PREFACE

This Handbook contains a compilation of Electron Paramagnetic Resonance (EPR) data of numerous semiquinones and related radicals. The Handbook is intended as a general reference guide to the structural studies of the radicals obtained by redox processes from natural and synthetic quinones and quinols. A chief difficulty in the general utility of EPR spectroscopy as an analytical tool is that even closely related radicals may furnish widely different spectra. When the spectra are analyzed in terms of splitting constants, however, the similarities between related radicals become apparent immediately. In organizing the Tables, therefore, effort has been made to attach importance to these similarities. Furthermore, variations in the splitting constants due to solvent, pH, or temperature effects have been located with the particular radical in order to make the data readily accessible; hopefully the clarity of presentation is not, therefore, compromised.

For the benefit of the newcomers to the field a short introduction to the principles of EPR is given, together with instructive examples which show how to correlate a radical structure with its EPR spectrum.

The Handbook should serve workers in a number of fields, especially since there is a growing interest in a variety of aspects of semiquinone chemistry. Besides the use in the structural characterization of numerous quinones/quinols the semiquinones are also useful for the following: as effective probes for studying intermolecular effects originating from counter ion and solvent association; for examining electronic theories of free radicals; and also for the insight one might get with systems where quinones/semiquinones participate, including blood clotting (menaquinones), aging (tocoquinones), energy conserving systems (plasto- and ubiquinones), and systems where the compounds act as insect and microbial controlling agents.

The editor is most grateful to the members of the Advisory Board for their useful criticisms and expert help. Special thanks are due to the many colleagues who generously provided compounds for analysis; these EPR analyses have been incorporated whenever possible.

The editor is pleased to acknowledge the expeditious and skillful help of several members of the technical staff at the Chemistry Department, Aarhus University, and owes a particular debt to the members of the Physical Chemistry Division for their valuable suggestions during the preparation of the manuscript.

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July 1983
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TABLE OF CONTENTS

Introduction ......................................................................................... 1
Assignments ......................................................................................... 1

Principles of EPR ................................................................................ 3
Radicals ............................................................................................... 4

Hyperfine Splittings ............................................................................ 5
Determinations of Splitting Constants from Experimental Spectra .......... 9
Assignment of Splitting Constants ......................................................... 12
The g-Factor ......................................................................................... 14

An Analytical Application .................................................................... 17

Semiquinone Spectra ........................................................................... 23

Explanation to Tables .......................................................................... 55
Location of Radicals ............................................................................. 55
Splitting Constants .............................................................................. 55

Tables .................................................................................................. 57

I. Anions ............................................................................................... 57

Benzosemiquinone Anions ................................................................. 57
I.1 1,2-Benzosemiquinones ................................................................. 57
I.2 1,3-Benzosemiquinones ................................................................. 66
I.3 1,4-Benzosemiquinones ................................................................. 67
I.3.1 2'-Substituted Phenyl-1,4-Benzosemiquinones ......................... 81
I.3.2 3'-Substituted Phenyl-1,4-Benzosemiquinones ......................... 82
I.3.3 4'-Substituted Phenyl-1,4-Benzosemiquinones ......................... 83
I.3.4 Polysubstituted Aryl-1,4-Benzosemiquinones ......................... 84
I.3.5 Imidazo- and Triazolo-1,4-Benzosemiquinones ....................... 85
I.4 Pyrogallol Semiquinones — Dianions ............................................ 87
I.5 Pyrogallol Semiquinones — Monoanions ...................................... 90
I.6 4-Oxido-1,2-Benzosemiquinones ................................................ 91
I.6.1 2'-Substituted 5-Phenyl-4-Oxido-1,2-Benzosemiquinones ......... 96
I.6.2 3'-Substituted 5-Phenyl-4-Oxido-1,2-Benzosemiquinones ......... 97
I.6.3 4'-Substituted 5-Phenyl-4-Oxido-1,2-Benzosemiquinones ........ 98
I.6.4 Polysubstituted 5-Phenyl-4-Oxido-1,2-Benzosemiquinones ....... 99
I.6.5 2'-Substituted 6-Phenyl-4-Oxido-1,2-Benzosemiquinones ......... 100
I.6.6 3'-Substituted 6-Phenyl-4-Oxido-1,2-Benzosemiquinones ......... 101
I.6.7 4'-Substituted 6-Phenyl-4-Oxido-1,2-Benzosemiquinones ......... 102
I.6.8 Polysubstituted 6-Phenyl-4-Oxido-1,2-Benzosemiquinones ....... 103
I.7 4-Hydroxy- and 4-Alkoxy/Aryloxy-1,2-Benzosemiquinones .......... 104
I.8 2-Hydroxy- and 2-Alkoxy/Aryloxy-1,4-Benzosemiquinones .......... 107
I.9 Benzosemiquinones with Four Key Oxygens [1,2,3,4] .................. 111
I.10 Benzosemiquinones with Four Key Oxygens [1,2,3,5] .................. 114
I.11 Benzosemiquinones with Four Key Oxygens [1,2,4,5] .................. 117
I.12 Benzosemiquinones with Five and Six Key Oxygens ................. 122
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.13.1</td>
<td>Bicyclobenzosemiquinones</td>
<td>124</td>
</tr>
<tr>
<td>I.13.2</td>
<td>Semiquinones Derived from 3',6'-Dihydroxybenzobicyclo[2.2.1]hept-2-ene</td>
<td>125</td>
</tr>
<tr>
<td>I.13.3</td>
<td>Semiquinones Derived from 3',6'-Dihydroxybenzobicyclo[2.2.2]oct-2-ene</td>
<td>128</td>
</tr>
<tr>
<td>I.13.4</td>
<td>Semiquinones Derived from 3',6'-Dihydroxybenzobicyclo[2.2.1]hepta-2,5-diene</td>
<td>129</td>
</tr>
<tr>
<td>I.13.5</td>
<td>Semiquinones Derived from 3',6'-Dihydroxybenzobicyclo[2.2.2]octa-2,5-diene</td>
<td>132</td>
</tr>
<tr>
<td>I.14</td>
<td>Semiquinone Radicals Derived from Triptycene</td>
<td>134</td>
</tr>
<tr>
<td>I.15.1</td>
<td>Naphthosemiquinones with Two Key Oxygens</td>
<td>137</td>
</tr>
<tr>
<td>I.15.2</td>
<td>Naphthosemiquinones with Three Key Oxygens</td>
<td>143</td>
</tr>
<tr>
<td>I.15.3</td>
<td>Naphthosemiquinones with Four to Eight Key Oxygens</td>
<td>149</td>
</tr>
<tr>
<td>I.15.4</td>
<td>Bicyclonaphthosemiquinones</td>
<td>157</td>
</tr>
<tr>
<td>I.16.1</td>
<td>Anthrasemiquinones with Two Key Oxygens</td>
<td>159</td>
</tr>
<tr>
<td>I.16.2</td>
<td>Hydroxy- and Alkoxyanthrasemiquinones</td>
<td>162</td>
</tr>
<tr>
<td>I.17</td>
<td>Phenanthrasemiquinone Anions</td>
<td>167</td>
</tr>
<tr>
<td>I.18.1</td>
<td>Tropone Anion Radicals and Tropolonyl Radicals</td>
<td>169</td>
</tr>
<tr>
<td>I.18.2</td>
<td>Benztpolonyl Radicals</td>
<td>171</td>
</tr>
<tr>
<td>I.19</td>
<td>Diphenosemiquinones</td>
<td>173</td>
</tr>
<tr>
<td>I.20</td>
<td>Semiquinones Derived from Diquinones</td>
<td>174</td>
</tr>
<tr>
<td>I.21</td>
<td>Diarylfuran Semiquinone Derivatives</td>
<td>178</td>
</tr>
<tr>
<td>I.22.1</td>
<td>3',4'-Dioxidoflavonoid Anion Radicals — B-Ring Semiquinones</td>
<td>181</td>
</tr>
<tr>
<td>I.22.2</td>
<td>2',3',4'- and 3',4',5'-Trioxidoflavonoid Anion Radicals — B-Ring</td>
<td>184</td>
</tr>
<tr>
<td>I.22.3</td>
<td>3',4',6'-Trioxidoflavonoid Anion Radicals — B-Ring Semiquinones</td>
<td>187</td>
</tr>
<tr>
<td>I.22.4</td>
<td>Radicals of Some Flavones — A-Ring Radicals</td>
<td>189</td>
</tr>
<tr>
<td>I.23</td>
<td>Oxidocoumarine Radicals</td>
<td>191</td>
</tr>
<tr>
<td>II.1</td>
<td>Phenoxy Radicals</td>
<td>194</td>
</tr>
<tr>
<td>II.2</td>
<td>2-Hydroxy- and 2-Alkoxyphenoxyl Radicals</td>
<td>199</td>
</tr>
<tr>
<td>II.3</td>
<td>3-Hydroxy- and 3-Alkoxyphenoxyl Radicals</td>
<td>202</td>
</tr>
<tr>
<td>II.4.1</td>
<td>4-Hydroxy- and 4-Alkoxyphenoxyl Radicals</td>
<td>203</td>
</tr>
<tr>
<td>II.4.2</td>
<td>Chromanlyoxyl Radicals</td>
<td>211</td>
</tr>
<tr>
<td>II.5</td>
<td>Pyrogallol Derived Phenoxy Radicals</td>
<td>213</td>
</tr>
<tr>
<td>II.6</td>
<td>Pyrogalloquinone Radicals</td>
<td>216</td>
</tr>
<tr>
<td>II.7</td>
<td>Phenoxy Radicals with Three Key Oxygens [1,2,4]</td>
<td>217</td>
</tr>
<tr>
<td>II.8</td>
<td>Phlorogluconol Radicals</td>
<td>219</td>
</tr>
<tr>
<td>II.9</td>
<td>Phenoxy Radicals with Four Key Oxygens [1,2,4,5]</td>
<td>221</td>
</tr>
<tr>
<td>II.10</td>
<td>1- and 2-Naphthyloxy Radicals</td>
<td>222</td>
</tr>
<tr>
<td>II.11</td>
<td>Anthranlyoxyl and Bianthrone Radicals</td>
<td>225</td>
</tr>
</tbody>
</table>
### III. Cations

