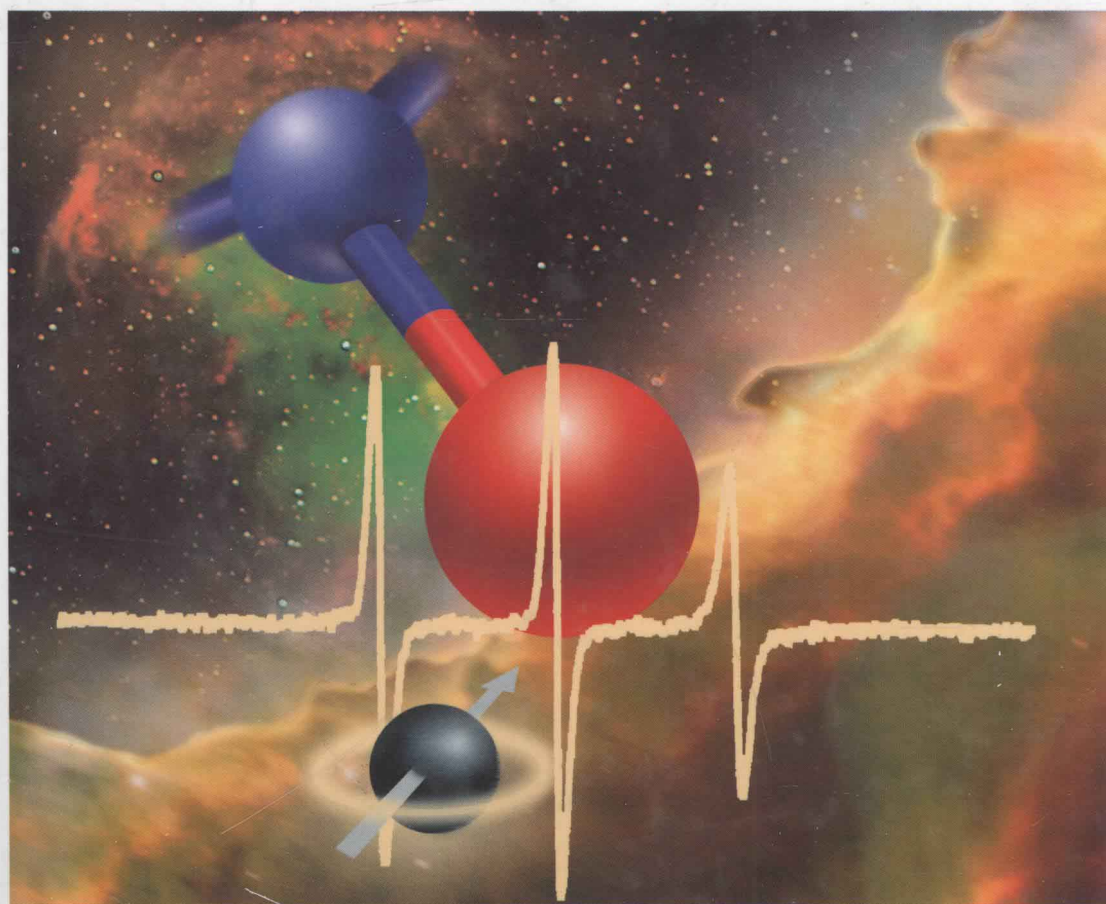


G. I. Likhtenshtein, J. Yamauchi,  
S. Nakatsuji, A. I. Smirnov, R. Tamura

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# Nitroxides

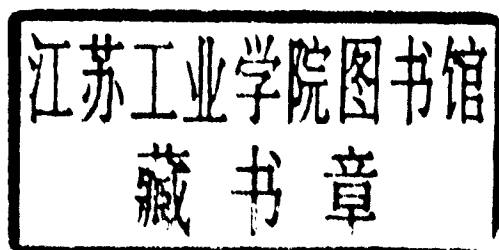
Applications in Chemistry, Biomedicine,  
and Materials Science



*Gertz I. Likhtenshtein, Jun Yamauchi,  
Shin'ichi Nakatsuji, Alex I. Smirnov,  
and Rui Tamura*

