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# LANDOLT-BÖRNS

Zahlenwerte und Funktionen  
aus Naturwissenschaften und Technik

*Neue Serie*

Gesamtherausgabe: K.-H. Hellwege

Gruppe II: Atom- und Molekularphysik

Band 9

Ergänzung und Erweiterung zu Band 1

**Magnetische Eigenschaften freier Radikale**

Teil d 1

**Organische Anion-Radikale**

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G. Placucci · H. B. Stegmann · K. B. Ulmschneider

Herausgeber: H. Fischer und K.-H. Hellwege



Springer-Verlag Berlin · Heidelberg · New York 1980

*Zahlenwerte und Funktionen aus Naturwissenschaften und Technik*/Landolt-Börnstein. – Berlin, Heidelberg, New York: Springer. Parallelt.: Numerical data and functional relationships in science and technology. N.S./Gesamthrg.: K.-H. Hellwege. Gruppe 2, Atom- und Molekularphysik

NE: Hellwege, Karl-Heinz [Hrsg.]; Landolt-Börnstein, ...; PT. Bd. 9. Magnetische Eigenschaften freier Radikale. Erg. u. Erw. zu Bd. 1 / Hrsg.: H. Fischer u. K.-H. Hellwege. Teil d. 1. Organische Anion-Radikale / A. Berndt ... - 1980.

ISBN 3-540-08884-9 (Berlin, Heidelberg, New York)  
ISBN 0-387-08884-9 (New York, Heidelberg, Berlin)

NE: Fischer, Hanns [Hrsg.]; Berndt, Armin [Mitarb.]

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Printed in Germany

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Typesetting, printing and bookbinding: Universitätsdruckerei H. Stürtz AG Würzburg

2163/3020-543210



## **Vorwort**

Bei dem vierten (und letzten) Teilband II/9d des Ergänzungsbandes II/9 zu dem 1965 veröffentlichten Band II/1 der Neuen Serie, „Magnetische Eigenschaften freier Radikale“, sind zwei Änderungen des ursprünglichen Planes, wie er in den bisher erschienenen Teilbänden abgedruckt wurde, nötig geworden.

Die wichtigste ist sachlicher Art: die vorgesehenen Tabellen über spinmarkierte Biomoleküle werden noch nicht erscheinen. Die tabellarische Bearbeitung des Gebietes ist nach ausführlicher Diskussion mit den Fachkollegen auf einen späteren Zeitpunkt verschoben.

Trotz dieser Kürzung ist der Teilband II/9d noch so umfangreich, daß er aus technischen Gründen geteilt werden mußte. Wie der im Umschlag-Deckel abgedruckte Plan zeigt, enthält jeder Teil in sich abgeschlossene Sachgebiete. Der hier vorgelegte Teil II/9d1 behandelt die organischen Anion-Radikale.

Der letzte Teil, II/9d2, wird die organischen Kation-Radikale und Polyradikale behandeln. Er wird Anfang 1980 erscheinen und auch das kumulative Substanzenverzeichnis für den gesamten Band II/9 und den Band II/1 enthalten.

Unser Dank gilt wie immer den Autoren für ihre schnelle und sachkundige Arbeit und die angenehme Zusammenarbeit. Zu danken ist wiederum auch der Landolt-Börnstein-Redaktion, besonders Frau H. Weise, für ihre Mühe bei der Fertigstellung des Manuskriptes und beim Lesen der Korrekturen sowie dem Springer-Verlag für die sorgfältige Betreuung bei der Buchherstellung. Dieser Band wird wie alle anderen Landolt-Börnsteinbände ohne Zuschüsse von anderer Seite publiziert.

Darmstadt/Zürich, Oktober 1979

**Die Herausgeber**

## Preface

For the fourth and last subvolume, II/9d, of the supplement II/9 to volume II/1 of the New Series, "Magnetic properties of free radicals" published in 1965, it was necessary to modify the original program printed in the parts published up to now.

The main alteration concerns the planned tables on spin labelled biomolecules which will not be published within volume II/9. After thorough discussions with specialists, the compilation of data in this field has been postponed.

In spite of this, part II/9d is still so voluminous that it has to be divided. As the survey given on the inside of the front cover shows, each part is treating a well-defined field. The present part, II/9d1, is dealing with organic radical anions.

The last part, II/9d2, will refer to the organic radical cations and polyradicals. It will be published early in 1980 and will also contain the cumulative index of substances for the whole volume II/9 and for volume II/1.

We again wish to thank the authors for their quick and experienced work as well as for the agreeable cooperation, the Landolt-Börnstein office, especially Frau H. Weise, for their untiring and careful checking of manuscripts and galleys, and Springer Verlag for their customary care in the preparation of the volumes which are published without financial support from any other source.

Darmstadt/Zürich, October 1979

The Editors

## **Survey**

### **Part a**

Atoms, Inorganic Radicals, and Radicals in Metal Complexes

### **Part b**

Organic C-Centered Radicals

### **Part c1**

Organic N-Centered and NO Radicals

### **Part c2**

Organic O-, P-, S-, Se-, Si-, Ge-, Sn-, Pb-, As-, Sb-Centered Radicals

### **Part d1**

Organic Anion Radicals

### **Part d2**

Organic Cation Radicals and Polyradicals  
Index of Substances for Volumes II/1 and II/9

## **Übersicht**

### **Teil a**

Atome, anorganische Radikale und Radikale in Metallkomplexen

### **Teil b**

Organische Radikale mit C als Zentralatom

### **Teil c1**

Organische Radikale mit N als Zentralatom und NO-Radikale

### **Part c2**

Organische Radikale mit O, P, S, Se, Si, Ge, Sn, Pb, As, Sb als Zentralatom

### **Teil d1**

Organische Anion-Radikale

### **Teil d2**

Organische Kation-Radikale und Polyradikale  
Substanzenverzeichnis für die Bände II/1 und II/9

# Contents

## Magnetic properties of free radicals Part d1 : Organic anion radicals

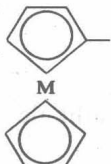
### General introduction

H. FISCHER, Physikalisch-Chemisches Institut der Universität Zürich, Switzerland

|   |                            |   |
|---|----------------------------|---|
| A | Definitions and substances | 1 |
| B | Magnetic properties        | 1 |
| C | Arrangement of the tables  | 2 |
| D | Important monographs       | 3 |
| E | Symbols and abbreviations  | 3 |
|   | Symbols                    | 3 |
|   | Abbreviations              | 4 |

