Organic Structures from Spectra

Fourth Edition

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PREFACE

The derivation of structural information from spectroscopic data is an integral part of Organic Chemistry courses at all Universities. At the undergraduate level, the principal aim of such courses is to teach students to solve simple structural problems efficiently by using combinations of the major techniques (UV, IR, NMR and MS), and over more than 25 years we have evolved a course at the University of Sydney, which achieves this aim quickly and painlessly. The text is tailored specifically to the needs and philosophy of this course. As we believe our approach to be successful, we hope that it may be of use in other institutions.

The course has been taught at the beginning of the third year, at which stage students have completed an elementary course of Organic Chemistry in first year and a mechanistically-oriented intermediate course in second year. Students have also been exposed in their Physical Chemistry courses to elementary spectroscopic theory, but are, in general, unable to relate it to the material presented in this course.

The course consists of about 9 lectures outlining the theory, instrumentation and the structure-spectra correlations of the major spectroscopic techniques and the text of this book corresponds to the material presented in the 9 lectures. The treatment is both elementary and condensed and, not surprisingly, the students have great difficulties in solving even the simplest problems at this stage. The lectures are followed by a series of 2-hour problem solving seminars with 5 to 6 problems being presented per seminar. At the conclusion of the course, the great majority of the class is quite proficient and has achieved a satisfactory level of understanding of all methods used. Clearly, the real teaching is done during the problem seminars, which are organised in a manner modelled on that used at the E.T.H. Zurich.

The class (typically 60 - 100 students, attendance is compulsory) is seated in a large lecture theatre in alternate rows and the problems for the day are identified. The students are permitted to work either individually or in groups and may use any written or printed aids they desire. Students solve the problems on their individual copies of this book thereby transforming it into a set of worked examples and we find that most students voluntarily complete many more problems than are set. Staff (generally 4 or 5) wander around giving help and tuition as needed, the empty alternate rows of seats

making it possible to speak to each student individually. When an important general point needs to be made, the staff member in charge gives a very brief exposition at the board. There is a $1^1/_2$ hour examination consisting essentially of 4 problems and the results are in general very satisfactory. Moreover, the students themselves find this a rewarding course since the practical skills acquired are obvious to them. There is also a real sense of achievement and understanding since the challenge in solving the graded problems builds confidence even though the more difficult examples are quite demanding.

Our philosophy can be summarised as follows:

(a) Theoretical exposition must be kept to a minimum, consistent with gaining of an understanding of the parts of the technique actually used in solving the problems. Our experience indicates that both mathematical detail and description of advanced techniques merely confuse the average student.

(b) The learning of data must be kept to a minimum. We believe that it is more important to learn to use a restricted range of data well rather than to achieve a nodding acquaintance with more extensive sets of data.

(c) Emphasis is placed on the concept of identifying "structural elements" and the logic needed to produce a structure out of the structural elements.

We have concluded that the best way to learn how to obtain "structures from spectra" is to practise on simple problems. This book was produced principally to assemble a collection of problems that we consider satisfactory for that purpose.

Problems 1 – 277 are of the standard “structures from spectra” type and are arranged roughly in order of increasing difficulty. A number of problems are groups of isomers which differ mainly in the connectivity of the structural elements and these problems are ideally set together (*e.g*. problems 2 and 3, 22 and 23; 27 and 28; 29, 30 and 31; 40 and 41; 42 to 47; 48 and 49; 58, 59 and 60; 61, 62 and 63; 70, 71 and 72; 77 and 78; 80 and 81; 94, 95 and 96; 101 and 102; 104 to 107; 108 and 109; 112, 113 and 114; 116 and 117; 121 and 122; 123 and 124; 127 and 128; 133 to 137; 150 and 151; 171 and 172; 173 and 174; 178 and 179; 225, 226 and 227; 271 and 272; and 275 and 276). A number of problems exemplify complexities arising from the presence of chiral centres (*e.g*. problems 189, 190, 191, 192, 193, 222, 223, 242, 253, 256, 257, 258, 259, 260, 262, 265, 268, 269 and 270); or of restricted rotation about peptide or amide bonds (*e.g*. problems 122, 153 and 255), while other problems deal with structures of compounds of biological, environmental or industrial significance (*e.g*. problems 20, 21, 90, 121, 125, 126, 138, 147, 148, 153, 155, 180, 191, 197, 213, 252, 254, 256, 257, 258, 259, 260, 266, 268, 269 and 270).

Problems 278 - 283 are again structures from spectra but with the data presented in a textual form such as might be encountered when reading the experimental section of a paper or a report.

In the 4th Edition of "Organic Structures from Spectra" we have introduced problems dealing with quantitative analysis using NMR spectroscopy and problems 284 - 291 involve the analysis of mixtures of compounds.

In this edition, we have also introduced a series of problems using two-dimensional NMR. Problems 292 - 309 represent a graded series of exercises introducing COSY, NOESY, C-H Correlation and TOCSY spectroscopy as aids to spectral analysis and as tools for identifying organic structures from spectra.

Problems 310 – 332 deal with more detailed analysis of NMR spectra - this tends to be a stumbling block for many students. There are two worked solutions (to problems 91 and 121) in an Appendix as an illustration of a logical approach to solving problems. However, with the exception that we insist that students perform all routine measurements first, we do not recommend a mechanical attitude to problem solving - intuition has an important place in solving structures from spectra as it has elsewhere in chemistry.

Bona fide instructors may obtain a list of solutions by writing to the authors or EMAIL: L.Field@unsw.edu.au or FAX: (61-2)-9385-8008

We wish to thank Dr Ian Luck in the School of Chemistry at the University of Sydney, and Dr Hsiulin Li and Dr Adelle Shasha in the School of Chemistry at the University of New South Wales who helped to assemble the additional samples and spectra in the 4th edition of this book. Thanks are also due to the many graduate students and research associates who, over the years, have supplied us with many of the compounds used in the problems.

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S Sternhell

J R Kalman October 2007

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