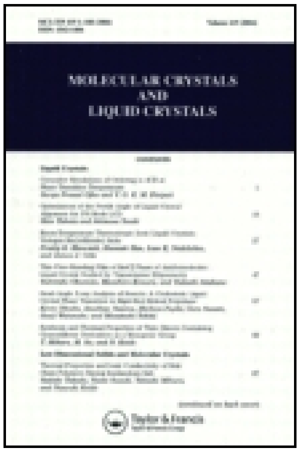

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Endor/Triple Study of Heterocyclic-Substituted Nitronyl Nitroxide Radicals: Influence of Heteroatoms on the Intramolecular π-Spin Density Distribution

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ENDOR/TRIPLE STUDY OF HETEROCYCLIC-SUBSTITUTED NITRONYL NITROXIDE RADICALS: INFLUENCE OF HETEROATOMS ON THE INTRAMOLECULAR π-SPIN DENSITY DISTRIBUTION

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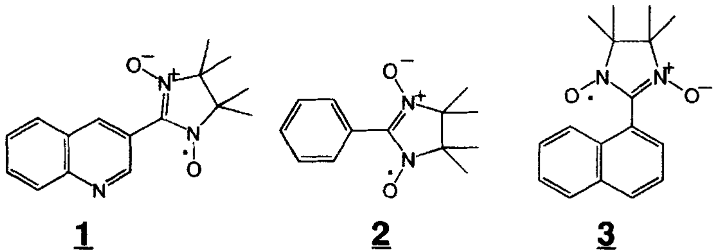
Abstract The influence of introducing heteroatom into carbon-based π-conjugation on the intramolecular π-spin density distribution was examined for three kinds of nitronyl nitroxide radical molecules. The magnitudes and relative signs of the π-spin densities for a heterocyclic substituted nitronyl nitroxide radical, 3-quinolyl nitronyl nitroxide were determined by liquid-phase ^{1}H-ENDOR and TRIPLE spectroscopy. A pronounced negative spin density ($\rho = -0.032$) was found in the 2- or 4-position of the quinolyl ring. The ρ value is about 3/2 times as large as that of the non-heterocyclic molecules, phenyl nitronyl nitroxide and 1-naphtyl nitronyl nitroxide. The mechanism for the enhanced amplitude of the negative spin polarization in the quinolyl derivative is explained in terms of the topological relation between the heteroatom and the nitronylnitroxide group.

INTRODUCTION

The magnetism of organic molecule-based materials has been attracting ever-increasing interest after the discovery of the first purely organic ferromagnet, *p*-NPNN.[1,2] In recent years much efforts have been devoted to both understanding the mechanism of intermolecular ferromagnetic interactions and developing new ferromagnetic materials.[3] The intramolecular exchange interaction (intramolecular spin polarization) as well as crystal packing is crucial to the intermolecular magnetic interactions in the crystals of the molecule-based magnets. In the light of the intramolecular spin polarization effect of a stable organic radical family, α-substituted nitronyl nitroxide derivatives,[4-6] the unequivocal, experimental determination of their π-spin density distribution is important from the viewpoint of building blocks of organic magnets. The experimental determination of the π-spin density distribution of the nitronyl nitroxide molecules has been reported only for a few derivatives by neutron diffraction,[7-9] NMR,[5] and liquid-phase electron-nuclear multiple resonance (ENMR) spectroscopy.[10]

In this paper, we discuss the π-spin density distribution for three kinds of nitronyl nitroxide derivatives elucidated by means of liquid-phase ENMR spectroscopy. The present ENMR study is focused on the influence of the introduction of heteroatoms into carbon-based aromatic π-conjugation on the π-spin density distribution. The molecules under study are 3-quinolyl nitronyl nitroxide (1),[11-13] phenyl nitronyl nitroxide (2),[10] and 1-naphtyl nitronyl nitroxide (3) [13] (Figure 1). From the isotropic hyperfine coupling constants (hfcc's, A) obtained by liquid-phase proton-(^{1}H-)ENDOR (electron nuclear double resonance) spectroscopy, the magnitudes of the π-spin densities at the aromatic ring carbon sites are determined. The relative signs of the π-spin densities are determined by general-TRIPLE (electron nuclear nuclear triple resonance) spectroscopy and INDO MO calculations are invoked for their interpretation. The π-spin density of 1 is compared with that of 2[10] which has a nitrogen-free phenyl substituent. A liquid-phase ENDOR spectrum of 3 is also measured and compared with that of 1 as another example of non-heterocyclic π-radical.