## **Nitroxides**

Applications in Chemistry, Biomedicine,  
and Materials Science



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**Nitroxides**

## ***Further Reading***

M. Kaupp, M. Bühl, V. G. Malkin (Eds.)

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## Preface

Stable nitroxide radicals have proved to be effective tools in solving many problems in chemistry, physics, biology, and biomedicine at the molecular level. The nitroxide labels are used as “molecular rulers” to measure the distances between chosen groups and to measure the size, form, and micro-relief of objects of interest. The labels provide information that helps the scientist to understand the structure and molecular dynamics of individual molecules, polymers, liquid crystals, enzymes, proteins, membranes, and nucleic acids and how they function. Recently, new important developments of nitroxides as redox-probes, spin-traps, imaging and pharmacokinetic reagents, and magnetic materials have been reported. Nitroxide derivatives are successfully used for the investigation of chemical kinetics, photo-physical, and photochemical processes. Therapeutic and clinical applications of nitroxides appear to be a new advance in medicine.

This volume covers all aspects of this field. It also critically discusses recent results obtained with the use of nitroxides and gives an analysis of developments in the field in the future.

This book is a view of the area by a group of scientists with long-term experience in the investigation of chemistry, physicochemistry, biochemistry, and biophysics of nitroxides. It is not intended to provide an exhaustive survey of each topic but rather a discussion of their theoretical and experimental background, and recent developments. The literature of nitroxides is vast and many scientists have made important contributions in the area so that it is impossible in the space allowed in this book to give a representative set of references. The authors apologize to those they have not been able to include. More than 1100 references are given, which should provide a key to essential relevant literature.

In Chapters 1 to 3 (J. Yamauchi) of the present monograph, the general theoretical, and experimental background is expounded for magnetic properties and ESR techniques. Chapter 4 (A. Smirnov) describes recent advances in modern ESR technique and related areas, which to a considerable extent were stimulated by the growing requirements of nitroxide application in biology and biomedicine. Fundamentals, recent results in preparation, and basic chemical properties of nitroxides are the main subject of Chapter 5 (S. Nakatsuji).

Chapters 6 and 7 (G.I. Likhtenshtein) offer a brief outline of principles and current results in nitroxide application as spin-labels and spin-probes in the

investigation of the molecular dynamics and microstructure of biological and non-biological objects, and as redox-probes and spin-traps. An important role of nitroxides as spin pH-meters, spin oximeters, and reactive radical-nitron adducts is elucidated. These chapters form the basis for subsequent profound studies of molecular properties of various objects such as polymers, inorganic materials, complexes of nitroxides with paramagnetic metals, photochemical systems, and so forth (Chapter 8 by G.I. Likhtenshtein). Advantages in a new area, the construction and investigation of magnetic materials on the basis of nitroxides are the subjects of Chapter 9 (R. Tamura). Chapter 10 (G.I. Likhtenshtein) discusses recent results from the utilization of the spin-labeling method for the investigation of molecular structure, dynamics, and functional activity of proteins, enzymes, biomembranes, nucleic acids, and polysaccharides. The concluding Chapter 11 (G.I. Likhtenshtein) considers biomedical, therapeutic, and clinical applications of nitroxides in areas which appear to be of great importance for human wellbeing.

Chemical, biochemical, biomedical, and material researchers may find in this book knowledge about fundamentals, instrumentation, data interpretation, capacity, and recent advances in nitroxide applications. It will help them to understand how nitroxides can help to solve their own problems. Physicists and experts in ESR instrumentation may learn about current problems and achievements in various areas of chemistry and molecular biology, and in the rapidly developing field of the application of nitroxides in biomedicine and medicine in particular. The book is also suited as a subsidiary text for instructors, graduate, and undergraduate students of university biochemical and chemical departments.

The authors are very grateful to Drs A. Rockenbauer, V. Khramtsov, F. Villamena, and A. Wasserman for their valuable advice and fruitful discussions. Finally, the authors are deeply indebted to Dr H. Tsue for his generous help in the preparation of the manuscript.

