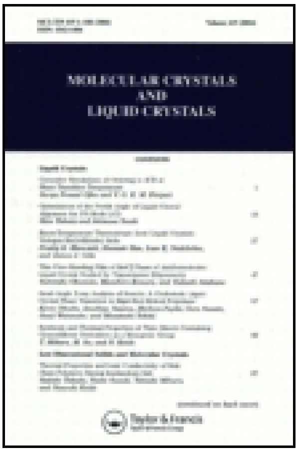


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

II-Spin Density Determination of Phenylnitronyl Nitroxide Radical: A Liquid-Phase Endor/Triple Study

Takeji Takui [a], Yozo Miura [b], Kunio Inui [b], Yoshio Teki [c], Makoto Inoue [a] & Koichi Itoh [c]

[a] Department of Chemistry, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka, 558, Japan

[b] Department of Applied Chemistry, Faculty of Engineering, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka, 558, Japan

[c] Department of Material Science, Faculty of Science, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka, 558, Japan

Version of record first published: 24 Sep 2006.

To cite this article: Takeji Takui , Yozo Miura , Kunio Inui , Yoshio Teki , Makoto Inoue & Koichi Itoh (1995): II-Spin Density Determination of Phenylnitronyl Nitroxide Radical: A Liquid-Phase Endor/Triple Study, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 271:1, 55-66

To link to this article: http://dx.doi.org/10.1080/10587259508034038

Mol. Cryst. Liq. Cryst., 1995, Vol. 271, pp. 55–66
Reprints available directly from the publisher
Photocopying permitted by license only

Π-SPIN DENSITY DETERMINATION OF PHENYLNITRONYL NITROXIDE RADICAL: A LIQUID-PHASE ENDOR/TRIPLE STUDY

TAKEJI TAKUI,[1] YOZO MIURA,[2] KUNIO INUI,[2] YOSHIO TEKI,[3] MAKOTO INOUE,[1] and KOICHI ITOH[3]
[1]Department of Chemistry and [3]Department of Material Science, Faculty of Science, and [2]Department of Applied Chemistry, Faculty of Engineering, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558, Japan

Abstract The molecular building block of the first well-characterized purely organic crystalline ferromagnet is 4,4,5,5-tetramethyl-3-oxide-2(p-nitrophenyl)-2-imidazolin-1-yloxyl doublet radical. Among the diverse subjects of organic molecular crystalline ferromagnetism, the spin density distribution of the molecular building unit gives fundamental bases for understanding the underlying mechanism. In this work, an attempt has been made to determine experimentally the magnitudes and relative signs of the π-spin densities on the aromatic ring carbon sites (except the site 1) of 4,4,5,5-tetramethyl-3-oxide-2-phenyl-2-imidazolin-1-yloxyl doublet radical (abbreviated to 2-phenylnitronyl nitroxide) by liquid-phase ENDOR/TRIPLE spectroscopy. A series of partially deuterated 2-phenylnitronyl nitroxide compounds have given an unequivocal experimental identification of the ring protons: the spin densities of the ortho (2',6'), meta (3',5'), and para (4') proton are $\rho^{ortho} = -0.023$, $\rho^{meta} = +0.013$, and $\rho^{para} = -0.0207$, respectively, and $\sum_i \rho^i = -0.0407$. The results show that 2-phenylnitronyl nitroxide undergoes negative spin polarization in the phenyl ring because the negative spins exceed the positive ones. The results have been compared with those obtained from polarized neutron diffraction measurements on the single crystal of 2-(p-nitrophenyl)-nitronyl nitroxide by Schweizer et al. The INDO calculation has been tested, indicating that the calculation gives an overestimation a great deal for the hyperfine coupling constants of the aromatic protons.

INTRODUCTION

Organic molecular based magnetism[1,2] (abbreviated to organic magnetism) has been the topic of wide-increasing interest in many fields of both pure and applied science for the last decade.[3,4] This is due to the fact that the study of organic magnetism has conveyed important and intriguing conceptual advances in chemistry and physics. This is partly due to the rich variety of novel physical phenomena and properties which organic magnetic materials are expected to exhibit both macro- and mesoscopically, and due to their potential applications as the future technology in materials science.[3c,5]

Recently, the first purely organic molecular crystalline ferromagnet has emerged.[6,7] The molecular building block is 4,4,5,5-tetramethyl-3-oxide-2-(p-nitropyenyl)-2-imidazolin-1-yloxyl doublet radical (abbreviated to 2-(p-nitrophenyl)nitronyl nitroxide), which is depicted in Figure 1 ($X = p\text{-}NO_2$). Among isomorphous crystal forms of 2-(p-nitrophenyl)nitronyl nitroxide only the β phase crystal exhibits bulk ferromagnetism ($Tc \sim 0.6K$).