1 (3-QNNN) 2 (PNN) 3 (1-NAPNN)

FIGURE 1 α-Substituted nitronyl nitroxide radicals, 3-quinolyl nitronyl nitroxide (3-QNNN), phenyl nitronyl nitroxide (PNN, 2) and 1-naphtyl nitronyl nitroxide (1-NAPNN, 3).

EXPERIMENTAL

The nitronylnitroxide radicals were synthesized by the reported method.[6] The liquid-phase cw-ESR, ^{1}H-ENDOR and ^{1}H-TRIPLE spectra of the radical molecules were recorded in mineral oil solutions (10^{-5} M) at temperature range of T= 282~293 K on Bruker ESR/ENDOR spectrometers ESP300/350 and ESP380E/360. The solutions were degassed before the ENMR measurements.

RESULTS AND DISCUSSION

cw-ESR and ^{1}H-ENDOR of 3-QNNN

The liquid-phase ESR spectrum of <u>1</u> exhibited hyperfine structure characteristic of two equivalent nitrogen nuclei as shown in Figure 2. Hyperfine splittings due to methyl or quinolyl-ring protons and ring nitrogen are unresolved in the spectrum.

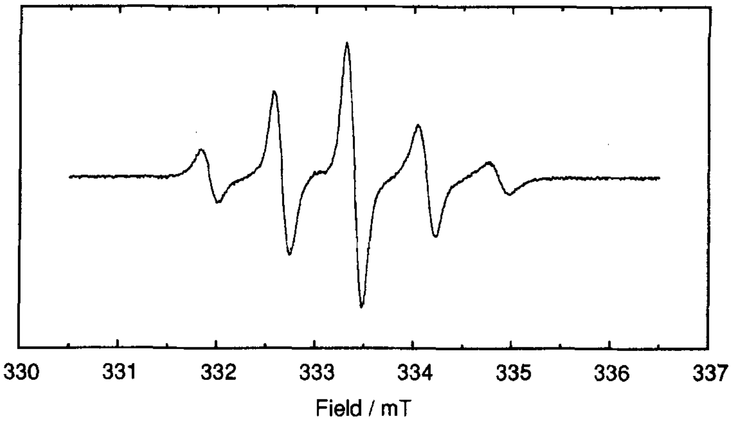


FIGURE 2 Liquid-phase ESR spectrum of 3-QNNN (1) observed in mineral oil at 293 K. The microwave frequency was 9.3692 GHz.

For doublet (S=1/2) radicals, the ENDOR signal with the hfcc value of $|A_i|$ smaller than $2\nu_H$ appears at

$$\nu_{\pm} = \nu_H - A_i m_S/h = \nu_H \pm A_i/2h \qquad (m_S = -1/2 \text{ or } +1/2), \tag{1}$$

where ν_H is the NMR frequency of free proton. The hfcc $|A_i|$ is determined from the separation between a pair of the ENDOR transitions at $\nu_{\pm}$. As depicted in Figure 3, three pairs of ENDOR signals were found for a mineral oil solution of 1 at 282 K by monitoring the most intense central ESR line at 333.4 mT in Figure 2;

$$|A_1|/h = 0.59 \text{ MHz}, |A_2|/h = 0.9 \sim 1.1 \text{ MHz}, |A_3|/h = 2.02 \text{ MHz}. \qquad (2)$$

^{1}H-ENDOR signal intensity is proportional to the number of equivalent protons if the protons in the system experience similar spin relaxation processes in the weak limit of radiofrequency (RF) irradiation. The integrated intensity ratio of the ENDOR signals of **1** suggests that the innermost pair with the hfcc of A_1 is attributable to the twelve methyl protons. The hfcc value, $|A_1|/h = 0.59$ MHz, is nearly equal to that of phenyl nitronyl nitroxide radical.[10] The other two kinds of ENDOR signals with $|A_2|$ and $|A_3|$ are assignable to quinolyl ring protons. All the ring-protons are expected to be inequivalent considering the molecular structure. However, the signals from the ring protons are not fully resolved in the observed spectrum but grouped into two pairs of broad signals with $|A_2|$ and $|A_3|$.