### 12 Semidiones and related species

M. LEHNIG, Lehrstuhl für organische Chemie der Universität Dortmund, Germany

|                |                                                                                                                                                                                                                                                     |    |
|----------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 12.0           | Introduction                                                                                                                                                                                                                                        | 5  |
| 12.1           | Semidiones $[R-CO^-(=C-C)_n-CO^+-R'; n=0, 1, 2, 3]$                                                                                                                                                                                                 | 6  |
| 12.1.1         | 1,2-Semidiones $(R-CO^-=CO^+-R'; n=0)$                                                                                                                                                                                                              | 6  |
| 12.1.1.1       | Anion radicals from $\alpha$ -keto aldehydes ( $R=H$ )                                                                                                                                                                                              | 6  |
| 12.1.1.2       | Anion radicals from dionic systems ( $R, R' \neq H$ )                                                                                                                                                                                               | 10 |
| 12.1.1.2.1     | Anion radicals from noncyclic diketones                                                                                                                                                                                                             | 10 |
| 12.1.1.2.1.1   | Anion radicals from 2,3-diketones ( $R=CH_3, R'=alkyl$ )                                                                                                                                                                                            | 10 |
| 12.1.1.2.1.2   | Anion radicals from 3,4-diketones ( $R=C_2H_5, R'=alkyl$ )                                                                                                                                                                                          | 15 |
| 12.1.1.2.1.3   | Anion radicals from 4,5-diketones ( $R=CH_2CH_2CH_3, R'=alkyl$ )                                                                                                                                                                                    | 16 |
| 12.1.1.2.1.4   | Anion radicals from biacyls ( $R=R'=alkyl, R, R' \neq CH_3, C_2H_5, CH_2CH_2CH_3$ )                                                                                                                                                                 | 17 |
| 12.1.1.2.1.5   | Anion radicals from 1-aryl-1,2-diketones ( $R=aryl, R'=alkyl, aryl$ )                                                                                                                                                                               | 22 |
| 12.1.1.2.1.6   | Anion radicals from ferrocenyl and ruthenocenyl diketones                                                                                                                                                                                           |    |
|                | <br>$(R = \text{cyclopentadienyl ring with substituent } R, M = \text{metal atom}, R' = \text{cyclopentadienyl ring with substituent } R')$ , $R' = alkyl, aryl$ | 27 |
| 12.1.1.2.2     | Anion radicals from cyclic dionic systems                                                                                                                                                                                                           | 30 |
| 12.1.1.2.2.1   | Anion radicals from homocyclic diketones                                                                                                                                                                                                            | 30 |
| 12.1.1.2.2.1.1 | Anion radicals from cyclobutane- and cyclobutenedionic systems                                                                                                                                                                                      | 30 |
| 12.1.1.2.2.1.2 | Anion radicals from cyclopentane- and cyclopentenenedionic systems                                                                                                                                                                                  | 34 |
| 12.1.1.2.2.1.3 | Anion radicals from cyclohexane- and cyclohexenedionic systems                                                                                                                                                                                      | 38 |
| 12.1.1.2.2.1.4 | Anion radicals from cycloheptane- and cycloheptenedionic systems                                                                                                                                                                                    | 44 |
| 12.1.1.2.2.1.5 | Anion radicals from cyclooctane, cyclononane-, etc., -diones                                                                                                                                                                                        | 45 |
| 12.1.1.2.2.2   | Anion radicals from heterocyclic dionic systems                                                                                                                                                                                                     | 46 |
| 12.1.1.2.2.2.1 | Anion radicals from oxa-, aza-, and diazacyclopentane- and cyclopentenenedionic systems                                                                                                                                                             | 46 |
| 12.1.1.2.2.2.2 | Anion radicals from aza-, oxa-, and thiacyclohexanedionic systems                                                                                                                                                                                   | 47 |

|                                                                                                                                                   |     |
|---------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 12.1.1.3 Anion radicals from $\alpha$ -keto acids ( $R=H$ , alkyl, $R'=OH$ )                                                                      | 49  |
| 12.1.1.4 Anion radicals from $\alpha$ -keto acid esters and amides ( $R=$ alkyl, aryl, $R'=O$ -alkyl, S-alkyl, $N(alkyl)_2$ )                     | 50  |
| 12.1.1.5 Anion radicals from oxalic acid esters, thioesters, and amides ( $R, R'=O$ -alkyl, S-alkyl, $NH_2$ , $NH$ -alkyl, $N(alkyl)_2$ )         | 52  |
| 12.1.2 1,4-, 1,6-, 1,8-Semidiones ( $n=1, 2, 3$ )                                                                                                 | 56  |
| 12.1.2.1 Anion radicals from dionic and tetrionic systems                                                                                         | 56  |
| 12.1.2.1.1 Anion radicals from noncyclic 1,4-diketones ( $R, R'=$ alkyl, aryl)                                                                    | 56  |
| 12.1.2.1.2 Anion radicals from cyclic diketones and tetraketones                                                                                  | 56  |
| 12.1.2.1.2.1 Anion radicals from dionic and tetrionic systems                                                                                     | 56  |
| 12.1.2.1.2.1.1 Anion radicals from homocyclic diketones: carbonyl groups belonging to the same ring                                               | 56  |
| 12.1.2.1.2.1.1.1 Anion radicals from cyclopentanedionic systems                                                                                   | 56  |
| 12.1.2.1.2.1.1.2 Anion radicals from cyclohexanedionic systems                                                                                    | 57  |
| 12.1.2.1.2.1.1.3 Anion radicals from cycloheptane- and cyclooctanedionic systems                                                                  | 58  |
| 12.1.2.1.2.1.2 Anion radicals from homocyclic diketones and tetraketones: carbonyl groups belonging to different rings                            | 60  |
| 12.1.2.1.2.2 Anion radicals from heterocyclic dionic systems                                                                                      | 62  |
| 12.1.2.2 Anion radicals from fumaric, maleic, and hexanedienedioic acids                                                                          | 64  |
| 12.1.2.3 Anion radicals from fumaric and maleic acid esters and amides                                                                            | 66  |
| 12.1.2.4 Anion radicals from maleimides and maleic anhydrides                                                                                     | 68  |
| 12.2 Thiosemidiones ( $R-CS^-=CS^*-R'$ , $R-CO^-=CS^*-R'$ )                                                                                       | 73  |
| 12.2.1 Anion radicals from $\alpha$ -thioketo acid amides ( $R=$ alkyl, phenyl, $R'=N(alkyl)_2$ )                                                 | 73  |
| 12.2.2 Anion radicals from thiooxalic esters, thioesters, and amides ( $R, R'=O$ -alkyl, S-alkyl, $NH_2$ , $NH$ -alkyl, $N(alkyl)_2$ )            | 75  |
| 12.3 Semitriones ( $R-CO^-=CO^*-CO-R'$ )                                                                                                          | 79  |
| 12.3.1 Anion radicals from trionic systems                                                                                                        | 79  |
| 12.3.1.1 Anion radicals from noncyclic triketones ( $R, R'=$ aryl)                                                                                | 79  |
| 12.3.1.2 Anion radicals from cyclic trionic systems                                                                                               | 79  |
| 12.3.1.2.1 Anion radicals from homocyclic triketones                                                                                              | 79  |
| 12.3.1.2.2 Anion radicals from heterocyclic trionic systems                                                                                       | 80  |
| 12.3.2 Anion radicals from pyrovoylformic and mesoxalic acid esters and amides ( $R=CH_3$ , O-alkyl, $N(alkyl)_2$ , $R'=O$ -alkyl, $N(alkyl)_2$ ) | 82  |
| 12.4 Anion radicals from aromatic polycarbonyl and -thiocarbonyl compounds and polycarboxylic acids                                               | 83  |
| 12.4.1 Anion radicals from dialdehydes and keto aldehydes                                                                                         | 83  |
| 12.4.2 Anion radicals from di- and tetraketones                                                                                                   | 85  |
| 12.4.3 Anion radicals from polycarboxylic acids                                                                                                   | 88  |
| 12.4.4 Anion radicals from anhydrides and thioanhydrides                                                                                          | 91  |
| 12.4.5 Anion radicals from esters and thioesters                                                                                                  | 93  |
| 12.4.6 Anion radicals from imides                                                                                                                 | 100 |
| 12.4.7 Anion radicals from thiophthalates                                                                                                         | 104 |
| 12.5 References for 12.1...12.4                                                                                                                   | 107 |

### 13 Semiquinones and related species

K.B. ULSCHNEIDER, Tübingen, and H.B. STEGMANN, Institut für Organische Chemie der Universität Tübingen, Germany

|                                      |     |
|--------------------------------------|-----|
| 13.0 Introduction                    | 112 |
| 13.0.1 General remarks               | 112 |
| 13.0.2 Arrangement of the tables     | 112 |
| 13.1 Semiquinone anion radicals      | 113 |
| 13.1.1 Carbocycles                   | 113 |
| 13.1.1.1 <i>o</i> -Benzosemiquinones | 113 |



