

STUDIES IN ANALYTICAL CHEMISTRY I

**STRUCTURAL ANALYSIS
OF ORGANIC COMPOUNDS**

by Combined
Application of Spectroscopic Methods

J. T. CLERC
E. PRETSCH
J. SEIBL

STUDIES IN ANALYTICAL CHEMISTRY I

**STRUCTURAL ANALYSIS
OF ORGANIC COMPOUNDS**

by Combined
Application of Spectroscopic Methods

STUDIES IN ANALYTICAL CHEMISTRY

Editorial Board

E. PUNGOR (Budapest), W. SIMON (Zürich),
J. INCZÉDY (Veszprém)

Volume 1 Structural Analysis of Organic Compounds by Combined Application of Spectroscopic Methods (Clerc, Pretsch, Seibl)

Volume 2 The Principles of Ion-Selective Electrodes and of Membrane Transport (Morf)

Volume 3 Nondestructive Activation Analysis (Amiel, editor)

0657-6
C629

STUDIES IN ANALYTICAL CHEMISTRY 1

25/10/81
31

STRUCTURAL ANALYSIS OF ORGANIC COMPOUNDS

by Combined
Application of Spectroscopic Methods

J. T. CLERC

E. PRETSCH

J. SEIBL

Swiss Federal Institute of Technology

Zürich, Switzerland



ELSEVIER SCIENTIFIC PUBLISHING COMPANY

Amsterdam-Oxford-New York 1981

*The distribution of this book is being handled
by the following publishers*

for the U.S.A. and Canada
Elsevier/North-Holland, Inc.

52 Vanderbilt Avenue
New York, New York 10017, U.S.A.

*for the East European countries, China,
Korean People's Republic, Cuba,
People's Republic of Vietnam and Mongolia*
Akadémiai Kiadó, The Publishing House of the
Hungarian Academy of Sciences, Budapest

for all remaining areas

Elsevier Scientific Publishing Company
1 Molenwerf

P. O. Box 211, 1014 AG Amsterdam, The Netherlands

Library of Congress Cataloging in Publication Data

Clerc, Thomas.

Structural analysis of organic compounds by combined
application of spectroscopic methods.

(Studies in analytical chemistry; 1)

Bibliography: p.

Includes index.

1. Spectrum analysis. 2. Chemistry, Organic.

I. Pretsch, Ernő, 1942— joint author.

II. Seibl, Josef, 1924— joint author. III. Title.

IV. Series.

QD272.S6C58 547.1:22 80-26703

ISBN 0-444-99748-2 (Vol. 1)

ISBN 0-444-41941-1 (Series)

© Akadémiai Kiadó, Budapest 1981

Joint edition published by

Elsevier Scientific Publishing Company, Amsterdam, The Netherlands and
Akadémiai Kiadó, The Publishing House of the Hungarian Academy
of Sciences, Budapest, Hungary

Printed in Hungary

CONTENTS

33		
34		
35		
36		
37		
38		
39		
40		
41		
42		
43		
44		
45		
46		
47		
48		
49		
50		
51		
52		
53		
54		
55		
56		
57		
58		
59		
60		
61		
62		
63		
64		
65		
66		
67		
68		
69		
70		
71		
72		
73		
74		
75		
76		
77		
78		
79		
80		
81		
82		
83		
84		
85		
86		
87		
88		
89		
90		
91		
92		
93		
94		
95		
96		
97		
98		
99		
100		

Mass spectrum	33
Infrared spectrum	34
Proton and carbon-13 NMR spectra	34
PROBLEM 2	36
Elemental composition and structural features	38
Structural assembly	38
Comments	39
Mass spectrum	39
Infrared spectrum	39
Proton NMR spectrum	40
Carbon-13 NMR spectrum	41
PROBLEM 3	42
Elemental composition and structural features	44
Structural assembly	44
Comments	45
Mass spectrum	45
Infrared spectrum	46
Proton NMR spectrum	47
Carbon-13 NMR spectrum	48
PROBLEM 4	50
Elemental composition and structural features	52
Structural assembly	52
Comments	53
Mass spectrum	53
Infrared spectrum	53
Carbon-13 NMR spectrum	53
PROBLEM 5	54
Elemental composition and structural features	55
Structural assembly	56
Comments	57
Mass spectrum	57
Infrared spectrum	57
Proton NMR spectrum	58
Carbon-13 NMR spectrum	58
PROBLEM 6	60
Elemental composition and structural features	61
Structural assembly	62
Comments	62
Mass spectrum	62
Infrared spectrum	63
Proton NMR spectrum	64
Carbon-13 NMR spectrum	65
PROBLEM 7	66
Elemental composition and structural features	67
Structural assembly	68