The subject of organic molecular crystalline ferromagnetism is diverse. Particularly despite the existence of the anisotropy due to crystallographic directions, purely organic crystalline ferromagnets composed of light atoms with small spin-orbit interactions are expected to be ideal isotropic ferromagnets, together with spin glasses as the so far best known examples of amorphous magnets characterized by small remnant anisotropies. Purely organic molecular crystalline ferromagnets are also anticipated to exhibit low dimensionality. Extensive studies including the heat capacity and μon spin rotation measurements below 1K have been made by Kinoshita's group on this crystalline ferromagnet in order to disclose its particular structure-magnetism relationship.[7e] Also an attempt has been made by Yamaguchi's group to reproduce the observed long-range ferromagnetic ordering temperature by means of a quantum chemical calculation based upon the precise knowledge of the β phase crystal structure, taking into account all the intermolecular exchange interactions and packing modes.[8] It turns out that a breakthrough in understanding the underlying mechanism for this purely organic crystalline ferromagnetism is required to be associated with the precise knowledge of the spin density distribution of the constituent molecule, most preferably in the crystal.

2-Substituted phenylnitronyl nitroxide also has frequently been exploited as a pertinent monomer unit for quasi 1D purely organic polymer ferromagnets,[1g,9] where the molecular design is based on topologically controlled π spin polarization (through-bond approach).[1] The through-bond approach to organic magnetism has essentially invoked the robust spin polarization of the π electron network in organic molecules. In view of materials challenges, it is of essential importance to characterize 2-substituted phenylnitronyl nitroxide in terms of spin polarization since organic high-spin polymers have been emerging.[10]

The precise determination of the spin density distribution, particularly of the π-conjugated atomic sites, is not only essential for rationales, in terms of molecular orbital picture, for underlying mechanisms of organic magnetism from a microscopic viewpoint, but also tests in a quantitative sense the general validity of the above quantum chemical calculation,[8] providing the possible calculation of other physical parameters depending on the microscopic details of the system. Obviously, the knowledge obtained from the crystalline ferromagnet is of crucial importance for the designing of organic molecular amorphous magnets as well as for better control of the characteristics for future potential applications.[3c,5] Thus, we present in this paper an unequivocal experimental determination of the spin density distribution of 2-phenylnitronyl nitroxide (see Figure 1 (X=H)), focusing on its phenyl proton hyperfine coupling constants (hfccs). The determination has been carried out by liquid-phase ^{1}H-ENDOR/TRIPLE spectroscopy. In order to obtain an unambiguous spectral assignment of the phenyl protons, we have synthesized a series of deuterium labeled 2-phenylnitronyl nitroxide radicals. The spin density distribution has been compared with that obtained by polarized neutron scattering studies of the crystal of 2-phenylnitronyl nitroxide. In addition, an INDO calculation of the hfccs has been carried out for the comparison with the observed ones.

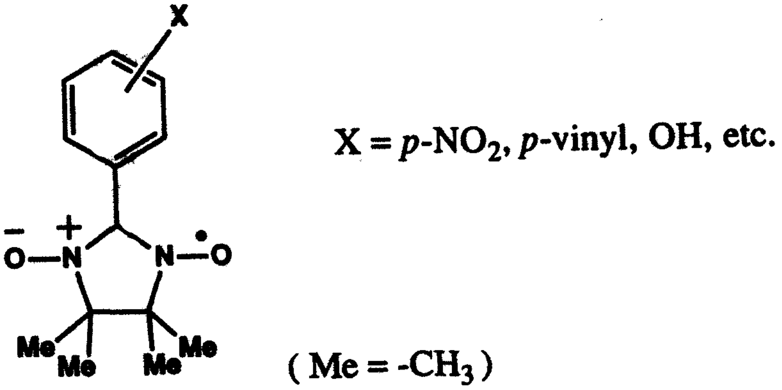


FIGURE 1 2-Substituted phenylnitronyl nitroxides. X=H: 2-phenylnitronyl nitroxide.

