

Spectroscopic Methods in Organic Chemistry

Manfred Hesse

University of Zürich

Herbert Meier

University of Mainz

Bernd Zeeh

BASF Limburgerhof

Translated by Anthony Linden and Martin Murray

221 Figures, 100 Tables



1997

Georg Thieme Verlag Stuttgart · New York

Contents

| | |
|---|----|
| Chapter 1 | |
| UV/Vis Spectroscopy | 1 |
| 1. Theoretical Introduction | 1 |
| 1.1 Electronic Transitions | 1 |
| 1.2 Light Absorption and the Spectrum | 4 |
| 2. Sample Preparation and Measurement of Spectra | 7 |
| 3. Chromophores | 9 |
| 3.1 Individual Chromophoric Groups and their Interactions | 9 |
| 3.2 Olefins, Polyenes | 10 |
| 3.3 Benzene and Benzenoid Aromatics | 14 |
| 3.4 Carbonyl Compounds | 17 |
| 4. Applications of UV/Vis Spectroscopy | 20 |
| 5. Derivative Spectroscopy | 22 |
| 6. Chiroptical Methods | 22 |
| Literature | 26 |
| Chapter 2 | |
| Infrared and Raman Spectroscopy | 29 |
| 1. Introduction | 29 |
| 2. Basic Principles and Selection Rules | 30 |
| 3. IR Spectrometers | 32 |
| 3.1 Classical (Scanning) IR Spectrometers | 32 |
| 3.2 Fourier-Transform IR Spectrometers | 33 |
| 4. Sample Preparation | 34 |
| 4.1 Measurements in the Gas Phase | 34 |
| 4.2 Measurements on Liquids | 35 |
| 4.3 Measurements in Solution | 35 |
| 4.4 Measurements in the Solid State | 35 |
| 5. The IR Spectrum | 36 |
| 6. Overview of Characteristic Absorptions | 40 |
| 7. IR Absorptions of Single Bonds to Hydrogen | 44 |
| 7.1 C-H Absorptions | 44 |
| 7.2 (O-H) and (N-H) Absorptions | 45 |
| 8. IR Absorptions of Triple Bonds and Cumulated Double Bonds | 47 |
| 9. IR Absorptions of Double Bonds | 48 |
| 10. Typical IR Absorptions of Aromatic Compounds | 52 |
| 11. IR Absorptions in the Fingerprint Region | 53 |
| 12. Examples of IR Spectra | 55 |
| 13. Information Technology as an Aid to IR Spectroscopy | 65 |
| 14. Quantitative IR Spectroscopy | 65 |
| 15. Raman Spectroscopy | 66 |
| 15.1 The Raman Effect | 66 |
| 15.2 Selection Rules | 67 |
| 15.3 Raman Spectrometers | 69 |
| 15.4 Applications | 69 |
| Literature | 70 |
| Chapter 3 | |
| Nuclear Magnetic Resonance Spectroscopy | 71 |
| 1. Fundamental Physical Principles | 71 |
| 1.1 The Resonance Phenomenon | 71 |
| 1.2 Chemical Shift | 73 |
| 1.3 Spin-Spin Coupling | 74 |
| 1.4 Line Widths | 83 |
| 1.5 Intensity | 84 |