## Contents

|                                                                                    |     |
|------------------------------------------------------------------------------------|-----|
| 13.1.1.1.1 Unsubstituted and monosubstituted <i>o</i> -benzosemiquinones . . . . . | 113 |
| 13.1.1.1.2 Disubstituted <i>o</i> -benzosemiquinones . . . . .                     | 133 |
| 13.1.1.1.3 Trisubstituted <i>o</i> -benzosemiquinones . . . . .                    | 149 |
| 13.1.1.1.4 Tetrasubstituted <i>o</i> -benzosemiquinones . . . . .                  | 153 |
| 13.1.1.1.5 Polycyclic <i>o</i> -benzosemiquinones . . . . .                        | 158 |
| 13.1.1.2 <i>m</i> -Benzosemiquinones . . . . .                                     | 159 |
| 13.1.1.3 <i>p</i> -Benzosemiquinones . . . . .                                     | 162 |
| 13.1.1.3.1 Unsubstituted and monosubstituted <i>p</i> -benzosemiquinones . . . . . | 162 |
| 13.1.1.3.2 Disubstituted <i>p</i> -benzosemiquinones . . . . .                     | 192 |
| 13.1.1.3.3 Trisubstituted <i>p</i> -benzosemiquinones . . . . .                    | 220 |
| 13.1.1.3.4 Tetrasubstituted <i>p</i> -benzosemiquinones . . . . .                  | 221 |
| 13.1.1.3.5 Polycyclic <i>p</i> -benzosemiquinones . . . . .                        | 236 |
| 13.1.1.4 Pyrogallolsemiquinones . . . . .                                          | 242 |
| 13.1.1.5 Benzosemiquinones derived from 1,2,4-trihydroxybenzene . . . . .          | 249 |
| 13.1.1.6 Benzosemiquinones derived from polyhydroxybenzenes . . . . .              | 273 |
| 13.1.2 Naphthosemiquinones . . . . .                                               | 275 |
| 13.1.2.1 Naphthosemiquinones derived from 1,2-dihydroxynaphthalenes . . . . .      | 275 |
| 13.1.2.2 Naphthosemiquinones derived from 1,4-dihydroxynaphthalenes . . . . .      | 280 |
| 13.1.2.3 Naphthosemiquinones derived from other dihydroxynaphthalenes . . . . .    | 290 |
| 13.1.2.4 Naphthosemiquinones derived from trihydroxynaphthalenes . . . . .         | 290 |
| 13.1.2.5 Naphthosemiquinones derived from naphthazarine . . . . .                  | 298 |
| 13.1.2.6 Naphthosemiquinones derived from other tetrahydroxynaphthalenes . . . . . | 303 |
| 13.1.3 Anthrasemiquinones . . . . .                                                | 304 |
| 13.1.4 Phenanthrenesemiquinones . . . . .                                          | 318 |
| 13.1.5 Semiquinones from other carbocyclic compounds . . . . .                     | 322 |
| 13.1.5.1 Semiquinones derived from tropolone . . . . .                             | 322 |
| 13.1.5.2 Diphenosemiquinones and related anions . . . . .                          | 324 |
| 13.1.5.3 Acenaphthenesemiquinones and related anions . . . . .                     | 327 |
| 13.1.5.4 Ferrocenosemiquinones and related anions . . . . .                        | 330 |
| 13.1.5.5 Other carbocyclic semiquinones . . . . .                                  | 331 |
| 13.1.5.6 Indophenolsemiquinones . . . . .                                          | 333 |
| 13.2 Semiquinone anions from heterocyclic compounds . . . . .                      | 334 |
| 13.2.1 Nitrogen heterocycles . . . . .                                             | 334 |
| 13.2.1.1 Pyridinesemiquinones . . . . .                                            | 334 |
| 13.2.1.2 Indole- and benzindolesemiquinones . . . . .                              | 337 |
| 13.2.1.3 Imidazobenzosemiquinones . . . . .                                        | 339 |
| 13.2.1.4 Other N-heterocyclic semiquinones . . . . .                               | 341 |
| 13.2.2 Oxygen heterocycles . . . . .                                               | 343 |
| 13.2.2.1 Dibenzofuransemiquinones . . . . .                                        | 343 |
| 13.2.2.2 Semiquinones from fluoresceine and related systems . . . . .              | 344 |
| 13.2.2.3 Other O-heterocyclic semiquinones . . . . .                               | 347 |
| 13.2.3 Sulfur heterocycles . . . . .                                               | 347 |
| 13.3 Semiquinone cation radicals . . . . .                                         | 351 |
| 13.3.1 Benzosemiquinone cations . . . . .                                          | 351 |
| 13.3.2 Naphthosemiquinones cations . . . . .                                       | 357 |
| 13.3.3 Diphenosemiquinone cations . . . . .                                        | 358 |
| 13.3.4 Anthrasemiquinone cations . . . . .                                         | 359 |
| 13.3.5 Other semiquinone cations from carbocyclic compounds . . . . .              | 359 |
| 13.4 Charge-transfer complexes of quinones . . . . .                               | 361 |
| 13.4.1 With organic donors . . . . .                                               | 361 |
| 13.4.2 Adsorbed quinones . . . . .                                                 | 365 |
| 13.5 References for 13.1-13.4 . . . . .                                            | 367 |