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>III. 1 Phenol Radicals with One Key Oxygen</td>
<td>227</td>
</tr>
<tr>
<td>III. 2 Phenol Radicals with Two Key Oxygens [1,2]</td>
<td>230</td>
</tr>
<tr>
<td>III. 3 Phenol Radicals with Two Key Oxygens [1,3]</td>
<td>234</td>
</tr>
<tr>
<td>III. 4 1,4-Dihydroxy/Alkoxybenzene Derived Radicals</td>
<td>235</td>
</tr>
<tr>
<td>III. 5 Phenol Radicals with Three Key Oxygens [1,2,3]</td>
<td>242</td>
</tr>
<tr>
<td>III. 6 Phenol Radicals with Three Key Oxygens [1,2,4]</td>
<td>246</td>
</tr>
<tr>
<td>III. 7 Phloroglucinol Radicals</td>
<td>247</td>
</tr>
<tr>
<td>III. 8 Phenol Radicals with Four Key Oxygens [1,2,3,4] and [1,2,3,5]</td>
<td>249</td>
</tr>
<tr>
<td>III. 9 Phenol Radicals with Four Key Oxygens [1,2,3,4,5]</td>
<td>252</td>
</tr>
<tr>
<td>III. 10 Phenol Radicals with Five and Six Key Oxygens</td>
<td>255</td>
</tr>
<tr>
<td>III. 11 1,4-Dihydroxy/Alkoxyanthracene Derived Radicals</td>
<td>257</td>
</tr>
<tr>
<td>III. 12 9,10-Dihydroxy/Alkoxyanthracene Derived Radicals</td>
<td>259</td>
</tr>
</tbody>
</table>

### IV. Semiquinone-Cation Complexes

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV. 1.1 1,2-Benzosemiquinone-Cation Complexes</td>
<td>261</td>
</tr>
<tr>
<td>IV. 1.2 4-Substituted 1,2-Benzosemiquinone-Cation Complexes</td>
<td>265</td>
</tr>
<tr>
<td>IV. 1.3 Diorganothallium(III)-1,2-Benzosemiquinone Complexes</td>
<td>267</td>
</tr>
<tr>
<td>IV. 1.4 3,5-Di-t-butyl-1,2-Benzosemiquinone-Cation Complexes</td>
<td>272</td>
</tr>
<tr>
<td>IV. 1.5 3,6-Di-t-butyl-1,2-Benzosemiquinone-Cation Complexes</td>
<td>283</td>
</tr>
<tr>
<td>IV. 1.6 Tetrahalogeno-1,2-Benzosemiquinone-Cation Complexes</td>
<td>296</td>
</tr>
<tr>
<td>IV. 1.7 1,4-Benzosemiquinone-Cation Complexes</td>
<td>304</td>
</tr>
<tr>
<td>IV. 1.8 Tetrasubstituted-1,4-Benzosemiquinone-Cation Complexes</td>
<td>317</td>
</tr>
<tr>
<td>IV. 1.9 Benzosemiquinone-Cation Complexes with Three Key Oxygens [1,2,3] and [1,2,4]</td>
<td>321</td>
</tr>
<tr>
<td>IV. 1.10 Some 1,2-Benzosemiquinone TI-Metal Complexes, Solvent Effects</td>
<td>324</td>
</tr>
<tr>
<td>IV. 2.1 1,2-Naphthosemiquinone-Cation Complexes</td>
<td>326</td>
</tr>
<tr>
<td>IV. 2.2 1,4-Naphthosemiquinone-Cation Complexes</td>
<td>330</td>
</tr>
<tr>
<td>IV. 3 9,10-Anthrasemiquinone-Cation Complexes</td>
<td>331</td>
</tr>
<tr>
<td>IV. 4 Phenanthrenesemiquinone-Cation Complexes</td>
<td>333</td>
</tr>
<tr>
<td>IV. 5 Acenaphthenesemiquinone-Cation Complexes</td>
<td>336</td>
</tr>
<tr>
<td>IV. 6.1 Dithieno-1,2-Benzosemiquinone-Cation Complexes</td>
<td>338</td>
</tr>
<tr>
<td>IV. 6.2 Dithieno-1,4-Benzosemiquinone-Cation Complexes</td>
<td>343</td>
</tr>
</tbody>
</table>

### V. Isotopes: $^{13}$C and $^{17}$O

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>V. 1 1,2-Benzosemiquinones</td>
<td>345</td>
</tr>
<tr>
<td>V. 2 1,3-Benzosemiquinones</td>
<td>348</td>
</tr>
<tr>
<td>V. 3.1 1,4-Benzosemiquinones</td>
<td>349</td>
</tr>
<tr>
<td>V. 3.2 1,4-Benzosemiquinones, Cations, and Neutral Species</td>
<td>352</td>
</tr>
<tr>
<td>V. 3.3 Substituted 1,4-Benzosemiquinones</td>
<td>353</td>
</tr>
<tr>
<td>V. 3.4 2,5-Dio xo-1,4-Benzosemiquinones</td>
<td>355</td>
</tr>
<tr>
<td>V. 4 Miscellaneous Radicals</td>
<td>356</td>
</tr>
</tbody>
</table>

References ................................................................................. 357

EPR Monographs ........................................................................ 367

Abbreviations ............................................................................ 369
Compound Index ........................................................................................................... 371
Subject Index ............................................................................................................. 377
INTRODUCTION

Semiquinones are relatively stable free radicals formed by one-electron reduction of quinones or by one-electron oxidation of quinols. Thus, in alkaline media, the 1,4-benzo-semiquinone radical anion ($Q^-$) appears as an intermediate in the process

\[
\begin{align*}
\text{Q} & \xrightarrow{\text{Red}} \text{Q}^+ \xrightarrow{\text{Ox}} \text{Q}^- \\
\text{O} & \xrightarrow{\text{Red}} \text{O}^+ \xrightarrow{\text{Ox}} \text{O}^-
\end{align*}
\]

A semiquinone is by virtue of the odd number of electrons amenable to electron paramagnetic resonance (EPR) spectroscopy. In general, the protons in the molecule split the EPR signal from the unpaired electron into a unique splitting pattern, called the hyperfine structure. Although the pattern may consist of hundreds of individual lines, it can be completely described in terms of a small number of splitting constants, in fact constituting a "structural fingerprint" of the semiquinone.

Moreover, since redox processes of the type (1) occur without significant structural changes, the EPR spectrum of a semiquinone identifies the parent quinone or quinol as well. This, in connection with the inherent high sensitivity of EPR spectroscopy, has made EPR spectra of semiquinones an important analytical tool in the study of naturally occurring quinones and quinols. The analytical application rests on the substantial and rapidly growing body of published semiquinone spectra, obtained from chemically well-defined compounds.

The present compilation of splitting constants was undertaken primarily to give ready access to the available reference data, thus enhancing the analytical potential of the EPR method in studies involving quinones and related compounds.

The tables comprise representative results for all reported semiquinone-radicals derived from quinones or quinols having six-membered quinone rings without heteroatoms, supplemented by data for other radicals derived from mono- and polyhydric phenols and naphthols. Five- and seven-membered quinone rings are represented byacenaphthenoquinones and tropolones, respectively.

The compilation is based on the literature as covered by Chemical Abstracts from 1958 to the beginning of 1983. As a rule, all EPR data concerning the classes of radicals mentioned are included. Omissions are made, however, where the description or interpretation of the results was found inadequate and where new, accurate data supersede older ones. Data from some 200 unpublished spectra run in the editors laboratory are included to fill "gaps" in some of the tables and to augment the very scanty information on certain groups of radicals, e.g., the anthrasemiquinones.

ASSIGNMENTS

The assignment of observed hyperfine splitting constants to nuclei at specific sites is crucial for any interpretation in terms of molecular properties. Most splitting constants included in the tables were originally assigned by the authors. However, conflicting or incomplete assignments in the literature are not uncommon. All assignments entered into the tables have been critically revised in the light of the newest evidence, empirical rules for substituent effects, and, finally, trends within a family of related radicals, e.g., an anion radical and its complexes with various cations. The assignments thus obtained are internally consistent and agree with the available evidence.
Where an assignment deviates from that given by the authors, the reference is marked with a superscript plus sign (e.g., $27^+\)  

The data, comprising hyperfine splitting constants, g-factor, solvent system, and method of radical generation, are organized in five sections under the headings Anions, Neutral Species, Cations, Semiquinone-Cation Complexes, and Isotopes ($^{13}C$ and $^{17}O$).

To facilitate the use of the tabulated data, a brief introduction to the analysis of EPR spectra is given. Moreover, a collection of semiquinone spectra is shown in order to illustrate characteristic features. The analytical application of EPR spectroscopy is shown with examples of determinations of quinones/quinols in crude plant extracts.
PRINCIPLES OF EPR*  

A free electron placed in a magnetic field, \( H \), will be found in either of two Zeeman states having an energy separation proportional to the strength of the field. This is accounted for by assigning to the electron a spin angular momentum with quantum number \( S = \frac{1}{2} \), and an associated magnetic moment. It follows from the quantum mechanics of angular momentum that the electron can be in either of \( 2S + 1 = 2 \) states, associated with the values \((\pm \frac{1}{2})\) of the "magnetic" quantum number \( m_s \), which specifies the orientation of the magnetic moment in the external field.

