Organic Spectroscopy

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THIRD EDITION

palgrave

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First edition 1975
Reprinted six times
Second edition 1987
Reprinted once
Third edition 1991
Reprinted 2002

Published by
PALGRAVE
Houndmills, Basingstoke, Hampshire RG21 6XS and
175 Fifth Avenue, New York, N.Y. 10010
Companies and representatives throughout the world

PALGRAVE is the new global academic imprint of
St. Martin's Press LLC Scholarly and Reference Division and
Palgrave Publishers Ltd (formerly Macmillan Press Ltd).

ISBN 978-1-4039-0684-7   ISBN 978-1-349-15203-2 (eBook)
DOI 10.1007/978-1-349-15203-2

This book is printed on paper suitable for recycling and
made from fully managed and sustained forest sources.

A catalogue record for this book is available
from the British Library.

12 11
03 02 01

This edition is manufactured in India and is authorised for
sale only in India, Bangladesh, Pakistan, Nepal and Sri Lanka.

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Preface to the First Edition

This book is an introduction to the application of spectroscopic techniques in organic chemistry. As an introduction it presupposes very little foreknowledge in the reader and begins at a level suitable for the early student. Each chapter is largely self-contained, beginning with a basic presentation of the technique and developing later to a more rigorous treatment. A supplement to each of the principal chapters covers recent and recondite areas of the main fields, so that the book will also serve to refresh and update the postgraduate student's knowledge. Sufficient correlation data are given to satisfy the average industrial or academic user of organic spectroscopic techniques, and these tables and charts constitute a useful reference source for such material.

SI units are used throughout, including such temporarily unfamiliar expressions as *relative atomic mass* and *relative molecular mass*. A major break with the British conventions in organic nomenclature has also been made in favor of the American system (thus, 1-butanol rather than butan-1-ol). This step is taken both in recognition of the vast amount of chemical literature that follows American rules (including the UKCIS computer printouts) and in the expectation that these conventions will in due course be adopted for use by more and more British journals and books.

Chapter 1 takes a perspective look at the electromagnetic spectrum, and introduces the unifying relationship between energy and the main absorption techniques.

The next four chapters deal with the four mainstream spectroscopic methods—methods which together have completely altered the face of organic chemistry in little over a decade and a half. Most students will use infrared spectroscopy first (chapter 2), and nuclear magnetic resonance spectroscopy will follow (chapter 3). Electronic spectroscopy is more limited in scope (Chapter 4), and mass spectroscopy (chapter 5) is the most recent and, in general, the most expensive. Chapter 6 provides both

worked and problem examples in the application of these techniques, both singly and conjointly.

The emphasis throughout has been unashamedly 'organic', but interpretative theory has been included even where controversy exists: the theory of nuclear magnetic resonance is particularly satisfying and logical when treated semiempirically, but infrared theory is often conflicting in its predictions, mass spectroscopy theory is often speculative and electronic theory can be very mathematical. These strengths and weaknesses are emphasized throughout.

Students of chemistry, biochemistry or pharmacy at university or college will hopefully find the book easy to read and understand: the examples chosen for illustration are all simple organic compounds, and chapter 6 includes problems at an equally introductory level (so that students can *succeed* in problem-solving!). It is likely that the chapter supplements will be studied by students at honours chemistry degree or postgraduate level, and on the whole this is reflected in degree of complexity.

The author is reluctant to admit it, but he graduated at a time when no spectroscopic technique (other than X-ray crystallography) was taught in the undergraduate curriculum. He hopes that his own need to learn has given him a sympathetic insight into those dark areas that students find difficult to understand, and that the treatment accorded them in this book reflects their travail. His own colleagues have been of immense support, and did not laugh when he sat down to play. He thanks them all for it.

Heriot-Watt University, Edinburgh, January 1975

WILLIAM KEMP

Preface to the Second Edition

When first produced, this book tapped into a floodstream of progress in the application of spectroscopy to organic chemistry, and the unabated flow of developments has made a second edition necessary and timely.

The developments have not been entirely spectroscopic *per se*, but have been associated with the considerable reduction in the cost of computers, so that new spectroscopic information can be elicited, and the data then manipulated in new ways, too. This is equally true in the parallel working of spectroscopy with chromatography, and a new section is devoted to outlining this successful marriage.

A major area of expansion is in the coverage of nuclear magnetic resonance, where carbon-13 NMR is now given equal prominence with proton NMR, although the theory is developed around a protocentric *Weltanschauung*. New tables of data, new worked examples and more problem examples (with answers) give a student-oriented coverage of all interpretative applications of NMR.