Comments	69
Mass spectrum	69
Infrared spectrum	69
Proton NMR spectrum	69
Carbon-13 NMR spectrum	70
PROBLEM 8	72
Elemental composition and structural features	74
Structural assembly	75
Comments	76
Mass spectrum	76
Infrared spectrum	77
Proton NMR spectrum	77
Carbon-13 NMR spectrum	77
PROBLEM 9	78
Elemental composition and structural features	80
Structural assembly	82
Comments	83
Mass spectrum	83
Infrared spectrum	83
Proton NMR spectrum	83
Carbon-13 NMR spectrum	85
PROBLEM 10	86
Elemental composition and structural features	88
Structural assembly	89
Comments	89
Mass spectrum	89
Infrared spectrum	90
Proton NMR spectrum	90
Ultraviolet spectrum	91
PROBLEM 11	92
Elemental composition and structural features	93
Structural assembly	94
Comments	94
Configuration of oximes	94
Spectroscopic features of long aliphatic chains	95
Infrared spectrum	96
Mass spectrum	96
PROBLEM 12	98
Elemental composition and structural features	99
Structural assembly	101
Comments	102
Mass spectrum	102
Proton NMR spectrum	103
Carbon-13 NMR spectrum	103

PROBLEM 13	104
Elemental composition and structural features	106
Structural assembly	107
Comments	107
Mass spectrum	107
Infrared spectrum	108
Proton NMR spectrum	108
PROBLEM 14	110
Elemental composition and structural features	111
Structural assembly	112
Comments	114
Mass spectrum	114
Infrared spectrum	114
Proton NMR spectrum	114
Carbon-13 NMR spectrum	115
PROBLEM 15	116
Elemental composition and structural features	118
Structural assembly	118
Comments	119
Mass spectrum	119
PROBLEM 16	120
Elemental composition and structural features	121
Structural assembly	123
Comments	124
Mass spectrum	124
Infrared spectrum	124
Proton NMR spectrum	125
Carbon-13 NMR spectrum	125
PROBLEM 17	126
Elemental composition and structural features	128
Structural assembly	130
Comments	130
Mass spectrum	130
Proton and carbon-13 NMR spectra	131
Infrared spectrum	133
PROBLEM 18	134
Elemental composition and structural features	136
Structural assembly	137
Comments	138
Mass spectrum	138
Infrared spectrum	138
Nuclear magnetic resonance spectra	139

PROBLEM 19	140
Elemental composition and structural features	141
Structural assembly	142
Comments	144
Mass spectrum	144
Infrared spectrum	144
Proton NMR spectrum	145
Carbon-13 NMR spectrum	145
PROBLEM 20	146
Elemental composition and structural features	148
Structural assembly	149
Comments	150
Mass spectrum	150
Infrared spectrum	150
Proton NMR spectrum	151
Ultraviolet spectrum	151
PROBLEM 21	152
Elemental composition and structural features	154
Structural assembly	155
Comments	155
Mass spectrum	155
Proton NMR spectrum	156
Carbon-13 NMR spectrum	156
PROBLEM 22	158
Elemental composition and structural features	160
Structural assembly	161
Comments	161
Mass spectrum	161
Infrared spectrum	162
Proton NMR spectrum	162
Carbon-13 NMR spectrum	162
PROBLEM 23	164
Elemental composition and structural features	166
Structural assembly	167
Comments	169
Mass spectrum	169
Infrared spectrum	170
Proton NMR spectrum	170
Carbon-13 NMR spectrum	170
PROBLEM 24	172
Elemental composition and structural features	173
Structural assembly	174
Comments	175
Mass spectrum	175
Infrared spectrum	176

Proton NMR spectrum	176
Carbon-13 NMR spectrum	177
PROBLEM 25	178
Elemental composition and structural features	180
Structural assembly	181
Comments	184
Mass spectrum	184
Proton and carbon-13 NMR spectra	184
Ultraviolet spectrum	185
PROBLEM 26	186
Elemental composition and structural features	187
Structural assembly	188
Comments	190
Mass spectrum	190
Carbon-13 NMR spectrum	190
PROBLEM 27	192
Elemental composition and structural features	193
Structural assembly	194
Comments	197
Structural assembly	197
Mass spectrum	198
Infrared spectrum	198
Carbon-13 NMR spectrum	199
PROBLEM 28	200
Elemental composition and structural features	202
Structural assembly	202
Comments	204
Mass spectrum	204
Infrared spectrum	204
Proton NMR spectrum	205
PROBLEM 29	206
Elemental composition and structural features	207
Structural assembly	208
Comments	209
Mass spectrum	209
Proton NMR spectrum	209
Carbon-13 NMR spectrum	210
Ultraviolet spectrum	211
PROBLEM 30	212
Elemental composition and structural features	214
Structural assembly	214

