

Applications of Dynamic NMR Spectroscopy to Organic Chemistry, by MICHINORI ŌKI, VCH Verlagsgesellschaft, Weinheim, Federal Republic of Germany, 1985, xii + 423 pages, \$ 92.50, DM 208.00.

This book forms Volume 4 of the series "Methods in Stereochemical Analysis", edited by Alan P. Marchand. The text is largely a comprehensive collection of applications of dynamic n.m.r. spectroscopy (^1H -, ^{13}C -, and ^{19}F -n.m.r. methods) taken from the mainstream of physical organic chemistry. The word "dynamic" refers here to the n.m.r. spectroscopy of interconverting molecular species, and the principal parameter that is derived from such studies is the free energy of activation (ΔG^\ddagger), or barrier to interconversion.

The relative free-energies of various conformers may often be of more interest to the carbohydrate chemist, but this subject is given only limited attention. Despite the availability of some data in the literature on the barriers to conformational interconversion of carbohydrate derivatives, none of these examples are described.

Chapter 1, "General Considerations", offers a very useful discussion of the basic techniques and parameters, including coalescence phenomena, lineshape analysis, examples of spin exchange, the use of lanthanide shift-reagents, and a comparison of the reliability of the data obtained by the dynamic n.m.r. method with that of those measured by other n.m.r. methods, and non-n.m.r. methods.

Chapter 2, "Restricted Rotation about a Partial Double Bond", describes dynamic n.m.r. studies of amides, esters, conjugated double-bond systems, enamines, and aromatic compounds.

Chapter 3, "Restricted Rotation about a Formal Double Bond", discusses examples where the rather high barrier to rotation in normal alkenes is lowered by interaction with other, nearby double-bonds, or electron-withdrawing or -donating groups.

Chapter 4, "Racemization-Topomerization by Rotation about an sp^2 - sp^2 Bond", outlines substituent effects on the barriers to rotation of biphenyl derivatives, chiral 1,3-butadienes and acid anilides, and aromatic ketones and acid derivatives.

Chapter 5, "Restricted Rotation about a Trigonal to Tetrahedral Bond", describes barriers to rotation about the bonds between alkyl and aryl groups, restricted rotation in alkenes and carbonyl compounds, gearing of alkyl groups, and rotations in a number of cyclophane derivatives.

Chapter 6, "Rotation about Tetrahedral to Tetrahedral Bonds", relates to rotations in simple alkanes and their derivatives, and also to more complex compounds, such as 9,9'-bifluorenyls and various tryptycene derivatives.

Chapter 7, "Conformational Changes in Ring Compounds", is probably of most interest to carbohydrate chemists, and there are sections on six-, seven-, and eight-membered (and larger) rings, including those that are saturated, unsaturated,

or heterocyclic. The elegant, low-temperature studies of F. A. L. Anet and co-workers receive appropriate attention in this Chapter.

Chapter 8, "Stereodynamics of Amines and Imines", includes discussions of the complexities of processes that involve inversion about a nitrogen atom combined with internal rotation about various single bonds. These two facets can be distinguished by the application of appropriate techniques.

Chapter 9, "Application to Chemical Reactions", describes applications of the dynamic n.m.r. technique to the study of processes that involve bond formation and cleavage, including detection of fast reactions that cannot be monitored conveniently on the laboratory time-scale.

The book also contains two useful appendices: I. "Relationships Among Various Activation Parameters", and II. "Specification of Conformations". Let the prospective reader should presume that the latter appendix refers to the use of such symbols as C_1 and ${}^4C_1(D)$, *etc.*, it should be pointed out that this discussion actually involves the application of the Cahn-Ingold-Prelog sequence rule, specifically to aliphatic, alkenic, and aromatic derivatives. The use of the words "configuration" or "configurational isomers" is almost completely avoided in this book. Thus, isomeric structures that might commonly be referred to as configurational isomers are described instead as conformers about a rotational axis.

The chapters are well referenced, and the text contains eight figures, 1,327 well drawn formulas, and 109 tables of useful data, principally barriers to rotation and conformational interconversion. However, no experimental n.m.r. spectra are reproduced. There are relatively few errors in the book, which covers the literature for the period 1956-1983, with a few references for 1984.

It is difficult to imagine a student course that would be as specialized as the material presented in this book. Therefore, it appears to be more suitable either for library use, or for the personal library of the professional scientist who has a special interest in the subject matter. In view of the large quantity of material in the book, it seems to be fairly priced.

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