Pulsed Fourier Transform methods make it possible to observe NMR from even the most unfavorable of magnetic nuclei, and multinuclear spectrometers are now less expensive and esoteric than before—a brief look at nitrogen-15 and oxygen-17 NMR is included in deference to their importance to organic chemists. Time and money are still needed to record NMR from these nuclei, but the interpretation of the spectra is no more difficult than for carbon-13 (and usually much simpler than for the proton); the book emphasizes these simplicities.

Infrared spectroscopy has undergone a renaissance with the advent of extremely sensitive Fourier Transform instruments, but although the spectra can be obtained from small (and very unusual) samples, the structural application of the method is not much different from before.

New techniques and devices have appeared in ultraviolet spectroscopy and in mass spectroscopy and these are introduced as part of the updating of the text.

Two changes in units have been agreed internationally, and in accordance with new recommendations chemical shift in NMR is now quoted as, for example, δ 7.3 (and not 7.3 δ), and mass-to-charge ratios in MS are quoted in units of m/z (and not m/e).

Throughout these alterations and expansions the character of the book has survived, particularly in the use of simple examples to illustrate sophisticated science. Hopefully they will enhance its usefulness not only for reference but also in learning.

Heriot-Watt University, Edinburgh, 1986

W. K.

Preface to the Third Edition

Since the publication of the second edition, the rate of change in these various fields of spectroscopy has maintained its pace. Some of the developments have been in instrumentation rather than in the exploitation of new spectroscopic phenomena, but this has led to the ready availability of spectra which were regarded, only a few years ago, as in the exotic class. As a consequence of these advances, we are witnessing changes in the emphases which the organic spectroscopist places on particular techniques: his time will be spent more with the carbon-13 and proton NMR spectra than with the infrared and ultraviolet.

The publication of a third edition has been centered around three main themes. The first change acknowledges a need to minimize discussion of obsolete instruments or techniques, and many more details of spectrometer operation have been added; Fourier Transforms and computers are no longer optional extras in the spectroscopy laboratory.

The second change is in the introduction of almost one hundred new student exercises throughout the book, in the form of both worked 'examples' (showing the working of a model problem, with a model answer to the question) and problem 'exercises' for the student to practice, having seen the method demonstrated in the model; answers to all of these self-assessment exercises are given at the back of the book. Several more difficult problems have also been added.

The third and major change is to the chapter on nuclear magnetic resonance, which has been considerably extended to take cognizance of its position as the preeminent method for structural determination in organic chemistry. This has been done mainly through the use of the Supplements, so that the beginning student can still come to grips with the simpler ideas of NMR and thereafter, at his or her own developing pace, tackle the conceptual complexities of rotating frames, pulse angles, and the like.

For students coming fresh to spectroscopy, it is difficult to anticipate how each of the methods can help in deducing the structure of an organic compound, and so an extended introduction in chapter 1 sets out a

comparison among them; even then, much of this will need to be reread *post hoc* before any perspective can be gained. Progress in the development of one technique may also downvalue a particular strength of another; a clear example of this is in the way that NMR has stolen IR thunder in the analysis of substitution patterns in benzene rings, identification of alkyl groups (methyl, ethyl, isopropyl, *tert*-butyl), differentiation of aldehydes from ketones from esters, and so on.

In infrared spectroscopy, relatively cheap Fourier Transform infrared (FTIR) spectrometers have become more readily available and it is quite probable that all new instruments designed by the major manufacturers will be based on FTIR, although the dispersive instruments at present in use throughout the world will expect to live on for a time yet. Because of this important imminent change, the section on infrared instrumentation has been completely rewritten, with FTIR spectroscopy brought out from the Supplement to its proper place in equal prominence with dispersive instrumentation. In addition to the principal advantages of FTIR instruments (speed and sensitivity), the spectral data are digitized, allowing many manipulations such as spectral subtraction: an example of this has been included. To minimize the chore of having to skip back and forth from text to spectrum, most of the infrared spectra are now annotated with assignments for the bands.