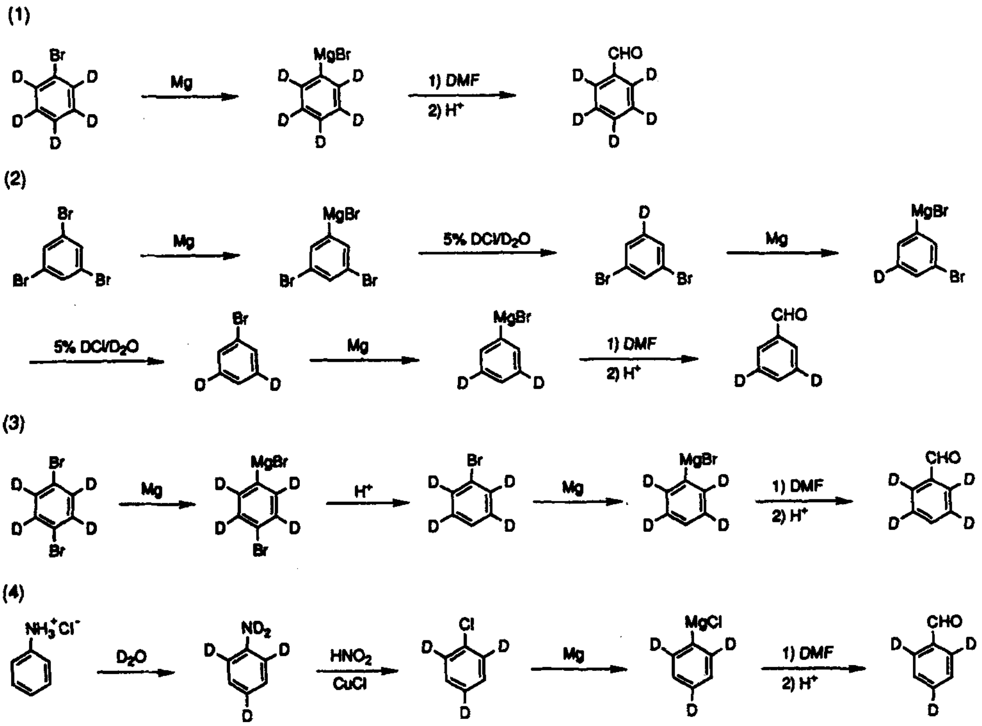
RESULTS AND DISCUSSION

Liquid-Phase ESR and ^{1}H-ENDOR Spectra of 2-Phenylnitronyl Nitroxide Radicals

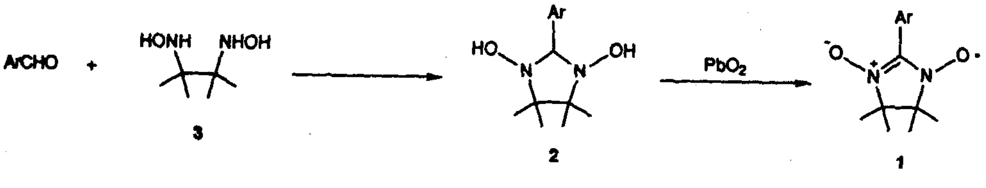
The synthetic pathways corresponding to non-deuterium labeled 2-phenylnitronyl nitroxide radical a and deuterium labeled ones b–e are shown in Scheme I and II. Experimental details will be published elsewhere.

Liquid-phase ESR spectra of 2-substituted nitronyl nitroxide radicals usually exhibit only hyperfine structures characteristic of two equivalent nitrogen nuclei as shown in Figure 2, and hyperfine splittings due to protons are rarely resolved except for 2-methyl substituted one because of a large amount of the localization of an unpaired electron on the two equivalent NO sites, indicating a salient feature of

Scheme I



Scheme II



a: Ar = C_6H_5
b: Ar = C_6D_5
c: Ar = 3,5-$D_2C_6H_3$
d: Ar = 2,3,5,6-D_4C_6H
e: Ar = 2,4,6-$D_3C_6H_2$

the singly occupied molecular orbital (SOMO) of 2-substituted nitronyl nitroxide radicals. Neither a liquid-phase ESR spectrum of perdeuterated (b) nor partially deuterated 2-phenylnitronyl nitroxide radical (c–e) showed additional hyperfine splittings in mineral oil. This partly arises from unresolved hyperfine lines due to the twelve protons of the four methyl groups. Efforts to label all the methyl protons with deuterium were made, but the complete deuteration of the methyl protons was unsuccessful.