The electronic energy is given by

\[
E(m_s) = E_0 + \beta g_e H m_s
\]

where \( E_0 \) represents the energy in the absence of the magnetic field, \( \beta \) is the Bohr magneton \((9.274 \times 10^{-21} \text{ erg G}^{-1})\), and \( g_e \) a dimensionless constant, the electronic g-factor with the value 2.002319. In an EPR experiment transitions are induced between Zeeman states in a strong magnetic field, by means of microwave radiation of proper frequency \( \nu_0 \), determined by the resonance condition

\[
\hbar \nu_0 = \Delta E = E(m_s = \frac{1}{2}) - E(m_s = -\frac{1}{2})
\]

or with Equation 2

\[
\hbar \nu_0 = \beta g_e H
\]

The level diagram and the EPR spectrum of a (hypothetical) sample of free electrons are depicted in Figure 1.

* The following outline is intended to serve as an introduction to the EPR studies in solution. For more detailed information, one of the authoritative reference texts listed under EPR monographs should be consulted.
In Figure 1 the EPR spectrum is represented as absorption vs. field strength, since in the normal experimental procedure the microwave frequency, \( \nu_0 \), is held constant whereas \( H \) is varied until the resonance condition (Equation 3) is met. The field at which the absorption line occurs, is called the resonance field, \( H_r \). Note the slope of the energy levels is determined by \( g_e \).

**RADICALS**

The spins of electrons bound in molecules are usually paired, so that most molecules with an even number of electrons have no net magnetic moments due to the electrons. Such molecules do not respond to magnetic fields in the way required to yield an EPR spectrum. On the other hand, radicals having an odd number of electrons behave in the EPR experiment much like free electrons. In molecular quantum mechanics the electronic ground state of radicals is assigned an electron spin \( S = \frac{1}{2} \). Strictly speaking, this quantum number characterizes the full electronic state of the radical rather than a single electron. However, in accordance with molecular orbital theory and the Aufbau principle, it has proved convenient to attribute the magnetic properties of the radical to the spin of a single electron occupying a specific molecular orbital. This so-called unpaired electron represents the radical as far as the EPR spectrum is concerned. Hence the description given above for a sample of free electrons applies to a sample of radicals, as well, if \( g_e \) in Equation 3 is substituted by the \( g \)-factor of the unpaired electron, i.e., the value required to represent the magnetic moment of the radical.
HYPERFINE SPLITTINGS

Semiquinone radicals give rise to spectra exhibiting from one to hundreds of lines disposed in a centrosymmetric pattern of total spread up to 30 G. The line pattern or hyperfine structure arises from interaction between the magnetic moment of the unpaired electron and one or more atomic nuclei. Many commonly occurring nuclei possess magnetic moments associated with spins.* The spin quantum number assigned to nuclei is denoted \( I \) and has one of the values \( 0, \frac{1}{2}, 1, 3/2 \ldots \) depending on the nucleus in question. A nucleus with spin \( I \) has \( 2I + 1 \) substates labeled by the magnetic quantum number \( m \), \( m = I, I-1, I-2 \ldots -I \). The states correspond to different orientations of the nuclear moment in an external magnetic field.

In a radical containing a nucleus with spin \( I \neq 0 \), the magnetic moment of the unpaired electron may interact with the local magnetic field set up by the nuclear moment. Since the local field experienced by the unpaired electron depends on the quantum number \( m \), so do the energy levels of the electron. In fact, for each value of \( m \), there are \( 2I + 1 \) closely spaced levels (Figure 2). If the external field is much stronger than the local fields and the radicals are dissolved in a low-viscosity solvent so that they tumble rapidly, the possible EPR transitions are simply obtained from the resonance condition

\[
h \nu = g\beta H + a'm_i \quad (4)
\]

where the term \( a'm_i \) appears as a result of the interaction with the local field. For fixed frequency, \( \nu \), \( 2I + 1 \) equidistant EPR lines of equal intensity, each associated with a particular value of \( m_i \), are observed at the resonance fields

\[
H(m_i) = H_o - am_i \quad (5)
\]

where \( H_o = h\nu/g\beta \) is the resonance field in the absence of magnetic nuclei, and \( a = a'/g\beta \) is the hyperfine splitting constant measured in Gauss.

Identical nuclei in identical chemical environments within a radical will give rise to the same hyperfine splitting. Such nuclei are called equivalent. A radical containing \( n \) equivalent nuclei of spin \( I \) yields equidistant EPR lines at the resonance fields

\[
H(m^e_1, m^e_2, \ldots, m^e_n) = H_o - a \sum_{j=1}^{n} m^e_j \quad (6)
\]

There are \( (2I + 1)^n \) different sets \( (m^e_1, m^e_2, \ldots, m^e_n) \), each specifying a transition in the EPR spectrum. However, the right-hand side of Equation 6 yields only \( 2nI + 1 \) different resonance fields, or distinct EPR lines. Hence all but the two outermost EPR lines are degenerate, so that the observed relative intensities increase towards the center of the spectrum. For nuclei with spin \( I = \frac{1}{2} \) the relative intensities are given by the binomial coefficients of order \( n \) (Pascal's triangle, see Scheme 1) and for spin \( I = 1 \) by the trinomial coefficients and so on.

These results may be generalized to radicals containing \( r \) groups of equivalent nuclei. If the \( i \)'th group contains \( n^i \) equivalent nuclei with spin \( I^i \) and splitting constant \( a^i \), then the number of lines in the spectrum is given by the product

\[
N = \prod_{i=1}^{r} (2n^i I^i + 1) \quad (7)
\]

These lines are positioned at the resonance fields given as

\[
H(m^{i,j}_{1}) = H_o - \sum_{i=1}^{r} a^i \sum_{j=1}^{n^i} m^{i,j} \quad (8)
\]

where \( i \) labels the groups of equivalent nuclei and \( j \) labels the nuclei within the groups. The number of individual transitions is given by the product

\[
D = \prod_{i=1}^{r} (2I + 1)^{n_i} \tag{9}
\]

Since \( N < D \) if there are equivalent nuclei, a number of transitions will coincide to produce degenerate lines in the spectrum. The outermost lines are always nondegenerate, however. This implies that \( D \) may be expressed in terms of the height \( h(k) \) of the \( k \)'th line as

\[
D = \sum_{k=1}^{N} \frac{h(k)}{h(1)} \tag{10}
\]

The linear field separation between the two outermost lines in the spectrum called the total width (TW), may be expressed by means of Equation 8 as

\[
TW = 2 \sum_{i=1}^{r} n_i' a^i \tag{11}
\]

Examples include the following:

1. **Radical with a single proton with splitting constant \( a \):** \( r = n = 1, I = \frac{1}{2} \), and \( m_i = \pm \frac{1}{2} \), and therefore two resonance fields are obtained from Equation 6

\[
H_1 = H_o - \frac{1}{2} a \\
H_2 = H_o + \frac{1}{2} a
\]

The spectrum consists of two lines of equal intensity, separated by \( a \) as shown in Figure 2. As usual in EPR spectroscopy the spectrum is represented as the first derivative of the absorption curve.

![EPR Spectrum Diagram](image-url)
Scheme 1
BINOMIAL, TRINOMIAL, AND TETRANOMIAL COEFFICIENTS GIVING THE RELATIVE LINE INTENSITIES OBSERVED FROM n NUCLEI OF SPIN I = 1/2, 1, AND 3/2, RESPECTIVELY

<table>
<thead>
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<th>n</th>
<th>Relative intensities</th>
<th>N</th>
<th>D</th>
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<td>N = n + 1</td>
<td>D = 2ⁿ:</td>
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</tr>
<tr>
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</tr>
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</tr>
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<td>8</td>
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<td>16</td>
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</tr>
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<tr>
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<td>1 8 28 56 70 56 28 8 1</td>
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<td>256</td>
</tr>
<tr>
<td>9</td>
<td>1 9 36 84 126 126 84 36 9 1</td>
<td>10</td>
<td>512</td>
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<table>
<thead>
<tr>
<th>I = 1</th>
<th>N = 2n + 1</th>
<th>D = 3ⁿ:</th>
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<tr>
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<tr>
<td>5</td>
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<td>6</td>
<td>1 6 21 50 90 126 141 125 90 50 21 6 3</td>
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<table>
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<td></td>
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<tr>
<td>4</td>
<td>1 4 10 20 31 40 44 40 31 20 10 4 1</td>
<td>13 256</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2. Radical with two equivalent protons: r = 1, n = 2, I = 1/2, m₁ = ±1/2. The spectrum contains three lines (Equation 7). The resonance fields obtained from Equation 6 are

\[
\begin{align*}
H(\frac{1}{2}, \frac{1}{2}) &= H_0 - a \\
H(\frac{1}{2}, -\frac{1}{2}) &= H_0 \\
H(-\frac{1}{2}, \frac{1}{2}) &= H_0 \\
H(-\frac{1}{2}, -\frac{1}{2}) &= H_0 + a
\end{align*}
\]

The spectrum is a triplet with the relative intensities 1:2:1 and line separation equal to a as shown in Figure 3.
1. The smallest splitting constant is equal to the separation $H(2) - H(1)$ (or $H(N) - H(N - 1)$).

2. If $h(1) \approx h(2)$, the smallest splitting stems from a single proton (cf. Figure 2), and the second-smallest splitting constant then equals $H(3) - H(1)$. If on the other hand, $h(2) \approx 2h(1)$ or $h(2) \approx 3h(1)$, then the smallest splitting stems from two or three equivalent nuclei, respectively. This rule applies to $I = \frac{1}{2}$ nuclei only.