January 2008

*The authors*

## Symbols and Abbreviations

### Symbols

$\alpha$	electron spin quantum number $m_s = 1/2$ angle, alternating parameter anisotropic exchange parameter
$\alpha_n$	nuclear spin quantum number $m_1 = 1/2$
$\beta$	spin quantum number $m_s = -1/2$ angle
$\beta_n$	nuclear spin quantum number $m_1 = -1/2$
$\delta_{ij}$	Kronecker $\delta$
$\theta$	angle Curie-Weiss constant
$\Delta H$	line-width
$\Delta H_{1/2}$	half height line-width
$\Delta H_{pp}$	peak-to-peak line-width
$\Delta H_{msl}$	maximum-slope line-width
$\Delta H_{\omega 1/2}, H_{\omega pp}$	line-width in frequency
$\epsilon_0$	dielectric constant
$\epsilon_F$	Fermi energy
$\eta$	$ J'/J $
$\Gamma$	molecular field coefficient
$\gamma$	gyromagnetic ratio exchange interaction parameter anisotropic exchange parameter
$\gamma_n$	nuclear gyromagnetic ratio
$\phi$	molecular orbital relaxation function
$\Psi$	molecular orbital
$\psi$	atomic orbital
$\nu$	frequency
$\mu$	magnetic permeability
$\mu_0$	magnetic permeability of free space



$\mu_B$	Bohr magneton
$\mu_n$	nuclear Bohr magneton
$\mathcal{H}$	Hamiltonian
$\rho$	spin density, life-time probability
$\Lambda$	$\Lambda_{\mu\nu}$ -tensor
$\Lambda_{\mu\nu}$	second order perturbation of spin-orbit interaction
$\lambda$	spin-orbit coupling constant
$\tau, \tau_c$	correlation time, life time
$\tau_C$	correlation time
$\omega$	(angular) frequency
$\omega_C$	cyclotron frequency
$\omega_L$	Larmorfrequency
$\chi$	magnetic susceptibility
$\chi_{\parallel}$	parallel magnetic susceptibility
$\chi_{\perp}$	perpendicular magnetic susceptibility
$\chi_{\text{dia}}, \chi_{\text{para}}, \chi_{\text{TIP}}$	diamagnetic, paramagnetic, and temperature-independent paramagnetic magnetic susceptibility
$A$	hyperfine coupling constant
$A_{\text{aniso}}$	anisotropic hyperfine splitting $A_x, A_y, A_z$ or $A_{xx}, A_{yy}, A_{zz}$
$A_{\text{dip}}$	dipolar hyperfine tensor
$A_{\text{iso}}$	average of $A$ -tensor
$A_{\text{sol}}$	hyperfine coupling constant in solution
$A_0$	hyperfine tensor of Fermi contact term
$A_0$	Fermi contact hyperfine coupling constant
$B$	magnetic induction
$B_j$	Brillouin function
$C$	Curie constant Coulomb integral
$c$	light velocity
$D$	<b>D</b> -tensor
$D$	zero-field splitting parameter
$E$	energy, zero-field splitting parameter
$F$	force
FT	Fourier transformation
$G$	Gaussian (function) complex magnetization autocorrelation function
$g$	$g$ -value
$g_e$	free electron $g$ -value
$g_n$	nuclear $g$ -value
$g_{\text{iso}}$	average of $g$ -tensor
$g_{\text{sol}}$	$g$ -value in solution
$h$	Planck constant

$\backslash$	
$H, H$	magnetic field (strength)
$H_1$	oscillating magnetic field
$H_a$	anisotropic field
$H_e$	exchange field
$H_C$	coercivity (coercive force)
$H_{cr}$	critical field
$H_{eff}$	effective field
$H_{dip}$	dipolar field
$H_{ex}$	exchange field
$H_{mol}, H_{mol}$	Wiss molecular field
$I$	nuclear spin operator
$I$	nuclear spin angular momentum
	light intensity
$I$	nuclear spin quantum number
	function of $\eta$
$J$	total angular momentum operator
$J$	total angular momentum
$J$	quantum number of total angular momentum
	exchange integral
	spectral density
	power spectrum
$J$	the resonance integral or coupling factor
$K$	anisotropy constant
$k$	Boltzmann constant
	rate constant
$L$	orbital angular momentum operator
	unitary matrix
$L$	L-band
$L$	orbital angular momentum
$L$	quantum number of orbital angular momentum
$L$	Lorentzian (function)
	Langevin function
$l$	azimuthal quantum number
$M$	magnetization
$M$	magnetization ( $M_x, M_y, M_z, M_0$ )
$M_S$	saturation magnetization
$M_r$	residual magnetization
$m$	magnetic moment
$m_{eff}, m_{eff}$	effective magnetic moment
$m_e$	mass of electron
$m_p$	mass of proton
$m_i$ ( $i = l, S, I$ )	quantum number
$n$	principal quantum number
$Q_{ij}^i$	McConnell proportionality