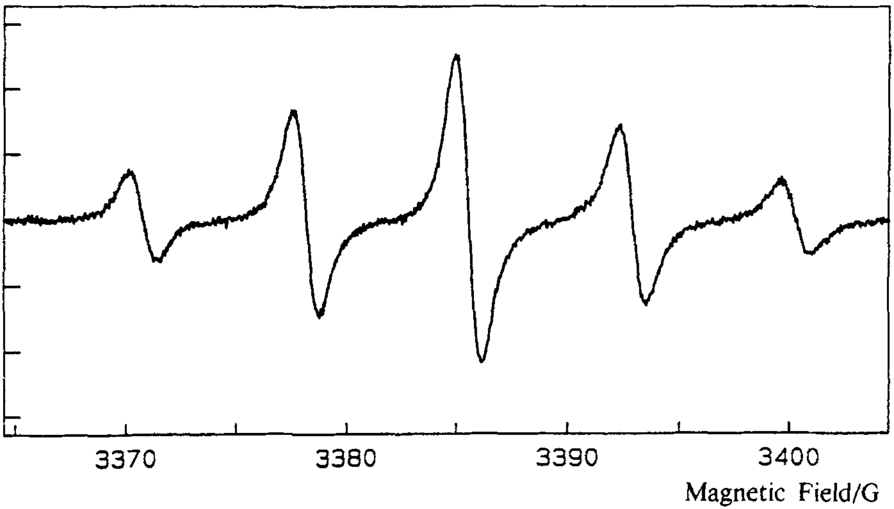
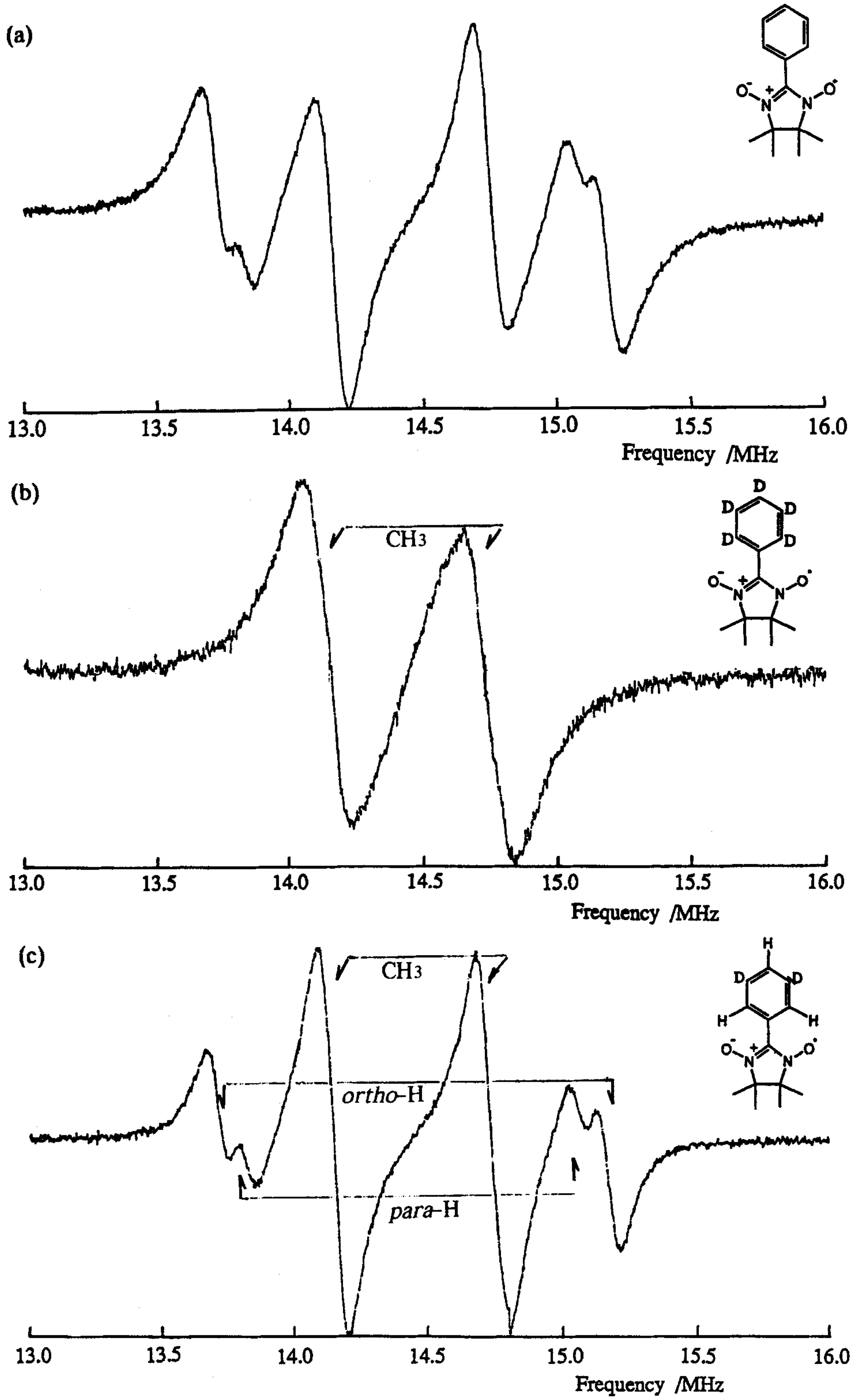


FIGURE 2 Liquid-phase ESR spectrum of 2-phenylnitronyl nitroxide observed in mineral oil at 280K. The microwave frequency was 9.626541GHz.

Figure 3a shows a liquid-phase ^{1}H-ENDOR spectrum of non-deuterated 2-phenylnitronyl nitroxide **a** in mineral oil observed at room temperature. The most intense central ESR line was monitored in order to observe ENDOR transitions. The spectrum was obtained using CAT technique with a frequency modulation depth of 9.88 kHz and a phase-sensitive detection frequency of 12.5 kHz. The modulation depth was approximately a tenth of the ENDOR linewidth. Further resolution improvement was not obtained with the modulation depth reduced.

In the case of the doublet (S=1/2) radical, the ^{1}H-ENDOR signal assignable to the hfcc value smaller than $2\nu_n^H$ appears at frequencies $\nu_\pm = |\nu_n^H \pm A_i/2|$ to a good approximation, where ν_n^H stands for NMR frequency for free proton (ν_n^H=14.461 MHz in Figure 3a) and A_i for the proton hfcc. A_i can be determined directly from the separation between a pair of the ENDOR transitions $\nu_\pm$. It is worth noting that assuming that radio frequency power is constant in the limited range of swept frequency and $|A_i| < |2\nu_n^H|$ the proton signal intensity is nearly proportional to the


(a)
O
N
N
O
13.0
13.5
14.0
14.5
15.0
15.5
16.0
Frequency /MHz
(b)
D
D
D
D
D
CH3
13.0
13.5
14.0
14.5
15.0
15.5
16.0
Frequency /MHz
(c)
H
D
D
H
H
CH3
ortho-H
para-H
13.0
13.5
14.0
14.5
15.0
15.5
16.0
Frequency /MHz