3. When all but one splitting constant, $a'$, have been determined, $a'$ may be obtained as

$$a' = \frac{1}{2n'\eta'} \left( TW - 2 \sum_{i=1}^{n' - 1} n'\eta'a_i \right) \quad (12)$$

Example 1 — 2-Methoxy-1,4-benzosemiquinone (No. 446).* As shown in Figure 5, 28 lines are observed. First the total number $P$ of protons associated with splittings is determined via Equation 9, which for $I = \frac{1}{2}$ becomes

$$D = 2^p$$

or, by means of Equation 10

$$2 \sum_{k=1}^{28} h(k)/(h(1) + h(28)) = 2^p$$

yielding

$$2^p \sim 62 \text{ or } P = 6$$

By Rule 1, $a^1 = H(2) - H(1)$. Furthermore, since $h(1) \approx h(2)$, Rule 2 yields $a^2 = H(3) - H(1)$. Since $h(3)$ is $\approx 3h(1)$, a 1:3:3:1 intensity pattern is searched for. This pattern is exhibited by the lines 1, 3, 5, and 8, indicating the presence of three equivalent protons with splitting constant $a^2$. The 8th-line spectrum (Figure 5b) constructed from $a^1(1H)$ and $a^2(3H)$ can be superimposed on the lines 1 through 5, 7, and 8, and 11, so that the first line not accounted for is line number 6. Hence $H(6) - H(1)$ is equal to $a^3$ (Figure 5c) and, since $h(6) \approx h(1)$, only one proton is associated with $a^3$. Hence the splitting constant of the 6th proton remains to be determined by Rule 3, $a^4 = TW - (a^1 + 3a^2 + a^3)$, with $TW = H(28) - H(1)$.

According to Equation 7 the spectrum should contain 32 lines rather than 28. However, a reconstruction of the spectrum by means of Equation 8 shows an accidental overlap of lines in the center, so that the lines 13 to 16 each contain two components of intensity 1 and 3, respectively.

Example 2 — 5-(2-Carboxylatoethyl)-4-oxido-1,2-benzosemiquinone (No. 402). This experimental spectrum (Figure 6) contains some lines (marked by arrows) from an unknown radical. Such spurious EPR lines are frequently encountered. They should be clearly marked before an analysis of the main spectrum is attempted. Usually spurious lines may be recognized through a different rate of decay and a different spectral centerpoint (g-factor). The number of protons involved in the spectrum is determined, as in the first example, from

$$D = 2^p = 2 \sum_{k=1}^{33} h(k)/(h(1) + h(33)) = 76$$

* Number from the chapter on Explanation of Tables.
3. **Radical with three protons, two being equivalent:** \( r = 2, n^1 = 1, n^2 = 2 \), with splitting constants \( a^1 \) and \( a^2 \). The resonance fields are obtained from Equation 8. The appearance of the spectrum depends on the relative magnitude of \( a^1 \) and \( a^2 \) as illustrated in Figure 4.

![Figure 3](image)

![Figure 4](image)

The number of lines derived from Equation 7 is six (four if \( a^1 = a^2 \)). For \( a^1 = 2a^2 \) only five lines appear due to *accidental* degeneracy. The spectrum (Figure 4c) is characteristic of three equivalent protons, e.g., from a methyl group.

**Determination of Splitting Constants from Experimental Spectra**

The analysis of reasonably well-resolved EPR spectra from the type of radicals considered in this handbook is illustrated through two examples, for simplicity chosen so that all hyperfine splittings arise from protons \((I = \frac{1}{2})\). A few simple rules are often helpful in the analysis. Assume that the spectrum to be analyzed consists of \( N \) lines which are numbered consecutively from left to right, and that the resonance field and height of line \( k \) are \( H(k) \) and \( h(k) \), respectively. Then the rules may be expressed:
FIGURE 5.
Radical: 2-Methoxy-1,4-benzosemiquinone (no. 447)
Solvent: w/EtOH
Method: Oxidation in an alkaline medium
$\Delta H$/Gauss: 0.602($a^1$), 0.788($a^2$), 2.029($a^3$), 3.601($a^4$)
$Lw$/Gauss: 0.054
Again six protons are involved since the value of D is closer to 2\textsuperscript{a} than to either 2\textsuperscript{b} or 2\textsuperscript{c}. The spectrum consists of three 11-line subspectra with the same hyperfine structure and with relative intensities close to the ratios 1:2:1. This indicates a large splitting from two equivalent protons, the splitting constant a\textsuperscript{f} being immediately obtainable as H(12) - H(1). By Rule 1 a\textsuperscript{e} is found as H(2) - H(1) and, since h(2) \approx 2h(1), two equivalent protons are associated with a\textsuperscript{e} (Figure 6a). This accounts for the lines 1, 2, and 3 so that a\textsuperscript{f} is equal to H(4) - H(1). As shown in Figure 6b, a\textsuperscript{g} stems from a single proton. By Rule 3, a\textsuperscript{d} is finally determined as a\textsuperscript{d} = TW - (2a\textsuperscript{e} + 2a\textsuperscript{f} + a\textsuperscript{g}). A reconstruction of the spectrum from Equation 8 shows that the lines 6, 17, and 28 are composite lines formed by accidental overlap of two components of equal intensity.

In order to check the analysis, a reconstruction of the spectrum is usually made. For simple, well-resolved spectra like the foregoing examples, a stick-plot diagram calculated from Equation 8 suffices. However, when the number of lines increases and overlap between lines becomes frequent, a computer simulation taking the lineshape into account is required.
The first derivative of a Lorentzian curve (Figure 7) closely matches the shape of EPR lines from radicals in diluted liquid solutions ($<10^{-4}M$), as illustrated in Figures 17 and 18b. As shown in Figure 18a a stick-plot diagram may be insufficient to confirm the analysis of the spectrum, since a detailed comparison with the experimental curve is not feasible. The derivative signal in Figure 7 is increasing and the one in Figure 17 decreasing on the left-hand side. This phase difference is totally irrelevant for the spectral analysis, and recorded spectra of either phase occur throughout in the literature and in this handbook.

If the EPR spectrum is recorded on paper, the set of splitting constants and the linewidth are adjusted by trial and error until the calculated spectrum closely matches the experimental spectrum (cf. Figure 61). If, on the other hand, the EPR spectrometer is interfaced to a computer, the analysis of the digitally recorded spectrum may be refined by an iterative least-squares parameter adjustment. The experimental spectra shown in this handbook have been analyzed digitally.

Assignment of Splitting Constants
The assignment of splitting constants to nuclei at specific sites in the radical requires some care. Splittings due to nuclei in substituents may often be recognized immediately, as illustrated by Examples 1 and 2 above. Thus in Example 1, the splitting constant $a^2$ associated with three equivalent protons evidently belongs to the methoxyl group. Similarly, in Example 2 the constants $a^1$ and $a^2$ belong to two pairs of equivalent methylene protons. From the general experience that the unpaired electron density decreases with distance from the radical nucleus, the large constant $a^1$ is assigned to the $\alpha$-methylene protons and $a^2$ to the $\beta$-methylene protons.
Assignment of splitting constants to the aromatic protons of the radical nucleus frequently requires comparison of data for a family of radicals obtained from a basic structure through substitution. The following discussion applies to the aromatic protons only. The most direct assignment results from site-specific substitution with deuterium, which affects only the splitting constant $a_H$ belonging to the substituted atom. Taking the spin and magnetic moment of the deuteron into account, $a_H$ may be expressed

$$a_H = 1.44 (TW_H - TW_D) \quad (13)$$

where $TW_H$ and $TW_D$ are the total widths of the fully protonated and monodeuterated radicals, respectively. This procedure has been widely used to identify splitting constants associated with labile protons (such as hydroxyl protons) where $TW_D$ may be obtained simply by preparing the radical sample in a deuterated solvent.

All substituents other than deuterium change the distribution of the unpaired electron in the radical, and the splitting constants of the aromatic protons change accordingly. For certain substituents, such as alkyl groups or halogen atoms, the changes are often quite small, so that the splitting constants of the aromatic protons may still be recognized. Thus the assignments for a family of substituted radicals may sometimes be made without taking recourse to deuterium substitution.

The assignment of the five splitting constants of 4-oxido-1,2-naphthosemiquinone (No. 590, Scheme 2) illustrates the procedure. Consider first the derived radicals Nos. 593, 602, 603, and 604, where the 3-position has been blocked by a phenyl group from which no hyperfine splitting is observed. In each of the bromosubstituted species, the three remaining proton splittings are practically unaffected, allowing an unambiguous assignment at the positions 5 to 8. Comparison of the splittings of the radicals Nos. 591 and 593 indicates that the phenyl group has no specific influence on the splitting constants. Hence the assignment made for radical No. 593 applies to the unsubstituted radical No. 590 as well, suggesting in turn that the splitting from the proton at position 3 has the value 0.25 G.
The changes of the splitting constants of the aromatic protons induced by neighboring substituents may be used to assist the assignments, especially in monosubstituted radicals. The basic assumption is that the effects of substituents on the splitting constants of the protons are additive.

If \( a_i^0 \) is the splitting constant of the proton at position \( i \) in the unsubstituted radical and \( a_i^j \) is the value of that constant observed when a given substituent, \( R_j \), is introduced at position \( j \), the \textit{additivity principle} may be expressed

\[
a|_k = a_i^j + a_i^k - a_i^0
\]

where \( a|_i^k \) is the value of the constant belonging to position \( i \), measured when the substituents \( R_j \) and \( R_k \) are introduced at position \( j \) and \( k \), respectively. The width of the spectrum of the unsubstituted radical is

\[
T(o) = \sum_{\ell=1}^{n} a^o_{\ell}
\]

Similarly, for the radicals substituted at position \( j \), and at the positions \( j \) and \( k \), the widths may be expressed

\[
T(j) = \sum_{\ell \neq j} a^j_{\ell} \text{ and } T(j,k) = \sum_{\ell \neq j,k} a^j_{\ell,k}
\]

where any contribution from the substituents has been subtracted. With these expressions, Equation 14 leads to

\[
\sum_{i \neq j,k} a|_i^{j,k} = T(j,k) = (T(j) - a^j_i) + (T(k) - a^k_i) - (T(o) - a^o - a^0_i)
\]

If only a single set of equivalent positions in the radical is considered, and \( R_j \) is taken equal to \( R_k \), it follows that

\[
T(j) = T(k), \quad a^j_i = a^k_i, \text{ and } a^o = a^0_i
\]

Hence Equation 15 may be written

\[
a^j_i = a^o + T(j) - \frac{1}{2}(T(o) + T(j,k))
\]

Thus the splitting constant at position \( k \) may be predicted from three appropriate spectral widths, \( T \), and the splitting constant of the equivalent protons in the unsubstituted radical. The following chart illustrates the assignment of the three splittings from the aromatic protons in monosubstituted 1,4-benzoquinones by means of Equation 16.