## 14 Anion radicals from nitro compounds

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|                                                                                                                                   |     |
|-----------------------------------------------------------------------------------------------------------------------------------|-----|
| 14.0 Introduction . . . . .                                                                                                       | 376 |
| 14.1 Nitro compounds without double bonds conjugated with the NO <sub>2</sub> group . . . . .                                     | 377 |
| 14.1.1 Nitroalkanes (including arylnitroalkanes) without heteroatoms (except as substituents of phenyl rings) . . . . .           | 377 |
| 14.1.1.1 Primary nitroalkanes . . . . .                                                                                           | 377 |
| 14.1.1.2 Secondary nitroalkanes . . . . .                                                                                         | 381 |
| 14.1.1.3 Tertiary nitroalkanes . . . . .                                                                                          | 384 |
| 14.1.2 Nitroalkanes containing fluorine . . . . .                                                                                 | 386 |
| 14.1.3 Nitroalkanes containing chlorine . . . . .                                                                                 | 388 |
| 14.1.4 Nitroalkanes containing oxygen . . . . .                                                                                   | 390 |
| 14.1.4.1 Primary nitro compounds . . . . .                                                                                        | 390 |
| 14.1.4.1.1 Primary nitro compounds with OH, O <sup>-</sup> , OR bound to carbon bearing the NO <sub>2</sub> group (α-C) . . . . . | 390 |
| 14.1.4.1.2 Primary nitro compounds with OH, OR bound to β, γ, δ carbon . . . . .                                                  | 392 |
| 14.1.4.1.3 Primary nitro compounds with COR, CO <sub>2</sub> <sup>-</sup> , COOR bound to α, β, γ carbon . . . . .                | 395 |
| 14.1.4.1.4 Primary nitro compounds with oxygen-containing rings . . . . .                                                         | 398 |
| 14.1.4.2 Secondary nitro compounds . . . . .                                                                                      | 399 |
| 14.1.4.3 Tertiary nitro compounds . . . . .                                                                                       | 401 |
| 14.1.5 Nitroalkanes containing sulfur bound to carbon . . . . .                                                                   | 402 |
| 14.1.5.1 Primary nitro compounds . . . . .                                                                                        | 402 |
| 14.1.5.2 Secondary nitro compounds . . . . .                                                                                      | 404 |
| 14.1.5.3 Tertiary nitro compounds . . . . .                                                                                       | 406 |
| 14.1.6 Nitroalkanes containing nitrogen . . . . .                                                                                 | 406 |
| 14.1.6.1 Primary nitro compounds . . . . .                                                                                        | 406 |
| 14.1.6.1.1 Primary nitro compounds with NH <sub>2</sub> , NHR, NR <sub>2</sub> substituents . . . . .                             | 406 |
| 14.1.6.1.2 Primary nitro compounds with N <sub>3</sub> , CON, CN substituents . . . . .                                           | 407 |
| 14.1.6.2 Secondary nitro compounds . . . . .                                                                                      | 409 |
| 14.1.6.3 Tertiary nitro compounds . . . . .                                                                                       | 409 |
| 14.1.7 Nitroalkanes containing phosphorus bound to carbon . . . . .                                                               | 410 |
| 14.1.8 Nitroalkanes containing arsenic . . . . .                                                                                  | 414 |
| 14.2 Nitro compounds with double bonds conjugated with the NO <sub>2</sub> group . . . . .                                        | 414 |
| 14.2.1 Nitroalkenes . . . . .                                                                                                     | 414 |
| 14.2.1.1 Nitroalkenes with alkyl substituents . . . . .                                                                           | 414 |
| 14.2.1.2 Nitrodienes and acylnitroalkenes . . . . .                                                                               | 417 |
| 14.2.1.3 Phenyl substituted nitroalkenes . . . . .                                                                                | 418 |
| 14.2.2 1,1-Dinitroalkenes . . . . .                                                                                               | 420 |
| 14.2.3 Acyl nitro-compounds . . . . .                                                                                             | 421 |
| 14.2.4 Anions from 1,1-dinitroalkanes . . . . .                                                                                   | 421 |
| 14.2.4.1 Anions from 1,1-dinitroalkanes with alkyl and cycloalkyl substituents . . . . .                                          | 421 |
| 14.2.4.2 Anions from 1,1-dinitroalkanes with vinyl, aryl, acyl, cyano, and nitro substituents . . . . .                           | 424 |
| 14.2.5 Anions from dinitro- and trinitrocyclohexadienes . . . . .                                                                 | 426 |
| 14.2.5.1 1,3-Dinitrocyclohexadienes . . . . .                                                                                     | 426 |
| 14.2.5.2 1,5-Dinitrocyclohexadienes . . . . .                                                                                     | 428 |
| 14.2.5.3 1,3,5-Trinitrocyclohexadienes . . . . .                                                                                  | 429 |
| 14.3 Aromatic mononitro compounds . . . . .                                                                                       | 430 |
| 14.3.1 Isocyclic compounds . . . . .                                                                                              | 430 |
| 14.3.1.1 Isocyclic compounds derived from benzene . . . . .                                                                       | 430 |
| 14.3.1.1.1 Unsubstituted nitrobenzene (various solvents and gegenions) and deuterated nitrobenzenes . . . . .                     | 430 |
| 14.3.1.1.2 Nitrobenzenes containing substituents without double bonds conjugated with the aromatic ring . . . . .                 | 449 |
| 14.3.1.1.2.1 Aliphatic substituents . . . . .                                                                                     | 449 |
| 14.3.1.1.2.1.1 Open chain alkyl substituted nitrobenzenes . . . . .                                                               | 449 |
| 14.3.1.1.2.1.2 Nitrobenzenes with cycloalkyl substituents . . . . .                                                               | 463 |

|                                                                                                                             |     |
|-----------------------------------------------------------------------------------------------------------------------------|-----|
| 14.3.1.1.2.1.3 Nitrobenzenes with condensed aliphatic rings (including spirocyclic rings and paracyclophane)                | 465 |
| 14.3.1.1.2.1.4 Nitrobenzenes with condensed bicyclic rings (including triptycene)                                           | 468 |
| 14.3.1.1.2.2 Nitrobenzenes with halogen and halogen containing substituents                                                 | 471 |
| 14.3.1.1.2.2.1 Fluoro- and fluoroalkylnitrobenzenes                                                                         | 471 |
| 14.3.1.1.2.2.2 Chloro- and chloroalkylnitrobenzenes                                                                         | 479 |
| 14.3.1.1.2.2.3 Bromonitrobenzenes                                                                                           | 488 |
| 14.3.1.1.2.2.4 Iodonitrobenzenes                                                                                            | 490 |
| 14.3.1.1.2.3 Nitrobenzenes with oxygen and oxygen containing substituents                                                   | 493 |
| 14.3.1.1.2.3.1 Oxygen directly bound to ring                                                                                | 493 |
| 14.3.1.1.2.3.1.1 Nitrophenols, nitrophenolates, dihydroxynitrobenzenes                                                      | 493 |
| 14.3.1.1.2.3.1.2 Nitroanisoles, alkoxy- and aryloxy-nitrobenzenes                                                           | 499 |
| 14.3.1.1.2.3.2 Nitrobenzenes with oxygen in $\beta$ -position to ring (including oxiranes and dioxolan rings)               | 503 |
| 14.3.1.1.2.3.3 Nitrobenzenes with C=O in $\beta$ -position to ring                                                          | 505 |
| 14.3.1.1.2.4 Nitrobenzenes with sulfur and sulfur containing substituents                                                   | 505 |
| 14.3.1.1.2.5 Nitrobenzenes with nitrogen containing substituents                                                            | 508 |
| 14.3.1.1.2.5.1 Directly bound $\text{NH}_2$ , $\text{NHR}$ , $\text{NR}_2$ , $\text{NR}_3$ and $\text{N}=\text{C}=\text{S}$ | 508 |
| 14.3.1.1.2.5.2 $\beta$ -N (including $\beta\text{-NO}_2$ )                                                                  | 513 |
| 14.3.1.1.2.6 Nitrobenzenes with phosphorus containing substituents                                                          | 515 |
| 14.3.1.1.2.6.1 Phosphorus directly bound to ring                                                                            | 515 |
| 14.3.1.1.2.6.2 Phosphorus in $\beta$ -position to ring                                                                      | 515 |
| 14.3.1.1.2.7 Nitrobenzenes with arsenic containing substituents                                                             | 518 |
| 14.3.1.1.2.8 Nitrobenzenes with silicon containing substituents                                                             | 519 |
| 14.3.1.1.2.9 Nitrobenzenes with germanium containing substituents                                                           | 522 |
| 14.3.1.1.2.10 Nitrobenzenes with boron containing substituents                                                              | 522 |
| 14.3.1.1.2.11 Nitrobenzenes with mercury containing substituents                                                            | 523 |
| 14.3.1.1.3 Nitrobenzenes containing substituents with double bonds conjugated with the aromatic ring                        | 524 |
| 14.3.1.1.3.1 Vinylnitrobenzenes (including those derived from 1,1-diphenylethylene and stilbene)                            | 524 |
| 14.3.1.1.3.2 Acylnitrobenzenes                                                                                              | 529 |
| 14.3.1.1.3.2.1 Formyl-, acetyl-, and benzoylnitrobenzenes                                                                   | 529 |
| 14.3.1.1.3.2.2 $\text{COOH}$ , $\text{COO}^-$ , $\text{COOR}$ substituted nitrobenzenes                                     | 534 |
| 14.3.1.1.3.2.3 $\text{CONH}_2$ , $\text{CONR}_2$ substituted nitrobenzenes                                                  | 542 |
| 14.3.1.1.3.3 $\text{CSNHR}$ , $\text{CSNR}_2$ , and $\text{CSSR}$ substituted nitrobenzenes                                 | 544 |
| 14.3.1.1.3.4 $\text{C}=\text{NOR}$ substituted nitrobenzenes                                                                | 545 |
| 14.3.1.1.3.5 $\text{SO}_x\text{R}$ substituted nitrobenzenes                                                                | 546 |
| 14.3.1.1.3.5.1 $\text{SOR}$ substituted nitrobenzenes                                                                       | 546 |
| 14.3.1.1.3.5.2 $\text{SO}_2\text{R}$ substituted nitrobenzenes                                                              | 548 |
| 14.3.1.1.3.5.3 $\text{SO}_3^-$ substituted nitrobenzenes                                                                    | 551 |
| 14.3.1.1.3.6 N-nitrobenzenes containing $-\text{N}=\text{N}-\text{R}$ and $-\text{N}^+\equiv\text{N}$ substituents          | 552 |
| 14.3.1.1.4 Nitrobenzenes containing substituents with triple bonds conjugated with the aromatic ring                        | 553 |
| 14.3.1.1.4.1 Ethynyl substituted nitrobenzenes                                                                              | 553 |
| 14.3.1.1.4.2 Cyano substituted nitrobenzenes (nitrobenzonitriles)                                                           | 554 |
| 14.3.1.1.4.3 Nitriloxide substituted nitrobenzenes                                                                          | 559 |
| 14.3.1.1.5 Nitrobenzenes containing substituents with $6\pi$ electrons                                                      | 559 |
| 14.3.1.1.5.1 Cyclopentadienyl substituted nitrobenzenes                                                                     | 559 |
| 14.3.1.1.5.2 Phenylnitrobenzenes                                                                                            | 560 |
| 14.3.1.1.5.2.1 Nitrodiphenyl                                                                                                | 560 |
| 14.3.1.1.5.2.2 Di-, tri-, tetra-, and pentaphenylnitrobenzenes                                                              | 563 |
| 14.3.1.1.6 Nitrobenzenes with diphenyl substituents                                                                         | 565 |
| 14.3.1.1.7 Nitrobenzenes with naphthyl substituents                                                                         | 566 |
| 14.3.1.1.8 Nitrobenzenes with anthracenyl substituents                                                                      | 567 |
| 14.3.1.2 Nitroferrocene                                                                                                     | 570 |
| 14.3.1.3 Nitrotropolones                                                                                                    | 570 |
| 14.3.1.4 Nitronaphthalenes                                                                                                  | 571 |
| 14.3.1.4.1 1-Nitronaphthalenes                                                                                              | 571 |
| 14.3.1.4.2 2-Nitronaphthalenes                                                                                              | 572 |