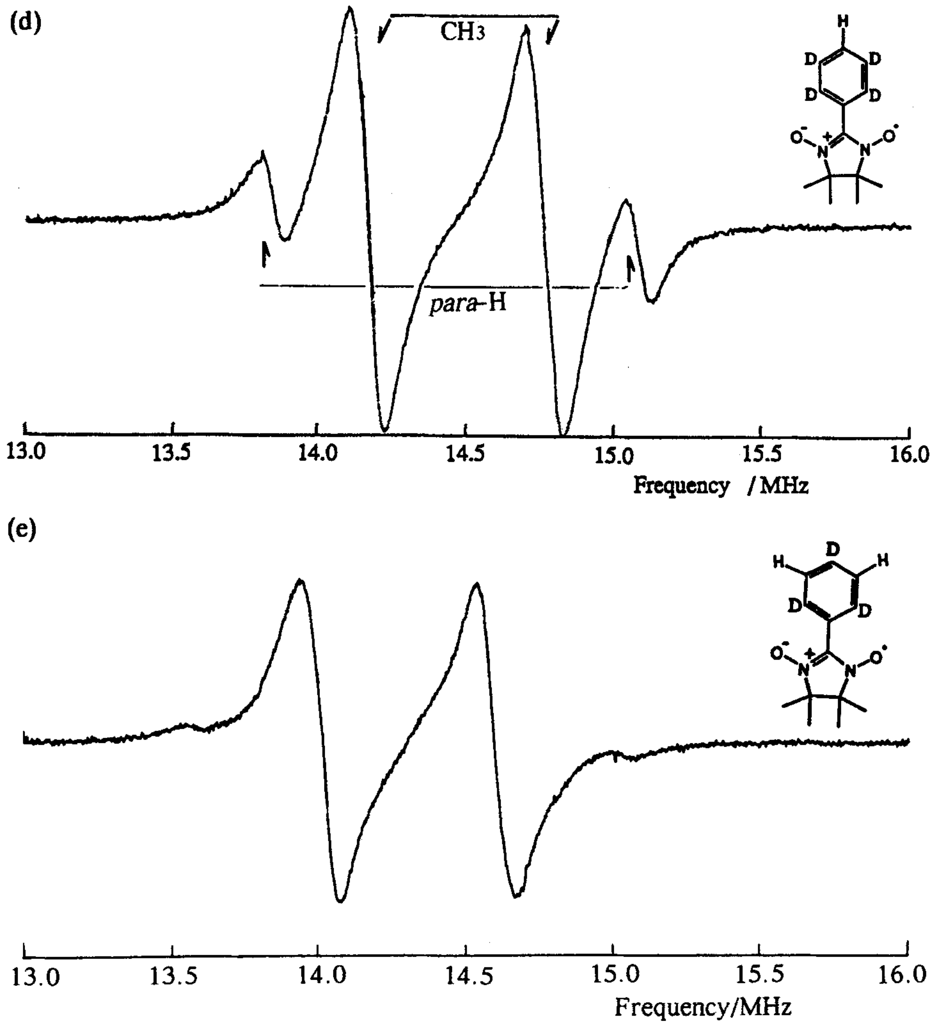


FIGURE 3 Liquid-phase ^{1}H-ENDOR spectra of non-deuterated **a** and partlly deuterated 2-phenylnitronyl nitroxides **b**-**e** observed in mineral oil at ambient temperature. The pair of arrows designates the proton assignment.
(e)The meta and methyl proton signals overlap each other. The outermost trace signals were due to partially deuterated 2-phenylnitronyl nitroxide radicals produced by undesired reactions of o- or p-proton substitution.

number of equivalent protons with particular hfccs if protons in the system experience similar spin relaxation processes. The condition of $|A_i| < |2\nu_n{}^H|$ assures that the variation of the ENDOR transition probability as a function of the transition frequency is small. The integrated signal intensity ratio of the innermost intense pair in relative to the other pairs in Figure 3a suggested that the innermost pair signal was attributable to the twelve methyl protons, the outermost pair to ortho- and/or meta-phenyl protons, and the remaining one with a weak intensity to para-phenyl proton. A close study of the lineshape of the innermost pair suggested that there occurred overlapping signals with an hfcc value (ca. 0.82 MHz) a little larger than those of the dominant components (ca. 0.58 MHz). The hfcc value of 0.82 MHz was assigned to meta-phenyl protons. The masking of the component (0.82 MHz) seen in Figure 3a was confirmed in the spectral analyses of partially deuterated 2-phenylnitronyl nitroxides. Three well-separated pairs of the signals in Figure 3a give directly three sets of the proton hfccs; $|A_1|=0.576$ MHz, $|A_2|=1.310$ MHz, and $|A_3|=1.454$ MHz. The hfcc for the masked components was estimated to be $|A_4|=0.82$ MHz.

Figure 3b shows a ^{1}H-ENDOR spectrum of perdeuterated 2-phenyl-2',3',4',5',6'-d_5-nitronyl nitroxide **b** in mineral oil observed at 297K. No trace signal arising from undesired partially deuterated 2-phenylnitronyl nitroxides was detected as seen in Figure 3b, indicating that successful synthetic processes were carried out. A pair of the observed signals with a broad linewidth unequivocally arise from the approximately equivalent twelve protons of the methyl groups of the imidazol ring.

Figure 3c shows a ^{1}H-ENDOR spectrum of partially deuterated 2-phenyl-3',5'-d_2-nitronyl nitroxide **c** in mineral oil observed at 283K. The outermost pair was assigned to the two ortho-phenyl protons (A_3^{ortho}), the innermost pair to the methyl protons ($A_1^{CH_3}$) of the imidazol ring, and the remaining pair with the weakest intensity to the single para-phenyl proton (A_2^{para}), respectively.