It should be emphasized that the additivity principle only applies to set of spectra obtained under strictly similar conditions with respect to solvent system, temperature, and method of radical generation. Moreover, any instrument drift during the experiment may lead to incorrect and highly misleading T-parameters. Violation of the additivity principle may often be attributed to conformational differences between the radicals in the set.

The g-Factors

Determination of g-factors (Equations 4 and 5) involves measurement of \( H_o \), and the microwave frequency \( v_o \). For a group of related radicals such as the semiquinones the variation
### Chart 1

**ASSIGNMENT OF OBSERVED SPLITTING CONSTANTS (GAUSS) OF SUBSTITUTED 1,4-BENZOSEMIQUINONE ANIONS BY ADDITIVITY RULES**

<table>
<thead>
<tr>
<th>Substituents</th>
<th>( a^* )</th>
<th>( a_1^* )</th>
<th>( a_2^* )</th>
<th>( a_3^* )</th>
<th>( T(2) )</th>
<th>( T(2,3) )</th>
<th>( T(2,5) )</th>
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<td>6.44</td>
<td></td>
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<td>1.92</td>
<td>3.62</td>
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* Variations of \( a^* \) are due to different compositions of solvent.
* Values in parenthesis are calculated by means of Equation 16, simplified to \( a_1^* = T(j) - a^* - \frac{1}{2}T(j,k) \).
* Experimental value not available.
of the values of $H_0$ at constant $\nu_0$ is of the order $10^{-4}$. Hence the g-factors are most conveniently determined by comparing the positions of the spectra on the magnetic field scale with that of a standard radical with known g-factor, thus bypassing the absolute determination of $H_0$ and $\nu_0$. The spectrum of the radical $U$, for which the g-factor is to be determined, is run simultaneously with that of the standard radical $S$. Denoting the resonant fields $H_U$ and $H_S$, the g-factor of $U$ is related to the one of the standard $g_S$ by the equation

$$g_U = g_S \left(1 - \frac{\Delta H}{H_S + \Delta H}\right)$$

where $\Delta H = H_U - H_S$.

A convenient standard for the determination of g-factors of semiquinones is tetrahydroxy-1,4-benzoquinone, which easily converts to a radical (No. 520) with a single narrow line. The recommended experimental conditions and the radical characteristics for the g-factor standard (No. 520)* are

1. Solvent: Alkaline water, $10^{-1} M$ NaOH
2. Concentration: $10^{-1} M$ in above solvent
3. Radical formation: Flushing the solution with atmospheric oxygen
4. Spectrum: One narrow line; peak-to-peak linewidth 30 mG (minimum observed)
   Line surrounded by two $^{13}$C satellites at $^{13}$C) = 0.66 G (see Figure 21)
5. g-Factor: 2.00487 at 25°C
6. Stability: Several hours at best; radical decays continuously

* For a list of other standards, see Wertz and Bolton, loc. cit. EPR Monographs.
AN ANALYTICAL APPLICATION

Many quinones and quinols occurring in plants may be detected and identified by EPR spectroscopy in crude alcoholic extracts of the plant material, since these compounds can be simply converted to the relatively stable semiquinone radicals in alkaline media by an appropriate redox process. Most other radicals that might arise are too short lived to be detected, so that no chemical purification of the extracts is required. As an example, the results of a semiquantitative determination of juglone, 2-methyljuglone, and hydroquinone in crude plant extracts are shown in Scheme 3. For details of this and other applications, see References 15, 16, and 456.
Scheme 3
NATURALLY OCCURRING QUINONES/QUINOLS DETECTED AND IDENTIFIED BY EPR

a) Juglone (observed as 5-hydroxy-1,4-naphthoquinone, no. 613)\(^a\)

![Scheme 3 Diagram](image)

**Observed in:**
- Juglandaceae (leaves)
  - *Carya alba* (0.14)\(^a\)
  - *C. cordiformis* (blank)
  - *C. glabra* (blank)
  - *C. luciniosa* (0.10)
  - *C. ovalis* (blank)
  - *C. ovata* (blank)
- *Juglans cathayensis* (0.31)
- *J. cinerea* (0.31)
- *J. dracoruza* (0.44)
- *J. hindsii* (0.09)
- *J. mandshurica* (0.28)
- *J. nigra* (0.42)
- *J. regia* (0.44)
- *J. rupestris* (0.29)
- *J. sieboldiana* (0.57)
- *J. stenocarpa* (0.28)
- *Pterocarya fraxinifolia* (0.59)
- *P. hubeiensis* (0.38)
- *P. rhoifolia* (0.33)
- *P. stenoptera* (0.37)

**FIGURE 8.** Spectrum observed from leaf extract of *Pterocarya fraxinifolia*. For experimental details, see no. 613, Table 1.15.2 (Reference 16).
b) 2-Methyljuglone (observed as 5-hydroxy-2-methyl-1,4-naphthoquinone, no. 614)

![Chemical structure of 2-Methyljuglone]

Observed in:
- Droceraceae (leaves)
- Drosera binata
- Plumbaginaceae (leaves, roots)
- Ceratostigma plumbaginoides

FIGURE 9. Spectrum observed from root extract of Ceratostigma plumbaginoides. For experimental details, see no. 614, Table 1.15.2 (Reference 16).

c) Hydroquinone (observed as 1,4-benzoquinone, no. 107)

![Chemical structure of Hydroquinone]

Observed in:
- Asteraceae (leaves)
- Senecio elegans
- Ericaceae
  - Arctostaphylos alpina
  - Vaccinium vitis-idaea
- Lamiaceae (leaves)
  - Dracocephalum ruyschiana
  - Origanum vulgare
Scheme 3 (continued)

NATURALLY OCCURRING QUINONES/QUINOLS DETECTED AND IDENTIFIED BY EPR

Lycopodiaceae (leaves, dried)
- Lycopodium cunningii
- L. hastatum
- L. hippurideum
- L. sp. aff. crassum
- L. sp. aff. rufescens
- L. tetragonum

Rosaceae (leaves)
- Pyrus amygdaliformis (0.31)
- P. amygdaliformis var. persica (0.17)
- P. betulaefolia (0.18)
- P. communis (0.35)
- P. elaeagrifolia (0.18)
- P. elaeagrifolia var. kotschyanum (0.22)
- P. nivalis (0.17)
- P. pusilla (<0.02)
- P. salicifolia (0.06)
- P. salicifolia var. pendula (<0.02)
- P. serrulata (0.11)
- P. ussuriensis (0.20)
- P. ussuriensis var. hondoensis (0.19)
- P. communis × nivalis (0.17)
- Sorbus aria × P. communis (<0.02)
  (sorbopyrus auricularis)
- P. calleryana var. faurei (blank)
- Cydonia oblonga (blank)

Rubiaceae (flowers)
- Galium mollugo

Rutaceae (flowers)
- Phellodendron amurense
- P. japonicum
- P. sachaliense
Saxifragaceae (leaves)

- *Bergenia bifolia* (0.10)
- *B. busiana* (0.09)
- *B. ciliata* (blank)
- *B. cordifolia* (0.22, red leaves)
- *B. cordifolia* (0.06, green leaves)
- *B. crassifolia* (<0.02)
- *B. ligulata* (blank)
- *B. subsiliata* (0.18)

* All semiquinones observed in w/EtOH (alkaline).
* Figure shows milligrams of compound per grams of dry weight.
SEMIQUINONE SPECTRA

The following collection contains 50 high-resolution EPR spectra analyzed digitally with the simplifying assumption of constant linewidth. The experimental conditions used in generating radicals are given in abbreviated form (see Explanation to Tables). The instrumental settings (Instr. sett.) applied are stated in the following order:

1. Scan width (4 G, 10 G, etc.)/scan time (sec, min)
2. Filter time constant (sec)
3. Microwave power (mW)
4. Number of accumulated scans (acc)

The spectra were run on a Bruker® ER 200 EPR spectrometer or a Varian® E-15 EPR spectrometer with a modulation frequency of 12.5 and 10 kHz, respectively. The spectra were stored digitally as 4000 discrete signals (resolution, 2.5 mG per interval for a 10-G spectrum).