|                                                                                                                                                                     |     |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 14.3.2 Heterocyclic aromatic mononitro compounds . . . . .                                                                                                          | 572 |
| 14.3.2.1 5-membered rings . . . . .                                                                                                                                 | 572 |
| 14.3.2.1.1 Nitrofurans . . . . .                                                                                                                                    | 572 |
| 14.3.2.1.2 Nitrothiophenes . . . . .                                                                                                                                | 578 |
| 14.3.2.1.2.1 2-Nitrothiophenes . . . . .                                                                                                                            | 578 |
| 14.3.2.1.2.2 3-Nitrothiophenes . . . . .                                                                                                                            | 582 |
| 14.3.2.1.2.3 Nitrothienothiophenes . . . . .                                                                                                                        | 583 |
| 14.3.2.1.3 Nitrothiazoles . . . . .                                                                                                                                 | 584 |
| 14.3.2.1.3.1 2-Nitrothiazoles . . . . .                                                                                                                             | 584 |
| 14.3.2.1.3.2 4-Nitrothiazoles . . . . .                                                                                                                             | 584 |
| 14.3.2.1.3.3 5-Nitrothiazoles . . . . .                                                                                                                             | 585 |
| 14.3.2.1.4 Nitroimidazoles . . . . .                                                                                                                                | 586 |
| 14.3.2.1.4.1 2-Nitroimidazoles . . . . .                                                                                                                            | 586 |
| 14.3.2.1.4.2 4-Nitroimidazoles . . . . .                                                                                                                            | 587 |
| 14.3.2.1.4.3 5-Nitroimidazoles . . . . .                                                                                                                            | 588 |
| 14.3.2.2 6-membered rings . . . . .                                                                                                                                 | 589 |
| 14.3.2.2.1 Nitropyridines . . . . .                                                                                                                                 | 589 |
| 14.3.2.2.1.1 2-Nitropyridines . . . . .                                                                                                                             | 589 |
| 14.3.2.2.1.2 3-Nitropyridines . . . . .                                                                                                                             | 590 |
| 14.3.2.2.1.3 4-Nitropyridines . . . . .                                                                                                                             | 594 |
| 14.3.2.2.2 Nitropyridine <i>N</i> -oxides . . . . .                                                                                                                 | 600 |
| 14.3.2.2.3 Nitropyrimidines and related compounds (nitrouracil, nitroorotic acid, nitrobarbituric acid) . . . . .                                                   | 604 |
| 14.3.2.3 Condensed ring systems . . . . .                                                                                                                           | 608 |
| 14.3.2.3.1 Nitrodibenzo- <i>p</i> -dioxin . . . . .                                                                                                                 | 608 |
| 14.3.2.3.2 Nitrophenothiazine 5-oxide . . . . .                                                                                                                     | 608 |
| 14.3.2.3.3 Nitrophenoxatellurin . . . . .                                                                                                                           | 608 |
| 14.3.2.3.4 Nitrocycl[3,2,2]azine . . . . .                                                                                                                          | 609 |
| 14.4 Aromatic dinitro compounds . . . . .                                                                                                                           | 609 |
| 14.4.1 Isocyclic compounds . . . . .                                                                                                                                | 609 |
| 14.4.1.1 Isocyclic compounds derived from benzene . . . . .                                                                                                         | 609 |
| 14.4.1.1.1 Nitro groups bound to the same aryl ring . . . . .                                                                                                       | 609 |
| 14.4.1.1.1.1 <i>o</i> -Dinitrobenzenes . . . . .                                                                                                                    | 609 |
| 14.4.1.1.1.1.1 Unsubstituted <i>o</i> -dinitrobenzenes . . . . .                                                                                                    | 609 |
| 14.4.1.1.1.1.2 Substituted <i>o</i> -dinitrobenzenes . . . . .                                                                                                      | 611 |
| 14.4.1.1.1.2 <i>m</i> -Dinitrobenzenes . . . . .                                                                                                                    | 614 |
| 14.4.1.1.1.2.1 Unsubstituted <i>m</i> -dinitrobenzene . . . . .                                                                                                     | 614 |
| 14.4.1.1.1.2.2 Substituted <i>m</i> -dinitrobenzenes . . . . .                                                                                                      | 621 |
| 14.4.1.1.1.2.2.1 Substituted <i>m</i> -dinitrobenzenes without conjugated double bonds . . . . .                                                                    | 621 |
| 14.4.1.1.1.2.2.2 Substituted <i>m</i> -dinitrobenzenes with conjugated double bonds . . . . .                                                                       | 628 |
| 14.4.1.1.1.2.2.3 Substituted <i>m</i> -dinitrobenzenes with conjugated triple bonds and aryl rings . . . . .                                                        | 633 |
| 14.4.1.1.1.3 <i>p</i> -Dinitrobenzenes . . . . .                                                                                                                    | 634 |
| 14.4.1.1.1.3.1 Unsubstituted <i>p</i> -dinitrobenzenes . . . . .                                                                                                    | 634 |
| 14.4.1.1.1.3.2 Substituted <i>p</i> -dinitrobenzenes . . . . .                                                                                                      | 639 |
| 14.4.1.1.2 Nitro groups bound to different aryl rings . . . . .                                                                                                     | 641 |
| 14.4.1.1.2.1 Directly connected rings . . . . .                                                                                                                     | 641 |
| 14.4.1.1.2.1.1 <i>o,o'</i> -Dinitrodiphenyl . . . . .                                                                                                               | 641 |
| 14.4.1.1.2.1.2 <i>m,m'</i> -Dinitrodiphenyl . . . . .                                                                                                               | 642 |
| 14.4.1.1.2.1.3 <i>p,p'</i> -Dinitrodiphenyl . . . . .                                                                                                               | 642 |
| 14.4.1.1.2.2 Rings connected by saturated links . . . . .                                                                                                           | 643 |
| 14.4.1.1.2.2.1 Dinitrodiphenylmethanes, dinitrodiphenyloxides, dinitrodiphenylsulfides . . . . .                                                                    | 643 |
| 14.4.1.1.2.2.2 Dinitro-9,10-dihydro-9,10-methano-anthracenes, dinitro-9,10-dihydro-9,10-ethano-anthracenes, dinitrotritycene, dinitro[2,2]paracyclophanes . . . . . | 645 |
| 14.4.1.1.2.2.3 Rings connected by unsaturated links . . . . .                                                                                                       | 646 |
| 14.4.1.1.2.2.3.1 Anions from dinitrodiphenylmethanes and dinitrofluorene . . . . .                                                                                  | 646 |
| 14.4.1.1.2.2.3.2 1,1-Di( <i>p</i> -nitrophenyl)ethylene . . . . .                                                                                                   | 647 |
| 14.4.1.1.2.2.3.3 Dinitrobenzophenones, dinitrobenzil . . . . .                                                                                                      | 648 |
| 14.4.1.1.2.2.3.4 4,4'-Dinitrostilbenes . . . . .                                                                                                                    | 650 |