Figure 3d shows a ^{1}H-ENDOR spectrum of partially deuterated 2-phenyl-2',3',5',6'-d_4-nitronyl nitroxide **d** in mineral oil observed at 283K. Both Figure 3b and 3d exclusively show that the ENDOR transition yielding $|A_2|=1.310$ MHz in Figure 3a is assigned to the para-phenyl proton. No trace signal from undesired deuterated compounds was observed.

Figure 3e shows a liquid-phase ^{1}H-ENDOR spectrum of partially deuterated 2-phenyl-2',4',6'-d_3-nitronyl nitroxide **e** in mineral oil observed at 283K. The overlapping line with the hfcc value of 0.82 MHz was attributed to the two meta-phenyl protons (A_4^{meta}).

Determination of Relative Signs for Proton Hfccs by ^{1}H-TRIPLE Resonance

The determination of the relative signs of the proton hfccs is of crucial importance for understanding the magnetic properties on the basis of the microscopic details of the system. An attempt to experimentally determine the relative signs was made by electron-nuclear-nuclear TRIPLE resonance spectroscopy as shown in Figure 4. The detection of a significant TRIPLE effect was hampered by the intense signals from the methyl protons of the imidazol ring. The relative signs of the hfccs in Figure 3 were, however, determined by means of general TRIPLE technique except the sign for the meta-phenyl proton. For the complete determination, the deuterium substitution of the four methyl groups is required.

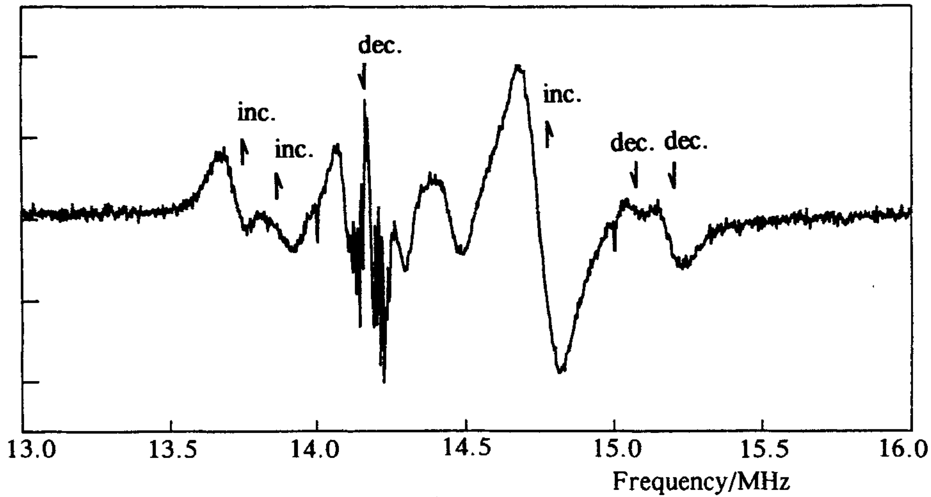


FIGURE 4 Liquid-phase general ^{1}H-TRIPLE spectrum of non-deuterated 2-phenylnitronyl nitroxide observed in mineral oil at 290K. The pump frequency was 14.18MHz.

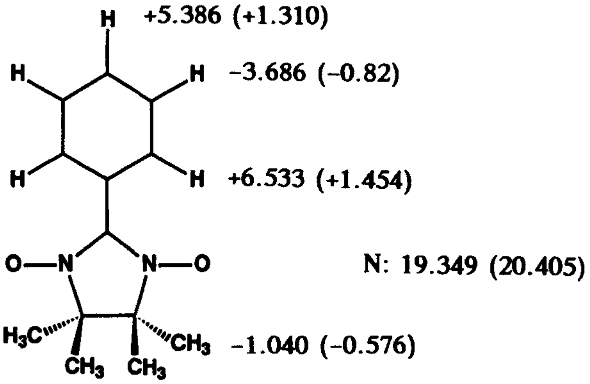


FIGURE 5 Observed and calculated hfccs in units of MHz for all the protons of 2-phenylnitronyl nitroxide. The observed hfcc values are in parentheses.

Comparison of Observed Proton Hfccs with Calculated Ones by INDO MO Method

In Figure 5 are summarized both the observed and calculated hfccs for all the protons of 2-phenylnitronyl nitroxide. The calculated hfccs were obtained by the INDO MO method assuming 50 degree of the dihedral angle between the 2-phenyl and imidazol ring and the molecular structural parameters of 4'-substituted 2-