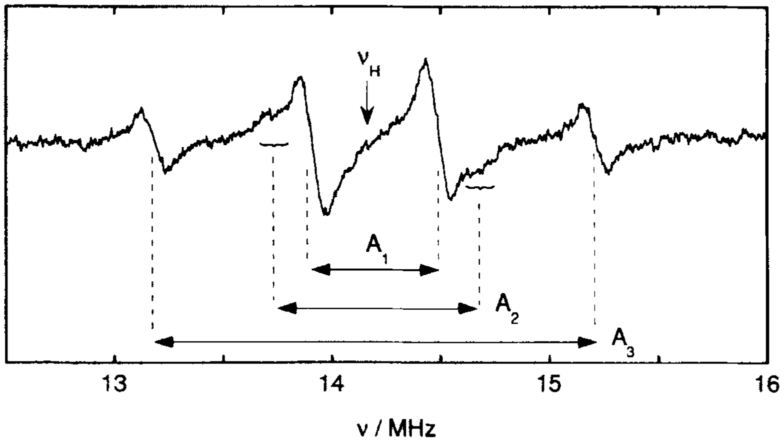


FIGURE 3 Liquid-phase ^{1}H-ENDOR spectrum of 3-QNNN (**1**) observed in mineral oil at 282 K. ν_H indicates the NMR frequency of free proton. A_1, A_2 and A_3 show the hfcc's of the three pairs of ENDOR signals.

^{1}H-TRIPLE of 3-QNNN

The TRIPLE transitions belonging to the same m_S-manifold (m_S=+1/2 or -1/2 for a doublet radical) as that of an RF-pumped transition diminish their intensity, while those belonging to another m_S-manifold gain their intensity. From the assignment of m_S together with the relation in Equation (1), the relative signs of hfcc's, A_i's, can be determined in TRIPLE measurements.

The relative signs of hfcc's, A_1, A_2 and A_3, of 1 were determined from the TRIPLE spectra as shown in Figure 4. The TRIPLE effect, the change in intensity of the ENDOR transitions in the presence of the RF-pumping, is clearly seen in Figures 4(b) ~ 4(e) as compared with the ENDOR spectrum in 4(a): A_2 and A_3 are in the same sign and the both are opposite to A_1.

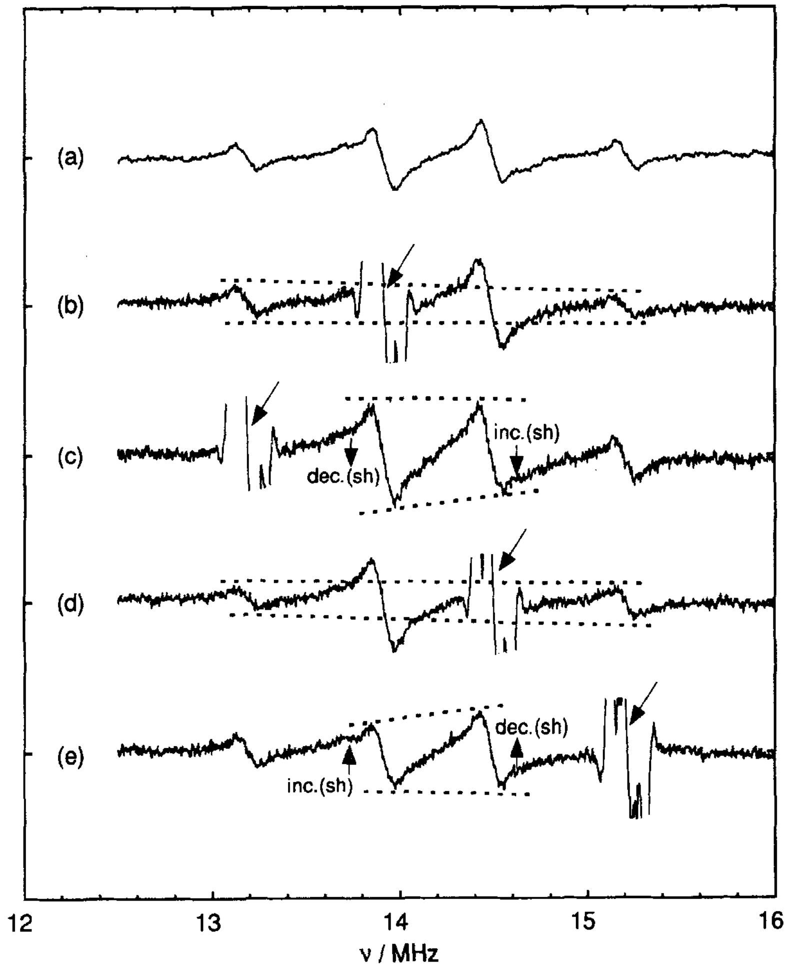


FIGURE 4 Liquid-phase general ^{1}H-TRIPLE spectra of 3-QNNN (1) observed in mineral oil at 282 K (b ~ e) as compared with the ^{1}H-ENDOR spectrum (a). The oblique arrows designate the pump frequencies; (b) 13.914 MHz, (c) 13.184 MHz, (d) 14.499 MHz, and (e) 15.215 MHz. The dashed lines represent the TRIPLE effects appearing in the pairs of ENDOR signals. The TRIPLE effects of the weak shoulders are shown by the arrows in (c) and (e); "inc.(sh)" and "dec(sh)." denote the increase and decrease in the shoulder intensity, respectively.

