

## 12 Nitroxide radicals and polynitroxides

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### 12.1 Introduction

#### 12.1.1 General remarks

This is the third edition of this compilation, and is meant to cover the literature from 1987/88 to 2000. Since the previous edition the number of publications dealing with nitroxides has increased steadily, and the present volume includes a few thousands entries. This compilation is nevertheless not exhaustive, in the sense that it does not include all the nitroxides reported in the above time interval, and is mainly addressed to those species that did not appear in the previous two editions. Already described nitroxides have been included when their spectral parameters differed significantly from those already reported or when they had been produced through not obvious or new chemical processes. Although in many cases the reported nitroxides are originated by treatment of the corresponding amines, hydroxylamines, or *N*-oxides with a variety of oxidizing agents (e.g. peracids, metal oxides, etc.), the vast majority of nitroxides derive from spin-trapping experiments whereby transient radical species are converted to more persistent spin adducts (nitroxides) by reacting them with either nitroso compounds (both aliphatic and aromatic) or with nitrones (both acyclic or cyclic). In some cases biradicals can be converted to cyclic alkyl-alkoxynitroxides by a “double” trapping with nitric oxide.

Owing to their generally high persistence, there has been a continuing exploiting of nitroxides as spin labels and spin probes. Thus, for example, several studies have been oriented at determining the viscosity of organic and/or biological media through a study of custom designed and synthesized spin probes.

While a large number of spin-trapping experiments have been carried out with purely mechanistic purposes, being addressed to intercepting free radicals intervening in organic reactions, an enormous amount of work has been dedicated to the trapping of radicals generated in biological systems in order to evaluate the nature, and possibly the extent, of the radical damage induced in these systems by the exposure to ionizing radiations or by chemical reactions resulting in the production of highly reactive species, as for example the hydroxy radical. In many of these cases, however, the trapped radicals are part of a very complex molecule, such as a protein, a nucleic acid, etc., and it is not possible to exactly define the structure of the spin adducts. These nitroxides have therefore been omitted from the tables in Sects. 12.2–12.5. Two research groups have been mainly operating in this field, and because their results pertaining to these nitroxides may be of general interest, a number of references to their relevant work are given in the end of this introductory section.

Section 12.5 dealing with polynitroxides only covers species containing two or more nitroxidic functions. Mononitroxides in higher spin states (e.g. the diradical cation or anion of a nitroxide) are reported as a note to the entry of the corresponding nitroxides. In this section, the values of zero field splitting parameters *D* and *E* are given by default in  $\text{cm}^{-1}$ . When data refer to different units, these are expressly indicated.

#### 12.1.2 Classifications

The nitroxides have been divided into two broad families: acyclic nitroxides and cyclic nitroxides. The former are further divided into aliphatic, aliphatic-aromatic, aromatic nitroxides. Aliphatic derivatives are further divided according to the extent of substitution of the carbon bound to the nitrogen atom of the nitroxidic function. Cyclic nitroxides are divided according to the nature of the ring containing the

nitroxidic nitrogen atom. Acyl, vinyl, and iminyl nitroxides as well as nitroxides with a leading atom other than carbon are also considered.

### 12.1.3 Abbreviations and acronyms

A list of the most common abbreviations and acronyms used through the tables in Sects. 12.2–12.5 follows. Other less common abbreviations not included in the list are explained in a note to the relevant entry. For the sake of brevity, whenever in a page the same abbreviation appears more than once, the explanation is only reported the first time.

ACN = Acetonitrile  
 AIBN = Azobisisobutyronitrile  
 BHP = *tert*-Butylhydroperoxide  
 BOOB = Di-*tert*-butyl peroxide  
 BPB = *tert*-Butylperoxybenzoate  
 $\alpha$ ,  $\beta$ ,  $\gamma$ -CD =  $\alpha$ ,  $\beta$ ,  $\gamma$ -Cyclodextrine  
 CPBA = *m*-Chloroperbenzoic acid  
 DBNB = 2,6-Dibromonitrosobenzene  
 DBNBS = 2,6-Dibromonitrosobenzen-4-sulphonic acid, sodium salt  
 DBPO = Di-*tert*-butylperoxyoxalate  
 DEPMPO = 5-(Diethoxyphosphoryl)-5-methylpyrroline *N*-oxide  
 DEPPO = 5-(Diethoxyphosphoryl)-5-phenylpyrroline *N*-oxide  
 DME = 1,2-dimethoxyethane  
 DMF = Dimethylformamide  
 DMSO = Dimethylsulfoxide  
 DPN = Diphenyl nitrone  
 EDTA = Ethylenediaminetetraacetic acid  
 GSH = Glutathione (reduced form)  
 LLE = Laboratory light exposure  
 M<sub>2</sub>PyO = 6,6-dimethyl-3,4,5,6-tetrahydropyridine *N*-oxide  
 M<sub>3</sub>PO = 2,5,5-Trimethylpyrroline *N*-oxide  
 M<sub>4</sub>PO = 3,3,5,5-Tetramethylpyrroline *N*-oxide  
 MDN = Methyl-*N*-duryl nitrone  
 MNP = 2-Methyl-2-nitroso propane  
 MPO = 2-Methyl-1-pyrroline *N*-oxide  
 MPPO = 5-Methyl-5-phenylpyrroline *N*-oxide  
 NADPH = Nicotinamide adenine dinucleotide phosphate, reduced form  
 NB = Nitrosobenzene  
 ND = Nitrosodurene  
 NNP = 2-Nitro-2-nitroso propane  
 NPBA = *p*-Nitroperbenzoic acid  
 PBN =  $\alpha$ -Phenyl-*N*-*tert*-butyl nitrone  
 PMNB = Pentamethoxynitrosobenzene  
 POBN =  $\alpha$ -(4-Pyridyl-1-oxide)-*N*-*tert*-butyl nitrone  
 PPCN = (Phosphorylated photochromic nitrone) = 5'-{*N*-[2-(Di-ethoxyphosphoryl)propan-2-yl]-*N*-oxidoazaniumylidenemethyl}-1,3,3-trimethylspiro-{indoline-2,3'-naphtho[2,1-b][1,4]oxazine}  
 PPN =  $\beta$ -Diethoxyphosphoryl  $\alpha$ -phenyl-*N*-*tert*-butyl nitrone  
 4-PyOPN = {1-Diethoxyphosphoryl-1-methyl-*N*-[(1-oxidopyridin-1-ium-4-yl)methylidene]-ethylamine *N*-oxide  
 2-PyPN = *N*-[(Pyridinium-2-yl)methylidene]-1-diethoxyphosphoryl-1-methylethylamine *N*-oxide  
 3-PyPN = *N*-[(Pyridinium-3-yl)methylidene]-1-diethoxyphosphoryl-1-methylethylamine *N*-oxide