Only one manufacturer is still producing a low-cost continuous wave nuclear magnetic resonance spectrometer, all other instruments on the market being FTNMR machines. Superconducting magnets are now able to reach 14.1 T, corresponding to 600 MHz in proton frequency, and it is projected that 700 MHz will be achievable—with a stable magnet—in a few years' time. Unlike infrared spectra, where the spectrum will often look the same whether it has been recorded on a grating or on an FTIR instrument, proton NMR spectra from CW instruments exhibit 'ringing' and therefore do not look the same as those from FTNMR machines (even if the field strength is unchanged). The older literature, and most of the spectra catalogs, contain only CW spectra, whereas new spectra are virtually always from the FTNMR mode, and one consequence of this for the student is the necessity to recognize these differences: the interpretation of a spectrum from either mode (all other things being equal) poses the same challenges. Thus, in this third edition, a few of the simple first-order proton spectra shown in earlier editions at 60 MHz CW have been retained, but most of the CW spectra have been replaced by FTNMR spectra, from 80 MHz up to 600 MHz: the additional abilities of FT instruments to record DEPT spectra and 2-D spectra are also exemplified.

It has been decided to follow IUPAC recommendations and to eliminate almost completely the use of the terms 'high field', 'low field', 'upfield' and 'downfield' from the book. The fact that almost all new NMR instruments are FTNMR machines (in which the field strength is constant) means that it

is in the interests of new students to refer exclusively to relative chemical shift positions in the context of 'lower frequency' and 'higher frequency', respectively, even though these terms may initially be unfamiliar to former users. Discussion of techniques with outdated usefulness has been eliminated (spin tickling) or severely curtailed (INDOR).

There have been few changes in the science of ultraviolet and visible spectroscopy since the second edition, and in mass spectrometry the major change of interest to the compass of this book has been the ubiquitous availability of computerized data handling. This has been reflected in the discussion of the subject: the importance of library searching as a means of compound identification has also been given increased prominence. An additional section deals with laser ionization, and its importance, particularly in surface analysis.

The development of separation science (mainly chromatography) has continued steadily in parallel with the development of spectroscopy, but especially dynamic growth is taking place in those joint techniques in which the separation of mixtures is coupled with spectroscopic analysis of the separated constituents, as in supercritical fluid chromatography-mass spectrometry (SFC-MS) or gas chromatography-Fourier Transform infrared spectroscopy (GC-FTIR). The discussion of these so-called *hyphenated techniques* has been extended in recognition of their importance and novelty, and their derived acronyms have been included in Appendix 2, as a guide through the maze.

As must ever be the case, thanks are due to the many people who have helped in this revision by supplying information or argument, but especial thanks must go to my colleague Dr Alan Boyd for the amount of work involved in rerunning so many of the NMR spectra (and in carrying out the musical Fourier Transforms in chapter 1).

Heriot-Watt University, Edinburgh, 1990

W.K.

Acknowledgments

The author wishes to place on record his grateful thanks to the many people who supplied material, information, spectra and a share of their valuable time; comments critical and encouraging were received from many colleagues, and changes in this edition reflect these indications.

The book, in its third edition, is being jointly published for the first time by W. H. Freeman, New York, and much advice has been accepted from chemists in the USA to try and meet the needs of students there. Some early help came from Dr Donna Wetzel, Rohm and Haas, Bristol, Pennsylvania; Dr Daniel F. Church, Louisiana State University; Dr William Closson, State University of New York; Dr John Gratzner, Purdue University; and Dr Neil Schore, University of California. The entire manuscript was read by Prof. George B. Clemans, of Bowling Green State University, and Prof. Harold M. Bell, of Virginia Tech.: their many suggestions for improvement have been incorporated wherever possible. Gary Carlson, of W. H. Freeman, was responsible for inviting the whole project to the USA, and for arranging its review by faculty on that side of the Atlantic.

CHAPTER 1. The portraits of Isaac Newton and Joseph Fourier at the chapter head are reproduced with the permission, respectively, of The Royal Society of Chemistry, London, England, and Librairie Larousse, Paris, France. The music featured in figure 1.6 had Ailsa Boyd on clarinet, Iona Boyd on violin and the author on bagpipes: the recording and subsequent Fourier Transformation were by Dr Alan Boyd, of Heriot-Watt University.

CHAPTER 2. The infrared spectra reproduced in this chapter were recorded on a Perkin-Elmer Model 700 infrared spectrophotometer, with the exceptions of figures 2.10 and 2.11, which were recorded, respectively, on a Perkin-Elmer Model 1720-X FTIR spectrometer (by Dr Iain McEwan, of Heriot-Watt University) and a Pye-Unicam Model SP3-100 instrument. The photographs at the chapter head were supplied by Perkin-Elmer, and show examples of the Models 1600 and 1700 series. The correlation charts

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