When A_1(methyl) <0 is assumed, the hfcc values of 3-QNNN are determined as follows;

$$A_1/h = -0.59 \text{ MHz}, A_2/h = +0.9 \sim +1.1 \text{ MHz}, A_3/h = +2.02 \text{ MHz}. \tag{3}$$

Assignment of Hfcc's and π-Spin Densities on Aromatic Ring Carbon Sites

In order to complete the assignment of the hfcc's for 1, the hfcc values of the quinolyl-ring protons were calculated by the UHF-INDO MO method.[14] The molecular geometry of 1 obtained from the X-ray crystal structure analysis[11] was used in the MO calculations. It has been shown that the INDO method overestimates the hfcc's of the aromatic ring protons for PNN (2) but reproduces the relative magnitude of the observed values.[10] According to the ratio of the calculated to the observed hfcc's of 2, the calculated hfcc's for 1 are scaled down by 22%. The result is shown in Figure 5(a).

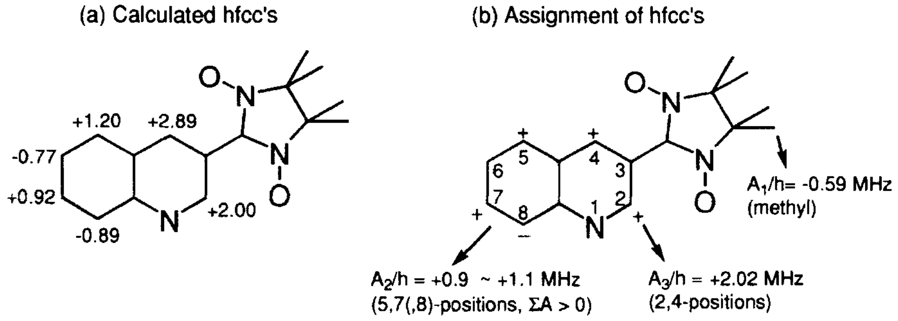


FIGURE 5 Calculated hyperfine coupling constants (hfcc's) in units of MHz (a) and the assignment of the observed hfcc's for the protons (b) of 3-QNNN (1).

From the comparison of the observed hfcc's with the calculated ones, A_3 is assigned to the protons at 2- or 4-position of the quinolyl ring. To the other protons at 5- to 8-positions are assigned the smaller hfcc A_2 as shown in Figure 5(b). Since A_2 of the broad shoulder-signal is positive in sign as described above, the ENDOR signals from the 5- and 7-protons presumably dominate in the shoulder signals. The ENDOR signal from the 6-proton, for which the smallest hfcc is expected in the MO calculation, probably overlaps with the intense innermost signal from the methyl protons.

The π-spin densities (ρ's) of the quinolyl-ring carbon sites were calculated from the observed hfcc's by assuming that McConnell's relationship,

$$A=\rho Q, \quad (Q=-63.2\ \text{MHz}), \tag{4}$$

holds for the π-electron system of **1**. The π-spin densities ρ(i)'s on the i-th carbon sites of the quinolyl ring are calculated as;

$\rho(2\text{ or }4) = -0.032,$
$\rho(5\text{ or }7) = -0.014 \sim -0.017.$

π-Spin Density Distribution of Heterocyclic and Non-Heterocyclic Substituted Radicals

The π-spin densities on the phenyl carbon sites of **2** are ρ(ortho)=-0.023, ρ(meta)=+0.013, and ρ(para)=-0.021.[10] The largest spin density $|\rho(2\text{ or }4)|=0.032$ observed for the molecule **1** is about 3/2 times as large as that of **2**: A pronounced negative spin density has been found in the quinolyl-derivative of nitronyl nitroxide, **1**. The ENDOR spectra of the three kinds of α-substituted nitronyl nitroxide molecules in this study, **1**, **2**, and **3**, are compared in Figure 6. It is obvious that the molecule **1** has the largest separation between the pair of ENDOR transitions, *i.e.*, the largest spin density on the aromatic ring carbon sites.

