.⁷ The reason is that the spin density comes from the two superimposed contributions: π -electron delocalization and σ -electron spin polarization. We suppose that the advantage of our work is unambiguous evidence that, in the pure σ -electron systems with fixed geometry, spin polarization is the dominating, if not the only, mechanism of spin propagation.

Alternation of spin density may be stemmed from the direct movement of an unpaired electron by delocalization; it is supposed to occur as a tumbling of electron when it jumps from one atom to another. However, this mechanism seems unbelievable, and it has no physical reasoning. An alternative behavior of spin densities unambiguously indicates that the main contribution into the spin propagation stems from the spin polarization mechanism. It implies that an unpaired electron on some atom attracts an electron of the chemical bond with the same spin but repulses another electron with the opposite spin. It results in the spin polarization of chemical bond accompanied by the partition of different spins on the neighboring atoms. The physical background of spin polarization follows from the universal Pauli principle: a virtual triplet spin state lies lower in energy than a singlet spin state. Quantitatively, spin polarization is characterized by exchange energy; a good agreement between experimental and calculated spin densities confirms that quantum models satisfactorily reproduce exchange interactions of electrons in spin molecules.

The sign of spin density is a key parameter to design purely organic ferromagnetic materials. In organic spin molecules unpaired electrons occupy an upper molecular orbital, being localized mainly on the 'surface' of the electron shells so that intermolecular exchange interaction responsible for the spin alignment is negative. It arranges spins of neighboring, even high spin molecules, opposite to each other, so that the total macroscopic spin is zero. For this reason, even solid oxygen is diamagnetic.

Suppose that spin molecules in a crystal or glass are arranged in such a remarkable manner that one molecule positive spin density regions face another molecule negative spin density regions and this alternation of spin density signs holds for the whole bulk. The negative inter-spin exchange interaction aligns these two spin subsystems in opposite directions: the positive spin densities are oriented in one direction and the negative densities, in the opposite one. However, the positive spin densities are much larger than the negative ones, so that the macroscopic total spin corresponds to the ferromagnetic alignment. It means that the purely organic ferromagnetism may be designed *via* anti-ferromagnetic interactions. This idea was first formulated by McConnell¹⁸ and later generalized for all molecule-based magnets;^{2,19} it attracts renewed interest in relation to nanomagnets and magnetic nanocatalysts.^{20,21}

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2015.07.010.

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