

Contents

Preface ix

Abbreviations and Symbols xi

A General Part 1

1 Physical Fundamentals of Electron Spin Resonance 3

- 1.1 Spin and Magnetic Moment of Electron 3
- 1.2 Zeeman Splitting and Resonance Condition 4
- 1.3 Spin-lattice Relaxation 6
- 1.4 Line-width and Line-form 8

2 Paramagnetic Organic Species and Their Generation 10

- 2.1 Spin Multiplicity 10
- 2.2 Neutral Radicals 13
- 2.3 Radical Ions 19
- 2.4 Triplets: Electron–Electron Magnetic Interaction 27

3 Electron–Nuclear Magnetic Interaction 37

- 3.1 Nuclear Magnetism 37
- 3.2 Hyperfine Splitting of ESR Signal 39

4 Spin Density, Spin Population, Spin Polarization, and Spin Delocalization 49

- 4.1 Concepts 49
- 4.2 π Radicals 56
- 4.3 σ Radicals 75
- 4.4 Triplet States 79
- 4.5 Calculations of Spin Populations 80

5 Multiresonance 83

- 5.1 Historical Note 83
- 5.2 ENDOR 84

5.3	TRIPLE Resonance	94
5.4	ELDOR	96
6	Taking and Analyzing ESR Spectra	97
6.1	Instrumentation	97
6.2	g_e Factor	99
6.3	Optimal Conditions	102
6.4	Unravelling Hyperfine Pattern	109
6.5	Assignment and Sign of Coupling Constants	127
6.6	Ion Pairing	141
6.7	Intramolecular Dynamic Processes	153
B	Special Part	167
7	Organic Radicals Centered on One, Two, or Three Atoms	169
7.1	C-, N-, and O-centered Radicals	169
7.2	Si-, P-, and S-centered Radicals	186
7.3	CC-, NN-, and OO-centered Radicals	189
7.4	NO- and NO ₂ -centered Radicals	200
7.5	PO-, PP-, SO-, SS-, and SO ₂ -centered Radicals	208
8	Conjugated Hydrocarbon Radicals	210
8.1	Theoretical Introduction	210
8.2	Odd Alternant Radicals	217
8.3	Odd Nonalternant Radicals and Radical Dianions	224
8.4	Even Alternant Radical Ions	229
8.5	Even Nonalternant Radical Ions	254
8.6	Radicals and Radical Ions with a Perturbed π Perimeter	261
8.7	Radical Ions of Phanes	278
8.8	Radical Ions of Radialenes	287
9	Conjugated Radicals with Heteroatoms	290
9.1	Neutral Radicals	290
9.2	Radical Anions of Electron Acceptors	302
9.3	Radical Cations of Electron Donors	346
9.4	Radical Cations with Special Structures	366
9.5	Radical Ions of Multi-redox Systems	372
10	Saturated Hydrocarbon Radicals	375
10.1	Radical Cations of Alkanes	375
10.2	Structurally Modified Radical Cations	380
11	Biradicals and Triplet-state Molecules	386
11.1	Biradicals	386

11.2	Molecules in Photoexcited Triplet State	389
11.3	Molecules in Ground or Thermally Accessible Triplet State	393
	Appendices	405
A.1	Nitroxyls as Spin Labels and Spin Adducts	405
A.2	Hyperfine Splitting by Alkali-Metal Nuclei in Counterions of Radical Anions	409
	References	415
	Index	447