Part 3

Short supplementing essays

Degree of unsaturation. Calculation of number of double bond equivalents	219
General information from mass spectra	220
Evidence for elemental composition from isotope peak intensities	221
Evidence for elemental composition in low resolution mass spectra	223
High resolution data	224
Impurities in mass spectra	225
Prediction of infrared stretching frequencies	226
Overtone, combination bands, Fermi resonance	227
Band shapes and intensities in infrared spectra	228
Spurious bands in infrared spectra	229
Rules for the interpretation of proton NMR spectra	229
General rules	229
Rules for first order spectra	230
Higher order spectra	231
Simplification of higher order spectra	235
Application of higher magnetic field strength	235
Application of shift reagents	239
Computer simulation of spectra	242
Off-resonance decoupled spectra	245
Signal intensities in carbon-13 NMR spectra	248
Saturation	248
Nuclear Overhauser effect	249
Other influences	250
Intensities of solvent signals	250
Influence of molecular symmetry and conformational equilibria on NMR spectra	251
Introduction	251
Influence of symmetry properties on the NMR spectra	251
Fast conformational equilibria	252
Examples	252
Bulk susceptibility corrections	254
Solvents in ultraviolet spectroscopy	254
Interactions of chromophores	255

Appendix

Isotope distribution pattern of all natural elements in the periodic system	259
Mass correlation table	260

Mass spectra of some important solvents which occur frequently as impurity in mass spectra of organic samples	266
Infrared absorption spectra of some common solvents and suspension agents	268
Estimation of the proton chemical shifts in substituted alkanes	270
Estimation of the chemical shifts of olefinic protons	270
Estimation of the proton chemical shifts in substituted benzene	272
Estimation of the carbon-13 chemical shifts in aliphatic compounds	273
- Steric corrections S	274
Conformational corrections C	274
Estimation of the chemical shifts of olefinic carbon atoms	276
Estimation of the carbon-13 chemical shifts in substituted benzene	277
Estimation of the carbon-13 chemical shifts in substituted pyridine	279
Subject index	281
Structures of compounds	285

Preface

Spectroscopic methods have taken over the lion's share of organic analysis within the last two to three decades and one or more of them are employed in all chemical laboratories. Meanwhile it has become widely appreciated that for structural analysis the most efficient use of these modern methods is made by their combined application wherever possible, because they provide complementary information which increases their overall effectiveness. The importance of the subject has caused the appearance of a large number of texts dealing with the individual methods at fundamental as well as advanced levels. However, treatments of their combined application are surprisingly scarce and many of the practical aspects, which are so important in everyday work, are essentially neglected.

From the response to our joint teaching of the subject of organic structural analysis by combined application of spectroscopic methods, we have been led to the conclusion that a treatment of some examples demonstrating different ways of approach and reasoning and including remarks and hints about practical analytical aspects would be welcome. The following text is an attempt to implement these suggestions. We chose a set of problems intended to cover as much variety in chemical structure and spectroscopic argument as possible, carry out exemplifying interpretations and comment on specific practical aspects of the problem solving procedure. We hope not to annoy the readers by English which falls somewhat short of Oxford grade.

Our special thanks go to Prof. Dr. Sev Sternhell for his critical reading of the manuscript. His expert competence in the subject has contributed significantly to improving the text and is gratefully acknowledged. We also thank Dr. A. Neszmélyi for going over the manuscript and for critical comments, H.-P. Meier for technical assistance in reproducing the spectra and Dr. R. Schwarzenbach, Dr. R. Büchi and Dr. A. Villiger for their engaged help in collecting samples and data. -

Spectroscopic methods have been used in all three cases and one or more of them are included in all chemical laboratories. Although it has become widely appreciated that structural analysis is most frequently of the molecular weight is made by their combined application, whether possible because they provide complementary information which ignores their overall character. The importance of the subject has caused the appearance of a large number of papers dealing with the individual methods at fundamental as well as advanced levels. However, treatments of their combined application are surprisingly scarce and many of the practical aspects, which are so important in everyday work, are essentially neglected.

From the response to our joint teaching of the subject of organic structural analysis by combined application of spectroscopic methods, we have been led to the conclusion that a treatment of some examples demonstrating different ways of approach and reasoning and including examples and some other practical difficulties would be welcome. The following text is an attempt to implement these suggestions. We show a set of problems intended to cover much variety in chemical structure and spectroscopic argument as possible, carry out exemplifying interpretations and comment on specific practical aspects of the problem solving procedure. We hope not to annoy the readers by English which falls somewhat short of Oxford grade.

Our special thanks go to Prof. J. S. Stewart for his critical reading of the manuscript. His expert comments on the subject has contributed significantly to improving the text and is gratefully acknowledged. We also thank Dr. A. Newman for going over the manuscript and for critical comments, H. P. Meyer for technical assistance in reproducing the spectra and Dr. R. Schwarzenbach, Dr. K. Büchi and Dr. A. Villiger for their engaged help in collecting spectra and data.

PART 1

INITIAL REMARKS

PART I

INITIAL REMARKS