| | | | | | |
|---------------------|---|-----|-----|---|-----|
| 2. | NMR Spectra and Molecular Structure | 86 | 2.1 | The Principle of the Mass Spectrometer | 220 |
| 2.1 | Molecules with "Rigid" Atomic Positions | 86 | 3. | Fragmentation of Organic Compounds | 222 |
| 2.2 | Intramolecular Motion | 88 | 4. | The Main Fragmentation Reactions of Organic Compounds | 226 |
| 2.3 | Chemical Exchange Processes | 95 | 4.1 | α -Cleavage | 226 |
| 3. | ^1H NMR Spectroscopy | 100 | 4.2 | Benzyl and Allyl Cleavage | 232 |
| 3.1 | Sample Preparation and Measurement of Spectra (CW and PFT Techniques) | 100 | 4.3 | The Cleavage of "Non-activated" Bonds | 234 |
| 3.2 | ^1H Chemical Shifts | 103 | 4.4 | The Retro Diels-Alder Reaction (RDA Reaction) | 236 |
| 3.3 | ^1H , ^1H Coupling | 106 | 4.5 | The McLafferty Rearrangement | 240 |
| 3.4 | Coupling to Other Nuclei | 112 | 4.6 | The Onium Reaction | 241 |
| 3.5 | Correlation of ^1H Shifts with Structural Features | 113 | 4.7 | Loss of CO | 244 |
| 3.6 | Increment Systems for Estimating ^1H Shifts .. | 121 | 5. | Thermal Reactions in the Mass Spectrometer .. | 246 |
| 3.7 | ^1H NMR Data of Representatives of the Commoner Classes of Compounds | 124 | 5.1 | The Most Important Types of Thermal Reactions | 246 |
| 3.8 | Specialised Techniques | 124 | 5.2 | Recognition of Thermal Reactions | 249 |
| 4. | ^{13}C NMR Spectroscopy | 142 | 5.3 | Prevention of Thermal Reactions in the Mass Spectrometer | 250 |
| 4.1 | Sample Preparation and Measurement of Spectra | 142 | 6. | Mass Spectra of Contaminated Samples and Mixtures | 251 |
| 4.2 | ^{13}C Chemical Shifts | 145 | 6.1 | Solvent | 252 |
| 4.3 | ^{13}C , ^1H Couplings | 149 | 6.2 | Foreign Substances in Solvents | 252 |
| 4.4 | Coupling of ^{13}C to Other Nuclei (D, F, N, P) .. | 152 | 6.3 | Foreign Substances in Reagents | 253 |
| 4.5 | ^{13}C , ^{13}C Couplings | 154 | 6.4 | Materials from Laboratory Apparatus | 253 |
| 4.6 | Correlation of ^{13}C Shifts With Structural Features | 157 | 6.5 | Contaminants from Thin-layer Chromatography Plates | 253 |
| 4.7 | Increment Systems for the Estimation of ^{13}C Shifts | 159 | 7. | Isotopic Labelling Reactions | 254 |
| 4.8 | Special Methods | 163 | 7.1 | H/D Exchange Reactions | 254 |
| 5. | ^1H and ^{13}C NMR Data: Representative Examples of the Most Important Classes of Compounds .. | 185 | 7.2 | Transformations of Functional Groups Under Deuterating Conditions | 255 |
| 6. | NMR Spectroscopy of Other Nuclei | 202 | 7.3 | Determination of the Degree of Labelling | 256 |
| 6.1 | ^{19}F NMR Spectroscopy | 202 | 8. | Additional Methods and Concepts | 258 |
| 6.2 | ^{31}P NMR Spectroscopy | 204 | 8.1 | Chemical Ionisation (CI) | 258 |
| 6.3 | ^{15}N NMR Spectroscopy | 208 | 8.2 | Direct Chemical Ionisation (DCI) | 259 |
| 6.4 | Other Nuclei | 214 | 8.3 | Electrospray Ionisation (ESI) | 259 |
| Literature | | 215 | 8.4 | Fast Atom Bombardment (FAB) | 260 |
| Chapter 4 | | | 8.5 | Field Desorption (FD) | 261 |
| Mass Spectra | | 219 | 8.6 | Field Ionisation (FI) | 261 |
| 1. | Introduction | 219 | 8.7 | Field Ionisation Kinetic (FIK) | 261 |
| 2. | Instrumentation and the Recording of Spectra .. | 220 | 8.8 | Measurement of High Masses | 261 |

VIII Contents

| | | | |
|---|-----|---|-----|
| 8.9 Ionization Methods | 263 | 9. Tables for Use in Mass Spectrometry | 279 |
| 8.10 Cation Addition Mass Spectroscopy | 265 | 9.1 List of Frequently Occurring Ions and Characteristic Mass Differences Resulting From Mass Spectrometric and Chemical Reactions | 279 |
| 8.11 The Coupling of Other Instruments to Mass Spectrometers | 266 | 9.2 Mass Differences Between the Reactant and Product of Frequently Used Chemical Reactions | 292 |
| 8.12 Laser Desorption / Ionisation Mass Spectrometry (LDI) | 268 | 9.3 Isotopic Ratios in Compounds Containing Cl and Br | 294 |
| 8.13 Multiply Charged Ions | 268 | 9.4 Mass Spectra of Solvents | 297 |
| 8.14 The Memory Effect | 269 | 9.5 Mass Spectra of Volatile Contaminants | 301 |
| 8.15 Neighbouring Group Participation Reactions | 269 | 9.6 Mass Numbers and Abundances of the Isotopes of Naturally Occurring Elements | 304 |
| 8.16 Photoionisation (PI) | 272 | Literature | 307 |
| 8.17 Quadrupole Mass Analysers | 272 | | |
| 8.18 Secondary Ion Mass Spectrometry (SIMS) | 273 | Chapter 5 | |
| 8.19 Spectral Libraries | 273 | Combined Examples | 313 |
| 8.20 Stereoisomers | 273 | | |
| 8.21 Collision Activation (CA) | 274 | Index | 335 |
| 8.22 Tandem Mass Spectrometry | 275 | Concepts | 335 |
| 8.23 Thermal Desorption Mass Spectrometry (TD) | 277 | Types of Compounds and Functional Groups | 342 |
| 8.24 The Thermospray Ionisation Procedure (TSI) | 277 | Specific Compounds | 352 |
| 8.25 Metastable Signals | 277 | | |