<b>R</b>	relaxation term
<b>S</b>	spin operator (electron)
<b>S</b>	spin angular momentum (electron)
<b>S</b>	spin quantum number (electron)
<b>s</b>	spin quantum number $s = 1/2$ (electron)
	saturation factor
<b>Tr</b>	trace
<b>T<sub>i</sub></b> ( $i = x, y, z$ )	triplet basis functions
<b>T<sub>1</sub></b>	spin-lattice relaxation time
<b>T<sub>2</sub></b>	spin-spin relaxation time
<b>T<sub>C</sub></b>	Curie temperature
<b>T<sub>N</sub></b>	Neel temperature
<b>t</b>	time
<b>u</b>	magnetization
<b>v</b>	magnetization
<b>X</b>	X-ray, X-band
<b>z</b>	number of the nearest neighbor or the interchain paths

## Abbreviations

<b>CT</b>	charge-transfer
<b>CW-ESR</b>	continuous wave-electron magnetic resonance
<b>DANO</b>	di- <i>p</i> -anisyl nitroxide
<b>DDQ</b>	2,3-dichloro-5,6-dicyano- <i>p</i> -benzoquinone
<b>DEER</b>	double electron electron resonance
<b>DMPO</b>	5,5-dimethylpyrroline- <i>N</i> -oxide
<b>DPPH</b>	diphenyl picryl hydrazyl
<b>DQC</b>	double quantum coherence
<b>DTBNO</b>	di- <i>t</i> -butyl nitroxide
<b>ED-ESR</b>	echo detected ESR
<b>ELDOR</b>	electron double resonance
<b>ESR</b>	electron spin resonance
<b>ENDOR</b>	electron nuclear double resonance
<b>ESEEM</b>	electron spin echo envelope modulation
<b>FT-ESR</b>	Fourier transform-electron spin resonance
<b>hfcc</b>	hyperfine coupling constant
<b>hfs</b>	hyperfine splitting
<b>HOMO</b>	highest occupied molecular orbital
<b>HTS</b>	high temperature-series (expansion)
<b>IN</b>	imine nitroxide
<b>LCAO</b>	linear combination of atomic orbital
<b>LUMO</b>	lowest unoccupied molecular orbital
<b>MD</b>	molecular dynamics
<b>MM</b>	molecular mechanics

MO	molecular orbital
NMR	nuclear magnetic resonance
NMLP	nitroxide mediated leaving polymerization
NR, NRO·	nitroxide radical
NNR, NNRO·	nitronyl nitroxide radical
PBN	phenyl <i>t</i> -butyl nitron
POBN	$\alpha$ -(4-pyridyl-1-oxide)- <i>N</i> - <i>t</i> -butylnitron
SDSL	site-directed spin-labeling
SO	super oxide
SOD	super oxide dismutase
SOMO	singly occupied molecular orbital
SQUID	superconducting quantum interference device
PEDRI	proton electron double resonance imaging instrumentation
PELDOR	pulse electron-electron double resonance
ROS	reactive oxygen species
SIFTER	single-frequency technique for refocusing
TANOL	2,2,6,6-tetramethylpiperidin-4-ol-1-oxyl
TEMPOL	2,2,6,6-tetramethylpiperidiny-1-oxyl
TEMPO	2,2,6,6-tetramethylpiperidiny-1-oxy
TPV	1,3,5-triphenylverdazyl
PROXYL	2,2,5,5-tetramethylpyrrolidiny-1-oxy
TCNE	tetracyanoethylene
TCNQ	7,7,8,8-tetracyanoquinodimethane
TCNQF <sub>4</sub>	2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane
TMM	trimethylenemethane
TTF	tetrathiafulvalene bis(ethylenedithio)tetrathiafulvalene
TMTSF	tetramethyltetrathiafulvalene
TRESR	time-resolved electron spin resonance

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