|                                                                                         |     |
|-----------------------------------------------------------------------------------------|-----|
| 14.4.1.1.2.2.3.5 Dinitrotolans and related compounds . . . . .                          | 650 |
| 14.4.1.1.2.2.3.6 4,4''-Dinitro- <i>p</i> -terphenyl . . . . .                           | 651 |
| 14.4.1.1.2.2.3.7 1,1'-Bis-( <i>o</i> -nitrophenyl) ferrocenes . . . . .                 | 652 |
| 14.4.1.2 Dinitro compounds derived from tropolones . . . . .                            | 652 |
| 14.4.1.3 Dinitro compounds derived from naphthalene . . . . .                           | 653 |
| 14.4.1.3.1 1,4-Dinitronaphthalenes, 1,5-, 1,8-, 2,6-, 2,7-dinitronaphthalenes . . . . . | 653 |
| 14.4.1.3.2 Dinitroacenaphthalenes and dinitronaphthalic anhydrides . . . . .            | 655 |
| 14.4.1.3.3 Nitro groups bound to different naphthalene rings . . . . .                  | 656 |
| 14.4.1.4 Dinitro compounds derived from anthracene . . . . .                            | 656 |
| 14.4.2 Heterocyclic dinitro compounds . . . . .                                         | 657 |
| 14.4.2.1 5-membered rings . . . . .                                                     | 657 |
| 14.4.2.2 6-membered rings . . . . .                                                     | 657 |
| 14.4.2.2.1 3,5-Dinitropyridines . . . . .                                               | 657 |
| 14.4.2.2.2 Dinitrophenothiazines, dinitrophenooxatellurin . . . . .                     | 661 |
| 14.5 Aromatic trinitro compounds . . . . .                                              | 661 |
| 14.5.1 Trinitro compounds derived from benzene . . . . .                                | 661 |
| 14.5.1.1 1,3,5-Trinitrobenzene . . . . .                                                | 661 |
| 14.5.1.2 1,3,5-Trinitrobenzene containing substituents . . . . .                        | 663 |
| 14.5.2 Trinitro compounds derived from stilbene . . . . .                               | 666 |
| 14.5.3 Trinitro compounds derived from naphthalene . . . . .                            | 667 |
| 14.5.4 Trinitrotriptycene . . . . .                                                     | 667 |
| 14.6 Aromatic tetranitro compounds . . . . .                                            | 668 |
| 14.6.1 Tetranitro compounds derived from naphthalene . . . . .                          | 668 |
| 14.6.2 Tetranitro-9,10-dihydro-9,10-ethano-anthracene . . . . .                         | 669 |
| 14.6.3 Tetranitrophenothiazine-5-oxide . . . . .                                        | 669 |
| 14.7 References . . . . .                                                               | 670 |
| 14.7.1 Review articles . . . . .                                                        | 670 |
| 14.7.2 References for 14.1...14.6 . . . . .                                             | 670 |

## 15 Anion radicals from nitroso compounds

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|                                                                                     |     |
|-------------------------------------------------------------------------------------|-----|
| 15.0 Introduction . . . . .                                                         | 679 |
| 15.1 Nitroso compounds without double bonds conjugated with the N=O group . . . . . | 680 |
| 15.1.1 Aliphatic nitroso compounds . . . . .                                        | 680 |
| 15.1.1.1 Aliphatic nitroso compounds without heteroatoms . . . . .                  | 680 |
| 15.1.1.2 Aliphatic nitroso compounds containing halogens . . . . .                  | 680 |
| 15.1.1.3 Aliphatic nitroso compounds containing oxygen . . . . .                    | 681 |
| 15.1.1.4 Aliphatic nitroso compounds containing nitrogen . . . . .                  | 683 |
| 15.1.1.5 Aliphatic nitroso compounds containing phosphorus . . . . .                | 684 |
| 15.1.2 Nitrites . . . . .                                                           | 684 |
| 15.1.3 Nitrosamines . . . . .                                                       | 685 |
| 15.2 Nitroso compounds with double bonds conjugated with the N=O group . . . . .    | 687 |
| 15.2.1 Nitrosoalkenes . . . . .                                                     | 687 |
| 15.2.2 Acyl nitroso compounds . . . . .                                             | 688 |
| 15.2.3 Anions from 1,1-dinitrosoalkanes . . . . .                                   | 688 |
| 15.2.4 Anions from nitrosodinitroalkanes and from nitrosodinitromethanes . . . . .  | 689 |
| 15.3 Aromatic nitroso compounds . . . . .                                           | 690 |
| 15.3.1 Nitrosobenzene and substituted nitrosobenzenes . . . . .                     | 690 |
| 15.3.2 <i>m</i> -Nitronitrosobenzenes . . . . .                                     | 694 |
| 15.4 References for 15.1...15.3 . . . . .                                           | 697 |



**15A Anion radicals from boron compounds**

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|                                                           |     |
|-----------------------------------------------------------|-----|
| 15A.0 Introduction . . . . .                              | 698 |
| 15A.1 Anion radicals containing one boron atom . . . . .  | 699 |
| 15A.1.1 Trialkyl boranes . . . . .                        | 699 |
| 15A.1.2 Mono-, di-, and trivinyl boranes . . . . .        | 699 |
| 15A.1.3 Mono-, di-, and triaryl boranes . . . . .         | 701 |
| 15A.2 Anion radicals containing two boron atoms . . . . . | 705 |
| 15A.3 References for 15A.1 and 15A.2 . . . . .            | 706 |