4-PyPN = *N*-[(Pyridinium-4-yl)methylidene]-1-diethoxyphosphoryl-1-methylethylamine *N*-oxide

SG = Thiyl radical from glutathione

SPBN =  $\alpha$ -(2-Sulfophenyl)-*N*-*tert*-butyl nitron, sodium salt

SQUID = Superconducting quantum interference device susceptometer

TBNB = 2,4,6-Tribromonitrosobenzene

TEAP = Tetraethylammonium perchlorate

TEMPO = 2,2,6,6-Tetramethyl-1-piperidinyloxy

2-TFDMPO = 2-Trifluoromethyl-5,5-dimethylpyrroline *N*-Oxide

THF = Tetrahydrofuran

TMTHF = 2,2,5,5-Tetramethyl-3,4-dihydrofuran

TMPO = 3,3,5,5-Tetramethyl-1-pyrroline-1-oxide

TR-ESR = Time Resolved Electron Spin Resonance spectroscopy

### 12.1.4 Summary table

This summary table is to be used as a general guide to users of the data. The coupling-constant intervals given refer to the majority of the nitroxides within a given family. Nitroxides with spectral parameters outside these intervals have also been reported (see tables in Sects. 12.2–12.5).

Nitroxide radical	General structure	$a_N$ [mT]	$g$
Alkyl	$RN(O^\bullet)H$	1.20 ... 1.53	2.0061 ... 2.0065
Alkyl acyl	$RN(O^\bullet)C(O)R$	0.85 ... 0.65	2.0065 ... 2.0075
Alkyl alkoxy	$RN(O^\bullet)OR$	2.90 ... 2.40	2.0054 ... 2.0060
Alkyl amino	$RN(O^\bullet)NR_2$	1.80 ... 1.60	2.0058 ... 2.0064
Alkyl aryl	$RN(O^\bullet)Ar$	1.25 ... 1.05	2.0056 ... 2.0064
Alkyl boroxy	$RN(O^\bullet)OBR_2NR_3$	2.85 ... 2.65	2.0054 ... 2.0055
Alkyl phosphoryl	$RN(O^\bullet)P(O)R_2$	0.89 ... 1.08	2.0062 ... 2.0068
Alkyl germxyloxy	$RN(O^\bullet)OGerR_3$	2.85 ... 2.79	2.0052 ... 2.0055
Alkyl silyl	$RN(O^\bullet)SiR_3$	1.12 ... 1.06	2.0070
Alkyl silyloxy	$RN(O^\bullet)OSiR_3$	2.94 ... 2.82	2.0052 ... 2.0055
Alkyl thio	$RN(O^\bullet)SR$	1.85 ... 1.70	2.0062 ... 2.0070
Aryl	$ArN(O^\bullet)H$	0.87 ... 1.00	2.0060
Aryl alkoxy	$ArN(O^\bullet)OR$	1.6 ... 1.04	2.0052 ... 2.0062
Aryl amino	$ArN(O^\bullet)NR_2$	1.28 ... 0.60	2.0055 ... 2.0065
Aryl boroxy	$ArN(O^\bullet)OBR_2NR_3$	2.19 ... 2.15	2.0053 ... 2.0054
Aryl silyloxy	$ArN(O^\bullet)OSiR_3$	1.50 ... 1.24	2.0047 ... 2.0048
Aryl thio	$ArN(O^\bullet)SR$	1.63 ... 0.90	2.0056 ... 2.0075
Cyclodialkyl	(5-membered ring)	1.55 ... 1.35	2.0058 ... 2.0065
Cyclodialkyl	(6-membered ring)	1.60 ... 1.40	2.0058 ... 2.0065
Dialkyl	$RN(O^\bullet)R$	1.55 ... 1.40	2.0059 ... 2.0065
Diaryl	$ArN(O^\bullet)Ar$	1.05 ... 0.90	2.0055 ... 2.0063