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有机化合物结构鉴定

——光谱数据手册

Structure Determination of Organic Compounds

Tables of Spectral Data

(4th , revised and enlarged edition)

Ernö Pretsch, Philippe Bühlmann and Martin Badertscher

原著第4版，修订扩展版

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by Ernö Pretsch，Philippe Bühlmann and Martin Badertscher
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Preface

The ongoing success of the earlier versions of this book motivated us to prepare a new edition. While modern techniques of nuclear magnetic resonance spectroscopy and mass spectrometry have changed the ways of data acquisition and greatly extended the capabilities of these methods, the basic parameters, such as chemical shifts, coupling constants, and fragmentation pathways remain the same. However, since the amount and quality of available data has considerably increased over the years, we decided to prepare a significantly revised manuscript. It follows the same basic concepts, i.e., it provides a representative, albeit limited set of reference data for the interpretation of ^{13}C NMR, ^{1}H NMR, IR, mass, and UV/Vis spectra. We also added a new chapter with reference data for ^{19}F and ^{31}P NMR spectroscopy and, in the chapter on infrared spectroscopy, we newly refer to important Raman bands.

Since operating systems of computers become outdated much faster than printed media, we decided against providing a compact disk with this new edition. The limited versions of the NMR spectra estimation programs can be downloaded from the home page of the developing company (www.upstream.ch/support/book_downloads.html).

We thank numerous colleagues who helped us in many different ways to complete the manuscript. We are particularly indebted to Dr. Dorothée Wegmann for her expertise with which she eliminated many errors and inconsistencies of the earlier versions. Special thanks are due to Prof. Wolfgang Robien for providing us with reference data from his outstanding ^{13}C NMR database, CSEARCH. Another high-quality source of information was the Spectral Database System of the National Institute of Advanced Industrial Science and Technology (http://riodb01.ibase.aist.go.jp/sdbs/), Tsukuba, Ibaraki (Japan).

In spite of great efforts and many checks to eliminate errors, it is likely that some mistakes or inconsistencies remain. We would like to encourage our readers to contact us with comments and suggestions under one of the following addresses: Prof. Ernö Pretsch, Institute of Biogeochemistry and Pollutant Dynamics, ETH Zürich, CH-8092 Zürich, Switzerland, e-mail: pretsche@ethz.ch, Prof. Philippe Bühlmann, Department of Chemistry, University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN 55455, USA, e-mail: buhlmann@umn.edu, or Dr. Martin Badertscher, Laboratory of Organic Chemistry, ETH Zürich, CH-8093 Zürich, Switzerland, e-mail: badertscher@org.chem.ethz.ch.

Zürich and Minneapolis, November 2008

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1 Introduction

1.1 Scope and Organization

The present data collection is intended to serve as an aid in the interpretation of molecular spectra for the elucidation and confirmation of the structure of organic compounds. It consists of reference data, spectra, and empirical correlations from ^{1}H, ^{13}C, ^{19}F, and ^{31}P nuclear magnetic resonance (NMR), infrared (IR), mass, and ultraviolet–visible (UV/Vis) spectroscopy. It is to be viewed as a supplement to textbooks and specific reference works dealing with these spectroscopic techniques. The use of this book to interpret spectra only requires the knowledge of basic principles of the techniques, but its content is structured in a way that it will serve as a reference book also to specialists.

Chapters 2 and 3 contain Summary Tables and Combined Tables of the most relevant spectral characteristics of structural elements. While Chapter 2 is organized according to the different spectroscopic methods, Chapter 3 for each class of structural elements supplies spectroscopic information obtained with various techniques. These two chapters should assist users less familiar with spectra interpretation to identify the classes of structural elements present in samples of their interest. The four chapters with data from ^{13}C NMR, ^{1}H NMR, IR spectroscopy, and mass spectrometry are ordered in the same manner by compound types. These cover the various carbon skeletons (alkyl, alkenyl, alkynyl, alicyclic, aromatic, and heteroaromatic), the most important substituents (halogen, single-bonded oxygen, nitrogen, sulfur, and carbonyl), and some specific compound classes (miscellaneous compounds and natural products). Finally, a spectra collection of common solvents, auxiliary compounds (such as matrix materials and references), and commonly found impurities is provided with each method. Not only the strictly analogous order of the data but also the optical marks on the edge of the pages help fast cross-referencing between the various spectroscopic techniques. Because their data sets are less comprehensive, the chapters on ^{19}F and ^{31}P NMR and UV/Vis are organized somewhat differently. Although currently UV/Vis spectroscopy is only marginally relevant to structure elucidation, its importance might increase by the advent of high-throughput analyses. Also, the reference data presented in the UV/Vis chapter are useful in connection with optical sensors and the widely applied UV/Vis detectors in chromatography and electrophoresis.

Since a great part of the tabulated data either comes from our own measurements or is based on a large body of literature data, comprehensive references to published sources are not included. Whenever possible, the data refer to conventional modes and conditions of measurement. For example, unless the solvent is indicated, the NMR chemical shifts were normally determined with deuterochloroform. Likewise, the IR spectra were measured using solvents of low polarity, such as chloroform or carbon disulfide. Mass spectral data were recorded with electron impact ionization at 70 eV.

While retaining the basic structure of the previous editions, numerous reference entries have been updated and new entries have been added. Altogether, about 20% of the data is new. The chapter on ^{19}F and ^{31}P NMR is entirely new, and the section on IR spectroscopy now includes references to important Raman bands.

1.2 Abbreviations and Symbols

al	aliphatic
alk	alkyl
alken	alkenyl
ar	aromatic
as	asymmetric
ax	axial
comb	combination vibration
d	doublet
δ	IR: deformation vibration NMR: chemical shift
DFTMP	1,1-difluoro-1-(trimethylsilyl)methylphosphonic acid
DMSO	dimethyl sulfoxide
eq	equatorial
ε	molar absorptivity
frag	fragment
γ	skeletal vibration
gem	geminal
hal	halogen
ip	in plane vibration
J	coupling constant
liq	liquid
$M^{+\cdot}$	molecular radical ion
m/z	mass to charge ratio
$\tilde{\nu}$	wavenumber
oop	out of plane vibration
sh	shoulder
st	stretching vibration
sy	symmetric
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TMS	tetramethylsilane
vic	vicinal

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