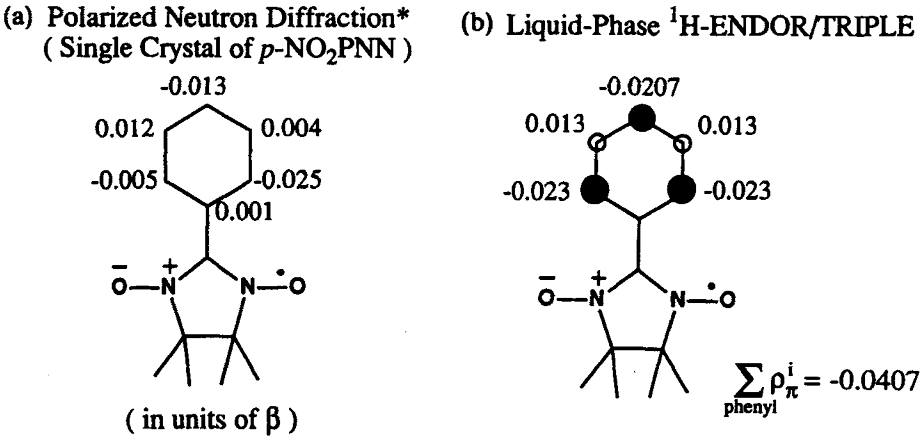
phenylnitronyl nitroxide which have been obtained by X-ray crystal analysis. Figure 5 shows that the INDO MO calculation reproduces the relative magnitude of the hfccs but overestimates their values, nearly four times larger for the phenyl proton and nearly two times larger for the methyl proton of the imidazol ring. The change in the dihedral angle effected only the slight reduction of the hfccs. On the other hand, the INDO MO calculation reproduced ca. 93% of the observed hfcc for the nitrogen nuclei of the imidazol ring.

π Spin Densities on Phenyl Carbon Sites and Comparison with Those from Polarized Neutron Scattering Experiments by Schweizer et al.

In Figure 6b are summarized the π spin densities ρ^is calculated from the observed hfccs assuming that McConnell relationship $A^i = Q\rho^i$ ($Q = -63.24$ MHz, i=ortho, meta, para) holds for the phenyl π system of 2-phenylnitronyl nitroxide. ρ^i ranges from ca. -0.023 to 0.013, indicating a small amount of the spin delocalization in the phenyl π system and the possible occurrence of negative π-spin polarization overwhelming the spin delocalization in the phenyl ring: $\Sigma_i\rho^i=-0.0407$ (i=ortho (2',6'), meta(3',5'), and para(4')) and the spin density on the carbon site 1' of the phenyl ring was not experimentally determined. The occurrence of the negative spin polarization in 2-phenylnitronyl nitroxide can be compared with the result from polarized neutron diffraction experiments by Schweizer et al. on the β phase single crystal of 2-(p-nitrophenyl)nitronyl nitroxide. As seen in Figure 6a, the reconstructed spin density distribution determined by the neutron scattering experiment[12] agrees with our result. The former which reflects the feature of the SOMO of 2-(p-nitrophenyl)nitronyl nitroxide was obtained as the average of the spin densities of the two distinguishable molecules in the crystal. The comparison is the highlighted part of the present work, giving crucial information about underlying mechanisms in the crystalline ferromagnet. Also more advanced and reliable theoretical calculations which reproduce the present result are to be invoked for a thorough understanding of underlying mechanisms in the first purely organic crystalline ferromagnet.

CONCLUSIONS

Using liquid-phase ^{1}H-ENDOR/TRIPLE spectroscopy we have given the complete determination of the hfccs for all the protons of 2-phenylnitronyl nitroxide, whose π spin density distribution can provide the precise and important microscopic knowledge of underlying mechanisms in the first purely organic molecular crystalline


(a) Polarized Neutron Diffraction* (Single Crystal of p-NO_2PNN)

(b) Liquid-Phase ^{1}H-ENDOR/TRIPLE

FIGURE 6 Experimentally determined π spin densities on the phenyl carbon sites and comparison with those from polarized neutron scattering experiments by Schweizer et al.[11] (a) By Shweizer et al. (b) This work.

ferromagnet composed of 2-(p-nitrophenyl)nitronyl nitroxide radical as the molecular building block. The electronic spin structure of 2-phenylnitronyl nitroxide has been characterized in terms of the π spin density distribution of the phenyl ring.

An unequivocal assignment of the ^{1}H-ENODR transitions has been carried out with the help of the deuterium substitution of the phenyl proton. The INDO MO calculation of the hfccs has been tested. It turned out that the INDO MO method gave an overestimation a great deal for the proton hfccs. From the experimental proton hfccs the π spin densities on the carbon sites in the phenyl ring have been derived, showing that a small amount of the spin delocalization ranging from -0.023 to 0.013 takes place in the phenyl π system. The results show that 2-phenylnitronyl nitroxide undergoes negative π spin polarization in the phenyl ring. The experimentally determined π spin density distribution reasonably agrees with the one obtained by Schweizer et al. from the polarized neutron diffraction experiments on the β phase single crystal of 2-(p-nitrophenyl)nitronyl nitroxide.

2-Substituted phenylnitronyl nitroxide as a pertinent monomer unit for polymer ferromagntes undergoes the negative spin polarization of the phenyl ring, which possibly hampers the topologically controlled spin polarization of extended polymeric systems. Knowledge of the spin density distribution of the constituent molecular unit serves as for the modeling of crystal molecular engineering in organic magnetism.

ACKNOWLEDGMENTS

The authors thank the computing centers of the Institute for Molecular Science, Okazaki and Osaka City University. This work has been supported by Grant-in-Aids for Scientific Research on Priority Areas "New Functionality Materials" and

"Molecular Magnetism", and by a Grant-in-Aid for General Scientific Research from the Ministry of Education, Science and Culture, Japan.