**16 Hydrocarbon anion radicals**

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|                                                           |     |
|-----------------------------------------------------------|-----|
| 16.0 Introduction . . . . .                               | 707 |
| 16.0.1 General remarks . . . . .                          | 707 |
| 16.0.2 Hyperfine splittings . . . . .                     | 707 |
| 16.0.3 g-Values . . . . .                                 | 707 |
| 16.1 Cyclic hydrocarbon anion radicals . . . . .          | 708 |
| 16.1.1 Monocyclic systems . . . . .                       | 708 |
| 16.1.1.1 Benzenes . . . . .                               | 708 |
| 16.1.1.2 Other single-ring compounds . . . . .            | 723 |
| 16.1.2 Polycyclic systems (condensed) . . . . .           | 731 |
| 16.1.2.1 Simple substituted naphthalenes . . . . .        | 731 |
| 16.1.2.2 Other substituted naphthalenes . . . . .         | 751 |
| 16.1.2.3 Other polycyclic compounds (condensed) . . . . . | 769 |
| 16.1.3 Polycyclic systems (non-condensed) . . . . .       | 798 |
| 16.1.3.1 Biphenyls . . . . .                              | 798 |
| 16.1.3.2 Bridged biphenyls . . . . .                      | 811 |
| 16.1.3.3 Other non-condensed cyclic compounds . . . . .   | 822 |
| 16.1.4 Bridged systems . . . . .                          | 834 |
| 16.1.5 Cyclophanes . . . . .                              | 838 |
| 16.1.6 Triptycenes . . . . .                              | 842 |
| 16.2 Non-aromatic hydrocarbon anion radicals . . . . .    | 844 |
| 16.3 References for 16.1 and 16.2 . . . . .               | 850 |

**17 Anion radicals from heterocyclic compounds**

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|                                                                                            |     |
|--------------------------------------------------------------------------------------------|-----|
| 17.0 Introduction . . . . .                                                                | 857 |
| 17.1 Nitrogen containing anion radicals . . . . .                                          | 858 |
| 17.2 Anion radicals of heterocycles containing O, S, and Se . . . . .                      | 883 |
| 17.3 Anion radicals of heterocycles containing P and Si . . . . .                          | 895 |
| 17.4 Anion radicals of heterocycles containing two or more different heteroatoms . . . . . | 898 |
| 17.5 References for 17.1-17.4 . . . . .                                                    | 903 |

## General introduction

### A Definition and substances

The free radicals considered in these tables are paramagnetic atoms, molecules and ions which derive their paramagnetism from a single unpaired *s*- or *p*-electron. They may be chemically stable or transient.

It is usual in organic chemistry to define a free radical as a paramagnetic molecule with one unpaired electron (see for instance: J. B. Hendrickson, D. J. Cram, G. S. Hammond: *Organic Chemistry*, 3rd ed. New York: McGraw-Hill 1970). However, alternatively all species can be classified as free radicals "that have a short lifetime in the gaseous phase under ordinary laboratory conditions" regardless of their electronic states (G. Herzberg: *The Spectra and Structures of Simple Free Radicals*. Ithaca: Cornell University Press 1971). The substances included in these tables are all paramagnetic and fulfill the first definition. Most of them also are transient and would fulfill the requirements of the alternative definition.

In particular, the tables include:

- Atoms and atomic ions in  $^2S$  and  $^2P$  states,
- Molecules or molecular ions which arise or may be thought to arise from the break of a single bond in a diamagnetic organic or inorganic molecule or molecular ion,
- Mono-(tri-, penta-, etc.)-negative or -positive ions of neutral organic or inorganic compounds,
- Several molecules which are paramagnetic in their normal binding states and have one unpaired electron (e.g. NO, NO<sub>2</sub>).

Not classified as free radicals are atoms or molecules in ground or excited electronic states with multiplicities larger than two (e.g. O<sub>2</sub>), transition metal ions and their complexes deriving their paramagnetic properties from *d*- or *f*-electrons, charge transfer complexes, aggregates of free radicals as for instance pairs of radicals not chemically linked to one another in solid matrices, and polyradicals, i.e. molecules or molecular ions, with more than one unpaired *s*- or *p*-electron and exchange couplings which are of the same order of magnitude as the hyperfine interactions.

The following tables deal with substances of type a) to d). In addition one table lists available information on polyradicals. It has been included because the magnetic properties of polyradicals often resemble those of the corresponding monoradicals.

Only compounds with unambiguously verified or at least very plausible structures are included. Papers which only state the presence of free radicals in a sample and do not give detailed structures nor magnetic properties of the radicals have not been reviewed. Also not reviewed are papers which deal exclusively with other topics than experimental determinations of magnetic properties of free radicals. Such papers may however be mentioned in footnotes or as further references at the appropriate entries.

The ordering of the substances classified as free radicals into subclasses is to be seen in the general table of contents. The ordering within the subclasses is explained, where not self-explanatory, in introductory sections to the individual tables.

### B Magnetic properties

The magnetic properties of free radicals are represented by the parameters describing their interaction with external magnetic fields and the parameters of intramolecular hyperfine interactions. For many free radicals, in particular  $^2S$ -atoms and radicals in liquid or solid environments where the orbital and rotational components of angular momentum are quenched, the parameters are conveniently given by the elements of the tensors *g* and *a<sub>λ</sub>* of the spin-Hamiltonian

$$\mathcal{H} = \mu_B \cdot \vec{S} \cdot \vec{g} \cdot \vec{H}_0 - \sum_{\lambda} \mu_N \cdot g_{N\lambda} \cdot \vec{I}_{\lambda} \cdot \vec{H}_0 + \sum_{\lambda} \vec{S} \cdot \vec{a}_{\lambda} \cdot \vec{I}_{\lambda}.$$

*g* is the spectroscopic splitting or *g*-tensor. It is symmetric, and for many radicals its principal elements deviate only slightly from the *g*-factor of the free electron

$$g_e = 2.002319278 \pm 0.000000006.$$

The isotropic part of *g*, i.e. the average of the principal elements,

$$g_{is} = \frac{1}{3} \sum_i g_{ii}$$

is called the *g*-factor of the free radical.

$a_\lambda$ , the hyperfine coupling tensor, describes the magnetic interaction between the electronic spin momentum and the nuclear spin momentum of the nucleus  $\lambda$  of the radical. If a radical contains several nuclei which interact with the electron spin, then there are several tensors  $a_\lambda$ . The coupling tensor is also often considered symmetric, its isotropic part

$$a_{is} = \frac{1}{3} \sum_i a_{ii}$$

is called hyperfine coupling constant or splitting parameter.

For polyatomic radicals in the gaseous phase the above spin-Hamiltonian does not apply. Here, the presence of unquenched orbital and rotational angular momenta necessitates the introduction of several magnetic hyperfine coupling constants to describe the interaction between one nucleus and the free electron. These are defined and explained in the introduction to the tables on inorganic radicals.

Polyradicals have magnetic properties derived from Zeeman ( $g$ ) and hyperfine ( $a$ ) interactions and in addition from exchange and dipolar coupling of the individual radical electrons. The display of the appropriate parameters is explained in the introduction to the tables on polyradicals.

There are a variety of techniques for the determination of the various parameters of the spin-Hamiltonian. Often applied are Electron Paramagnetic or Spin Resonance (EPR, ESR), Electron Nuclear Double Resonance (ENDOR), Electron Electron Double Resonance (ELDOR), Nuclear Magnetic Resonance (NMR), occasionally utilizing effects of Chemically Induced Dynamic Nuclear Polarization (CIDNP), Optical Detection of Magnetic Resonance (ODMR), Atomic Beam Spectroscopy and Optical Spectroscopy. The extraction of the magnetic parameters from the spectra obtained by application of these and related techniques follows procedures which may in detail depend on the technique, the state of the sample (gaseous, liquid, unordered solid, ordered solid) and on spectral resolution. For particulars, the reader is referred to the general references (D).

Further, magnetic moments of free radicals can be obtained from static susceptibility measurements. In the last years such determinations are rare, and they are only occasionally mentioned in the tables. For a list of references covering the literature up to 1964, see:

H. Fischer: Magnetic Properties of Free Radicals, Landolt-Börnstein, New Series, Group II, Vol. 1. Berlin, Heidelberg, New York: Springer 1965.