The spectra illustrate characteristic features for each example mentioned below (numbers in brackets are figure numbers):

1. Spectral changes from linewidth (Lw) variations (10)
2. Smallest \( a_{11} < \text{Lw} \) (40, 44, 47, 49, 50)
3. Smallest \( a_{11} = \text{Lw} \) (20, 25, 29, 34)
4. Line-broadening towards higher field (48, 56, 58, 59)
5. Line-broadening towards lower field (31)
6. Solvent dependence of splitting constants (60)
7. Simulations by computer (18, 38, 47—49)
8. Data subtractions by computer (12, 23)
9. Stick-plot diagram (18)
10. \(^{13}\text{C}\) splitting analysis (11)
11. Deuterium substitution (46)
12. Dissociation of hydroxyl proton (27, 52—55)
FIGURE 10. Simulations of doublet (1:1), triplet (1:2:1), and quartet (1:3:3:1) spectra with constant splitting ($a_H$) and linewidth (Lw) varied, or vice versa: $a_H$ and Lw in arbitrary unit.
FIGURE 11.
Radical: 5-Carboxylatopyrogallosemiquinone (no. 288)
Solvent: w/EtOH
Method: Ox alk
$\omega$/G: 1.088(2H), main triplet, lines out of scale
$\Delta$w/G: 0.190
Instr. sett.: 20 G/5 min. 0.03 sec, 0.1 mW

PARAMETERS USED IN SIMULATIONS

<table>
<thead>
<tr>
<th>Curve</th>
<th>Linewidth/G</th>
<th>$\omega$/G</th>
<th>Left (1:2:1)</th>
<th>Right (1:2:1)</th>
<th>Intensity (relative)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1.172</td>
<td>0.084</td>
<td>0.097</td>
<td>2.37</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>1.735</td>
<td>0.072</td>
<td>0.080</td>
<td>1.07</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>2.259</td>
<td>0.108</td>
<td>0.076</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>5.999</td>
<td>0.075</td>
<td>0.089</td>
<td>2.16</td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>7.733</td>
<td>0.087</td>
<td>0.123</td>
<td>1.10</td>
<td></td>
</tr>
</tbody>
</table>

Note: Top curve — Experimental spectrum consisting of signals from the radical containing no $^{13}$C nuclei (main triplet [2H, 1:2:1] at center) and from seven radicals each containing one $^{13}$C nucleus at a different position (satellite lines in pairs of 1:2:1 triplets). Since four of the seven carbon atoms are pairwise equivalent, only five distinct $^{13}$C spectra are observed with relative intensities 1:2:1:1:2:1 (cf. a to e in scheme). Curves a to e are simulated spectra of the radicals containing one $^{13}$C nucleus. Note that the linewidths of the left- and right-hand triplets are different.
FIGURE 12.
Radicals a: Mixture of three naphthazarin radicals (nos. 637, 649, and 655)
Solvent: DMF
Method: Re el
Instr. sett.: 20 G/2 min, 0.03 sec, 0.1 mW

Radical b: 2,3-Dimethoxynaphthazarin semiquinone (No. 655)
$\alpha$G: 0.548(2H), 1.806(2H)
Offset/G: $-0.104$ (relative to no. 637)
LwG: 0.104
Spectrum obtained by data subtraction: simulations of nos. 637 and 649 subtracted from spectra of Figure 12a

Radical c: 2-Methoxynaphthazarin semiquinone (no. 649)
$\alpha$G: 0.489(1H), 0.522(1H), 1.513(1H), 2.017(1H), 2.585(1H)
Offset/G: $-0.037$ (relative to no. 637)
LwG: 0.089
Spectrum obtained by data subtraction: simulations of nos. 637 and 655 subtracted from spectra of Figure 12a

Radical d: Naphthazarine semiquinone (no. 637)
$\alpha$G: 0.527(2H), 2.397(4H)
LwG: 0.075
Spectrum obtained by data subtraction: simulations of nos. 649 and 655 subtracted from spectra of Figure 12a
FIGURE 13.  
Radical: 1,2-Benzosemiquinone (no. 1)  
Solvent: w/EtOH  
Method: Ox alk  
\(a_v/G\): 0.88(2H), 3.65(2H)  
\(L_w/G\): ~0.05  
Instr. sett.: 20 G/4 min, 0.03 sec, 0.5 mW

FIGURE 14.  
Radical: 3-Methyl-1,2-benzosemiquinone (no. 2)  
Solvent: w/EtOH  
Method: Ox alk  
\(a_v/G\): 0.396(1H), 0.743(3H), 2.880(1H), 4.146(1H)  
\(L_w/G\): 0.045  
Instr. sett.: 20 G/5 min, 0.1 sec, 0.1 mW
FIGURE 15.
Radical: 4-Hydroxycarboxylatatomethyl-1,2-benzoquinone (no. 56)
Solvent: w/EtOH
Method: Ox alk (pH = 13.2)
a_\text{H}/G: 0.568(1H), 0.911(1H), 2.329(1H), 3.545(1H)
Lw/G: 0.043
Instr. sett.: 10 G/2 min, 0.03 sec, 0.05 mW, 8 acc

FIGURE 16.
Radical: 1,4-Benzosemiquinone (no. 107)
Solvent: w/EtOH
Method: Ox alk
a_\text{H}/G: 2.357(4H)
a(c)/G: 0.630 (positions 2, 3, 5, 6)
Lw/G: 0.074
Instr. sett.: 10 G/1 min, 0.03 sec
FIGURE 17.
Radical: 2-Phenyl-1,4-benzosemiquinone (no. 116)
Solvent: w/EtOH
Method: Ox alk
$\alpha_\text{G}/G$: 
$0.164(2H), 0.263(3H), 1.971(1H), 2.077(1H), 2.539(1H)$
$Lw/G$: 0.064
Instr. set.: 10 G/2 min, 0.03 sec, 0.05 mW, 4 acc

FIGURE 18. (a) Stick plot of No. 116; (b) computer simulation of no. 116.
FIGURE 19.
Radical: 6-Isopropyl-2-methyl-1,4-benzosemiquinone (no. 168)
Solvent: w/EtOH
Method: Ox alk
a_H/G: 1.356(1H), 1.760(1H), 1.833(1H), 2.237(3H)
Lw/G: 0.146
Instr. sett.: 20 G/2 min, 0.01 sec, 0.05 mW, 8 acc

FIGURE 20.
Radical: 2-(4-Carboxylatobutyl)-1,4-benzosemiquinone (no. 178)
Solvent: w/EtOH
Method: Ox alk
a_H/G: 0.055(2H), 1.708(1H), 1.733(2H), 2.462(1H), 2.515(1H)
Lw/G: 0.059
Instr. sett.: 20 G/2 min, 0.01 sec, 0.04 mW, 4 acc
Inset: (a) Line 1 enlarged; (b) line 1 simulated
Radical 1: 2-Carboxylato-1,4-benzosemiquinone (no. 192)
Solvent: w/EtOH
Method: Ox alk (pH ~13.2)
$\alpha_{pp}/G$: 2.061(1H), 2.430(1H), 2.630(1H)
$L_{w}/G$: 0.047

Radical 2: Tetraoxido-1,4-benzosemiquinone (no. 520; used as a g-factor standard)
Solvent: w
Method: Ox alk (pH ~13)
$\alpha(1^{13}C)/G$: 0.663
$L_{w}/G$: 0.051
Instr. sett.: 20 G/2 min, 0.1 sec, 0.1 mW

Radical: 2-Ethoxycarbonyl-1,4-benzosemiquinone (no. 196)
Solvent: w/EtOH
Method: Ox alk
$\alpha_{pp}/G$: 0.092(2H), 1.445(1H), 2.537(1H), 3.727(1H)
$L_{w}/G$: 0.049
Instr. sett.: 10 G/2 min, 0.03 sec, 0.25 mW
FIGURE 23a.
Radical 1: 2-Chloro-1,4-benzosemiquinone (no. 260)
a\textsubscript{p}/G: 2.147(1H), 2.241(1H), 2.459(1H)
Lw/G: 0.059

Radical 2: 1,4-Benzosemiquinone (no. 107)
a\textsubscript{p}/G: 2.359(4H)
Lw/G: 0.058
Solvent: w/EtOH
Method: Ox alk
Instr. sett.: 10 G/2 min, 0.1 sec, 0.06 mW, 4 ace

FIGURE 23b.
Data subtraction: simulation of no. 107 subtracted from spectra of Figure 23a
FIGURE 24.
Radical: 2-Bromo-1,4-benzosemiquinone (no. 261)
Solvent: w/EtOH
Method: Ox alk
$\sigma_{n}/G$: 2.159(1H), 2.355(1H), 2.367(1H)
$L_{w}/G$: 0.086
Instr. sett.: 10 G/2 min, 0.1 sec, 0.06 mW, 4 acc

FIGURE 25.
Radical: 4-Formylpyrogallol semiquinone anion (no. 278)
Solvent: w/EtOH
Method: Ox alk (pH ~13)
$\sigma_{n}/G$: 0.088(1H), 0.772(1H), 4.308(1H)
$L_{w}/G$: 0.071
Instr. sett.: 10 G/2 min, 0.03 sec, 0.06 mW, 2 acc
FIGURE 26.
Radical: 4-Carboxylatopyrogallol semiquinone anion (no. 283)
Solvent: w/EtOH
Method: Ox alk (pH ~13.7)
$\alpha_p$/G: 0.781(1H), 5.095(1H)
$Lw$/G: 0.063
Instr. sett.: 10 G/2 min, 0.03 sec, 0.1 mW, 2 acc

FIGURE 27.
Radical: 4-Carboxylatopyrogallol semiquinone (no. 302)
Solvent: w/EtOH
Method: Ox alk (pH ~13)
$\alpha_p$/G: 0.740(1H), 0.782(1H), 4.472(1H)
$Lw$/G: 0.036
Instr. sett.: 10 G/2 min, 0.03 sec, 0.1 mW
FIGURE 28.
Radical: 4-Methoxycarbonylpyrogallol semiquinone anion (no. 284)
Solvent: w/EtOH
Method: Ox alk (pH ~13.2)
$\omega$/G: 0.058(3H), 0.859(1H), 4.860(1H)
Lw/G: 0.036
Instr. sett.: 10 G/2 min, 0.03 sec, 0.04 mW, 4 acc