REFERENCES

1. (a)K. Itoh, *Chem. Phys. Lett.*, **1**, 235(1967). (b)E. Wasserman, R. W. Murray, W. A. Yager, A. M. Trozzolo, and G. Smolinsky, *J. Am. Chem. Soc.*, **89**, 5076(1967). (c)S. Morimoto, F. Tanaka, K. Itoh, and N. Mataga, *Preprints of Symposium on Molecular Structure (Chem. Soc. Japan)*, 67(1968). (d)N. Mataga, *Theor. Chim. Acta*, **10**, 372(1968). (e)K. Itoh, *Bussei*, **12**, 635(1971). (f)K. Itoh, *Pure & Appl. Chem.*, **50**, 1251(1978). (g)A. A. Ovchinnikov, *Theor. Chim. Acta*, **47**, 297(1978).
2. (a)H. M. McConnell, *J. Chem. Phys.*, **39**, 1910(1963). (b)H. M. McConnell, *Proc. R. A. Welch Found, Chem. Res.*, **11**, 144(1967).
3. (a)J. S. Miller, A. J. Epstein, and W. M. Reiff, *Chem. Rev.* **88**, 201(1988) and references therein. (b)J. S. Miller, A. J. Epstein, and W. M. Reiff, *Acc. Chem. Res.*, **22**, 114(1988) and references therein. (c)K. Itoh, *J. Appl. Magnetics Japan*, **14**, 9(1990). (d)T. Takui and K. Itoh, *J. Materials Sci. Soc. Japan (Zairyoh Kagaku)*, **28**, 315(1991) and references cited therein.
4. For a recent overview, see the following references.
   (a)J. S. Miller and D. A. Dougherty(eds.), *Mol. Cryst. Liq. Cryst.*, **176**, 1-562(1989). (b)L. Y. Chang, P. M. Chaikin, and D. O. Cowan(eds.), *Advanced Organic Solid State Materials* (MRS, 1990), P. 1-92. (c)D. Gatteschi, O. Kahn, J. S. Miller, and F. Palacio(eds.), *Molecular Magnetic Materials* (Kluwer Academic Publishers, 1991). (d)H. Iwamura and J. S. Miller(eds.), *Mol. Cryst. Liq. Cryst.*, **232/233**, 1-724(1993).
5. (a)T. Takui and K. Itoh, *Polyfile*, No. 314, 39(1990).(b)C. P. Landee, D. Melville, and J. S. Miller, *Magnetic Molecular Materials* ed. by D. Gatteschi, O. Kahn, J. S. Miller, and F. Palacio (Kluwer Academic Publishers, 1991). (c)J. S. Milller and A. J. Epstein, *Chemtech.*, **21**, 168(1991). (d)T. Takui, *Polyfile*, **29**, 120(1992). (e)J. S. Miller, *Adv. Mater.*, **6**, 322(1994).
6. (a)K. Awaga and Y. Maruyama, *Chem. Phys. Lett.*, **158**, 556(1989). (b)K. Awaga and Y. Maruyama, *J. Chem. Phys.*, **91**, 2743(1989). (c)K. Awaga, T. Inabe, U. Nagashima, and Y. Maruyama, *J. Chem. Soc. Chem. Commun.*, 1617(1989): ibid., 520(1990).
7. (a)P. Turek, K. Nozawa, D. Shiomi, K. Awaga, T. Inabe, Y. Maruyama and M. Kinoshita, *Chem. Phys. Lett.*, **180**, 327(1991). (b)M. Kinoshita, P. Turek, M. Tamura, K. Nozawa, D. Shiomi, Y. Nakazawa, M. Ishikawa, M. Takahashi, K. Awaga, T. Inabe, and Y. Maruyama, *Chem. Lett.*, 1225(1991). (c)M. Takahashi, P. Turek, Y. Nakazawa, M. Tamura, K. Nozawa, D. Shiomi, M. Ishikawa, and M. Kinoshita, *Phys. Rev. Lett.*, **67**746(1991). (d)M. Tamura, Y. Nakazawa, D. Shiomi, K. Nozawa, Y. Hosokoshi, M. Ishikawa, M. Takahashi, and M. Kinoshita, *Chem. Phys. Lett.*, **186**, 401(1991). (e) Y. Nakazawa, M. Tamura, N. Shirakawa, D. Shiomi, M. Takahashi, M. Kinoshita, and M. Ishikawa, *Phys. Rev.*, **B46**, 8906(1992). (f)M. Kinoshita, *Mol. Cryst. Liq. Cryst.*, **232**, 1(1993) and references cited therein.
8. M. Okumura, W. Mori, and K. Yamaguchi, *Mol. Cryst. Liq. Cryst.*, **232**, 35(1993) and references cited therein.
9. Y. Miura, K. Inui, F. Yamaguchi, M. Inoue, Y. Teki, T. Takui, and K. Itoh, *J. Polym. Chem. Polym. Chem. Ed.*, **30**, 959(1992) and references cited therein.
10. T. Kaneko, E. Tsuchida, H. Nishide, and K. Yamaguchi, to be published.
11. J. Schweizer et al., to be published: J. Schweizer, personal communication.
12. Preliminary results of ^{1}H-ENDOR measurements on 2-(p-nitrophenyl)nitronyl nitroxide showed no significant difference in the proton hfcc value between the two phenylnitronyl nitroxide radicals.