

Organic Structures from 2D NMR Spectra

L. D. Field, H. L. Li and A. M. Magill

School of Chemistry, University of New South Wales, Australia

WILEY

CONTENTS

Preface	vii
List of Figures	xi
List of Tables	xv
1 NMR Spectroscopy Basics	1
1.1 The Physics of Nuclear Spins	1
1.2 Basic NMR Instrumentation and the NMR Experiment	4
2 One-Dimensional Pulsed Fourier Transform NMR Spectroscopy	5
2.1 The Chemical Shift	7
2.2 ^1H NMR Spectroscopy	9
2.2.1 Chemical Shifts in ^1H NMR Spectroscopy	9
2.2.2 Spin-Spin Coupling in ^1H NMR Spectroscopy	10
2.2.3 Decoupling in ^1H NMR Spectroscopy	15
2.2.4 The Nuclear Overhauser Effect in ^1H NMR Spectroscopy	16
2.3 Carbon-13 NMR Spectroscopy	16
2.3.1 Decoupling in ^{13}C NMR Spectroscopy	17
2.3.2 Chemical Shifts in ^{13}C NMR Spectroscopy	18
2.4 Fluorine-19 NMR Spectroscopy	19
2.5 Phosphorus-31 NMR Spectroscopy	22
2.6 Nitrogen-15 NMR Spectroscopy	23
3 Two-Dimensional NMR Spectroscopy	25
3.1 General Principles	25
3.2 Proton-Proton Interactions	28
3.2.1 Correlation Spectroscopy – The COSY Experiment	28
3.2.2 Total Correlation Spectroscopy – The TOCSY Experiment	30
3.2.3 Nuclear Overhauser Spectroscopy – The NOESY Experiment	31
3.3 Carbon-Carbon Interactions	35
3.3.1 The INADEQUATE Experiment	35
3.4 Heteronuclear Correlation Spectroscopy	37
3.4.1 Heteronuclear Single Bond Correlation – The HSQC, HMQC and me-HSQC Experiments	37
3.4.2 Heteronuclear Multiple Bond Correlation – HMBC	38
4 Miscellaneous Topics	45
4.1 NMR Solvents	45
4.2 Reference Compounds and Standards	47
4.3 Dynamic Processes	48
4.3.1 Protons on Heteroatoms	49
4.3.2 Rotation about Partial Double Bonds	50
4.4 Second-Order Effects	51
4.5 Effect of a Chiral Centre on NMR Spectra	51

Contents

5	Worked Examples	55
5.1	General Principles	55
5.2	Worked Example 1	57
5.3	Worked Example 2	63
	Problems	71
	Index	309

Instructor's Guide and Solutions Manual to Organic Structures from 2D NMR Spectra

L. D. Field, H. L. Li and A. M. Magill

School of Chemistry, University of New South Wales, Australia

WILEY

CONTENTS

Preface	ix
Solutions Summary	1
Problem 1 (1-iodopropane)	7
Problem 2 (2-butanone)	11
Problem 3 (2-hexanone)	15
Problem 4 (ethyl propionate)	19
Problem 5 (ethyl 3-ethoxypropionate)	23
Problem 6 (4-acetylbutyric acid)	28
Problem 7 (3-ethoxypropionyl chloride)	32
Problem 8 (ethyl 3-chloropropionate)	36
Problem 9 (isoamyl acetate)	40
Problem 10 (<i>trans</i> -4-hexen-3-one)	45
Problem 11 (<i>trans</i> -2-octen-4-one)	50
Problem 12 (3-nitrobenzaldehyde)	55
Problem 13 (3-iodotoluene)	61
Problem 14 (8-hydroxy-5-nitroquinoline)	64
Problem 15 (2-bromo-3-picoline)	69
Problem 16 (<i>trans</i> -anethole)	72
Problem 17 (<i>cis</i> -2-pentene)	75
Problem 18 (<i>p</i> -tolyl benzoate)	79
Problem 19 (phenyl <i>p</i> -toluate)	86
Problem 20 (4-biphenyllyl acetate)	93
Problem 21 (4'-phenoxyacetophenone)	99
Problem 22 (4'- <i>tert</i> -butylacetophenone)	106

Problem 23 (2,2,4'-trimethylpropiophenone)	110
Problem 24 (<i>trans</i> -2-methyl-3-phenyl-2-propen-1-ol)	114
Problem 25 (methyl 4-ethoxybenzoate)	119
Problem 26 (methyl 3-(<i>p</i> -tolyl)propionate)	123
Problem 27 (4-(4'-methoxyphenyl)-2-butanone)	127
Problem 28 (ethyl 6-bromohexanoate)	132
Problem 29 (piperonal)	135
Problem 30 (<i>cis</i> -3-hexenyl benzoate)	139
Problem 31 (<i>trans</i> -2, <i>cis</i> -6-nonadienal)	146
Problem 32 (allyl glycidyl ether)	155
Problem 33 (3,4-epoxy-4-methyl-2-pentanone)	159
Problem 34 (dl-methionine)	162
Problem 35 (<i>N</i> -acetyl- <i>I</i> -leucine)	165
Problem 36 (isoamyl valerate)	170
Problem 37 ((<i>E</i>)-4-methyl-4'-nitrostilbene)	173
Problem 38 (2- <i>tert</i> -butyl-6-methylphenol)	181
Problem 39 (2-allyl-6-methylphenol)	186
Problem 40 (2-hydroxy-4-methoxybenzaldehyde)	194
Problem 41 (2'-hydroxy-5'-methylacetophenone)	198
Problem 42 (3'-fluoro-4'-methoxyacetophenone)	203
Problem 43 (<i>trans</i> -ferulic acid)	209
Problem 44 (sec-butyl 3-hydroxycinnamate)	215
Problem 45 (1-benzosuberone)	221
Problem 46 (dimethyl (3-bromopropyl)phosphonate)	228
Problem 47 (caffeine)	233
Problem 48 (benzyloxypropionitrile)	238
Problem 49 (cineole)	242
Problem 50 (thymoquinone)	246

Problem 51 (4-bromo-1-indanol)	251
Problem 52 (1-bromo-4-methylnaphthalene)	257
Problem 53 (carvacrol)	264
Problem 54 (acetoacetanilide)	272
Problem 55 (ethyl acetamidocyanoacetate)	277
Problem 56 (α -humulene)	283
Problem 57 (3,4-dihydro-2 <i>H</i> -benzopyran-3-carboxylic acid)	289
Problem 58 (quinidine)	296
Problem 59 (salbutamol)	312
Problem 60 (2-hydroxy-1-naphthaldehyde)	322
Problem 61 (6-methyl-4-chromanone)	329
Problem 62 (citronellal)	336
Problem 63 ((+)- <i>cis</i> -2-oxabicyclo-[3.3.0]oct-6-en-3-one)	344
Problem 64 (melatonin)	349
Problem 65 (carvone)	362
Problem 66 (haloperidol)	370