## C Arrangement of the tables

The following tables give the spin-Hamilton parameters  $g$  and  $a_\lambda$  of free radicals as determined mainly by spectroscopic measurements on liquid or solid samples. Gaseous phase di- and tri-atomic radicals are included in the tables on inorganic radicals. There is a special table on organic polyradicals and a collection of information on spin-labelled biomolecules.

For the display of the data the substances which are classified as free radicals are subdivided into several classes, and one individual table contains the information on the radicals of one particular class. Each table is headed by an introduction to the subject of the table which may specify the chemical species belonging to the class, details of the arrangement and ordering of the substances, and in some cases also special abbreviations. The table is followed by the list of references.

Within the individual tables the radicals are grouped into families. The data are arranged in columns in the following manner which, as far as possible, is applied to all species:

The *first* column describes the structure of the radical and contains the gross formula, the name (where useful and appropriate) and the structural formula (or a footnote referring to the structural formula).

The *second* column briefly describes the generation of the radical and specifies the matrix or solvent in which the radical was measured. For stable radicals (naturally occurring or synthesized by common chemical routes) the generation may not be specified.

The *third* column specifies the method used to determine  $g$  and  $a$ . The abbreviations for the methods most frequently used are explained in the list of abbreviations, p. 4.

If other abbreviations and other methods appear they are explained in footnotes. The third column also states the sample temperature during the measurement in units K. 300 normally means room temperature.

The *fourth* column ( $g$ -factor) states the absolute values of the elements of the  $g$ -tensor  $g$ . If for one radical four values are given, the first three are the principal elements of  $g$ , the fourth is the isotropic part  $g_{is}$ . If only one value is given without further explanation it is the isotropic part. Principal axes of  $g$  are not given. Errors are quoted in parentheses after the values.

The *fifth* column ( $a$ -value) contains the elements of the hyperfine coupling tensors  $a_\lambda$  of the coupling nuclei and states the nuclei. Where possible the signs of the tensor elements are given. The unit is mT (milli-Tesla), except for gaseous radicals where Mc/s ( $\equiv$  MHz) is applied. In many original papers Gauss or Mc/s are used as units.

The conversion is:

$$1 \text{ mT} \triangleq 10 \text{ Gauss} \triangleq 28.0247 (\text{g/g}_e) \text{ Mc/s}$$

If column five gives four values of  $a$  for one nucleus the first three are the principal elements of the coupling tensor, the fourth is the isotropic part. If only one value is given without further explanation it is the isotropic part. Errors are quoted in parentheses.

The nucleus to which the parameters belong is characterized by its chemical symbol, a left superscript may indicate the isotope, if another than the most abundant is meant. Entries within parentheses after the chemical symbol specify different positions of the nucleus in the radical (e.g.  $^{17}\text{O}(2)$ : The values belong to the isotope  $^{17}\text{O}$  in position 2 of the structural formula). If several nuclei with the same chemical symbol couple with the same hyperfine coupling constants the parameters are given only once and the number of equivalent nuclei is stated before the chemical symbol (e.g.  $3\text{H}$ : The values belong to 3 equivalent H atoms of the molecule).

The arrangement of columns four and five may differ for the cases of gaseous radicals and polyradicals from that described above. For these cases the entries are explained in the individual tables.

The *sixth* column (Ref./add. Ref.) lists the reference from which the data are taken. This reference is followed by additional references to the same subject. All references belonging to one individual table are found in the bibliography after that table.

The literature was considered for the period from 1964 to the end of 1975. For several tables literature of 1976 has also been included. Magnetic properties of free radicals published before March 1964 are to be found in:

H. Fischer: Magnetic Properties of Free Radicals, Landolt-Börnstein, New Series, Group II, Vol. 1. Berlin, Heidelberg, New York: Springer 1965.

## D Important monographs

- |       |                                                                                                                   |
|-------|-------------------------------------------------------------------------------------------------------------------|
| 67At1 | Atkins, P.W., Symons, M.C.R.: The Structure of Inorganic Radicals. Amsterdam: Elsevier 1967.                      |
| 67Ay1 | Ayscough, P.B.: Electron Spin Resonance in Chemistry. London: Methuen 1967.                                       |
| 67Ca1 | Carrington, A., McLachlan, A.D.: Introduction to Magnetic Resonance. Harper International 1967.                   |
| 67Ge1 | Gerson, F.: Hochauflösende ESR-Spektroskopie. Weinheim: Verlag Chemie 1967.                                       |
| 67Po1 | Poole, C.P., Jr.: Electron Spin Resonance. New York: Interscience 1967.                                           |
| 68Al1 | Alger, R.S.: Electron Paramagnetic Resonance. New York: Interscience 1968.                                        |
| 68Ka1 | Kaiser, E.T., Kevan, L.: Radical Ions. New York: Interscience 1968.                                               |
| 70Sc1 | Scheffler, K., Stegmann, H.B.: Elektronenspinresonanz. Berlin, Heidelberg, New York: Springer 1970.               |
| 72Ge1 | Geschwind, S., Editor: Electron Paramagnetic Resonance. New York: Plenum Press 1972.                              |
| 72Mu1 | Muus, L.T., Atkins, P.W., Editors: Electron Spin Relaxation in Liquids. New York: Plenum Press 1972.              |
| 72Sw1 | Swartz, H.M., Bolton, J.R., Borg, D.C.: Biological Applications of Electron Spin Resonance. New York: Wiley 1972. |
| 72We1 | Wertz, J.E., Bolton, J.R.: Electron Spin Resonance. New York: McGraw-Hill 1972.                                   |
| 73At1 | Atherton, N.M.: Electron Spin Resonance, Theory and Applications. New York: Halsted 1973.                         |
| 73Bu1 | Buchachenko, A.L., Wasserman, A.L.: Stable Radicals. Weinheim: Verlag Chemie 1973.                                |
| 73Ko1 | Kochi, J.K., Editor: Free Radicals. New York: Wiley 1973.                                                         |
| 73No1 | Norman, R.O.C., Editor: Electron Spin Resonance. London: The Chemical Society 1973ff.                             |
| 74Ca1 | Carrington, A.: Microwave Spectroscopy of Free Radicals. London: Academic Press 1974.                             |

## E Symbols and abbreviations

### Symbols

|                    |                                                                                          |                   |                                            |
|--------------------|------------------------------------------------------------------------------------------|-------------------|--------------------------------------------|
| $A_1, A_2$         | empirical parameters,<br>see vol. II/9a, section 1.1.4                                   | $\mu_N$           | nuclear magneton                           |
| $a, b, c, d$ [MHz] | magnetic hyperfine coupling<br>constants in Mega-Hertz,<br>see vol. II/9a, section 1.1.4 | $g$               | $g$ -tensor                                |
| $a_{is}$ [mT]      | isotropic part of $a$ in milli-Tesla                                                     | $g_{is}$          | isotropic part of $g$ ( $g$ -factor)       |
| $a_\lambda$ [mT]   | hyperfine coupling tensor of<br>nucleus $\lambda$ in milli-Tesla                         | $g_{N\lambda}$    | nuclear $g$ -factor of nucleus $\lambda$   |
| $\mu_B$            | Bohr magneton                                                                            | $\mathcal{H}$     | spin-Hamilton operator                     |
|                    |                                                                                          | $\vec{H}_0$       | external magnetic field vector             |
|                    |                                                                                          | $\vec{I}_\lambda$ | nuclear spin operator of nucleus $\lambda$ |
|                    |                                                                                          | $\vec{S}$         | effective electron spin operator           |
|                    |                                                                                          | $T$ [K]           | temperature in Kelvin                      |

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