FIGURE 29.
Radical: 4-Ethoxycarbonylpyrogallol semiquinone anion (no. 285)
Solvent: w/EtOH
Method: Ox alk
$\omega$/G: 0.048(2H), 0.847(1H), 4.865(1H)
Lw/G: 0.040
Instr. sett.: 10 G/2 min, 0.03 sec, 0.04 mW, 7 acc
FIGURE 30.
Radical: 5-Propoxycarbonylpyrogallol semiquinone anion (no. 291)
Solvent: w/EtOH
Method: Ox alk
$\alpha\nu/G$: 0.379(2H), 1.105(2H)
$Lw/G$: 0.089
Instr. sett.: 4 G/20 sec, 0.01 sec, 0.1 mW, 4 acc

FIGURE 31.
Radical: 5-Isopropoxycarbonylpyrogallol semiquinone anion (no. 298)
Solvent: w/EtOH
Method: Ox alk
$\alpha\nu/G$: 0.220(1H), 1.104(2H)
$Lw/G$: 0.054
Instr. sett.: 4 G/20 sec, 0.01 sec, 0.1 mW, 8 acc
FIGURE 32.
Radical: 4-Oxido-1,2-benzosemiquinone (no. 308)
Solvent: w/EtOH
Method: Ox alk
$\alpha_0/G$: 0.585(1H), 1.350(1H), 4.895(1H)
$L_w/G$: 0.035
Instr. sett.: 10 G/2 min, 0.03 sec, 0.036 mW, 5 acc

FIGURE 33.
Radical: 5-Hexyl-4-oxido-1,2-benzosemiquinone (no. 312)
Solvent: w/EtOH
Method: Ox alk
$\alpha_0/G$: 0.117(2H), 0.503(1H), 0.747(1H), 4.044(2H)
$L_w/G$: 0.090
Instr. sett.: 10 G/2 min, 0.03 sec, 0.04 mW, 4 acc
FIGURE 34.
Radical: 5-(2-Aminoethyl)-4-oxido-1,2-benzosemiquinone (no. 415)
Solvent: w/EtOH
Method: Ox alk
$\alpha_u/G$: 0.054(2H), 0.542(1H), 0.896(1H), 3.332(2H)
$L_w/G$: 0.060
Instr. sett.: 10 G/2 min, 0.03 sec, 0.04 mW, 4 acc

FIGURE 35.
Radical: 2-Isopropoxy-5-pentyl-1,4-benzosemiquinone (no. 465)
Solvent: w/EtOH
Method: Re DTN/alk
$\alpha_u/G$: 0.540(1H), 0.687(1H), 1.344(1H), 2.739(2H)
$L_w/G$: 0.180
Instr. sett.: 20 G/2 min, 0.03 sec, 0.1 mW, 18 acc
FIGURE 36.
Radical: 2-Isopropoxy-6-pentyl-1,4-benzosemiquinone (no. 468)
Solvent: w/EtOH
Method: Re DTN/alk
$\Delta H/G$: 0.528(1H), 0.608(1H), 1.440(2H), 2.753(1H)
Lw/G: 0.121
Instr. sett.: 10 G/2 min, 0.1 sec, 0.1 mW, 19 acc

FIGURE 37.
Radical: 1,2-Naphthosemiquinone (no. 557)
Solvent: w/EtOH
Method: Ox alk/H$_2$O.
$\Delta H/G$: 0.17(1H), 0.27(1H), 0.56(1H), 1.36(1H), 1.45(1H), 4.61(1H)
Lw/G: ~0.045
Instr. sett.: 20 G/8 min, 0.3 sec, 0.5 mW
FIGURE 38a.
Radical: 6-Methyl-1,4-naphthoquinone (no. 564)
Solvent: w/EtOH
Method: Ox alk
\( \alpha \)/G: 0.546(1H), 0.553(1H), 0.686(1H), 0.691(3H), 3.165(1H), 3.347(1H)
Lw/G: 0.051
Instr. sett.: 20 G/2 min, 0.03 sec, 0.04 mW, 16 acc.

FIGURE 38b. Computer simulation of No. 564.
FIGURE 39.
Radical: 6-Methyl-5-hydroxy-1,4-naphthosemiquinone (no. 617)
Solvent: w/EtOH
Method: Re DTN/alk
$\alpha_\nu$/G: 0.349(1H), 0.509(1H), 1.288(3H), 1.387(1H), 3.066(1H), 3.422(1H)
Lw/G: 0.044
Instr. sett.: 20 G/2 min, 0.03 sec, 0.04 mW, 15 acc

FIGURE 40.
Radical: 5-Methoxy-1,4-naphthosemiquinone (no. 619)
Solvent: w/EtOH
Method: Re DTN/alk
$\alpha_\nu$/G: 0.037(3H), 0.727(1H), 0.913(1H), 1.102(1H), 2.464(1H), 3.727(1H)
Lw/G: 0.058
Instr. sett.: 10 G/1 min, 0.03 sec, 0.05 mW
FIGURE 41.
Radical: 2-Oxidouanthrasemiquinone (no. 710)
Solvent: w/EtOH
Method: Re DTN/alk (pH ~ 13.2)
$\alpha_d/G$: 0.154(1H), 0.264(1H), 0.548(1H), 0.621(1H), 1.021(1H), 1.608(1H), 1.96(1H)
$Lw/G$: 0.071
Instr. sett.: 10 G/2 min, 0.03 sec, 0.3 mW

FIGURE 42.
Radical: 2-Methoxyanthrasemiquinone (no. 711)
Solvent: w/EtOH
Method: Re DTN/alk
$\alpha_d/G$: <0.015(3H), 0.310(1H), 0.338(1H), 0.737(1H), 0.785(1H), 0.788(1H), 1.081(1H), 1.237(1H)
$Lw/G$: 0.054
Instr. sett.: 10 G/2 min, 0.03 sec, 0.05 mW
FIGURE 43.
Radical: 1-Hydroxy-2-oxidoanthrasemiquinone (no. 713)
Solvent: w/EtOH
Method: Re DTN/alk (pH \(-13.6\))
\(a_p/G:\) 0.098(1H), 0.108(1H), 0.580(1H), 0.593(1H), 1.054(1H), 1.075(1H), 2.234(1H)
Lw/G: 0.043
Instr. sett.: 10 G/5 min, 0.1 sec, 4 acc

FIGURE 44.
Radical: 1-Hydroxy-4-methoxyanthrasemiquinone (no. 718)
Solvent: w/EtOH
Method: Re DTN/alk (pH \(-13.2\))
\(a_p/G:\) 0.026(3H), 0.142(1H), 0.396(1H), 0.454(1H), 0.891(1H), 0.958(1H), 1.954(1H), 2.177(1H)
Lw/G: 0.036
Instr. sett.: 10 G/2 min, 0.1 sec, 0.05 mW, 16 acc
FIGURE 45.
Radical: 1,4-Dihydroxyanthraquinone (no. 715)
Solvent: w/EtOH
Method: Re DTN/alk
\( \alpha_G: 0.520(2H), 0.554(2H), 0.905(2H), 2.084(2H) \)
\( Lw/G: 0.045 \)
Instr. sett.: 10 G/2 min, 0.03 sec, 0.3 mW

FIGURE 46.
Radical: 1,4-Dihydroxyanthraquinone (no. 715D)
Solvent: D\(_2\)O/EtOD
Method: Re DTN/NaOD
\( \alpha_G: 0.07(2D), 0.55(2H), 0.90(2H), 2.08(2H) \)
\( Lw/G: \sim 0.05 \)
Instr. sett.: 20 G/8 min, 0.3 sec, 0.2 mW
FIGURE 47a.
Radical: 1-Hydroxy-6-methoxyanthrasemiquinone (no. 721)
Solvent: w/EtOH
Method: Re DTN/alk (pH ~13.2)
$\alpha_{eq}$: 0.028(3H), 0.282(1H), 0.433(1H), 0.666(1H), 0.862(1H), 1.039(1H), 1.440(1H), 1.829(1H)
Lw:G: 0.043
Instr. sett.: 10 G/2 min, 0.03 sec, 0.04 mW, 23 acc

FIGURE 47b. Computer simulation of no. 721.
FIGURE 48a.
Radical: 1-Hydroxy-7-oxidoanthrasemiquinone (no. 722)
Solvent: w/EtOH
Method: Re DTN/alk (pH ~ 12.7)
\( g/G: \) 0.301(1H), 0.416(1H), 0.526(1H), 0.766(1H), 1.272(1H), 1.740(1H), 2.092(1H)
Linw/G: 0.033
Instr. sett.: 10 G/2 min, 0.03 sec, 0.035 mW, 36 ace

FIGURE 49a.
Radical: 1-Hydroxy-3-methyl-7-methoxyanthrasemiquinone (no. 724)
Solvent: w/EtOH
Method: Re DTN/alk
a/G: 0.026(3H), 0.333(1H), 0.344(1H), 0.800(1H), 1.124(1H), 1.208(1H), 1.247(1H), 1.370(3H)
Lw/G: 0.039
Instr. sett.: 20 G/5 min, 0.1 sec, 0.04 mW, 16 acc

FIGURE 49b. Computer simulation of no. 724.
FIGURE 50.
Radical: 1-Hydroxy-7-methoxyanthrasemiquinone (no. 723)
Solvent: w/EtOH
Method: Re DTN/alk
\[ a_H/G: 0.015(3H), 0.280(1H), 0.352(1H), 0.859(1H), 0.999(1H), 1.188(1H), 1.352(1H), 1.374(1H) \]
\[ L_w/G: 0.031 \]
Instr. sett.: 10 G/2 min, 0.03 sec, 0.04 mW, 8 acc

FIGURE 51.
Radical: 1,8-Dihydroxanthrasemiquinone (no. 725)
Solvent: w/EtOH
Method: Re DTN/alk
\[ a_H/G: 0.196(2H), 0.989(2H), 1.202(2H), 1.591(2H) \]
\[ L_w/G: 0.049 \]
Instr. sett.: 10 G/2 min, 0.01 sec, 25 acc
FIGURE 52.
Radical: 2-Hydroxy-3-oxidoanthrasemiquinone (no. 727)
Solvent: w/EtOH
Method: Re DTN/alk (pH ~12.2)

a/H: 0.602(2H), 1.133(2H), 1.350(2H)
Lw/G: 0.044
Instr. sett.: 10 G/2 min, 0.03 sec, 0.03 mW, 4 acc