CONCLUSION

The π-spin density distribution of the heterocyclic substituted derivative of nitronyl nitroxide radical, 3-QNNN (**1**) was investigated by liquid-phase ENMR spectroscopy and a pronounced spin density (ρ=-0.032) was found in the carbon sites of the heterocyclic substituent. The ρ value is about 3/2 times as large as that of the two kinds of non-heterocyclic molecules PNN (**2**) and 1-NAPNN (**3**). The enhanced ρ value is attributable to the introduction of the nitrogen atom into the quinolyl ring. The enhancement of the negative spin polarization in **1** should be related to the position of the ring-nitrogen site where the π-spin is presumably positively polarized. This is analogized with that the spin polarization of nitronyl nitroxide moiety itself is magnified by the exchange interaction of unpaired π-electron with the non-bonding electrons (n-π exchange interaction) at the nitroxide-nitrogen sites.[4-6]

The spin density of the nitronyl nitroxide radical molecules is mainly concentrated on the nitroxide groups, reflecting the feature of SOMO (singly occupied

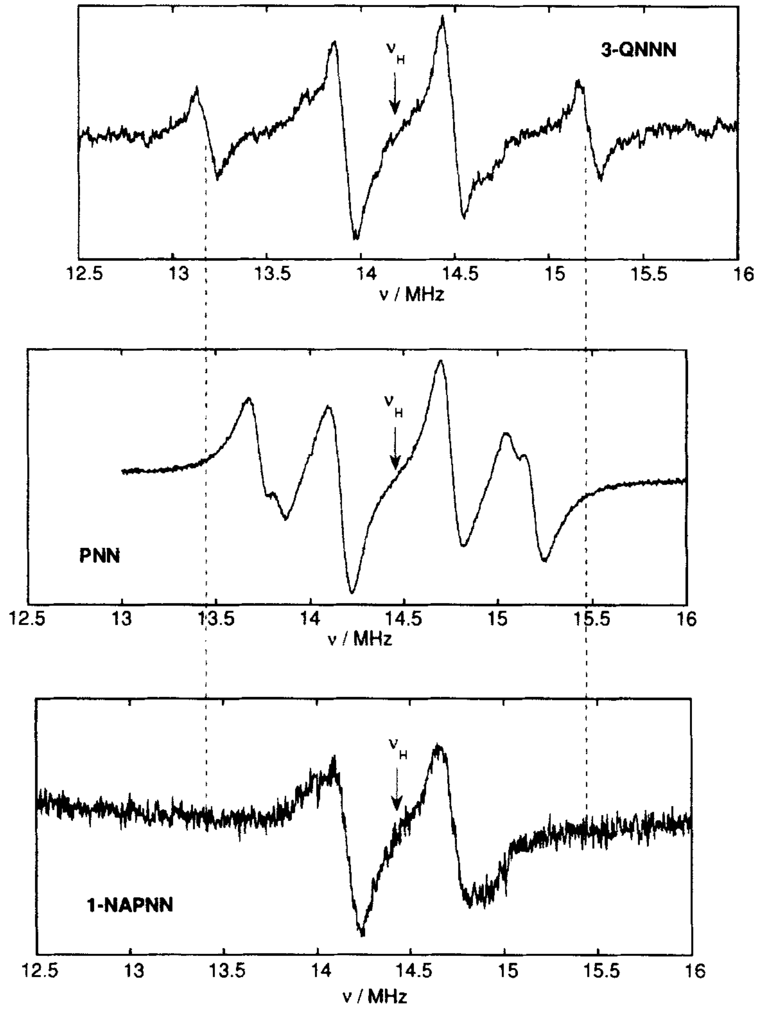


FIGURE 6 Comparison of ^{1}H-ENDOR spectra for 3-QNNN (**1**), PNN (**2**)[10] and 1-NAPNN (**3**). The frequency axes in the spectra are aligned with the NMR frequencies of free proton, ν_H. The dashed lines designate the largest hfcc found in the three kinds of radical molecules examined in this study.

molecular orbital) of the molecules, while the other frontier MO's usually have substantial amplitude in the π-conjugated substituents. In the light of the intermolecular orbital overlapping between the SOMO and the other frontier MO's of adjacent molecules in the crystal, which dominates the intermolecular exchange interactions,[15] the molecular design of the building blocks of organic magnets should include the control of π-spin density distribution as well as the establishment of robust spin polarization in the π-conjugated substituents. Therefore, it should be highlighted in this study that the negative π-spin density is enhanced by the factor of 3/2 in **1** by introducing the heteroatom into the π-conjugated substituent. In order to elucidate the mechanism for the enhanced amplitude of the π-spin density in the heterocyclic substituent, further investigation is needed which includes ENMR studies on molecules with partially deuterated ring-protons (for the refinement of the unresolved ENDOR signals) and on those with various position of the heteroatom relative to the nitronyl nitroxide group.

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