FIGURE 53.
Radical: 2,3-Dioxidoanthrasemiquinone (no. 728)
Solvent: w/EtOH
Method: Re DTN/alk (pH ~13.7)

a/H: 0.618(2H), 1.178(2H), 1.661(2H)
Lw/G: 0.059
Instr. sett.: 10 G/2 min, 0.03 sec, 0.03 mW
FIGURE 54.
Radical: 1,2-Dihydroxy-3-oxidoanthrasemiquinone (no. 731)
Solvent: w/EtOH
Method: Re alk (pH ~12.2)
a_H/G: 0.367(1H), 0.518(1H), 0.685(1H), 1.036(1H), 1.218(1H), 2.736(1H)
Lw/G: 0.049
Instr. sett.: 10 G/2 min, 0.03 sec, 0.3 mW, 12 ace

FIGURE 55.
Radical: 2,3-Dioxido-1-hydroxyanthrasemiquinone (no. 732)
Solvent: w/EtOH
Method: Re alk (pH ~13.7)
a_H/G: 0.437(1H), 0.583(1H), 0.613(1H), 1.147(1H), 1.185(1H), 2.940(1H)
Lw/G: 0.055
Instr. sett.: 10 G/5 min, 0.1 sec, 0.3 mW
FIGURE 56.
Radical: 1,4-Dihydroxy-2-oxidoanthrasemiquinone (no. 733)
Solvent: w/EtOH
Method: Re DTN/alk
a_\text{in.} G:\ 0.09(1H), 0.33(1H), 0.46(1H), 0.59(1H), 0.81(1H), 1.04(1H), 1.62(1H)
Lw/G: 0.050
Instr. sett.: 10 G/2 min. 0.03 sec. 0.3 mW. 9 ace

FIGURE 57.
Radical: 1,5-Dihydroxy-2-oxidoanthrasemiquinone (no. 734)
Solvent: w/EtOH
Method: Re DTN/alk (pH ~13.2)
a_\text{in.} G:\ 0.269(1H), 0.280(1H), 0.635(1H), 0.665(1H), 1.617(1H), 1.885(1H), 2.176(1H)
Lw/G: 0.042
Instr. sett.: 10 G/5 min. 0.1 sec
FIGURE 58.
Radical: 2,7-Dioxido-1-hydroxyanthrasemiquinone (no. 736)
Solvent: w/EtOH
Method: Re DTN/alk
a\textsubscript{q}/G: 0.209(1H), 0.380(1H), 0.592(1H), 0.804(1H), 1.250(1H), 2.264(1H)
Lw/G: 0.043
Instr. sett.: 10 G/2 min, 0.1 sec, 10 acc

FIGURE 59.
Radical: 1,4-Dihydroxy-6-oxidoanthrasemiquinone (No. 741)
Solvent: w/EtOH
Method: Re DTN/alk
a\textsubscript{q}/G: 0.187(1H), 0.429(1H), 0.565(1H), 0.582(1H), 1.679(1H), 1.979(1H), 2.730(1H)
Lw/G: 0.043
Instr. sett.: 10 G/2 min, 0.1 sec, 10 acc
**FIGURE 60.**
Radical: 3',4',5,6',7-Pentaoxido-2,3-dihydroflavonol anion radical (No. 876)
Method: Ox alk
Instr. sett.: 10 G/1 min, 0.03 sec, 0.1 mW

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Solvent DMSO:w (v/v)</th>
<th>$a_u$/G</th>
<th>Lw/G</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>2:8</td>
<td>0.196</td>
<td>1.604</td>
</tr>
<tr>
<td>b</td>
<td>2:3</td>
<td>0.199</td>
<td>1.594</td>
</tr>
<tr>
<td>c</td>
<td>2:2</td>
<td>0.209</td>
<td>1.574</td>
</tr>
<tr>
<td>d</td>
<td>2:1</td>
<td>0.214</td>
<td>1.523</td>
</tr>
</tbody>
</table>
FIGURE 61. (a) Simultaneous observation of four 16-line spectra from four conformers obtained from oxidation of 4,4'-dimethoxydiquinone. The arrows indicate pairwise the first and the last line for the four spectra. For structural details and EPR data see nos. 816 to 819, Table 1.20. (b) Simulation of the spectra in (a) obtained by a trial-and-error procedure. For data used see Table 1.20.
EXPLANATION TO TABLES

Location of Radicals

The radicals are located in the tables according to the characteristics of the radical nucleus, defined as the aromatic ring system including the oxygen atoms bound directly to the rings. These oxygen atoms are denoted as "key oxygens". All other functional groups attached to the rings are termed substituents.

A radical is indexed under the headings Anions (Table I), Neutral Species (Table II), or Cations (Table III), according to the total formal charge on the key oxygens, but irrespective of any formal charges on the substituents. Semiquinone anions, for which complexes with cations have been observed, are marked [C] in Table I. The EPR results for the complexes are listed separately in Table IV. Semiquinone-Cation Complexes. Splitting constants arising from $^{13}$C and $^{17}$O nuclei are listed in Table V. Isotopes. All entries in Table V appear also in one of the Tables I to IV, where the radicals are marked [I]. Radicals for which a spectrum is shown in the handbook are marked '.

In each table the entries are ordered with increasing number of rings in the radical nucleus and with increasing number of key oxygens. The detailed order is shown in the Table of Contents.

In Tables I to III the structure of each radical nucleus is shown with the numbering of carbon atoms adopted. In Table IV the basic structures of the semiquinone-cation complexes are similarly shown. Substituents are entered in the order H, C, N, P, S, F, Cl, Br, and I. In general, the names given are in accordance with IUPAC conventions. In the molecular formulas the abbreviations Me, Et, and Ph, are used for methyl, ethyl, and phenyl (C$_6$H$_5$), respectively. Asterisks or a, b in the formulas serve to link particular protons to the splitting constants similarly marked.

Splitting Constants

Unless otherwise stated, the splitting constants listed in the column a, refer to the aromatic proton at position (i) in the radical nucleus. Splitting constants arising from substituents at position (i) are listed also in the column a. Constants referring to protons in aliphatic substituents have numerical superscripts according to the scheme (SQ = semiquinone):

\[
\begin{array}{c|c|c}
1 & 2 & 3 \\
\hline
\text{SQ}-C-C-C & & \\
\text{C} & \text{C} & \\
2 & 3 & \\
\end{array}
\]

For example, 1.63$^1$ designates a splitting from either 3 protons from $-\text{CH}_3$, 2 protons from $-\text{CH}_2R$, or 1 proton from $-\text{CH}(R)R'$ or $-\text{CH} = C(R)R'$; and 0.22$^2$ designates a splitting from either 9 protons from $-C(\text{CH}_3)_3$, 6 protons from $-C(\text{CH}_3)_2R$, or 4 protons from $-C(\text{CH}_2R)_2R'$, etc.

The number of equivalent protons giving rise to a particular splitting must be derived from the name or the substituent formula. In case of nonequivalent methylene protons both observed splittings are shown with a superscript 1 (see, for example, Nos. 40 to 44 in Table I.1). Splittings from nuclei other than protons are labeled explicitly, e.g., F, Si, and 2N, for fluor, silicone, and two equivalent nitrogens. Where no splitting has been attributed to the nucleus/substituent, a u appears.

The organization of the tables requires that all splitting constants listed are assigned. It should be noted, however, that values deviating little from each other may be interchanged. In other cases where the assignments are tentative, the values of some constants are bracketed to indicate that they may be interchanged.
Since splitting constants are often reported without explicit indication of the accuracy, limits of errors are not given in the tables. They may be estimated as $\pm 3$ at the last decimal place.

In Tables I to IV absolute values of the splitting constants are given only, since the sign is not directly accessible in the EPR experiment. Aromatic proton splitting constants are negative with few exceptions, corresponding to positive spin densities at the carbon atoms. In Table V, Isotopes, the signs of the splitting constants are given.

Methods of radical generation are given in the tables in terms of the following abbreviations. For chemical methods:

1. Ox alk — autoxidation in an alkaline medium (NaOH) of quinols, phenols, etc.
2. Ox KOH — same as the above apart from the use of KOH instead of NaOH.
3. Ox agent(s) — oxidation with specified agent, e.g., I$_2$, KO$_2$, Ag$_2$O, PbO$_2$, etc.
4. Ox AlCl$_3$ — oxidation involving the combined action of AlCl$_3$ and a solvent, e.g., MeNO$_2$, CH$_2$Cl$_2$, PhMe. Method solely used to generate radical cations.
5. Re alk — reduction in an alkaline medium of quinones; reducing agent not specified.
6. Re agent(s) — reduction with specified agent, e.g., Zn, KO$_2$, DTN, etc.

For other methods:

1. Ox el — in situ electrolytic oxidation.
2. Re el — in situ electrolytic reduction.
3. Radiolysis — in situ radiolysis in an aqueous solution, saturated with N$_2$O to convert e$^-$ into OH$^-$.
4. Phot — in situ photolysis with ultraviolet or visible irradiation.

Spectra are recorded at room temperature (300 K) unless otherwise stated. If reported, composition of mixed solvents are expressed in vol%. Results from the editor’s laboratory are with 32% w/EtOH solvents; w/EtOH is stated in the tables only. The data are obtained from the Reference number stated first, unless otherwise indicated.

The radicals are numbered consecutively in the tables. For semiquinone-cation complexes the numbers begin with a capital letter C. A capital letter D after a number indicates a deuterated compound.
References
